ANALYSIS OF PHYSIOCHEMICAL PARAMETERS TO EVALUATE THE DRINKING WATER QUALITY IN SOME VILLAGES OF MEHKAR TALUKA, DISTRICT BULDANA (M. S.) INDIA

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ABSTRACT

Water is one of the most essential requirement natural resources. It is essential in the life of all living organisms including Plants, Animals and Human being. Ground water plays a pivotal role in human life. Drinking water plays a major role in metropolitan as well as in villages. It may contain chemicals like nitrates, sulphates, fluorides in dissolved state. Therefore, it is desirable to check the presence of these chemicals from drinking water because the intake from other sources like food or air may be difficult to avoid. the present Paper reveals analysis of drinking water quality and some of its physico-chemical parameters like temperature, pH, TDS, nitrate, total hardness, Alkalinity, Chloride, etc. of water samples in five villages of Mehkar Taluka, district Buldana, Maharashtra. The water samples were collected from different region of the villages and analyzed for the suitability of drinking purposes. The values of each parameters were found to be within the safe limits set by the WHO and Indian Standards.

Keywords: *Water sample analysis, drinking water quality, physico-chemical parameters, etc.*

Introduction

Drinking water[1] is key to sustainable development and essential to quality health and poverty reduction. Safe drinking water is essential to life and a satisfactory safe supply must be made available to all the living beings. Water is thus becoming a decisive factor for development and the quality of life. Therefore, drinking water intended for human consumption must not contain germs or harmful chemicals; because water contaminated with harmful germs and chemicals is the cause of scourge. That is good drinking water is not a extravagance but one of the most essential requirements of life. According to the World Health Organization (WHO), 89% of the world population consumes drinking water from improved drinking water sources. Improved drinking water sources include piped treated water connections, public standpipes and protected dug wells. However, improved drinking water sources can still be contaminated from various sources. Use of Bottled drinking water has been increased for the past 30 years. Worldwide demand of drinking water is increasing because of increasing population. Water quality[2] and suitability for use are determined by its taste, odour, colour, and concentration of organic and inorganic matters. Contaminants in the water can affect the water quality and consequently the human health. The potential sources of water contamination are geological conditions, industrial and agricultural activities, and water treatment plants. In many parts of the country available water is rendered non potable because of the presence of heavy metal in excess. WHO and reports of Indian Standards revealed that most of the diseases in developing countries arise from contaminated drinking water. The situation gets worsened during the summer season due to water scarcity and rain water discharge. Contamination of water assets available for domestic and consumption purposes loaded with heavy metal ions and harmful microorganisms is one of the causes of major health problems. Hence studies of physico-chemical parameters of underground water to find out whether it is fit for drinking and some other domestic uses.

Therefore, on observation of the above mentioned, it is of significance to study the drinking quality of water, especially in those regions, where water level is declining due to less precipitation and scarcity in the summer. The present paper describes the investigation of some physico-chemical parameters and drinking water quality of the 5 villages in Mehkar Taluka, district Buldana, Maharashtra, India. The physico-chemical parameters[3] of water sample investigation were pH, temperature, Alkalinity, Chloride, sulphate,

nitrate, total hardness and fluoride. All of the drinking water samples were randomly taken from the bore well, tap water, hand pump of residential and commercial areas of the selected five villages. The villages in Mehkar Taluka undertaken for this research work chosen were Deulgaon Mali, Dongaon, Lavhala, Loni and Vivekanand Nagar. All of the sampling locations are open for public such as tea-breakfast stalls and private houses. According to Census 2011 information, the Geographical details of villages from where the water samples are collected are as follows in Table - 1

Table- 1: Drinking water samples locations, numbers and source.

Name of the Village	Number	Village Code	Distance from		Source
			Taluka Place (Mehkar) (in Km)	District Headquarters (Buldana) (in Km)	
Deulgaon Mali	1	528945	12	58	Tap Water
Dongaon	2	529029	16	80	Tap Water
Lavhala	3	528931	22	44	Tap Water
Loni	4	528928	23	43	Tap Water
Vivekanand Nagar	5	528937	11	54	Tap Water

Materials and Methods

Sampling: All the water samples[4] were randomly collected taken from the tap water, hand pump and bore well of residential and commercial areas of the selected five villages. All of the premises from where the water samples are collected are open for public such as tea-breakfast stalls and private houses. The samples were numbered and collected in 1-liter polyethylene (PE) bottles, which were washed with deionized water before use. These sample bottles were sealed and placed in a dark environment at a constant temperature range of 4–10°C to avoid any contamination and the effects of light and temperature. For chemical analysis of collected water samples including pH, total dissolved solids (TDS), total hardness(TH),a representative water sampling was carried out from each location during the summer and winter times in a period of one year. During the summer, the temperature at the time of sampling was 41-43°C, while it was 21-23°C during the water sampling in winter. The average values of duplicate samples were used for graphical illustration. Each of the duplicate samples were analyzed for a number of parameters in the laboratory to determine the overall drinking water quality.

Onsite and Chemical Analysis: On-site analyses of pH[5], conductivity, and turbidity[6] were carried out at the site of sample collection following the standard protocols and methods of American Public Health Organization (APHA)[7]. The collected samples were estimated for Alkalinity, Chloride, sulphate, nitrate, total hardness and fluoride. The chemicals and reagent used for analysis were of analytical grade.

Statistical Analysis: All data generated were analyzed statistically by calculating the mean and compare the mean value with the acceptable standards. pH meter Equiptronics model was used to determine the pH of the samples, Titrimetric procedures were followed for the analysis of total hardness, alkalinity, Chloride, sulphate, nitrate and Fluoride. Borosilicate Glassware was used for all the estimations.

Result and Discussions:

The physico-chemical parameters obtained from analysis of water samples are presented in the **Table No. 2.** The various physico-chemical characteristics were analyzed for ground water from different sampling locations. The details of the average results were summarized in table 2.

pH: The pH value of water source determines the hydrogen ion concentration in water and indicates whether the water is acidic or alkaline. Most of the biological and chemical reactions are influenced by the pH of water. If pH is not within the acceptable limit, it damages the mucous membrane of cells. In the present reading all the ground water samples show fair pH values between 6.7 -7.8.

Total dissolved solids (TDS)[8]: The total dissolved solids in water are due to presence of all inorganic and organic substances. The solids can be salts of manganese, magnesium, potassium, sodium, calcium, carbonates, bicarbonates, chlorides, phosphates and other minerals. The high values of TDS results in gastrointestinal irritation to the any person but long time use of water with high TDS can cause kidney stones and heart diseases. In the present analysis, the TDS values were observed from 350 to 475 mg/l. The TDS value for all the ground water samples fall within the acceptable limit.

Total alkalinity (TA): The bases like Carbonates, bicarbonates, hydroxides, phosphates, nitrates, silicates, borates etc are responsible for alkalinity of water. Alkalinity provides information of natural salts present in water. The alkalinity values were recorded below the acceptable limit (50 - 80mg/l). So, All samples are within the desirable limit for drinking water 100 mg/l (WHO).

Total hardness (TH): Hardness[9] of water is an artistic quality of water and is caused by salts like carbonates, bicarbonates, sulphates and chlorides of calcium and magnesium. Hardness more than 300 mg/l may cause heart and kidney problems. The total hardness in ground water samples observed was beyond the desirable limit. All the ground water samples are quite hard and hence require suitable treatments before use.

Chloride (Cl^-): Chloride in ground water can be caused by industrial or household waste. The chloride concentration serves as an indicator of pollution by sewage. High chloride content in water bodies, harms agricultural crops, metallic pipes and harmful to people suffering due to cardiac and renal diseases. Most of the ground water samples show chloride concentration within the permissible limit (250 mg/l) of WHO.

Fluoride (F^-): Fluorine exists combining with other substances as fluoride. The main source of fluoride in ground water is fluoride bearing rock such as fluorspar, fluorite, cryolite, and fluorapatite. High fluoride content in ground water causes serious damage to the teeth and bones of human body, diseases caused called dental fluorosis and skeletal fluorosis. The value of fluoride concentration in ground water samples lie between 0.6 - 0.80 mg/l. All the ground water samples have fluoride concentration within permissible limit (1.0 mg/l) of WHO[10].

Nitrate (NO_3^-) Nitrate is an inorganic chemical that is highly soluble in water. Major sources of nitrate in drinking water include fertilizers, sewage and animal manure. High nitrate content may lead into Irritability, lack of energy, headache, dizziness, vomiting, and diarrhea. The Nitrate levels are found to be within the acceptable limit

Table No. 2: Analytical average results for different water quality parameters and Comparison with WHO Standards

Sr. No	Spots	pH (1)	Temp.(^oC) (2)	TA (3)	Cl^- (4)	NO_3^- (5)	TH (6)	F^- (7)	TDS (8)
1	Amdapur	6.7	33.2	69.5	108.6	32.4	524.57	0.78	574
2	Mera Kh	6.9	31.6	67.8	143.5	34.4	585.11	0.69	498
3	Mera Bk	7.4	32.6	72.5	142.2	36.5	582.15	0.78	442
4	Shelud	7.8	31.0	72.9	164.3	39.3	574.11	0.66	398
5	Mangrur Nawghare	7.5	32.0	69.3	129.4	39.9	590.12	0.69	412
6	WHO standard	6.5 - 8.5	30-34	100	200-600	20-45	100-500	1.2-1.5	500-1500

*All the results in the entries from (3) to (8) are in mg/l

Conclusion

It is observed that from the above data, ground water quality of the village is not so bad for drinking purpose but without prior treatment it is not suitable as it contains more total hardness beyond the permissible limits as recommended by WHO and Indian standards. The conclusion derived from these results is that some physico-chemical parameters examined were consistent with World Health

Organization standard for drinking water (WHO). And for such parameters that had mean values below the recommended WHO standard, water treatment plant should be built for these people to correct these anomalies.

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POTENTIOMETRIC ANALYSIS OF SINGLE COMPONENT PHARMACEUTICAL DRUG PARACETAMOL IN NON-AQUEOUS MEDIUM

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ABSTRACT

Potentiometric analysis of single component pharmaceutical drug paracetamol in non-aqueous medium by using isopropanol as the solvent and KOH in isopropanol as the titrant has been established. The drug paracetamol is distinctly acidic in nature and widely used in medicines and pharmaceuticals. Herein analysis of paracetamol was carried out by performing the titrations using a pair of glass and calomel electrodes. The method was found to be precise for assay of single component tablets and results obtained are comparable with those obtained by Indian Pharmacopoeia (IP) method.

Keywords *: Potentiometric analysis, drug paracetamol, non-aqueous medium*

Introduction

The potentiometric analysis of pharmaceutical drugs in non-aqueous medium has been reported earlier using the pairs of different electrodes[1-5]. For the analysis of single component pharmaceutical drugs, various methods are included in the pharmacopoeias[6-8]. In literature, the estimation of paracetamol by differentiating potentiometric titrations has been reported[9-11]. The potentiometric, pH-metric, spectrophotometric and colorimetric determinations of paracetamol were reported earlier in few communications[12-17]. The drug paracetamol was also analyzed by fluorimetry, voltametry, HPLC and UV spectrometry[18-21]. As the drug paracetamol is distinctly acidic, it could not be titrated directly with aqueous alkali due to its hydrolysis. The basic titrant is also superior to the alkoxide solvents, which are more susceptible to the atmospheric moisture and carbondioxide.

The aim of present work is to find out simple technique for analysis of common drugs which will help the determination of raw materials and products for quick check of spurious drugs that are feared to penetrate the markets. In this paper, potentiometric analysis of single component pharmaceutical drug paracetamol in non-aqueous medium was worked out using the solvent isopropanol and titrant KOH in isopropanol.

Material and Methods

The potentiometric titrations were carried out by using a digital potentiometer (Equiptronics, EQ-602). Glass and calomel electrodes were used as indicator and reference electrode respectively. Weighing of all the drugs and chemicals was made on Precisa-310-M (±0.001 g) balance. The chemicals and solvents of AR grade were used. All solvents were purified and made anhydrous by standard methods[22]. Care was taken to protect the titrant from atmospheric moisture and carbon dioxide. The drug paracetamol selected for present investigation was obtained from pharmaceutical laboratories and it is included in pharmacopoeias[6-8].

In this analysis, drug paracetamol containing ten tablets of the same batch were powdered. The powder containing 500 mg of the drug was weighed accurately, treated with 50 ml of isopropanol and stirred vigorously to dissolve the active components of drug. The common additives present in pharmaceuticals are calcium carbonate, sugars, gum etc. which are mostly insoluble in isopropanol. The solution was filtered, residue was washed two to three times with isopropanol and the volume of solution was made to 100 ml with isopropanol. An aliquot of 10 ml of solution was diluted to 20 ml with isopropanol and titrated potentiometrically with 0.1 M of solution of KOH in isopropanol using glass-calomel electrode pair. The titrant was standardized potentiometrically with 0.1 M benzoic acid in isopropanol. The end points were determined by plotting graphs and the amount of drug present in titrated weights of tablet powder was calculated. The amount of active component (drug) present in single tablet was calculated from the average weight. The same tablets

were then analyzed by method given in pharmacopoeias and results obtained were compared.

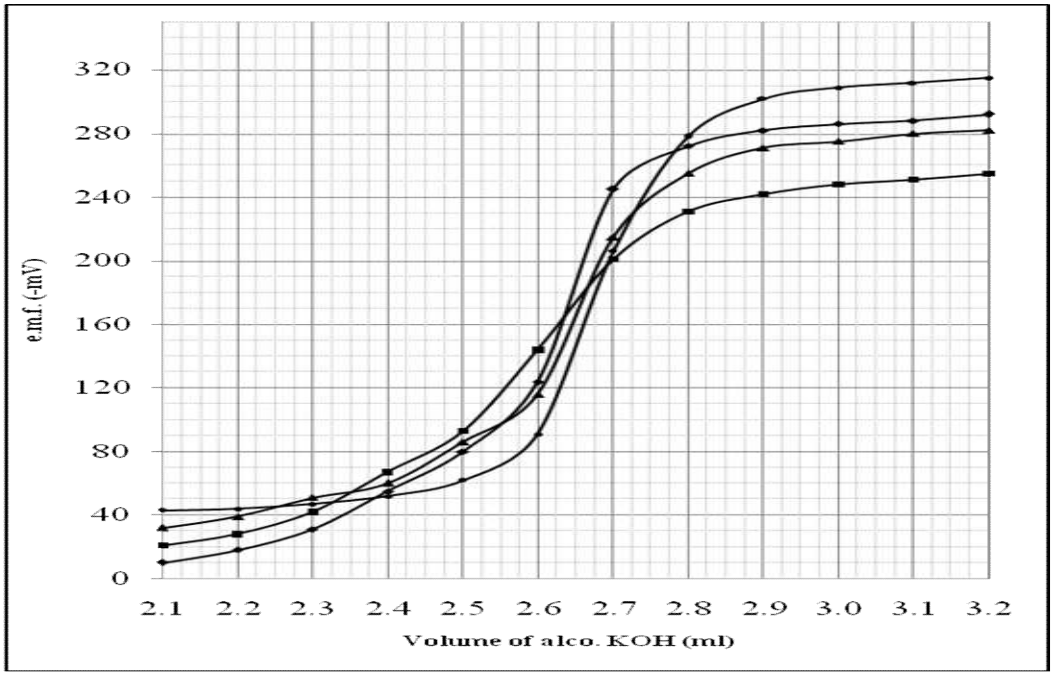
Results and Discussion

The drug paracetamol containing ten tablets of the same batch were powdered. The required quantity of powder was weighed accurately, extracted with isopropanol and the volume was made to 100 ml. An aliquot of 10 ml of solution was diluted to 20 ml with isopropanol and titrated potentiometrically with KOH in isopropanol. The titrant was standardized potentiometrically using standard benzoic acid in isopropanol. The weight of paracetamol present in single tablet was calculated. Same tablet was analyzed by IP method. The results obtained for four different brands of tablets are tabulated and it is found that, the non-aqueous potentiometric analysis gives fairly accurate and comparable results to those obtained by IP method (**Table 1)**. This method is better, accurate and simple than other methods reported in the literature. It is free from indicator error and interferences. The drug paracetamol gets hydrolyzed in presence of aqueous alkali but it is avoided in non-aqueous medium. The common additives present in the pharmaceuticals are calcium carbonate, sugars, gum etc. and as these are insoluble in isopropanol do not affect the results.

Table-1 : Analysis of single component pharmaceutical drug paracetamol

Sample	Label Claim (mg)	Weight Found (mg)	
		IP Method	Present Method
P1	500.0	499.67	499.91
P2	500.0	498.46	500.11
P3	500.0	498.56	499.86
P4	500.0	498.78	500.05

Graph-1 : Analysis of single component pharmaceutical drug paracetamol



Conclusion

The potentiometric analysis of single component pharmaceutical drug paracetamol in non-aqueous medium gave better results. As paracetamol is distinctly acidic, it could not be titrated directly with aqueous alkali because to its easy hydrolysis. The solvent isopropanol is found to be excellent for all titrations. The basic titrant, KOH in isopropanol was superior to the alkoxide solvents that are more susceptible to atmospheric moisture and carbondioxide. It gave better potentiometric breaks. The glass-calomel electrode pair gave

stable potentials which were quickly attained. The potentiometric breaks obtained using glass-calomel electrode pair were quite larger. In present work, method developed for analysis of acidic drug paracetamol is simple, precise and it can be used in common laboratories without use of any sophisticated instrument.

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STUDY OF 'TEMPERATURE, BOD, PH, DO' OF DISTILLERY WASTE WATER: BEFORE AND AFTER TREATMENT PROCESS

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ABSTRACT

Untreated effluent is found to have low contents of DO and high contents of BOD. According to the permissible limit suggested the BIS the untreated effluents is toxic to crop field so it is not permissible for irrigation. The results reflect that the treated effluents are not highly polluted and they satisfy the BIS values and therefore can be used for irrigation purposes. This paper study status of physicochemical parameters like Temperature, DO, BOD and pH values: before and after treatment of the distillery wastewater.

Keyword: *BOD, DO and pH, Distillery spent wash, physiochemical parameter, effluent.*

1. Introduction

In developing countries like India, the problems associated with wastewater reuse arise from its lack of treatment (Kaur, *et al.,*2012),Some industrial waste water contains harmful physicochemical parameters that not only affect crop growth but also reduce soil fertility.Effluent originating from distilleries known as spent wash leads to extensive soil and water pollution (Pant and Adholeya,2007).The distillery industry is one of them in this regard. Therefore, the present study is under taken to assess the level of physiochemical parameters of the distillery spent wash. These parameters will compare with BIS limit. The aim of this study was to analyze the dissolved oxygen and the biochemical oxygen demand.

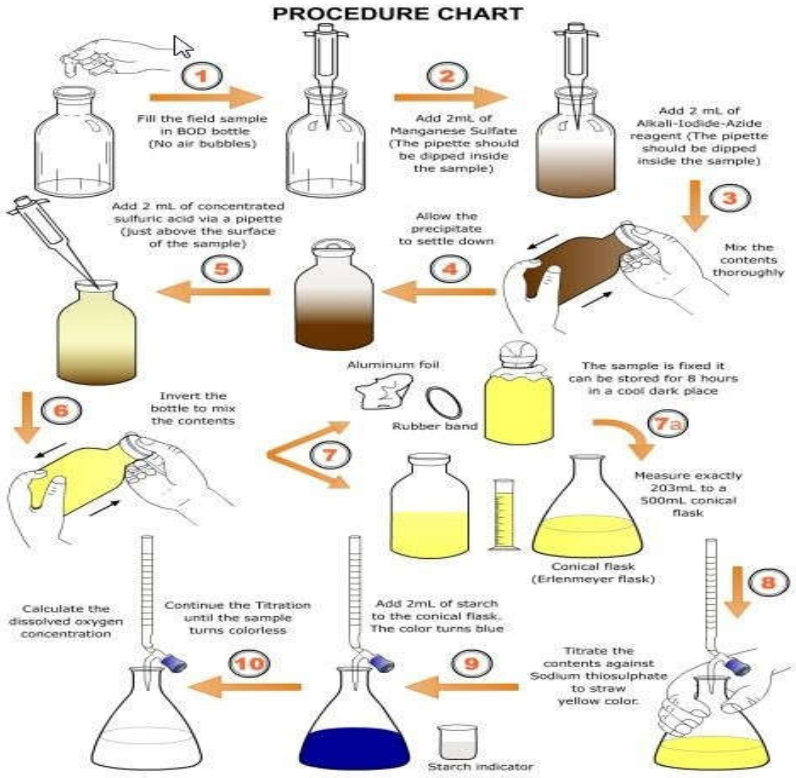
2. Methodology

a. Dissolve Oxygen

The presence of dissolved oxygen in wastewater is desirable because it prevents the formation of noxious odours.The presence of oxygen in water in dissolved form is necessary to keep it fresh. Dissolved oxygen is also important to aquatic life because detrimental effect can occur when DO levels drop below 4-5 mg/L, depending upon the aquatic species.Oxygen levels that remain below 1-2 mg/L for few hours can result in fish kills.

Dissolved oxygen is determined by Winkler's method: Fill the 125-water sample in BOD bottle, avoiding bubbles. Add 1 ml of each $MnsO_4$ and alkaline KI solutions. Shake the bottle thoroughly brownish collared precipitate will occur. Add 2 ml con.H_2SO_4 along the side of the bottle Then shake the bottle to dissolved precipitate. Take a 50 ml above solution in a 250 ml conical flask and titrate with 0.025N sodium thiosulphate using indicator as a starch. Noted the end point where the blue colour changes to colourless.

Chemical and Biological oxygen demand of the samples before and after the treatment were determined using potassium dichromate and Winkler's method (Yamuna, *et., al.*,2015)



b. Biological Oxygen Demand

The extent of oxygen consumed by the organic matter present in water sample is known as Biochemical Oxygen demand (BOD). The BOD of raw water will indicate the extent of organic matter present in the water. If sufficient oxygen is present in water, the useful aerobic bacteria production will flourish and cause the biological decomposition of waste and organic matter, thereby reducing the carbonaceous material from the water.The amount of oxygen required in the process until oxidation gets completed is known as BOD. Polluted waters will continue to absorb oxygen for many months, till the oxidation gets completed and it is not practically possible to determine this ultimate oxygen demand. Hence the BOD of water during the first five days at 200 C. The dissolved oxygen is measured after the period of incubation. The difference between the original oxygen content and the residual oxygen content will indicate the oxygen consumed by the water sample in five days. If BOD of water is zero it means that no oxygen is required and thus no organic matter is present.The extent of pollution of sewage and other industrial wastewater is also measured by determining the values of their BOD.

3. Results and discussion:

The results of the Parameters analysis in treated effluent and un treated effluent are given in table (1)

Table: -1 Observation Table Untreated Effluent

Sr. No.	Parameter	Treated Effluent	Untreated Effluent	BIS standard
1	Colour	Light Brown	Light Brown	-
2	Temperature	40 °C	38.9 °C	-
3	pH	4.5	7.2	6.5-9.0
4	DO	2.3 Mg/Lit	5.5 Mg/Lit	4-6 mg/l
5	BOD	7000 Mg/Lit	102 Mg/Lit	500000 mg/l

Results were supported by appreciable reduction in case of most of the parameters were observed, especially colour, BOD, etc. This is very significant from the toxicological

implications for discharging spent wash effluent in the water bodies. In the present study, the results indicate that the BOD content was very high before treatment it is about 7000 mg/lit and it is reducing after treatment 102 mg/lit. this results agreement with Tripathi, *et., al,* 2015) status of BOD, DO and pH values before and after treatment of the distillery wastewater. The aquatic region may not function correctly if BOD is high. Because of the low levels of DO, which is poisonous to plants, it is not suitable for irrigation.

Conclusion

It may conclude that treatment is an essential aspect of distillery wasted wash, with BOD concentration being the most critical treatment. Treated effluent of distillery plant which is well balanced of chemicals if it is diluted with other fresh water, will be suitable for irrigation purposes.BOD indicates the amount of organic matter present in the water. Therefore, a low BOD is an indicator of good quality water, while a high BOD indicates polluted water.

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SYNTHESIS OF PYRAZOLES AND THEIR ANTIBACTERIAL ACTIVITIES.

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ABSTRACT

As a part of systematic investigation of synthesis, spectral analysis and biological activity of some pyrazoles with aroylflavone on treatment with phenylhydrizine hydrochlorides ($PhNHNH_2.HCl$) in DMSO containing few drops of piperidine as medium. We got two series ,while carried out in different aromatic acids. In series, we got, 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(3-nitro phenyl) -1-pyrazole and 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(3'-nitrophenyl) -1-pyrazole. It has been revealed that, the use of piperidine in DMSO as the solvent in the above reaction influences the rate of the reaction and also the yield of the products.. All these compounds have been analyzed by UV, IR and NMR for the structure. The newly synthesized pyrazoles were screen for their antibacterial activities.

Keywords; *Pyrazoles, Aroylflavone, Antibacterial activities.*

Introduction

Pyrazole is a five membered heterocyclic compound containing two nitrogen atoms in the 1,2 positions placed in the heterocyclic ring. Many workers have synthesized different pyrazoles [1-7]. Heterocyclic compounds are very useful units in the fields of medicinal and pharmaceutical chemistry and have been reported to exhibit a variety of biological activities [8-13]. 3-aroylflavone on treatment with $NH_2OH.HCl$. It has been revealed that, the use of piperidine in DMSO as the solvent in the above reaction influences the rate of the reaction and also the yield of the products. 3-aroylflavone on treatment with NH2OH.HCl to gives final product. It has been well focused that, the presence of chlorosubstituted moieties is an important structural feature also, the present work were screen for their antibacterial activities.

It has been well established that the presence of 4-anisoyl (2-hydroxy-3, 5-dichloro) moieties is an important structural feature .Also 3-nitrphenyl groups present in pyrazoles hope that, the resulting molecule would exhibit promising biological properties as in table II

Experimental

All the glassware's used in the present work were of Pyrex quality. Melting points were determined in open capillary and are uncorrected. Purity of compounds was monitored on silica gel coated TLC plate. The IR spectra were recorded on `Perkin-Elmer 202` Infra red spectrophotometer 1310. The UV-VIS spectra were recorded on Systronics 119 spectrophotometer. The PMR spectra were recorded on Varian Mercury YH - 300 spectrometer in $CDCl_3$. The analytical data of compounds were highly satisfactory. All the chemicals used were of analytical grade. All the solvents used were purified by standard methods. Physical characterization data of all the compounds are given in Table-1.

The synthetic methods used in present work are given below along with their UV, IR and NMR data.

2-Hydroxyacetophenones (2)

2-Hydroxy-5-chloroactophenone (2a), m.p.56^{o}C and 2-hydroxy-3, 5-dichloroacetophenone, (2b), m.p. 53^{o}C were used as starting materials. The former was prepared by known method while the later was prepared by a new method invented by Rajput et al.

Preparation of 2-hydroxy-3, 5-dichloroacetophenone (2b)

2-Hydroxy-5-choloroacetophenone (3g) was dissolved in acetic acid (5ml). Sodium acetate (3g) was added to the reaction mixture and then chlorine in acetic acid reagent (20ml) (7.5 w/v) was added drop wise with stirring. The temperature of the reaction mixture was maintained below 20^{o}C. The mixture was allowed to stand for about 30 minutes. Finally it was poured into water with stirring. The pale yellow solid product thus separated was filtered

and crystallized from ethanol, m.p. 53°C yield 1.5g.

IR (KBr): 3040 (-OH phenolic stretching); 1660 (>C=O stretching); 1345 (-OH bending in phenol); 650 (C-Cl stretching).

PMR: □ 2.60 (s, 3H, -ArOCH$_3$); □ 7 to 8 (s,2H, -ArH); □ 12.11 (s, 1H, Ar-OH).

UV: 346nm.

Scheme-1

Preparation of 2-benzoyloxy -3, 5-dichloroacetophenone (3a)

2-Hydroxy-3,5-dichloroacetophenone (0.04 mol) and benzoyl- chloride (0.05mol) were dissolved in NaOH (10%) (30ml). The reaction mixture was shaken for about half an hour. The product thus separated was filtered, washed with water followed by sodium bicarbonate (10%) washing and then again with water. The solid product was crystallized from ethanol to obtain 2-benzoyloxy-3,5-dichloroacetophenone (3a), m.p.66°C, yield 76%.

IR (KBr): 3040 (-OH phenolic stretching); 1660 (>C=O stretching); 1345 (-OH bending in phenol); 650 (C-Cl stretching).

PMR: □ 2.60 (s, 3H, -ArOCH$_3$); □ 6.8 to 7.64 (m,2H, -ArH); □ 12.7 (s, 1H, Ar-OH).

UV: 346 nm.

Preparation of 1-(2-hydroxy-3,5-dichlorophenyl)-3-phenyl-1,3-propane-dione (4a):

2-Benzoyloxy-3,5-dichloroacetophenone (3a) (0.05 mol) was dissolved in dry pyridine (40ml). The solution was warmed up to 60°C and pulverized KOH (15g) was added slowly with constant stirring. After 4 hours of heating the reaction mixture was acidified by adding ice cold dil. HCl (1:1). The brownish yellow solid product thus separated was filtered, washed with sodium bicarbonate solution (10%) and finally again with water. It was then crystallized from ethanol acetic acid mixture to get 1-(2-hydroxy-3-dichloro-phenyl)-3-phenyl-1,3-propanedione(4a),m.p.110°C yield 75%.

IR (KBr): 3030 (-OH phenolic stretching); 1600 (>C=O stretching); 1170 (-OH bending in phenol); 790 (C-Cl stretching).

PMR: □ 3.60 (s, 3H, -ArOCH$_3$); □ 4.56 (s,2H –due to dione) □ 6.6 (s,6H, -ArH);
□ 12.75 (s, 1H, Ar-OH).

UV: 359 nm.

Preparation of 3-anisoyl-2-(3'-nitrophenyl)-6,8-dichloroflavanone(5a)

A mixture of 1-(2-hydroxy-3,5-dichlorophenyl)-3-phenyl-1,3 -propanedione (4a) (0.01mol) and 3-nitrobenzaldelyade (0.012 mol) was refluxed in ethanol (25ml) and piperidine (0.5 mol) for 15-20 min. After cooling, the reaction mixture was acidified with dil HCl (1:1) and the product thus separated, was crystallized from ethanol-acetic acid mixture to get the compound (5a), m.p.187°C yield 80%.

IR (KBr): 3070 (-OH phenolic stretching); 1650 (>C=O stretching); 1550 (-NO$_2$ stretching); 758 (C-Cl stretching).

PMR: □ 3.08 (s, 3H, -ArOCH$_3$); □5.3 (d,1H –CH$_A$-CH):□□5.9 (d,1H –CH-CH$_A$): □ 6.76 to 8.08 (m,10H, -ArH);

UV: 262 nm.

Formation of 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(3-nitrophenyl)-1-Phenyl pyrazole (6a):

A mixture of 3-anisoyl-2-(3-nitrophenyl)-6,8-dichloroflavone (5a), (0.01 mol) and PhNH NH$_2$OH.HCl (0.02 mol) was refluxed in DMSO (20ml) containing a few drops of piperidine (0.5 ml) for about 1.5 hrs. After cooling, the reaction mixture was acidified with dil. HCl (1.1). The product thus separated was filtered, washed first with sodium bicarbonate solution (10%) and then with water. Finally it was crystallized from ethanol-acetic acid mixture to get the compound(6a), m.p. 175°C, yield 75%.

IR (KBr): 3440 (-OH phenolic stretching); 1602 (>C=O stretching); 1554 (>C=N stretching); 810 (C-Cl stretching).

PMR: □ 3.01 (s, 3H, -ArOCH$_3$); □ 7.22 to 8.06 (m,15H, -ArH); □ 10.00 (s, 1H, -ArOH);

UV: 444.8 nm

Scheme-2

Preparation of 2-anisoyloxy-3, 5-dichloroacetophenone (3b)

2-Hydroxy-3,5-dichloroacetophenone (2b) (0.04mol) and anisic acid (0.05mol) were suspended in dry pyridine (30ml) and to this POCl$_3$ (3ml) was added drop wise with constant stirring and cooling. The reaction mixture was kept for overnight and then worked up by dilution and acidification with

ice cold HCl (50%) to neutralize pyridine. The solid product thus obtained was filtered washed with water followed by sodium carbonate (10%) washing and finally again with water. It was crystallized from ethanol to obtain 2-anisoyloxy-3,5-dichloroacetophenone (3b), m.p. 111°C and yield 74%.

IR (KBr): 3045 (-OH phenolic stretching); 1680 (>C=O stretching); 1365 (-OH bending in phenol); 670 (C-Cl stretching).

PMR: □ 2.65 (s, 3H, -ArOCH$_3$); □ 6 to 7.64 (m,2H, -ArH); □ 12.5 (s, 1H, Ar-OH)

Prepration of 1-(2-hydroxy-3,5-dichlorophenyl)-3-(4'-methoxypehnyl)-1,3-propanedione (4b)

2-Anisoyloxy-3,5-dichloroacetophenone (3b) (0.05 mol) was dissolved in dry pyridine (40 ml). The solution was warmed at about 60°C and pulverized KOH (0.15 mol) was added slowly with constant stirring. After 4 hours the reaction mixture was acidified with ice cold dil. HCl (1:1) and processed as described in (4a) to get the compound , 1-(2-hydroxy-3,5-dichlorophenyl)-3-(4'-methoxyphenyl)-1,3-propanedione (4b), m.p. 114°C, yield 75%.

IR (KBr): 3045 (-OH phenolic stretching); 1650 (>C=O stretching); 1160 (-OH bending in phenol); 760 (C-Cl stretching).

PMR: □ 3.50 (s, 3H, -ArOCH$_3$); □ 4.35 (s,2H –due to dione) □ 6.3 (s,6H, -ArH); □ 12.6 (s, 1H, Ar-OH)

UV: 348 nm

Preparation of 3-benzoyl-2-(3'-nitrophenyl)-6,8-dichloroflavanone(5b)

A mixture of 1-(2-hydroxy-3,5-dichlorophenyl)-3-(4'-methoxy-phenyl)-1,3-propanedione (4b) (0.01mol) and 3-nitrobenzaldenyde (0.012mol) was refluxed in ethanol(25ml) and piperidine (0.5 ml) for 15-20 min. After cooling, the reaction mixture was acidified with dil HCl (1:1) and the product thus separated, was crystallized from ethanol-acetic acid mixture to get the compound (5b) m.p.175°C yield 78%.

IR (KBr): 3065 (-OH phenolic stretching); 1645 (>C=O stretching); 1535 (-NO_2 stretching); 748 (C-Cl stretching).

PMR: □ 3.06 (s, 3H, -ArOCH$_3$); □5.8 (d,1H –CH$_A$-CH):□□5.6 (d,1H –CH-CH$_A$): □ 6.66 to 8.10 (m,10H, -ArH);

UV: 444 nm

Formation of 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(3-nitrophenyl)-1-Phenyl pyrazole (6b)

A mixture of 3-benzoyl-2-(3-nitrophenyl)-6,8-dichloroflavone (5b), (0.01 mol) and PhNH NH_2OH.HCl (0.02 mol) was refluxed in DMSO (20ml) containing a few drops of piperidine (0.5 ml) for about 1.5 hrs. After cooling, the reaction mixture was acidified with dil. HCl (1.1). The product thus separated was filtered, washed first with sodium bicarbonate solution (10%) and then with water. Finally it was crystallized from ethanol-acetic acid mixture to get the compound(6b), m.p. 175°C, yield 75%.

IR (KBr): 3420 (-OH phenolic stretching); 1610 (>C=O stretching); 1524 (>C=N stretching); 815 (C-Cl stretching).

PMR: □ 3.05 (s, 3H, -ArOCH$_3$); □ 7.00 to 8.00 (m,15H, -ArH); □ 10.00 (s, 1H, -ArOH);

UV: 425 nm

Results and Discussion

The compound (3a-6a) and (3b-6b) were studied the antibacterial activities against some human pathogens *S.aureus ,S.typhi ,C.gulkar ,A.niger* Species at 1000 µm gentamycine as a standard.DMF was used as solvent control using agar plate techniques.The zones of inhibition formed were measured in mm and are shown in Table 2. It gives following results. It was observed that,hetero atoms increase the antibacterial activity of compounds from (5a-6a) and (5b-6b).

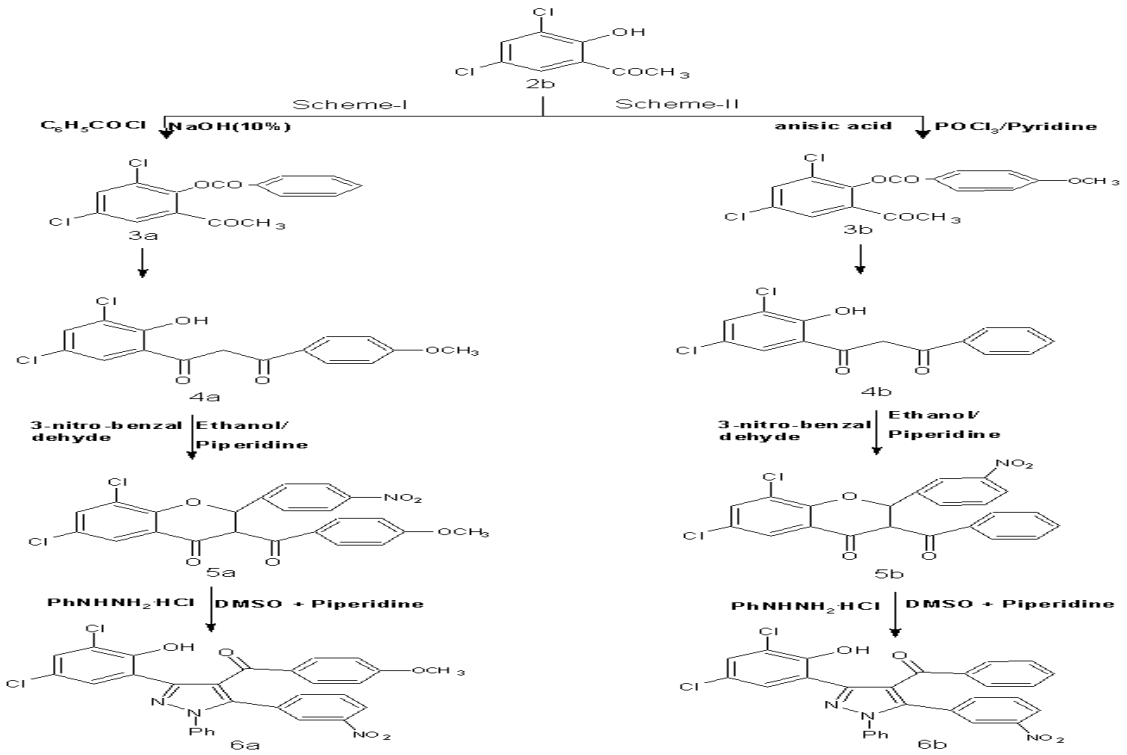
Table (1): Characterization data of synthesized new compound

Compound	Molecular Formula	M.P. (°C)	Yield (%)	Rf
2	$C_8H_6O_2Cl_2$	53	75	0.84
3a	$C_{15}H_{10}O_3Cl_2$	66	76	0.66
4a	$C_{15}H_{10}O_3Cl_2$	110	75	0.71
5a	$C_{23}H_{15}O_6\ NCl_2$	175	68	0.78
6a	$C_{29}H_{19}O_5N_3Cl_2$	190	75	0.72
3b	$C_{16}H_{12}O_4Cl_2$	66	76	0.66
4b	$C_{16}H_{12}O_4Cl_2$	114	75	0.81
5b	$C_{22}H_{13}O_5\ NCl_2$	187	80	0.65
6b	$C_{28}H_{17}O_4N_3Cl_2$	198	80	0.64

Table-2 Effects of newly synthesized compounds on Human pathogens

S. N.	Test Compounds	Zones of inhibition (mm)			
		Human Pathogens			
		S. aureus	***S. typhi***	***C. gulkar***	***A. niger***
1	2a	++	++	++	++
2	2b	++	++	+++	++
3	3a	++	+++	++	++
4	3b	+++	++	++	++
5	4a	++	+++	+++	+++
6	4b	+++	++	+++	+++
7	5a	+++	+++	+++	++++
8	5b	+++	+++	+++	+++
10	6a	++++	++++	++++	++++
11	6b	++++	++++	++++	++++

++++ Very Strongly active range
+++ Strongly active range
++ Moderately active range
\+ Weakly active range
\- Inactive range



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ROLE OF ALLOPATHY & AYURVEDA IN CONTROLLING COVID-19: A REVIEW

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ABSTRACT

In December 2019, COVID-19 takes place in Wuhan city of China. Due to this more than 210 countries and about 34 million people were died globally. COVID -19 is a viral disease, and the name of the virus is CORONA. The symptoms of COVID-19 are flu, cough, headache etc. Our whole world is suffering from the pandemic which is known as COVID-19. There are many scientists, researchers and healthcare centers are trying to cure from this pandemic with the help of the technologies and the medical science. Ayurveda and Allopathy have great approaches to cure from COVID-19. With the Ayurvedic and Allopathy treatment the Ministry of India also recommended that every individual should have to boost up the immunity and to increase the immunity they also recommended many home remedies. In Allopathy there are various antiviral drugs available which has been recommended by the doctors for the treatment of COVID-19 along with the treatment of Corona. At present the comparative analysis of the treatment of Ayurveda and Allopathic treatment for COVID-19 is carried out. On the basis of the symptoms and the conditions of the patient's there are various treatments in Ayurveda for COVID-19. The Allopathy treatment inhabits the viral infection by targeting the receptors which are responsible for spreading the virus. In this article, we have summarized the different treatments and the medicines which has been suggested by the Ayurveda and Allopathy and the strategies for the treatment of the COVID-19 which is a well-known as global pandemic.

Keywords: *COVID-19, the causes, Symptoms, Ayurveda, Allopath.*

Introduction

In the last few 10 years, there are different strains of corona viruses because of different strains it had presented the different health issues to the humans. Most commonly the coronavirus effects the respiratory system is (SARS-CoV) and the middle respiratory system get affected by the corona virus (MERS-CoV). The spread of the infection which is caused because of the coronaviruses is mostly increases due to the increase in the population, migration of peoples from one place to another place [1]. In 2003, severe acute respiratory syndrome coronavirus was one of the dangerous infectious diseases in the world for human being. Approximately 1800 humans were infected and 300 major cases were found in 2003 because of Severe acute respiratory syndrome The severe acute respiratory syndrome coronavirus (SARS-CoV-2019) emerged in 2019 in the month of December in Wuhan city of China, which again made the life of humans miserable with numerous fatal health issues and slowly and gradually this virus entrapped the whole world [2, 3]. The crown-shaped coronavirus leads to serious infections which was a brief part of the human SARS virus and affected the whole world which leads to a loss in business, tourism, and human life.

The World Health Organization (WHO) was declared the COVID-19 as an international pandemic; it takes place in our India at the end of the February. The symptoms of Corona are similar to the normal flu but in some patients there were mild symptoms, in some patients there were no symptoms and in some patients the symptoms there were very acute. The spread of the infection is spread so fast that the doctors, scientists and the researcher couldn't get any cure treatment as the lakhs of the people had already infected across the world. Before the doctors, scientists, and researchers could study and come up with a cure for treatment, this virus had already infected more than lakhs of people across the world with the human coronavirus pathogens, i.e., HCoV-22E and HCoV-OC43, which affects the upper respiratory tract. In 2005 the Netherland get affected by the pathogen in which CoV-NL63 and HCoV-HKU1. In 2012 the coronavirus is spread so speedily that Middle East, South Asia and Africa get affected 75%. The primary host of the coronavirus is bats whose pathogen is Pipistrellus bat which has a single-stranded positive RNA. is *Pipistrellus* bats which are single-stranded positive RNA bat viruses which are widely distributed during the coronavirus pandemic and very close to humans for infection [4–7]. We can also say that the Bats were the host of the pandemic

which affects the repository for spreading the in addition to that camels were also responsible for suspecting the infection.[8]. So the bats play a vital role for supply of the alpha and the beta coronavirus [9]. The pandemic which takes place in Wuhan i.e., SARS viruses was caused by the horseshoe bats, but after the study it has been discovered that the Bats were infected by the MERS virus species [10].

Pandemic Virus COVID-19

SAER-CoV is a infectious disease which can be transfer from one vertebrates to another vertebrates. It can be spread through the social contact as well as the migration [11]. The virus can be transfer through the genetic genome which has a basic protein which is known as replicas. The role of the replica is it help in the replication of the genetic genome which has the protein that is replicas. [12]. The symptoms of the coronavirus is like regular cold, fever, facing difficulty in breathing and it can propagate from one to another it means it is a transmission disease. The maximum duration for the recovery recommended by the doctors is 14-15 days. The preventive measures should be followed as per the prescription such as sanitization, social distancing, wearing a masks and the gloves. And the best remedy is the Self- quarantine so that the infection can be controlled.

During pandemic of COVID-19 the Ministry of AYUSH gives some preventive measure to control the spread of virus in people. The people were divided into four specific classifications along with characters and natural herbs for treatment which is tabulated in Table 1.

Table: 1 (Classification of characters and natural herbs)

Group	Characters	Hubs
No symptoms and also unexposed	Do not assimilate those people who do not have related side effects neither they have hazard issues. They doubtless they are most likely invulnerable from disease because of parthenogenesis	For purification of the body herbs like Allium sativum strip, Curcuma longa powder, Trachyspermum ammi seeds, and Loban were used whereas for respiratory tract Swarna Prashana, and mass prophylaxis of rasayana, Brahma Rasayana, Chyavanprasha or Amrit Bhallataka, Rasayana + Samhita were used
Mild symptoms	Have very less symptoms like fever, tiredness, cough, etc. and no need to be hospitalized. Home quarantine and to maintain social distance with family members too.	Nardiya, Ginger Root, Gojihvaadi Kashaya, Pippali rasayana, Sanjeevani vati, C. vati, Solanum surattense, Dashamul kwath, Talishadi Sitopaladi, and Yashtimadhu
Medium symptoms	Moderate to maximum symptoms. Took place with high hazard gathering. Severe symptoms like difficulty in breathing, pain in chest, and deafness; also, they can lose movement too. The patient took into consideration from initial stage and co-recommended with Ayurveda drugs.	P. rasayana, Laghu Vasant Glycyrrhiza glabra, Semecarpus anacardium, Tribhuvan keerti rasa Brihata Vata Chintamni rasa, Mrityunjaya rasa, and Siddha makardhvaja rasa
Quarantined	People who did not have any clear signs but still they are in danger because of contact history with patients. Tested on the idea of their contact history.	Sanjeevani vati, Chitrakadi vati, Guduchi (Tinospora cordifolia), Shunthi (Zingiber officinale), Haridra (C. longa), Sanjivani vati, T. cordifolia, Z. officinale, C. longa, Ocimum sanctum, Glycyrrhiza glabra, Adhatoda vasica, Andrographis paniculata, Swertia chirata, Moringa oleifera, Triphala

Role of Allopathic in COVID-19

In allopathy there are various treatment available to heal from the coronavirus such as oxygen therapy etc. The virus has the similar property like (HIV). There are different drugs which are used to cure from the coronavirus. The list of the medicine is as follows:

- Chloroquine and Hydroxychloroquine
- Ribavirin:
- Remdisivir:

- Dexamethasone

Role of Ayurveda in interpretation of the Patient's condition Diagnosis

The treatment is bases on the symptoms seen in the patients as well as the season. But still now the proper treatment for the COVID-19 is not yet found. The symptoms as those of a *nija jwara* (caused by the disequilibrium of the bodily doshas), a fever with *Vata-kapha* predominance and gave appropriate medicines, diet and regimen.

The final diagnosis was received supported the vast literature available on COVID-19 within the property right [7,8] and symptoms as reported by the patient. Fevers are classified consistent with the aggravated doshas (disease-causing factors), which allows us to know all kinds of latest and emerging fevers.

Pathophysiology *(*Samprapti)

In this *roga* (disease), the *Roga Marga* is *abhyantara,* SutraSthana, as jwara (fever), *svasa* (respiratory distress) and kasa (cough), the three major symptoms of COVID-19 belong to this roga marga. Abhyantara roga marga is one of the three roga margas or "pathways of disease" as described in Ashtanga Hrdayam. There is Pranavaha sroto dushti , Vimana Sthana, observed in this disease, as there is severe respiratory distress along with other symptoms, sometimes leading to death. The seat of affliction of this disease is primarily *Uras* (chest region).

Etiology

According to MWM, the etiology of this illness is now attributed to a completely unique novel virus belonging to the corona virus (CoV) family. It is now named SARS-CoV-2. In Ayurveda it is often can be classified/correlated with a Vata-kapha predominant fever with all the characteristics of a Janapadodhwamsa *vikara*. It is a highly contagious disease. The methods by which contagious diseases spread from one person to another is described in Susruta Samhita*:* Nidana Sthana*,*

The disease can spread eating with other person in the same plate, by sharing a bed, clothes, etc. It can be spread due to the body contact from infected person to the uninfected person.

Conclusion

COVID-19 is a worldwide pandemic which spreads with as great speed. So it is important to discover so new remedies or some preventive measure to cure form the coronavirus which is a viral disease. In the review the summary is given that how to medical science is utilizing the new therapy and preventive measure to cure from such a pandemic. Because of the rapid growth the rate of the infected peoples the death rate is also increases. . The most reassuring treatment is considered to be remdesivir, which is used as a antiviral drug for the patients. Oseltamivir has not presented with suitability, and corticosteroids are at the present not recommended. Whereas the homeopathy as well as Ayurveda also applicable to cure this patients. Therefore this study concludes that COVID-19 infections are often prevented by following government guidelines and opting immune-boosting Ayurveda routes.

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VISCOMETRIC STUDY OF OF SUBSTITUTED PYRAZOLE CARBOXYLIC ACID IN 70% METHANOL-WATER MIXTURE AT DIFFERENT TEMPERATURE UNDER PHYSICAL PROPARTIES

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ABSTRACT

viscometric study of of substituted pyrazole carboxylic acid in 70% methanol- water mixture at different temperature under physical proparties .Jones-Dole empirical equation analyzed the obtained data .we have studies thermodynamic parameters such as enthalpy change , entropy change and Gibbs free energy change. The interactions between solute-solute, solute-solvent and solvent–solvent interactions are studied.

keywords: *Substituted pyrazole carboxylic acid derivatives, Jones-Dole empirical equation and thermodynamic parameters.*

Introduction

Volumetric and viscometric studies of *N,N'*-bis(salicylaldehyde)-1,3 diaminopropane schiff base in ionic liquid - DMF solutions are reported. [1] Volumetric, viscometric and thermodynamic data gives valuable information about the solute-solute, solute-solvent and solvent–solvent interactions. [2] . Density and viscosity measurements have been studied for substituted 2,3-Dihydroquinazolin-4-(1H)-ones in 70% DMF-water at different temperatures [3] . Viscosity measurements play an important role in medicinal pharmaceutical, and drug chemistry. [4] Number of workers gives information about viscometric studies of some drug such as metformin hydrochloride, ranitidine hydrochloride and tramadol hydrochloride in aqueous solutions. [5] Viscometric studies on substituted 2,3-dihydroquinazolin-4(1H)- one in 70% DMF water have been reported. [6] Most of the modern drugs are studied by viscometric which containing heterocyclic nucleus [7] .Number of workers gives information about viscometric studies of some drug, metformin hydrochloride (MH), ranitidine hydrochloride (RH), and tramadol hydrochloride (TH) in aqueous solutions at different temperatures[8].

Viscosity measurements have been studied by Grunberg and Nissan [9], Hin [10], Tamura and Kurata [11], Katti and Chaudri [12], Sedgwick [13], McAllister [14], Krishnan and Laddha Model [15]. Viscometric study of complexes of poly(vinyl pyrrolidone) with Co^{2}+ was measured . [16] The density and viscosity measurement of (pyridoxine hydrochloride + water) and (thiamine hydrochloride + waterat different temperatures was given . [17] Viscosity for different molal concentration of L-Proline, L-Cerine and L-Histidine in dioxane-water mixture and evaluated the values of viscosity coefficients A and B of Jones-Dole equationhave investigated. [18] Determination of thermodynamic parameters of substituted azomethine drugs viscometrically was reported. [19] Viscosity and values of viscosity coefficients (A and B) of mixture of chromic anhidride, sodium dichromate, sodium chromate and water. They studied the solutesolute interaction, A series of compounds ethyl/methyl-4-(aryl)6-methyl-2-oxo/thioxo-1, 2, 3, 4-tetrahydropyridimidine-5-carboxylate under investigation for acoustical parameters in the present paper was reported.[20]Densities and viscosities of binary mixtures of n-decane + 1-pentanol, + 1-hexanol, + 1-heptanol at temperatures from 293.15 to 363.15 K and atmospheric pressure was studied. [21] Effect of Temperature on Viscosity of Substituted aminopyrimidine in 60% DMF-Water mixture are reported.[22]

Volumetric and viscometric Studies of *N,N'*-Bis(salicylaldehyde)-1,3 diaminopropane schiff base (Salpr) in ionic liquid + DMF solutions are reported. [23] Volumetric, viscometric and speed of sound measurements Studies on molecular interactions of some thiocyanate salts in coaqueous solutions of 1,3-Dioxolane + water is reported. [24] Co(III) complexes in water+alcohol mixtures regardingion association and solvation at different

temperatures are studied.[25] Viscometric Studies on Substituted-2, 3-Dihydroquinazolin- 4 (1H) -ones in 70%DMF-Water are done .[26] Comparison tests for the determination of the viscosity values of reference liquids by capillary viscometers and stabinger viscometer SVM 3001[27] Prediction of viscosity of biodiesel blends using various artificial model and comparison with empirical correlations have been reported.[28] Preparation, characterization, and viscosity studding the single-walled carbon nanotube nanofluids was studied.[29] Neural network for predicting the fragility index and the temperature-dependency of viscosity was studied.[30]

In the present work, viscometric study of substituted substituted pyrazole carboxylic acid is carried out at different temperatures by using their solutions of different concentrations.

Following substituted pyrazole carboxylic acid are used.

1) Ligand A (L_A)= 1- phenyl-3-(4'- methyl) phenyl-1H- pyrazol-4-carboxylic acid

2) Ligand B (L_B)= 1- phenyl-3-(4'- bromo) phenyl-1H- pyrazol-4-carboxylic acid

3) Ligand C (L_C)= 1- phenyl-3-(4'- ethyl) phenyl-1H- pyrazol-4-carboxylic acid

4) Ligand D (L_D)= 1, 3-diphenyl-1H- pyrazol-4-carboxylic acid

The solutions of ligands are prepared in the 70% methanol-water at different temperature (*T*= 295K, 300K, 305K and 310K) and at different concentration.

Experimental

The reported protocol used to synthesizes the ligand of physical parameters are to be explored.[31] Solvents and freshly prepared doubly distilled water are used to analyzed grade. The densities of pure solvent and solutions of various concentrations were measured at different temperatures using a specific gravity bottle. All the weights are taken on one pan digital balance (petit balance AD-50B) with an accuracy of ± 0.001 gm. Viscosities of the solutions are determined with the help of calibrated Ostwald viscometer (± 0.11% $Kgm^{-1}s^{-1}$). The flow time of solutions are measured by using digital clock (Racer Company) having an accuracy up to ±0.01Sec

Results and Discussion

To calculate the relative and specific viscosity the following empirical equations are useful.[32]

$$\eta_r = \frac{\eta}{\eta_o} = \frac{d_s \times t_s}{d_o \times t_o} \quad (1)$$

$$\eta_{sp} = (\eta_r - 1) \quad (2)$$

Where,

η_r = Relative viscosity
η_{sp} = Specific viscosity
η = Viscocity of solution
η_o = Viscosity of solvent
d_s = Density of solution
d_o = Density of solvent
t_s = Flow time for solution
t_o = Flow time for solvent

The viscosity data can be analyzed by Jones-Dole empirical equation.[33]

$$\frac{(\eta_r - 1)}{\sqrt{C}} = \frac{\eta_{sp}}{\sqrt{C}} = A + B\sqrt{C} \quad (3)$$

Where, *A* = Falkenhagen coefficient
B = Jones-Dole coefficient
C = Concentration of solutions

The Falkenhagen coefficient (*A*) reflects the solute-solute interactions while Jones-Dole coefficient (*B*) reflects the solute-solvent interactions.[34]

In present study with increase in concentration, the relative viscosity and density of the compounds increases. The increase in viscosity with increase in concentration credited to the increase in the solute-solvent interactions. The viscosity and density data for different ligands at different concentration is given in table no.1

Table1:Densities(d) and viscosities(η_r) of substituted pyrazole carboxylic acid derivatives at different concentration in 70% (Methanol+ water) solvent at 295K.

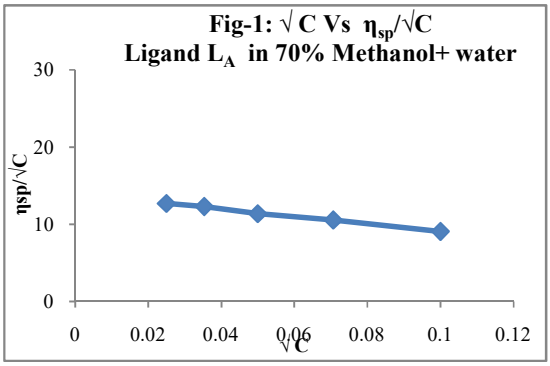
Conc. (C) mol/lit	L_A		L_B		L_C		L_D	
	Density (d)gm/cc	Relative Viscosity(η_r)	Density (d)gm/cc	Relative Viscosity(η_r)	Density(d) gm/cc	Relative Viscosity(η_r)	Density (d)gm/cc	Relative Viscosity (η_r)
0.01	1.0625	2.4727	1.0723	2.4741	1.0441	2.3012	1.0719	2.3262
0.005	1.0610	2.3218	1.0716	2.3218	1.0419	2.1710	1.0687	2.2281
0.0025	1.0590	2.2246	1.0673	2.2259	1.0412	2.0710	1.0682	2.1531
0.00125	1.0582	2.0971	1.0670	2.0969	1.0392	1.9862	1.0669	2.0579
0.000625	1.0574	1.8956	1.0683	1.8947	1.0380	1.8423	1.0659	1.8174

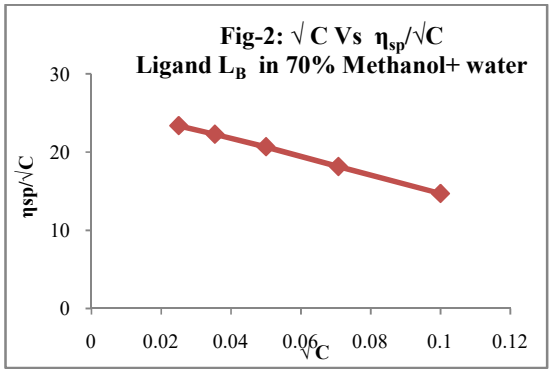
The graphs are plotted between √C versus $\eta_{sp}/\sqrt{C}$. The graphs for each system show the validity of Jones-Dole equation. The values of *A* and *B* have determined from the intercept and slope of √C versus $\eta_{sp}/\sqrt{C}$ respectively. The plots of √C versus $\eta_{sp}/\sqrt{C}$ for all four systems are shown in Fig. no. 1 to 5. From the table no. 2 the *B*-coefficient is found to be negative for all the systems and it is a measure of disorder introduced by the solute into the solvent in all the systems. The Falkenhagen coefficient-*A* is positive in all the systems and this coefficient reflects strong solute-solute interaction.

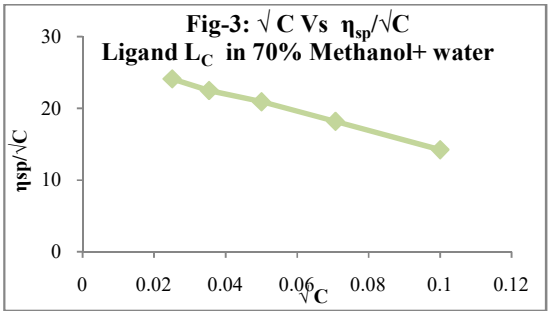
Viscometric study is performed for substituted pyrazole carboxylic acid at following different temperatures 295, 300, 305 and 310K. The experimental data of different ligands is presented in table no. 3.

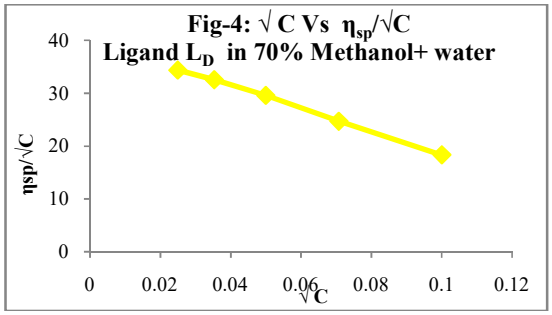
Table 2: *A* and *B* Coefficient values

Ligand + 70% Methanol-Water	*A* (lit$^{3/2}$ mol$^{-1/2}$)	*B* (lit mol^{-1})
L_A	14.828	-50.289
L_B	24.425	-112.12
L_C	25.310	-126.75
L_D	32.025	-218.57









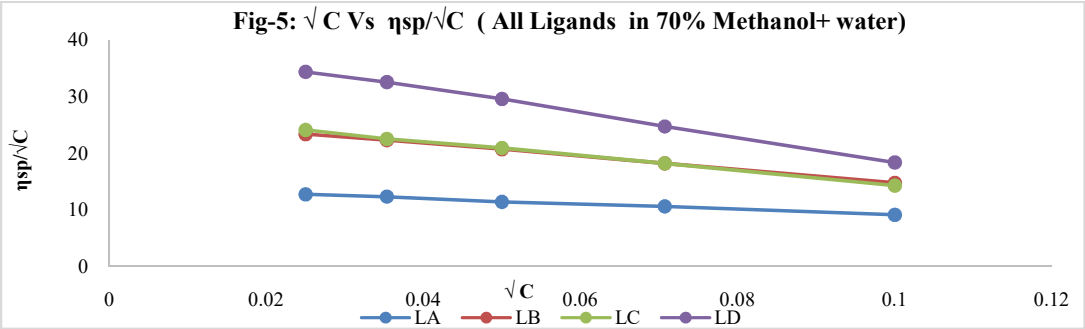


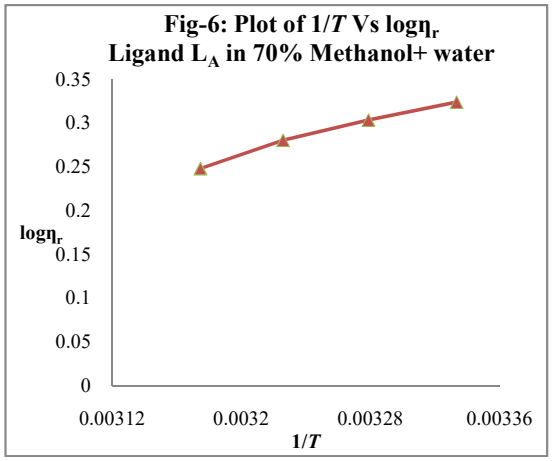
Table 3: Densites (d) and relative viscosities (η_r) of Substituted 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid derivatives of 0.01M concentration in 70% (Methanol+ Water) solvent at different temperature (*T*= 295, 300, 305,and 310K)

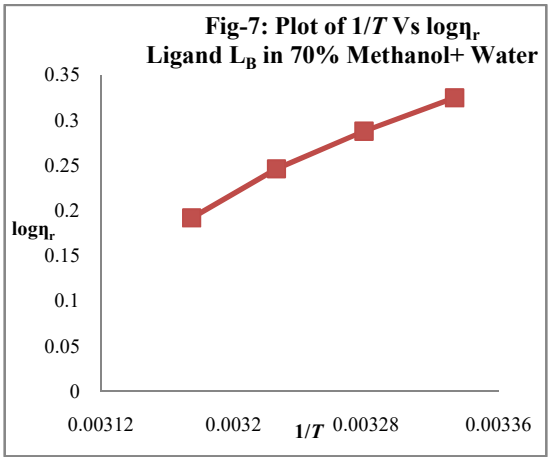
Temp. (K)	L_A		L_B		L_C		L_D	
	Density (d) gm/cc	Relative Viscosity (η_r)	Density (d) gm/cc	Relative Viscosity (η_r)	Density (d) gm/cc	Relative Viscosity (η_r)	Density (d) gm/cc	Relative Viscosity (η_r)
295	1.0630	2.1074	1.0724	2.3832	1.0437	1.0434	1.0720	2.3259
300	1.069	2.0102	1.0717	2.2211	1.1437	1.1429	1.0629	2.2038
305	1.0618	1.9049	1.0703	2.0829	1.2032	1.2026	1.0514	2.0259
310	1.0610	1.7679	1.0690	1.9930	1.1973	1.1968	1.0408	1.8790

The thermodynamic parameter Gibbs free energy change (ΔG), enthalpy change(ΔH) and entropy change (ΔS) are studied for substituted pyrazole carboxylic acid at different temperatures. All these thermodynamic parameters are calculated by plotting graphs between 1/T versus logη_r. These are shown in the fig. no. 6 to 10. These thermodynamic parameters for solutions of different ligands at various concentrations are presented in table no. 4. The values of ΔG and ΔH are found to be negative. The negative values of ΔG and ΔH indicate the reactions are spontaneous and exothermic respectively. The negative value of ΔS indicates that there is an association of solvent molecules around the ligand.

Table 4: Values of thermodynamic parameters for temperature difference(295 to 310K)

Ligands	ΔG (J mol^{-1})	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})
L_A	-1297.2	-4392.1	-97.83
L_B	-1033.4	-3336.3	-72.41
L_C	-1079.5	-3391.8	-75.36
L_D	-1807.2	1503.5	-45.15





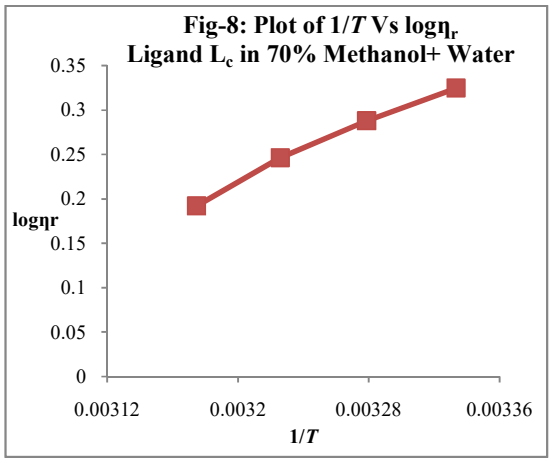


Fig-8: Plot of 1/*T* Vs logη_r
Ligand L_c in 70% Methanol+ Water

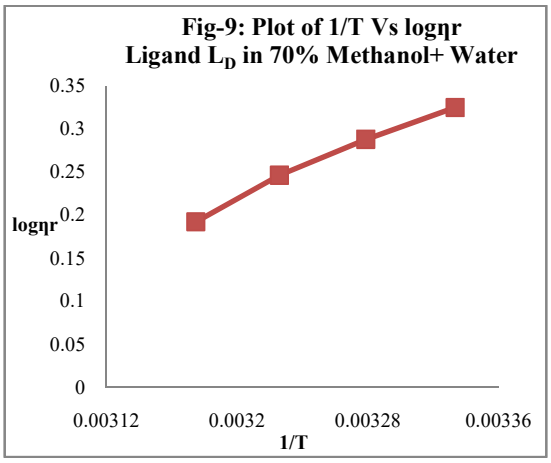


Fig-9: Plot of 1/T Vs logηr
Ligand L_D in 70% Methanol+ Water

Conclusions

In the present work, viscometric study is performed at different temperatures for substituted substituted pyrazole carboxylic acid. It is found that the density and relative viscosity increases as the concentration increases. And it is attributed to the concentration increases the increase in the solute-solvent interaction. *B*-coefficient is found to be negative for all the systems and it measures the disorder introduced by solute into the solvent. The Falkenhagen coefficient-*A* is positive in all the systems and this coefficient reflects strong solute-solute interaction in systems. The negative values of ΔG and ΔH indicates the reactions are spontaneous and exothermic. The negative values of ΔS indicate that there is an association of solvent molecules around the ligand.

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SYNTHESIS OF FLAVANONES AND THEIR SEED GERMINATION PROPERTIES

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ABSTRACT

As a part of systematic investigation, spectral analysis and seed germination (root and shoot elongation i.e Morphology) of chlorosubstituted flavanones from diketones, gives various series by using different aldehydes. As in series, 3-methoxy-8-chlorobenzoylflavanone,3-chlorobenzoyl-8-chloroflavanone,3-benzoyl-8-chloroflavanone.

kewords;- *Diketones, flavanones, root and shoot elongation.*

Introduction

Flavanones are group of common natural polyphenolic compound that are widely found in plant kingdom. It consists of two aromatic ring links through three Carbon bridge with a carbonyl function. Actually these are the class of Flavanoids, which can be subdivided into several classes such as chalcone, flavanones, isoflavanones, aurones etc. The flavanones are mainly distributed in citrus fruitsIn present study, various chlorosubstituted flavanones were synthesized from chlorosubstituted diketones and screened for their morphology (i.e. root and shoot elongation) against some crop plants. Flavanones and their analogues having attracted considerable attention because they possess antioxidant effect, cytotoxic, antimicrobial. Antinflamatory activities etc.

Larget R et.al.[1] reported substituted flavanone & studied as neuroprotective agents. Venkatramn et.al[2] synthesized the flavanone from chalcone by dehydrogenation with SeO2. Yoigtandes et.al. [3] reported the flavanone from flavanone by heating with I_2. Patill[4] synthesized flavanone from by using F2/DMSO as a dehydrogenating agent. Mayer A.M.et.al[5] synthesized cumarine and their role as growth regulators in several plants.. Korade D.L. et.al.[6] reported the effect of Anthracenes on seed germination of *Lolium multiflorum* plants. Gibba Z. et.al.[7] studied the effect of nitric oxide on germination of *Empress tree* seeds.Majumdar, G. p.[8] reported studied the cambial activities of root habit and shoot development in some plants.

The reaction of diketones with various aldehydes gives various flavanones these reactions carried out in presence of ethanol as energy transfer medium in aq.KOH.

It has been well established that, the presence of chlorosubstituted ketones present in flavanones, with the hope that the resulting molecules would exhibit promising root and shoot elongation as shown in table and graph.

Experimental Methods

All the glassware's used in the present work were of Pyrex quality. Melting points were determined in open capillary and are uncorrected. Purity of compounds was monitored on silica gel coated TLC plate. I.R. spectra were recorded on SHIMADZU Spectrophotometer in KBr palates. The analytical data of compounds were highly satisfactory. All the chemicals used were of analytical grade. All the solvents used were purified by standard methods. Physical characterization data of all the compounds are given in Table 1.

Result and discussion

The synthetic methods used in present work are given below along with their, IR data.

Acetylation of P- Chlorophenol

P – Chlorophenol 50 ml was mixed with acitic unhydride 60 ml & unhydrus sodium acetate 5 gm the mixture was refluxed for bout on 1 hrs. it was cooled and poured into cold water. Acetated layer was separated & washed with water several times finally it was purified by distillation and the distillate of compound was collected at about 232^0C. Yield 75%, B.P. 232^0C

2 – Hydroxy 5 – chloro-acetophenone

When Phenyl acetate (50ml) was mixed with anhydrous $AlCl_3$ (120gm) & heated at 120^0C for 45 min on oil bath. The reaction mixture was decomposed with ice cold water containing little hydrochloric acid to get crude ketone. It is purified by dissolving in acetic acid & allowing the solution to fall drop by drop into cold water with stirring. A slightly yellow powder was obtained having M.P. = 86^0C, Yield = 72%

2 – Benzoyloxy 5 - chloroacetophenone

2 – Hydroxy 5- Chloroacetophenone (0.04 mol) & (8.59 ml) Benzoyl Chloride (0.05 mol) were dissolved in NaOH (10 %) (30 ml). The reaction mixture was shaken for about 45 min. The product thus separated filtered, washed with water followed by sodium bicarbonate (10%) again with water. The solid product was crystallized from ethanol to obtain. 2 – benzoyloxy 5-chloroacetophenone white crystal is obtained having M.P. - 87^0C, Yield - 80%.

1 – (2-hydroxyl Phenyl) 5 – Chloro- 3 – Phenyl – 1, 3 – Propanedione:

2 – Benzoyloxy 5 - chloroacetophenone (1.5 gm) was dissolved in (40 ml) dry Pyridine. The solution was warmed up to 60^0C pulverized KOH (15gm) was added slowly with constant stirring. After 4 hours of heating then reaction mixture was acidified by adding ice cold HCl (1 : 1). The brownish yellow solid product thus separated was filtered, washed with sodium bicarbonate solution (10%) and finally again with water. It was then crystallized from ethanol-acetic acid mixture to get 1 – (2-hydroxyl phenyl) 5 – Chloro -3 – Phenyl – 1, 3 – Propanedione. M.P:121^0C, Yield – 75 %.

3 – benzoyl - 8 – chloro flavanone

A mixture of 1 – (2-hydroxyl phenyl- 5 – Chloro 3 – Phenyl – 1, 3 – Propanedione (0.01 mol) (3 gm) & Benzaldehyde (0.12 mol) (1 ml) was refluxed in ethanol (25 ml) and KOH (1 gm) for 15 – 20 min descried to get compound M.P. - 230^0C, Yield - 79%.

3 – Methory – 8-chloro benzoyl flavanone

A mixture of 1 – (2-hydroxyl phenyl)-3 – phenyl – 1, 3 – propanedione (0.01 mol) (3 gm) & anisaldehyde (0.12 mol.) (1 ml) was refluxed in ethanol (25 ml) & KOH (1 gm) for 15 -20 min. & process as descried to get compound, 3 – methoxy-8 – chloro benzoyl flavanone. M.P. - 251^0C, Yield – 72 %.

Table 1: Characterization data of synthesized new compound

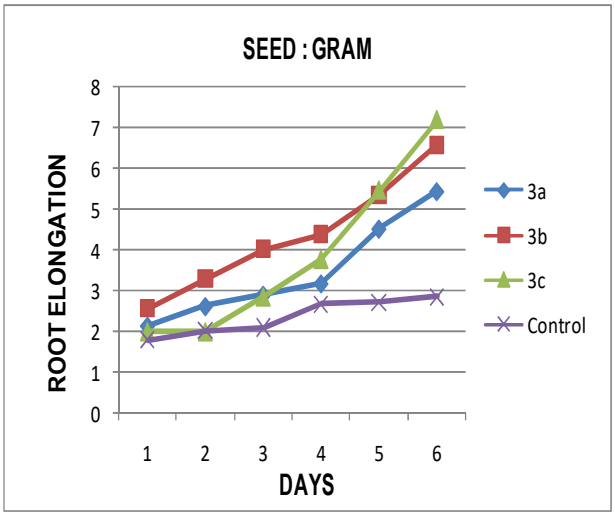
Compound	Molecular Formula	M.P. (^{o}C)	Yield (%)	Rf
3a	$C_{21}H_{13}O_3Cl$	230	79	0.76
3b	$C_{22}H_{16}O_4Cl$	251	75	0.78
3c	$C_{21}H_{14}O_3Cl_2$	240	75	0.79

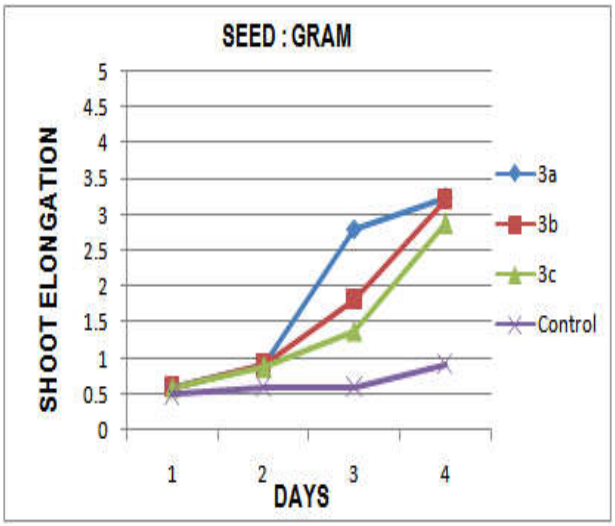
Table No. 1 : Seeds - Gram

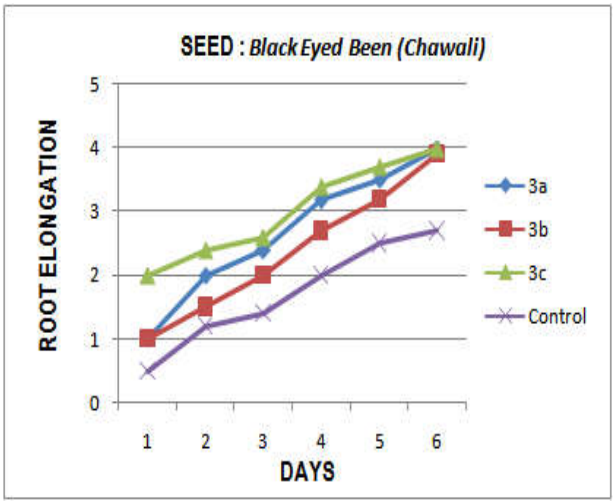
Sr. No.	Comp.	% of germination Day					Average length of root in cm. Day						Average length of shoot in cm. Day					
		2	4	6	8	10	2	4	6	8	10	12	2	4	6	8	10	12
1	3a	80%	100%				1	2	2.4	3.2	3.5	4			0.6	0.9	2.8	3.2
2	3b	80%	100%				1	1.5	2	2.7	3.2	3.9			0.6	0.9	1.8	3.2
3	3c	100%	100%				2	2.4	2.6	3.4	3.7	4			0.6	0.9	1.4	2.9
4	Control	80%	90%				0.5	1.2	1.4	2	2.5	2.7			0.5	0.6	0.6	0.9

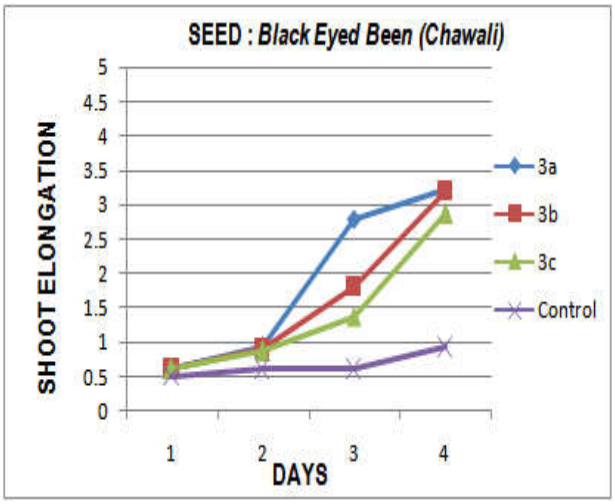
Table No. 2 : Seeds - Black Eyed Beans (Chawali)

Sr. No.	Comp.	% of germination Day					Average length of root in cm. Day						Average length of shoot in cm. Day					
		2	4	6	8	10	2	4	6	8	10	12	2	4	6	8	10	12
1	3a	80%	100%				2.1	2.6	2.9	3.2	4.5	5.4			0.6	0.9	2.8	3.2
2	3b	80%	100%				2.6	3.3	4.0	4.4	5.4	6.6			0.6	0.9	1.8	3.2
3	3c	80%	100%				2.6	3.3	4.0	4.4	5.4	6.6			0.6	0.9	1.8	3.2
4	Control	80%	90%				1.8	2	2.1	2.7	2.7	2.9			0.5	0.6	0.6	0.9









Conclusion

The present study was aimed at investigating the impact of newly synthesized chlorosubstituted flavanone on some crop plants viz: *Gram* and , Black Eyed Been (Chawali). The choice of these crops was based on their enormously vast utility and also the indispensability for the survival of the human race, all across the globe.

The efforts have been made to investigate and analyze the convergence and divergence effect of test compounds on the morphology of plants under investigation. It was interesting to note that, all the treated seeds exhibited remarkable roots and shoots elongation as compared to untreated ones.

When the growth of all the treated plants were compared among themselves, it was distinctly observed that, the change which is dominant

while applying the treated compound i.e. chlorosubstituted flavanones in *Gram, Black Eyed Been (Chawali).* In the initial stage vegetative growth was not significance but after 2nd interval it gradually increases and after 12 days roots and shoots elongation were dominant to a considerable extent. Thus there has been fair amount of satisfaction in crying out the present study. The encouraging results have surely contributed to the enthusiasm of the author. But honestly, this is just the beginning. There is a much scope for further study, and there is a long way to go.

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SYNTHESIS OF NEW 2-THIOHYDANTOIN

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ABSTRACT

2 hydroxy substituted calcone (I a-d) was dissolved in DMSO and mercuric acetate was added to it. The reaction mixture was refluxed for 2-3 hours and then diluted with water. The solid separated was crystallized from rectified sprit to give coumarone 3-one i.e. aurone (II a-d). Substituted aurone further refluxed with thiourea in ethanolic KOH for 3 hours gives substituted thiohydantoin. The structural elucidation of compound was done on the basis of analytical and spectral data.

***Keywords**: Synthesis, coumarone 3-one, mercuric acetate, thiourea, ethanolic KOH,.*

Introduction

Thiohydantoins are sulfur analogs of hydantoins with one or both carbonyl groups replaced by thiocarbonyl groups[1]. Among the known thiohydantoins, 2-thiohydantoins are most notably known due of their wide applications as hypolipidemic[2] , anticarcinogenic[3] , antimutagenic[4] , antithyroidal[5], antiviral (e.g., against herpes simplex virus, HSV)[6] , human immunodeficiency virus (HIV)[7] and tuberculosis[8], antimicrobial (antifungal and antibacterial)[9], anti-ulcer and anti-inflammatory agents[10], as well as pesticides[11]. Additionally, 2-thiohydantoins have been used as reference standards for the development of C-terminal protein sequencing[12] , as reagents for the development of dyes[13] and in textile printing, metal cation complexation and polymerization catalysis[14]. It is therefore not surprising that various different synthetic methods have been developed to prepare 2-thiohydantoin and its derivatives. Some of the most commonly used methods are the treatment of α-amino acids with acetic anhydride followed by ammonium thiocyanate[15] and the coupling reaction between α-amino acid derivatives and isothiocyanate[4a,12b,16]. Other preparative methods for 2-thiohydantoins include the reactions between thiourea and benzil[17]thiourea and α-halo acids[18] , oxazolinone and thiocyanate[19], amino amide and diimidazolethiocarbonate[20], and others[21] . In addition, some of the above reactions have been modified to take place under microwave irradiation[17c] and solid-phase[16a,22] or fluorous-phase [23] supported reaction conditions. However, the above methods often suffer from one or more synthetic limitations for large-scale preparation of 2-thiohydantoin derivatives due to their use of expensive, moisture sensitive and/or highly toxic starting materials and reagents. Moreover, the methods developed for combinatorial synthesis and used to prepare 2-thiohydantoin derivatives in small quantities for purposes like biological testing may not be feasible when operated on a large scale [22d,24]A Thiohydantoin derivative has also been reported as herbicidal[25]. Bucherer reaction has also been reported for the synthesis of thiohydantoin[26]. Sulfenylated thiohydantoins has also been reported as fungicides. Ant diabetic hydantoins have been synthesized by Japanese scientists[27]. 1-3-diglycidyl-5, 5-dimethyl hydantoin has been used for primed steel plate to give a good coating for weathering, alkali, acid and water resistance[28]. Some thiohydantoin derivatives have been used in the treatment of blood circulation disorder[29]. Some thiohydantoins have been reported as inhibitors of pyrimidine biosynthesis[30] ,5, 5-disubstituted thiohydantoins have also been synthesized for their anti HIV activity[31]. Synthesis of benzylidene derivatives of 3(2, 3, 4-chlorophenyl) thiohydantoins are reported for their anticonvulsant properties[32], 1-bromo thiohydantoins is reported where transposition of halogen atom from nitrogen to 3-alkyl group is studied[33]. 1-N-phenyl substituted 2-thiohydantoins derivatives were synthesized by Z. Jinpei et al for their antinociceptive activity[34]. Acetylation of 3-substituted 1-amino-thiohydantoins has been reported[35].

Reaction of 5-arylidene-3-phenyl-2-thiohydantoin with 2,3,4,6-tetra-o-acetyl-a-D-gluco-pyranosyl bromide are reported. The product is arylidene-phenyl [(tetra acetyl glycopyranosyl) thiohydantoin.[36]We now report a simple method for the preparation of 2-thiohydantoin derivatives that can easily be scaled up in the laboratory.

Experimental

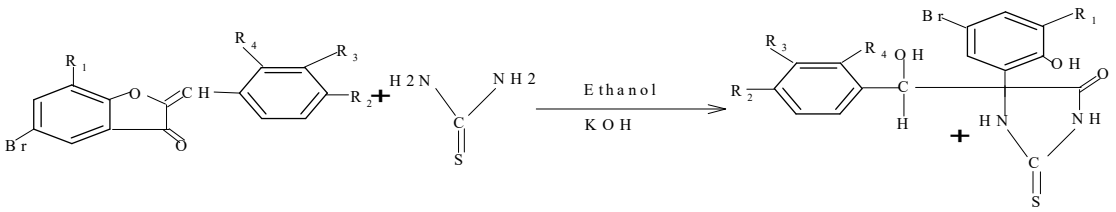
The melting points were taken in a capillary tube; IR spectra were recorded in Nijol,
1H NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard. The purity of
A synthesized compound was check by TLC. The structural elucidation of compound was done on the basis of chemical and spectral data.
The starting ketones were 2-hydroxy-5-bromo acetophenone (II a), 2-hydroxy-3-nitro-5-bromo acetophenone (II b).2-Hydroxy-5-bromo acetophenone (II a) was prepared from parabromo phenyl acetate (I a) by Fries migration using anhydrous AlCl3.2-Hydroxy-3-nitro-5-bromo acetophenone (II b) was prepared by nitration of 2-hydroxy-5-bromo acetophenone (II a).
Synthesized substituted acetophenone (II a&b) were condensed with substituted aldehyde separately to get corresponding chalcones (III a-d).
The above synthesized substituted chalcones (III a-d) were refluxed in DMSO medium in presence of mercuric acetate catalyst to yield 2-(substituted benzylidene)-7-substituted-5-bromo coumaran-3-one (IV a-d).
2-(substituted benzylidene) -7-substituted -5-bromo coumaran-3-one (IV a-d) was refluxed with urea in presence of alkaline medium and alcohol to get 2-substituted thiohydantoin (V a-d).

Preparation of 5-(2-hydroxy-3-nitro-5-chloro phenyl) 5-(ά-hydroxy-4-methoxy benzyl)-2-thiohydantion (II a)

2-(4' methoxy benzylidene)-5- bromo-7-nitro coumaran-3-one (I a) (0.01 mole) and urea (0.01 mole) were dissolved in 40 ml of ethanol. To this mixture 10 ml of 10% KOH was added drop wise with constant stirring, allowed to stand for 2 to 3 hours. The reaction mixture was refluxed for 3 hrs. Cooled and then diluted with ice cold water washed several time with 1% $NaHCO_3$ solution and then with distilled water. It was then crystallized from ethanol to get 5-(2-hydroxy-3-nitro-5-chloro phenyl) 5-(ά-hydroxy-4-methoxy benzyl)-2-hydantion**(II a)**.
The structure of compound **(II a)** has been supported by chemical and spectral data.

Properties of the compound (II a)

• Deep brown color crystalline solid m.p. 132^{o}C.
• It shows positive ferric chloride indicating non-involvement of phenolic –OH group.
• An IR spectrum was recorded in Nijol.
I. 3852 (-N-H, stretching).
II. 3853 (-N-H, stretching).
III. 3815-3801 (-OH group stretching).
IV. 1705 (Lactum cyclic C=O group stretching).
V. 1511 (-NO2 group symmetrical aromatic stretching).
VI. 1340 (-NO2 group unsymmetrical aromatic stretching).
VII 1251 (-NH bond stretching)
VIII. 1060 (-CHOH group stretching).
IX. 1480 cm-1 (C-Br group stretching).
• 1H NMR in CDCl3 with TMS as an internal standard.
I. 1.25 (s, 1H,-CH).
II. 3.9 (s, 3H, Ar-OCH3 group).
III. 6.3-6.4 (broad, 1H -OH).
IV. 6.8 (m, 6H, Ar-H).
V. 6.9-7.8δ (s, 1H, Ar-OH).
These chemical and spectral data shows that compound **(II a)** is got 5-(2-hydroxy-3- nitro -5-bromo phenyl) 5- (ά-hydroxy-4-methoxy benzyl)-2-thiohydantoin.
Similarly other compounds **(II b–II d)** were prepared by above method.



II a-d III a-d

Table 1: Synthesized compounds, M.P.'s and yields

S. No.	Compounds	R_1	R_2	R_3	R_4	M.P. (°C)	Yield (%)
1	IIa	NO_2	OCH_3	H	H	132-134	76
2	IIb	NO_2	H	H	OH	156-157	67
3	IIc	H	H	H	H	142-144	64
4	IId	H	H	NO_2	H	126-130	59

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OPTIMIZATION FOR ENERGY CONSUMPTION OF VAPOUR COMPRESSION REFRIGERATION SYSTEM IN DINSHAWS FOOD LIMITED, NAGPUR

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ABSTRACT

The aim of the project was to optimize the energy consumption by compressor in Refrigeration system at Dinshaws Dairy Food Ltd., Buttibori, Nagpur. When we surveyed the Industry, we found that there is problem of more power consumption in compressor which leads to higher production cost. Detail study of the plant, its layout and during discussion with the plant manager, it found that power consumption of the plant was suspected to be more. Detailed study of the plant, its layout was undertaken. Modification of the flow of the re frigerant was suggested. After suggestion, calculation of saving of the power consumption by the refrigeration system was found to be 0.8575KW

Keywords: *Refrigeration, Vapour compression system, Energy Consumption, Optimization*

Introduction

Dinshaws Dairy Food Ltd. is situated at Butibori, MIDC, Nagpur. An Ice Cream production plant is installed by YORK Company Ltd, Denmark. Their products are Carnivals, Family Packs, Candy(s), Cup's, etc. Dinshaws is one of the biggest ice cream producers in Asia. Their annual turnover is around Rs. 300 Crores. They have fully automated production plant. Whole refrigeration plant is controlled by PLC operated chamber.

Material and Method

The Refrigeration plant included the following components:

- Compressors
- 3-HP Compressor (Rotary type screw compressors)
- 11-Booster Compressor (Centrifugal compressors)
- Accumulator : Higher stage :- -33^0 C , $+40^0$ C Lower stage :- -7^0C
- Condenser:- Pre-heat Type
- Receiver : Diameter 1200mm, Length 6000mm
- Cooling Towers No.3
- Evaporators
- Tunnel : Spiral, Tray
- Cold Rooms
- Chillers
- Glycol Tank
- Refrigerant
- Ammonia (Primary Refrigerant)
- Brine (Secondary Refrigerant)Capacity of the plant:

100000 Litres /day - In summer season 50000 Litres /day - In winter season.

Ice cream manufacturing process: Process can be divided in the following steps:

1. Mixing	2. Pasteurization	3. Homogenization
4. Cooling	5. Ageing	6. Freezing
7. Filling / Packaging	8. Hardening	9. Storage and Distribution

Existing Ice–Cream Plant.

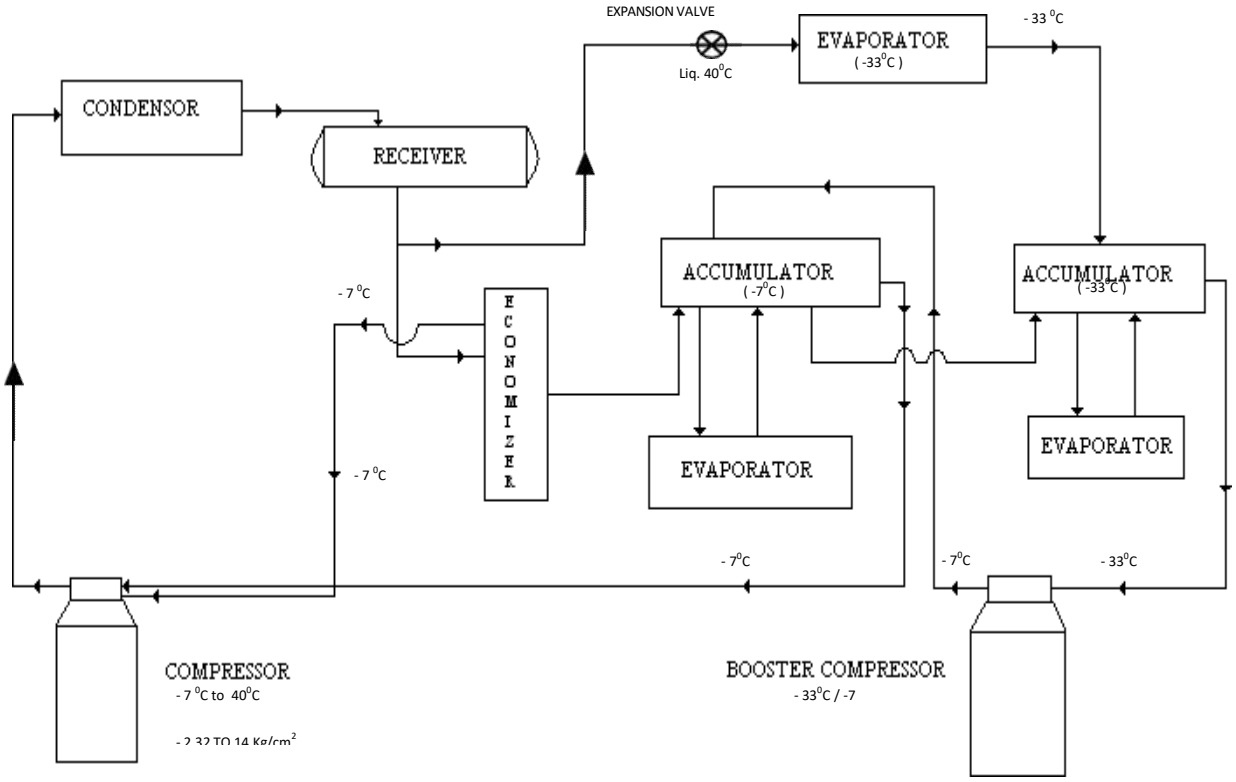

Fig.1 shows the flow diagram of refrigeration system for production of ice-cream. It consists of higher stage compressor, a booster compressor, condenser, receiver evaporator, two accumulators. The higher stage compressor is a rotary type screw compressor. The suction and discharge temperatures are -7^0C & $+40^0$C respectively. Second is a booster type centrifugal compressor whose suction & delivery temperatures are - 33^0C & -7^0C. It again consists of PHE condenser in which vapour refrigerant gives its latent heat to the surrounding medium. i.e. water which is circulated from a cooling tower. Vapour condensed and liquid refrigerant stored in a receiver. Refrigerant supplied to the evaporator continuously through the thermostatic expansion valve. In evaporator liquid refrigerant evapourates and takes its latent heat of vapour refrigerant from the surrounding medium which is generally brine (secondary refrigerant which takes part in actual cooling effect). After evaporation process vapour refrigerant collected in a accumulator, there are two accumulators maintained at -7^0C & -33^0C respectively. Accumulator is a device used for storage of refrigerant to supply the constant flowof vapour refrigerant to the compressor.

For each accumulator there is an evaporator which converts the refrigerant to the vapour for compressor, hence the cycle continues.

In this, booster compressors are connected to HP compressors such that as the load increases on the HP compressor one by one booster compressor get started. The load is in terms of temperature i.e. as the temperature in cold storage increases; compressor has to compress more refrigerant to get cooling effect.

Pressure Enthalpy & Temperature Entropy Diagram For Vapour Compr-ession Cycle

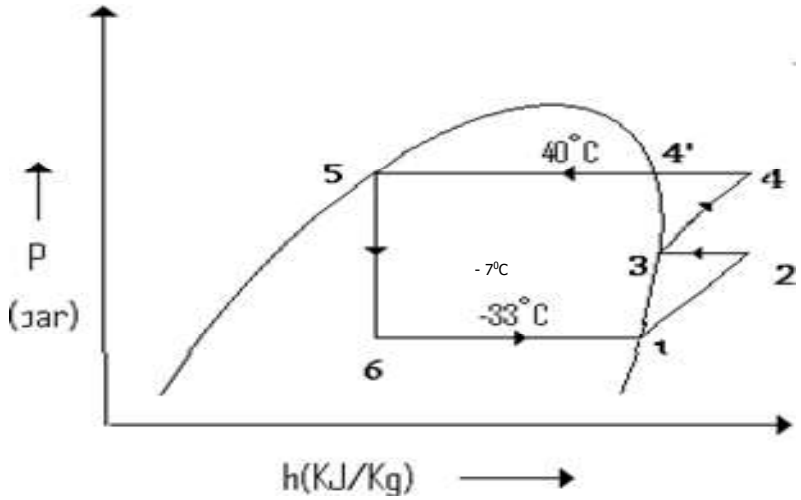

Fig.-2 – Pressure-Enthalpy Diagram Of Vapour Compression System (Existing)

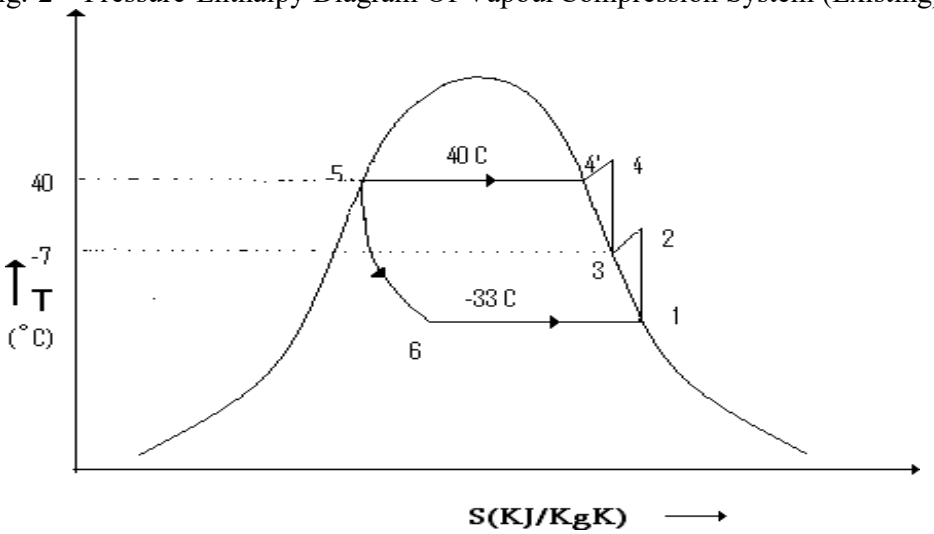

Fig.-3 – Temperature-Entropy Diagram of Vapour Compression System (Existing)

- Process 1 – 2: Compression process takes place isentropically. Vapour compress from -33^{0}C to -7^{0}C.
- Process 2 – 3: Desuperheating process take place vapour decreases the temperature & reach to dry saturated condition of temperature -7^{0}C.
- Process 3 – 4: At point 3 vapour enter in higher stage compressor and compress the refrigerant from temperature -7^{0}C to 40^{0}C.
- Process 4 – 4` : Desuper heating process takes place, vapours decreases the temperature & reach to dry saturated condition of temperature -7^{0}C.
- Process 4` – 5: Condensation process takes place, the superheated vapours enters the condenser, where heat is rejected at constant pressure, due to rejection of heat, the change of phase takes place. Latent heat removed and saturated liquid obtained at point 5.
- Process 5 – 6: Expansion process takes place and liquid refrigerant passed through expansion valve where liquid refrigerant throttle keeping the enthalpy constant and reducing the pressure. This wet vapour passes through evaporator at point 6, where it absorbs latent heat and convert it into saturated vapours and cycle is completed.
- Power required to drive the booster compressor is calculated 3.98KW and Second compressor is 4.38KW. So total power of the cycle is 8.36KW.
- Refrigeration effect of the system is 1029.5KJ/Kg.
- Mass flow rate of the refrigerant is 3.79Kg/min.

Modified Vapour Compression Refrigeration System

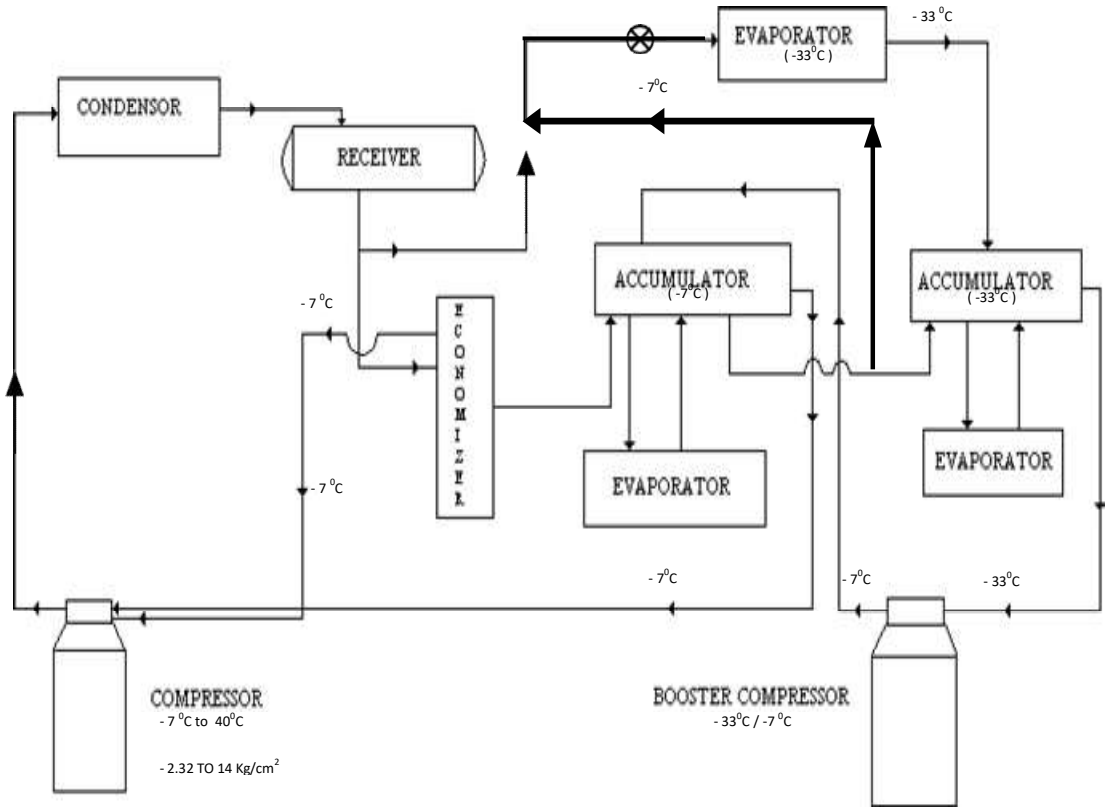

Fig. 4. Modified Flow diagram of vapour compression refrigeration system for production of Ice-cream

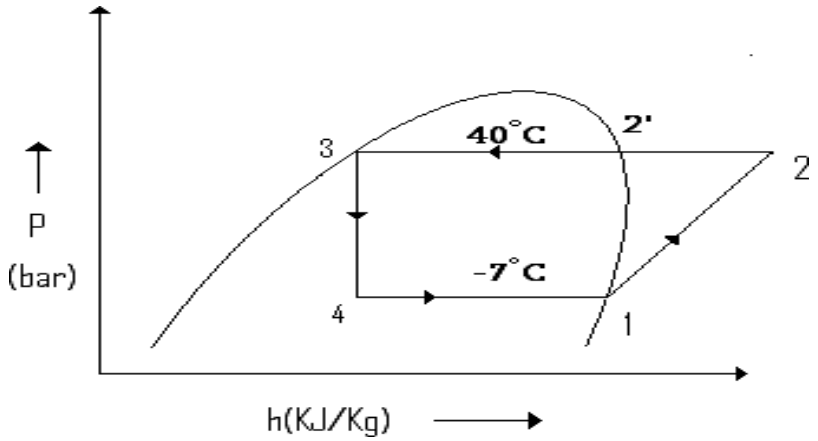

Fig.- 5 – Pressure-Enthalpy Diagram Of Vapour Compression System (Modified)

After studying the processes and operations carried out in the plant, the compressor is the major power consuming device. We studied the compressor suction and discharge temperature. We came to know that refrigerant has to travel from temperature range $+40^0$C to -33^0C for 65KW of refrigeration effect. As the suction temperature of compressor is -33^0C and discharge temperature $+40^0$C which consumed more power to drive the compressor so we thought that to change the inlet or outlet temperature of compressor. We found that there is a -7^0C vapour refrigerant is available in an accumulator. So we decided to give a -7^0C vapour refrigerant to the evaporator instead of $+40^0$C which reduce the load on a compressor. Now compressor compress the refrigerant from temperature - 33^0C to – 7^0C which required less

power than actual cycle.
Modified vapour compressor system work in two cycles which shown two different Pressure - Enthalpy & Temperature – Entropy diagram. As Shown in fig. 5, 7and fig. 6, 8. And according to these two cycles:-

1. Power required to drive the first compressor has calculated 4.237 KW and Second compressor is 3.28KW. So total power of the cycle is 7.51KW.
2. Refrigeration effect of the first system is 1063.25 KJ/Kg & second system is 1251.72 KJ/Kg.
3. Mass flow rate of the refrigerant in first systemis 3.66 Kg/min & second system is3.12Kg/min. Comparing the actual cycle compressor power andmodified cycle compressorpower, power saving is0.8575 KW and according to that, power saving in terms of rupees is

Power Saving In Terms Of Rupees:-

1 unit of Electricity = 1kWh
Rate/unit = 6 Rs. (Inclusive of All Taxes)Power saving = 0.8575kWh
Per day saving = 0.8575 × 24 = 20.58 KWh
Power Saving / year = 20.58 × 365= 7511.7KWh
Power saving in terms of money= 7511.7 × 6
Power saving in terms of money = 45070.2 Rs.
For Four Evaporator = 45070.2 × 4**= Rs. 180280.8**

4 Conclusions

After deep study of the flow diagram of refrigerant in Dinshaws Dairy Food Ltd . The power requirement for the existing refrigeration system was calculated. The calculations were also done by changing the path of refrigerant in the refrigeration cycle without changing the capacity of plant. It is found that the reduction of power consumption is around 1.0 KW. The saving in power increases the Coefficient Of Performance (COP) of the refrigerating plant.
The reduction in power consumption saves the electricity which ultimately increases company's profit. If the system will be modified by changing the refrigerant path in the cycle then the saving in the cost of electricity would be around Rs. 2 Lacs (Approx.) per annum which is an effective amount to improve company's profit.This project is being designed to reduce the power consumption of refrigeration system in Dinshaws Dairy Food Ltd. at Nagpur. The refrigeration system is studied and proposed work had found in the beginning. The power requirement for the existing refrigeration system was calculated. The calculations were also done by changing the pathof refrigerant in the refrigeration cycle without changing the capacity of plant. It is found that the reduction of power consumption is around 1.0 KW. The saving in power increases the Coefficient Of Performance (COP) of the refrigerating plant. The reduction in power consumption saves the electricity which ultimately increases company's profit. If the system will be modified by changing the refrigerant path in the cycle then the saving in the cost of electricity would be around Rs. 2 Lacs (Approx.) per annum which is an effective amount toimprove company's profit.

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GREEN CHEMISTRY: A TOOL FOR SUSTAINABLE DEVELOPMENT

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ABSTRACT:

Green chemistry which was initiated about three decades has attracted lot of attention. It is a multidisciplinary field which cover's areas such as synthesis, solvemts, catalysis, raw materials, products, efficient methods and many more.In the current globalized world green chemistry is becoming the most potent tool, the strength towards the sustainable and overall development. It is environmentally benign chemistry which reduces or eliminates the use and generation of hazardous chemicals and substances. The basic principle of green chemistry on which it works is the minimization of risks, hazards and pollution and maximising the efficiency by maintaining the cost and potential exposure. It includes all parts of chemistry and other disciplines that aims to minimize the negative effects and maximize the efficiency . There are many innovations in green chemistry such as synthesis, renewable products, catalysts, disposal of wastes, design of nontoxic chemicals and components, new formulations and many more. Therefore it is imperative to acknowledge the importance and values of this branch of chemistry to future generations. This paper addresses the importance, innovation and application of green chemistry for a sustainable development.

***Keywords:**, Green chemistry, multidisciplinary, sustainable development, design of safer chemicals, high efficiency.*

Introduction

In the last few decades trends such as climate change, population explosion, high degree of urbanisation, toxicity, scarcity of resources, energy and water have led to the initiation of sustainable practices in various sector's including industry, education and society. The ambition to improve standard of living and pure atmosphere the need for performance materials are required so that the gap between developed and developing nations get more narrower. These conditions has accelerated the development of materials based on green chemistry. The green chemistry is described as the movement towards more environment friendly chemical processes and synthesis. Nowadays green chemistry is regarded as a vital tool for the practice of chemistry and other branches of scienceto attain the sustainable development, by maintaining the balance with the environment. The concept of green chemistry was coined in 90's by the US Environmental Protection Agency (USEPA). Since then lot of research has been done in this field by developed nation's to achieve the optimum level of this branch. This fast moving concept is governed by some basic set of principles which move processes and products towards an economy based on renewable feedstock's which prevents chances of toxicity at the atomic or molecular levels. The chemical synthesis and products are designed and formulated so that to minimize the waste and side effects. The present era of globalization demands emphasis on safer and efficient products which can only be possible with the technology called as the green chemistry. There can be numerous applications of green chemistry in industries such as plastics, textile, pharmaceutical, renewable energy, pesticides, solvents, water purification, etc. It is believed that in the coming timegreen chemistry will change the face of science as a whole towards an economy based on renewable energy, green processes and bio based productions.

Green chemistry is commonly based on a set of 12basic principles proposed by Anastas and Warner. The principles includes instructions for chemist's and professionals to implement new chemical methods and novel ways of synthesis. The 12 principles are-

1. Prevention
2. Atom economy
3. Less hazardous chemical synthesis
4. Designing safer chemicals
5. Safer solvents and auxiliaries
6. Design for energy efficiency
7. Use of renewable feed stocks
8. Reduce derivatives
9. Design for degradation
10. Catalysis
11. Real time analysis for pollution prevention
12. Inherently safer chemistry for accident prevention

Thus the basic idea of green chemistry is to accomplish both transmateriliazation and dematerialization; through it's rational approach and metrics of principles. However to achieve the full potential of green chemistry a coordinated approach of factors like social, political, technological is required.

Implementation of green chemistry principles

In different chemical processes the waste products and the reagents used for synthesis, causes a severe threat to the environment. The exposure to hazardous chemicalscan be minimize in a simpler way by applying safe raw materials and intoxic procedure during the preparation. For example adipic acid is used for the production of polymers like nylon, Polyurethanes, lubricants, plasticizers, etc. This adipic acid is formed by benzene which is a potent carcinogen. However recently chemists have developed a method for the green synthesis of adipic acid by using raw materials like glucose which on action with genetically modified bacteria gets converted to adipic acid. Green chemistry emphasizes the use of renewable sources as raw materials and starting reactants. The production of biodiesel oil, is a perfect example of this. As the name indicates, biodiesel oil is produced from cultivated plants like soya beans and fats embedded in plants oil by extracting the glycerine from it. The advantage of using this nontoxic oil is obvious as on combustion it doesn't generates sulphur and nitrogen compounds which are serious threat for the environment.

Another threat to the environment are the organic solvents which are used during the synthesis of different compounds. They are released in the atmosphere by volatilization process especially in the case of volatile organic compounds (VOCs) . This problem can be minimized by using super critical fluids (SCFs) in chemical processes and synthesis which are harmless for humans and the environment. The use of SCFs is becoming very common to run the chemical reactions. The term SCF comprises the liquids and gases at their critical temperature (Tc) critical pressure (Pc). Above the critical point the liquid- vapour phase boundary disappears, while the present phase shows both the properties of liquid and the vapour. Due to this, the SCFs are able to dissolve many compounds with different polarity and molar masses. Some of the important fluids which have been in common use are the scCO2 and scH2O. CO2 as a SCF is frequently used as the solvent or medium for reactions, as it is inflammable, easily available and cheaper in cost. Room temperature ionic liquids are also considered to beenvironment friendly reaction media. However the lack of technology for the removal of products from the ionic fluid has limited their applications. But recently it has been found that CO2 can be used to extract non volatile organic compounds, from room temperature ionic liquids. The researches have shown that ionic liquids (using 1-butyl-3-methylimidazolium hexafluorophosphate) and CO2 shows very attractive phase behaviour. The solubility of CO2 in ionic liquids is substantial, reaching mole fraction as high as 0.5 at 10MPa. Inspite of this the two phase do not become completely miscible, so CO2 can be frequently used to extract compounds from the ionic liquids.

Green chemistry can also play a substantial role in analytical chemistry. Development of environmental monitoring techniques can lead to better knowledge of the state of environment and the processes that takes place in it. Due to the introduction of green analysis and evaluation new measuring techniques can be used to study the concentration of trace and micro trace components in samples. The novel techniques can also be used to study the acidic behavior of components in the environment, the ozone depletion phenomenon, change in the composition of air, increase in the concentration of persistent organic pollutants (POPs), etc. Thus the introduction of green tool into chemical laboratories and techniques can drastically reduce the instrumental costs and also the adverse effects on the environment which is caused by the liberation of chemicals and fumes. Nowadays many techniques have been used which are based on the rules of green chemistry. Some of them are.

X-ray fluorescence (XRF)
Solid phase extraction (SPE)
Surface acoustic wave (SAW)
Super critical fluid extraction (SCFE)

Mass spectroscopy with membrane interface (MIMS)
Green solvents
In-line analyzers
Out- line analyzers

Green nanotechnology: Nanotechnology is a potent tool of the present era and has variedapplications in almost every sector. Hence there is a general perception that nanotechnology will have a significant impact on the development of green and clean technologies with numerous environmental benefits.Nanotechnology with green approach is playing a vital role in purification of water, separation of different solvents, energy sector, manufacturing units, etc. As a matter of fact renewable energy applications are the areas where nanotechnology is ready to play a crucial role and probably it will be a large scale breakthrough across the globe. Nanotechnology applications could provide decisive technological momentum in the energy sector and will enhance the generation of sustainable energy support that will shift the equilibrium away from the fossil fuels which are the major cause of pollution. Although these transitions require a political will and funding. The technological foundation is there, all it takes thecorrect approach and proper laboratory facilities to make it happen. Thus nanotechnology can provide the required thrust to accelerate the energy supply with greener means.

Green catalysis: Lots of research work has been going on to provide a path or mechanism for the greener synthesis routesby using the catalyts which are nontoxic, efficient and degradable. Olefin metathesis is an example of a very atom economical reactions with potential to eliminate the waste associated with alternate multistage synthesis. A versatile method for forming the carbon-carbon bond in polar and nonpolar solvents has been carried out in the presence of green catalyts like Fe-TAML, enzymes, highly acidic dysprosium(lll) triflate (trifluoromethanesulphonate), Molybdenum disulphide coated on alumina, Cativa catalyst,etc.These catalysts have also been used during polymerisation, to construct ring systems, synthesis of natural products and in cyclisation of Polypeptides. Olefin metathesishas also been very useful in obtaining useful products from renewable resources. Unsaturated fatty acid esters and natural oils can also be used to produce nontoxic feed stocks and many natural products. Hydrogenation using H2 gas is another example of atom economical reaction which hashigh degree of utility in designing green synthesis mechanism and different pathwaysin order to phase out hazardous and wasteful hydride and boran reagents. Now the time has arrived to increase the safety of chemical processes, providing alternative to toxic reagents and avoid the generation of harmful pollutants by the extensive use of green catalyst. One such catalyst is Fe-TAML which is an environment friendly oxidizing agent . It's use provides an alternative to polluting oxidizing agents like Cl and metal based oxidants. Fe-TAML activated oxidants can be used instead of dangerous ClO2 gas and metals like Zn, Cu, Ti, etc. for different processes like bleaching, oxidation and deactivation of biological warfare.

Need for collaboration: There are many components and driver's of green chemistry. The promotion and commercial use of greener components, chemicals and techniques requires collaboration and communication between scientists, chemists, business leaders, politicians and common man. Designing different components and techniques requires lot of technicality and it can only be possible if there is an effective bonding between different branches of science. To implement green chemistry rules the market requires the inclusion of both the expertise andnontechnicalmanpower. Effective communication between different stakeholders is another criteria for the successful implementation of green technology as they use different technical terms and have different vested interests. However collaboration can be promoted with the creation of interdisciplinary research centres, which promotes fused action by including all the stake holders. The research centres can provide a common platform to discuss and identify key issues regarding the components of green chemistry. The components of green chemistry is actually the fusion of all the branches of science so

constructive collaboration is needed among all these branches.

Conclusion

Green chemistry is a tool which is being used to create a better, safer and efficient environment by minimizing the wastes and reducing the hazardous materials and chemicals. The future challenges in society, environment and resources needs the efficient and clean chemical process which can only be attained by the means of the green chemistry. It is a new smarter approach which can contribute towards the sustainable development of the society and the nation. The green chemistry rules are applied not only in synthesis, processing and manufacturing but are equally important innano, pharma, health and energy industries. The application of sample preparation techniques like SPME, SPE, ASE, etc. allows to obtain precise and accurate results. Green efforts are under going across the globe to design processes that initiates fromnon-polluting materials and requires no solvent to carry out the chemical reactions. Adoption of environmentally benign methods, new programs , government participation and funds are the important factors to replace the conventional methods by more greener and safer methods that forms the basis of green chemistry.

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SYNTHESIS, SPECTRAL STUDIES AND ANTI-MICROBIAL ACTIVITY OF NOVEL CHALCONES OF 2-ACETYL THIOPHENE

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ABSTRACT

Some new chalcones have been synthesized by the condensation of 2-acetyl thiophene with various aromatic aldehydes in 40% alkali. The synthesized compounds were identified by spectral data and screened for antimicrobial activity. Some of these compounds showed moderate to considerable anti-microbial activity.

Keywords: *Chalcone, Synthesis, Anti-microbial activity.*

Introduction

Chalcones are synthesized by Claisen – Schmidt condensation of aldehyde and ketone by base catalyzed followed by dehydration to yield chalcones. The synthesis of chalcone compounds incorporating with heterocyclic become the great importance in medicinal chemistry. The hetero atom products variety of application in the biological engineering and in other field of their specific structure. To the best of our knowledge acetyl thiophene involving different substituted aldehyde under basic condition reaction is unprecented. In continuation of our interest to developing novel synthetic methodologies and use of chalcones for organic synthesis. The compounds with the backbone of chalcones have been reported to possess various biological activities such as antimicrobial, anti-inflammatory, analgesic , antiulcerative, antimalarial, anticancer, antiviral and antioxidant activities. Antifungal activity of chalcones has been investigated by a number of researchers. Elemental sulfur has long been known to act as an antibacterial agent. Sulfur is present in antifungal agents of natural origin, e.g., Allium sativum (garlic), which is known to inhibit Candida albicans. The present work indicates that, when a thiophene ring was incorporated into a chalcone structure, the molecule exhibited antifungal activity.

The Chalcones display interesting biological activities, including anti malaria, anti inflammatory, cytotoxic, anticancer and antimicrobial activities. In the present study, some new chalcones **(1a-1f)** have been synthesized by the reaction of 2-acetyl thiophene with different aromatic aldehydes. The structures of the various synthesized compounds are assigned on the basis of elemental analyses, IR and 1H NMR spectral data. These compounds were also screened for their anti-microbial activity.

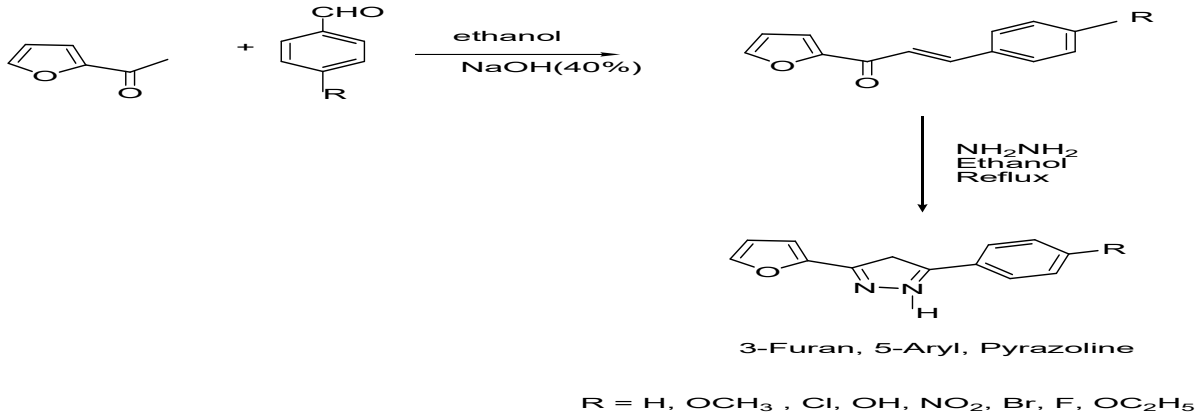
2. Materials and Methods

The melting point of the compounds were determined in open capillaries, using Eligo digital melting point apparatus and Melting points were determined on a capillary melting point apparatus and are uncorrected.expressed in degree Celsius and the values were uncorrected. IR spectra of the compounds were recorded onShimadzu 8201 spectrophotometer using KBr and the values are expressed in 4000-400 cm-1. 1H and 13C NMR spectra were recorded on Bruker AV 400 MHz Spectrophotometer using TMS as an internal standard and the values are expressed in δ ppm. All the solvents used were analytical grade. The purity of the compound was checked by TLC using silica gel plates.

General procedure for the preparation of chalcones (1a-1f)

Equimolar quantity of 2-Acetylthiophene (0.01 mol) and substituted aromatic aldehyde (0.01 mol) were dissolved in 20 ml of ethanol was cooled heated about 60^{o}C. In solution, 10 ml of 40% Sodium hydroxide solution was added drop wise The reaction mixture was magnetically stirred for 1h. Allow the solution to cool and acidify with dil.HCl. A flocculant precipitate was formed. The precipitate was filtered and washed with cold water and recrystallise from ethanol.

Scheme 1. Synthesis of some new chalcones of 2-acetyl thiophene



3. Results and Discussion

Physical data of compounds (**1a-1f**) are obtained and given in following table.

Compound	M.F.	M.P.(oC) Yield (%)
1a	$C_{13}H_9OSCl$	110 95
1b	$C_{13}H_{10}SO_2$	165 60
1c	$C_{13}H_9OSBr$	135 86
1d	$C_{14}H_{12}O_2S$	70 99
1e	$C_{15}H_{14}O_2S$	85 92
1f	$C_{13}H_9SNO_2$	280 76

Spectral data of the compounds (**1a-1f**) are obtained using various a spectral methods. Theresults discussed are given below.

1a - (2E)-3-(4-chlorophenyl)-1-(thiophene-2-yl) prop-2-en-1-one

Mp: 110^{0}C. IR (KBr) cm-1: 3527 (ArC-Hstr), 2924 (C-Hstrthiophene), 2854(C-Hstr alkene), 1743 (C=Ostr), 1651(C=Cstr), 802 (C-Hdef) and 677 (C-Clstr). 1HNMR (DMSO) ppm; 7.1-7.6 (Ar), 7.7 (Hβ =CH-Ar), 6.6 (Hα–CO-C=s). 13C NMR (CDCl3)ppm: 181 (-CO-), 128-134(Ar), 145 (Cβ), 112 (Cα).

1b – (2E)-3-(4-hydroxyphenyl)-1-(thiophen-2-yl) prop-2-en-1-one

Mp: 165^{0}C. IR (KBr) cm-1: 3516 (ArC-Hstr), 2924 (C-Hstr thiophene), 2856(C-Hstr alkene), 1805 (C=Ostr), 1651(C=Cstr), 1473 (C-Fstr) and 835 (C-Hdef). 1H NMR (DMSO)ppm; 7.4-7.7 (Ar), 7.3 (Hβ =CH-Ar), 6.9 (Hα –CO-C=). 13CNMR; (CDCl3)ppm: 181 (-CO-),126-140 (Ar), 145 (Cβ) 124 (Cα),

1c - (2E)-3-(4-bromophenyl)-1-(thiophen-2-yl) prop-2-en-1-one

Mp: 157^{0}C. IR (KBr) cm-1: 3446 (ArC-Hstr), 2924 (C-Hstrthiophene), 2854(C-Hstr alkene), 1745 (C=Ostr), 1649(C=Cstr), 671 (C-Brstr) and 889 (C-Hdef). 1H NMR (DMSO)ppm; 7.0-7.6 (Ar), 7.7 (Hβ =CH-Ar), 6.8 (Hα –CO-C=).13CNMR (CDCl3) ppm: 127-142 (Ar), 181 (-CO-), 145(Cβ),122 (Cα).

1d - (2E)-3-(4-methoxyphenyl)-1-(thiophen-2-yl) prop-2-en-1-one

Mp: 70^{0}C. IR (KBr) cm-1: 3454 (ArC-Hstr), 2922 (C-Hstrthiophene), 2854(C-Hstr alkene), 1743 (C=Ostr), 1649(C=Cstr), 979 (C-Sstr), 734 (C-Hdef), and 675 (C-Clstr). 1HNMR (DMSO) ppm; 8 (Hβ =CH-Ar), 7.3-7.7 (Ar), 7.2 (Hα –CO-C=). 13C NMR; (CDCl3)ppm: 129-138 (Ar), 192 (-CO-),143 (Cβ),128 (Cα).

1e - (2E)-3-(4-ethoxyphenyl)-1-(thiophen-2-yl) prop-2-en-1-one

Mp: 80^{0}C. IR (KBr) cm-1: 3454 (ArC-Hstr), 2922 (C-Hstr thiophene), 2854(C-Hstr alkene), 1743 (C=Ostr), 1649(C=Cstr), 979 (C-Sstr), 734 (C-Hdef), and 675 (C-Clstr). 1H NMR (DMSO) ppm; 8 (Hβ =CH-Ar), 7.3-7.7 (Ar), 7.2 (Hα –CO-C=). 13C NMR; (CDCl3)ppm: 129-138 (Ar), 192 (-CO-),143 (Cβ),128 (Cα).

1f – (2E)-3-(4-Nitrophenyl)-1-(thiophen-2-yl) prop-2-en-1-one

Mp: 280^{0}C. IR (KBr) cm-1: 2924 (C-Hstr thiophene), 2854(CHstralkene), 1743 (C=Ostr),

1635 (C=Cstr), 974 (C-Sstr), 889(C-Hdef) and 731(C-Hdef). 1H NMR (DMSO) ppm; 7.8 (Hβ=CH-Ar), 7.0-7.7 (Ar), 6.9 (Hα –CO-C=). 13C NMR;(CDCl3) ppm: 181 (-CO-), 145 (Cβ), 128-134 (Ar),

4. Antimicrobial Screening

Antimicrobial Activity - The purified products were screened for their antibacterial activity by using disc diffusion method. The nutrient agar broth prepared by the usual method, was inoculated aseptically with 0.5 ml of 24 hr old subculture of Staphylococcus aureus and Escherichia coli in separateconical flask at 400-500C and mixed well by gentle shaking.About 25 ml of the contents of the flask were poured andevenly spread in Petridis (90 mm in diameter) and allowedto set for two hrs. The cups (8mm in diameter) were formedby the help of borer in agar medium and filled with 0.1 ml (1mg/ml) solution of sample in acetone.

In antibacterial activity of chalcone derivatives (1a – 1e) were carried out using culture of Klebsiella aerogenes and Proteus Vulgaris by the disc diffusion method and the minimum inhibitory concentration (MIC) of these compounds were determined. Ciprofloxacin was used as the standard drug, where as dimethyl sulphoxide (DMSO) as solvent. The minimum inhibitory concentration (MIC) was evaluated by the micro dilution method of test compounds. more active against Klebsiella aerogenes. Compound 1e was better antibacterial activity against klebsiella aerogenes.

Antifungal Activity - Aspergillus nigerwas employed for testing antifungal activity by disc diffusion method. The culture was maintained on Sabouraud dextrose agar slants. Sterilized Sabouraud dextrose agar medium was inoculated with 72 hr old 0.5 ml suspension of fungal spores in a separate flask. About 25 ml of the inoculated medium was evenly spreader in a sterilized Petridis and allowed to set for 2 hr. The cups(8 mm in diameter) were punched in Petridis and loadedwith 0.1 ml (2 mg/ml) of solution of sample in acetone. Theplates were incubated at 20 – 2500C for 72 hr. After the completion of incubation period, the zones of inhibition growth is in the form of diameter in mm was measured. Along the test solution in each Petridis one cup was filled up with solvent which acts as control.

In antifungal activity of chalcone derivatives (1a – 1e) were carried out using the culture of Mucor racemosus, A. flavous and A. fumigatousby the disc diffusion method and the MIC of these compounds were determined. Nystatin used as the standard drug. The compound 1eshows high(35mm) antifungal activity against aspergillus fumigatous than other compounds (1a – 1e)

5. Conclusion

The present study of an efficient protocol for the Chalcones can be synthesized in good yields from aromatic aldehyde and ketone using the catalytic system of NaOH/ EtOH. The synthesized compounds were characterized by TLC, melting point, IR, NMR spectroscopy and elemental analysis. The results obtained from this study confirmed that the product has formed. The synthesized compounds 1a and 1b show significant antibacterial activity against Klebsiella aerogenes and Proteus vulgaris. Compounds 1cand1d showssignificant antifungal activity against Mucor rcemosus, A. flavousand A. fumigatous. Hence, it is concluded that thereis ample scope for further study in developing these as goodlead compounds.

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A GREEN CHEMICAL APPROACH FOR AN ULTRASONIC IRRADIATION: SYNTHESIS, CHARACTERIZATION OF 2-PHENYLAMINO-4-(2-IMINO-4-THIOBIURETO-5-YL-CARBAMI-DINO)-6- PHENYLIMINO-1, 3, 5-THIADIAZINE

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ABSTRACT

Novel series of 2-substitutedamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6- substitutedimino-1, 3, 5-thiadiazine [4a (i) to 4f (iv)] have been obtained by employing ultrasonic irradiation and conventional heating. The target compounds in higher yields in shorter reaction time compared with the conventional method were archived by ultrasonication. On the basis spectrum data and elemental analysis, the structures of all these compounds were established. The search for novel derivatives is of immense importance in research areas around the world for agricultural, pharmaceutical, and industrial applications

Keywords: *1, 3- Diformamidinothiacarbamide, 1, 3, 5-thiadiazines, synthesis, ultrasonic irradiation.*

Introduction

Now a day's in organic synthesis the ultrasound has been employed more and more frequently [1], as it improved the rate of reaction [2-3]. For meeting goals of the green chemistry and decreasing of the required energy for the reaction, the ultrasonic irradiation has proven to be an important tool [4]. The heterocyclic compounds having 1, 3, 5- thiadiazine enhanced pharmaceutical [5-6], medicinal [7-8], agricultural and industrial activities of the drugs and medicines. So the drugs or medicines containing thiadiazine nucleus are now used extensively in medical, biochemical and biotechnological faculties. The biological importance of the 1, 3, 5-thiadiazine derivatives is further emphasized by showing the presence of 1, 3, 5-thiadiazine ring in therapeutic agent 1, 3, 5- thiadiazine have been shown to possess brightening and fiber finishing properties in textile industry and used as fungicidal, [9] insecticidal [10] as well as medicinalcompounds. The same compounds have been synthesized by conventional and ultrasonication method.

Experimental Section

All chemicals used were of analargrade. Aryl/alkylisothiocyanate,Aryl/alkylisocyano-dichlorides were prepared according to literature method. [11] Melting points of all synthesized compounds were determined in open capillary. IR spectra were recorded on Perkin-Elmer spectrometer in the range 4000-400 cm^{-1} in KBr pellets. PMR spectra were recorded with TMS as internal standard using $CDCl_3$ and DMSO-d_6.TLC checked the purity of the compounds on silica gel-G plates with layer thickness of 0.3 mm. and result are cited in table1

Results and Discussion

The parent compound 1-formamidino-3-thioamido-N-substituted formamidinothiocarbamide [10] (1a-f) was prepared by refluxing the mixture of 1, 3-Diformamidinothiacarbamideand phenylisothiocyanate in acetone medium for 4 hr. The later were synthesized by conventional method and ultrasonic irradiation.

1) Synthesis of 2-phenylamino-4-(2-imino-4- thiobiureto-5-yl-carbami-dino)-6-phenylimino-1, 3, 5-thiadiazine[4a (i)] by conventional method

A reaction mixture of 1-formamidino-3-thioamido-N-phenylformamidinothiocarbamide (1a) and phenylisocyanodichloride (2) in 1:1 molar ratio was refluxed in carbon tetrachloride medium for 4-5 hours. After cooling the reaction mixture distilled off excess solvent, the solid crystals were separated out. And crystallized from aqueous Ethanol, dark brown crystals were isolated; yield 71%, m.p. 210°C.

It gives effervesces with sodium bicarbonate and acidic to litmus. Equivalent weight was found to be monohydrochlorides of [3a (i)]) which on basification with dilute ammonium hydroxide solution afforded light brown crystals of [4a(i)]. Similarly other compounds [3a (ii)] to [3f (iv)] were synthesized from (1a-1f) and which on basification yielded [4a (ii)] to [4f (iv)] by above mention method and enlisted in table1.

2) Synthesis of2-phenylamino-4-(2-imino-4- thiobiureto-5-yl-carbamidino)-6-phenylimino-1, 3, 5-thiadiazine[4a (i)] by Ultrasonication method

A reaction mixture of 1-formamidino-3-thioamido-N-henylformamidinothiocarbamide (1a) and phenylisocyanodichloride (2) via bath ultrasonication at different frequencies, temperature and time in presence of ethanol for 15 minutes. After cooling the reaction mixture distilled off excess solvent, the solid crystals were separated out. And crystallized from aqueous Ethanol, dark brown crystals were isolated; yield 88%, m.p. 210-12°C. Equivalent weight was found to be monohydrochlorides of [3a (i)]) which on basification with dilute ammonium hydroxide solution afforded crystals of [4a(i)]. Similarly other compounds [3a (ii)] to [3f (iv)] were synthesized from (1a-1f) and which on basification yielded [4a (ii)] to [4f (iv)] by above mention method and enlisted in table1.

Properties of (IIIa)

It is light brown crystalline solidhaving m.p. 210-12 ^{0}c. From analytical data; molecular formula is C17H16N8S2; IR spectra of compound shows □ (N-H) 3359.5cm^{-1}, (C-H)(Ar)2924.7cm^{-1}, □(C=N) 1642.2 cm^{-1}, □(C-N) 1294.3cm^{-1}, □(C=S) grouping 1173.7cm^{-1}, □(C-S) 778.3 cm^{-1}, □ (C=NH) grouping 1506.1cm^{-1}. The PMR spectrum of compound [3a (i)] was carried out in DMSO-*d6* and CDCl3. This spectrum distinctly displayed signals due to Ar-H protons at□7.04-7.71 ppm, Ar-NH protons at □ 6.48-6.87 ppm, and NH protons at □ 4.2-4.3 ppm. The signals at □ 2.7-3.1 ppm are due to moisture in DMSO-*d6* and 0.75-2.26 ppm is due to DMSO. From these spectral and chemical data the compound [4a (i)] is 2-phenylamino-4-(2-imino-4-thiobiureto-5-yl-carbamidino)-6-henylimino-1, 3,5-thiadiazine.

Table No. I

Physical data of the compounds [4a (i) to 4f (iv)]

Compounds	R	R1	Yield Conventional	Yield Ultrasonication	m.p. (^{0}C)
[4a(i)]	Phenyl	Phenyl	71	88	210
[4a(ii)]	Phenyl	p-Chlorophenyl	72	86	202
[4a(iii)]	Phenyl	Ethyl	76	81	192
[4a(iv)]	Phenyl	t-butyl	65	79	182
[4b(i)]	Ethyl	Phenyl	62	77	190
[4b(ii)]	Ethyl	p-Chlorophenyl	68	81	189
[4b(iii)]	Ethyl	Ethyl	73	89	177
[4b(iv)]	Ethyl	t-butyl	72	79	172
[4c(i)]	p-Chlorophenyl	Phenyl	68	73	207
[4c(ii)]	p-Chlorophenyl	p-Chlorophenyl	76	87	219
[4c(iii)]	p-Chlorophenyl	Ethyl	74	86	191
[4c(iv)]	p-Chlorophenyl	t-butyl	68	81	187
[4d(i)]	p-Tolyl	Phenyl	72	85	203
[4d(ii)]	p-Tolyl	p-Chlorophenyl	76	77	227
[4d(iii)]	p-Tolyl	Ethyl	59	76	187
[4d(iv)]	p-Tolyl	t-butyl	54	77	181
[4e(i)]	Methyl	Phenyl	62	81	184
[4e(ii)]	Methyl	p-Chlorophenyl	69	77	189
[4e(iii)]	Methyl	Ethyl	76	83	172
[4e(iv)]	Methyl	t-butyl	72	87	176
[4f(i)]	t-Butyl	Phenyl	77	89	184
[4f(ii)]	t-Butyl	p-Chlorophenyl	72	82	192
[4f(iii)]	t-Butyl	Ethyl	61	77	168
[4f(iv)]	t-Butyl	t-butyl	59	72	176

Conclusion

The end compounds [4a (i) to 4f (iv)] were prepared by using conventional heating and ultrasonic irradiation. The target compounds in higher yields in shorter reaction time compared with the conventional method were archived by ultrasonication. All the structure of the above compounds was in good conformity with Spectral and Analytical data.

Disclosure of conflict of interest

Authors wish to state that there is no conflict of interest on this work.

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ANALYSIS OF HEAVY METALS PRESENT IN MILK AND MILK PRODUCTS

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ABSTRACT

Milk and its products are one of the most important and prominent source of the energy for the large population of every country. Heavy metals are important contamination present in the milk samples because of the industrialization of the country and excessive use of the fertilizers and insecticides for the forming due to that create a soil pollution, water pollution and that indirectly comes in the dairy and dairy products. The present investigation was carried out to determine the concentration of lead, cadmium present in milk and milk products by using Atomic Absorption Spectroscopy and evaluate the potential health risks of metal to human via. consumption of milk and dairy products. A total four samples of milk and dairy products (milk, curd, butter and paneer) were collected from dairy shop in Akola city and conducted process know as pretreatment by using nitric acid, perchloric acid. The result showed the presence of heavy metals in the all the samples of milk and milk products. The heavy metal Lead (Pb) is found in more concentration as campare to normal value in case of Paneer but less concentration in all the other products. The high concentration of Cadmium (Cd) found in all the samples of the milk and milk product as compare to normal value.

***Keyword**: milk and milk products, heavy metal, Atomic absorption spectroscopy*

Introduction

Heavy metals are persistent contaminants in the environmental and create health hazards. They are released into the environment from natural as well as man-made activities. Some heavy metal (like Cu and Fe) are essential to maintain proper metabolic activity in living organisms other (like Pb and Cd) are nonessential and have no biological role However, at high concentration they can cause toxicity to living .Milk is the first food that human encounters which serves as a source of essential nutrients required for the biological function and growth during early stage of life. Milk become contaminated with heavy metal either through food stuff and water or through manufacturing and packaging process, it constitute a major food source around the world. Therefore monitoring heavy metals level in milk, is of great importance for nutritional toxicological and environmental purposes. Lead and Cadmium in milk and dairy products are of particular concern since they are largely consumed by infants children. Due to enormous development of industrial growth, heavy metals can be reached to the environment if we see in the industrial point of view then heavy metals reached to canals, rivers and other water bodies by the direct discharged or through the rain water. This contaminated water used for the agriculture purposes where the animals feeds are grown. That ultimately leads to contamination of milk and milk products.Treatment of industrial waste water by adsorption of heavy metals from industrial waste water is very crucial point to prevent the contamination of the water bodies some potential low cast sorbent for the heavy metal have been found effective. These low cast sorbent may be a more vibal option in developing countries.

But more advanced treatment technology like Nano- filtration, reverse osmosis and ion exchange should be needed for the effective removal of the heavy metals. However these technologies may not be economically feasible for the developing country.

There is a change in the milk manufacturing process may helpful to the decrees in the contamination of heavy metals. The water which is the prominent source of the

contamination of the heavy metals use for the drinking of animals and fooder of milking animals should be regularly monitored for the evaluate the content of heavy metals, precaution should be taken while handling the milk and milk products. Animal hearbs and land where they grow should be selected that should away from the any industrial area and any contaminated water bodies and fields where the use of excessive fertilizers and insecticides.

There should be regular practice for the heavy metal detection from the water bodies because heavy metals can cause serious health problems in child and elderly peoples because their high milk consumption rate. Rapid urbanization and industrialization and people not follow regulation and environmental pollution can result in elevated levels of heavy metals in milk and milk product hence the farmers should aware and educate about how to minimize the contamination.

Material and method

Collection and Sample Pre-treatment for heavy metals analysis

(Nitric acid, perchloric acid, decomposition method)

A total four sample were collected from dairy shop in Akola city. First take 2-5 ml of sample and place in the beaker were digested with nitric acid and perchloric acid until a transparent solution are obtained, after digestion sample were filtered and diluted to a suitable concentration. Adjust the PH of solution by adding distilled water up to 7, finally sample fills in the bottle and analyzed the heavy metal by using Atomic Absorption Spectroscopy.

The heavy metals like lead and cadmium concentration in the digested sample were measured using atomic absorption spectroscopy.

Result and discussion

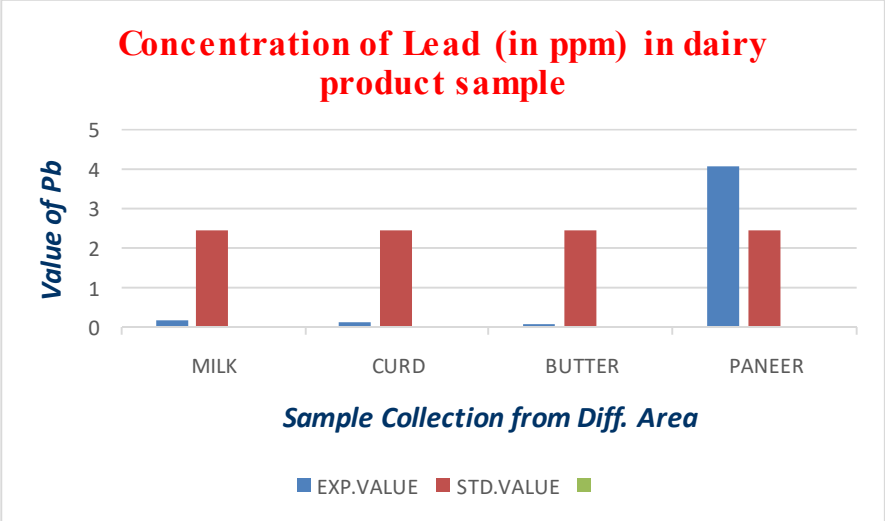
The concentration of heavy metal Pb & Cd present in milk and milk products are shown in the following table 1and 2 respectively.

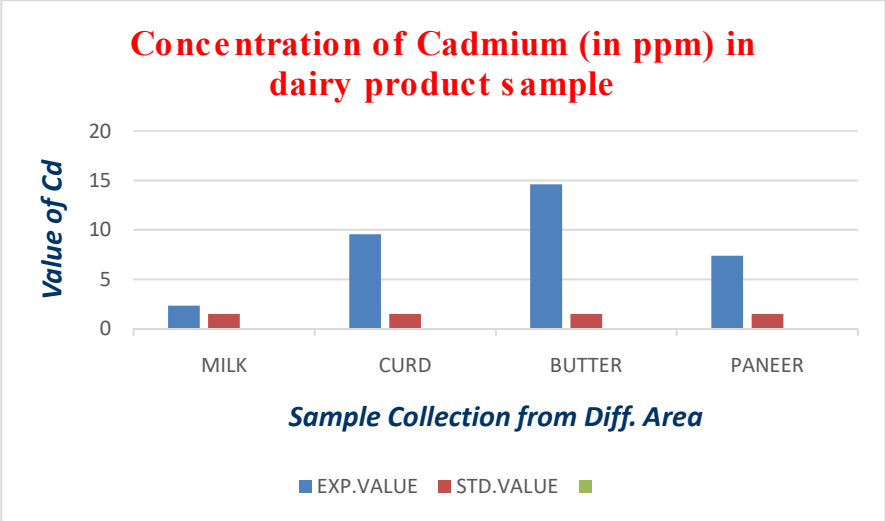
Table 1. Concentration of Lead (Pb) in ppm presents in milk and milk products (dairy) samples.

Sr. No.	Samples	Experimental value of Pb in ppm	Standard Value of Pb in ppm
1	Milk	-0.1698	2.5
2	Curd	-0.1486	2.5
3	Butter	-0.0743	2.5
4	Paneer	4.0758	2.5

Table 2. Concentration of Cadmium (Cd) in ppm presents in milk and milk products (dairy) samples

Sr. No.	Samples	Experimental value of Cd in ppm	Standard Value of Cd in ppm
1	Milk	2.3333	1.5
2	Curd	9.5333	1.5
3	Butter	14.6000	1.5
4	Paneer	7.4000	1.5





Conclusion

Taking into the consideration the level of heavy metals in the various collected samples of milk and milk products that affects the health of the people. More research ie required for the development of the effective, feasible and cost effective technology in future, for the detection of level of heavy metals from the milk and milk products that ultimately benefited for the people.

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NOVEL $CaCrO_4$: AN EFFICIENT PHOTOCATALYST FOR THE DEGRADATION OF METHYLENE BLUE UNDER VISIBLE LIGHT IRRADIATION

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ABSTRACT

The photocatalytic degradation of methylene blue has been investigated in aqueous suspension of calcium chromate prepared by three different methods under different conditions to study the impact of synthesis method on the efficiency of the photocatalyst for different applications. By measuring the change in substrate concentration as a function of irradiation time using UV-Visible spectroscopic analysis, the degradation was monitored. The photocatalytic degradation of methylene blue was studied using different parameters such as type of photocatalyst, catalyst concentration and substrate concentration to ascertain the optimum conditions for the reaction. The calcium chromate prepared by ultrasonic method was found to be more efficient as compared with sol gel and solid state methods.

Keywords: *Photocatalysis, methylene blue, calcium chromate, kinetics.*

Introduction

Water is a basic need of all living things. Water pollution has been caused by economic revolutions around the world, including population growth and industrialization. One of the pollutants in the water is the dyes wastewater of various textile industries.Large amounts of dyes are lost during the dyeing process in the textile industry, which is a major problem for the industry as well as a threat to the environment (1, 2). Therefore, the color of dye affluent has attracted increasing attention. Over the past decades, photocatalytic processes involving TiO_2 semiconductor particles under UV light radiation have been shown to be potentially beneficial and useful in the treatment of wastewater contaminants.

There are several studies related to the use of semiconductors in the photo mineralization of photo stable dyes (3-11). The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed (12, 13) extensively in the referred articles. When a semiconductor like TiO_2 absorbs a photon of energy equal to or greater than its band gap width, an electron can be promoted from the valence band to the conduction band (e_{cb}^-) which leavesan electron vacancy or "hole" in the valence band (h_{vb}^+). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with adsorbed species. Specially, h_{vb} hole may react with surface-bound H_2O or OH to produce the hydroxyl radical ($OH^\cdot$) ande$_{cb}^-$ picked up by oxygen to form superoxide radical anion ($O_2^{-\cdot}$) as indicated in eqs. 1 - 3. It has been suggested that the hydroxyl radicals ($OH^\cdot$) and superoxide radical anions ($O_2^{-\cdot}$) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the bleaching of the methylene blue.

$$TiO_2 + h\upsilon \longrightarrow e_{cb}^- + h_{vb}^+ \quad ..1$$

$$O_2 + e_{cb}^- \longrightarrow O_2^{-\cdot} \quad .....2$$

$$H_2O + h_{vb}^+ \longrightarrow OH^\cdot + H^+ \quad .....3$$

Previous studies have shown that heterogeneous photocatalytic oxidation processes can be used to extract coloring material from dye influencers in the presence of light. TiO_2 is the UV active material hence for its activation UV light is the must and natural sunlight contains very less amount of UV light which hinder its practical application in natural environment. To overcome the practical difficulties occurred in the TiO_2, researchers searching for the alternative photocatalyst compounds. From the view point of utilization of solar energy an extensive effort has been carried out to develop a visible light photocatalyst (14-15). Generally, there are two main strategies to develop visible light sensitive photocatalyst by improving the valence bands of the semiconductors. On the one hand, in the transition metal oxides doping by the anions, for example N, C, S and B the p orbital of non-metal and oxygen elements hybridize to heighten the top of the valence bands, thus narrowing the band gap. On the

other hand, in multi-metal oxides the s, p and d orbital of metals and oxygen hybridized each other to form proper valance band for photo oxidation of organic contaminations under visible light irradiation (16).

In this article we report the preparation of visible light sensitive chromium containing photocatalyst. Polycrystalline Calcium chromate ($CaCrO_4$) ceramic powders were synthesized by the conventional sol gel method, solid state reaction method and ultrasound method.$CaCrO_4$ have orthorhombic structure with 1.93 eV band gap and have a good photocatalytic activity than P25 Degussa. $CaCrO_4$ is nontoxic, quite stable in aqueous medium and activate under visible light are the advantages over TiO_2. Hence in the present study we use $CaCrO_4$ prepared by different methods to understand more about photocatalytic processes. Methylene blue has been selected as a model compound in this oxidation process.

Experimental details

The photochemical degradation of methylene blue (sd fine-chem) was studied in presence of $CaCrO_4$ prepared by different methods viz. ultrasonic, Reflux, Solid State reaction methods by using stoichiometric amount of $CaCl_2$(sd fine-chem) and K_2CrO_4 (sd fine-chem). The water used in all the studies was double distilled water. The samples prepared by ultrasonic, Reflux, Solid State reaction method was denoted as CAC-US, CaC-RF and CaC-SS here after. The pH of the resultant mixture was measured by using digital pH meter (systronics Model 335) and was found to be 5.6.

Synthesis of $CaCrO_4$

1. **Ultrasonic Method**: 100 ml 0.1N K_2CrO_4 Solution is taken in a beaker and kept in a ultrasonic bath for 15 min then drop wise slowly add 0.1 N 100 ml $CaCl_2$ solution to the above solution in ultrasonic bath then both these solutions are allow to reacts each other under ultrasonic condition for about 8 hrs. Then dark yellow colored precipitate of $CaCrO_4$ is obtained, filter it and then kept in an oven for 6 hrs for drying. The dried powder is removed and kept in dry glass bottle for further investigations.
2. **Reflux method**: 100 ml 0.1N K_2CrO_4 Solution and 0.1 N 100 ml $CaCl_2$ solution mix in a round bottom flask and allowed to reacts each other under reflux condition for about 1 hr. Then round bottom flask is removed and content is then filtered out with proper washing so that unreacted ions get removed and we get dark yellow colored precipitate of $CaCrO_4$ on the filter paper. This is then kept in an oven for 6 hrs for drying. The dried powder is removed and kept in dry glass bottle for further investigations.
3. **Solid state Reaction method:** In this method 1.9419 g of K_2CrO_4 and 1.6987 g of $CaCl_2$ both mixed on a thoroughly cleaned mortar with the help of pistol for about 2 hrs. Then the mixture is kept for drying in a oven for about 100 ^oC for 6 hrs. The dried powder is removed and kept in dry glass bottle for further investigations.

Photocatalytic investigation

The Photolysis of aqueous solution of methylene blue (MB) for 4 ppm and 200 mg of $CaCrO_4$ prepared by different methods was carried out in a circular glass reactor (designed and fabricated in our laboratory). Tungsten lamp (40W/230V/36D, Phillips, Essential) was used as a visible light source. During the photolysis experiment air was bubbled in a solution continuously as a source of oxygen. Aliquots of the reaction mixture were withdrawn and suspensions were filtered through 0.2 um millipore discs prior to determination of methylene blue quantitatively by using UV-Visible spectrophotometer (ShimadzuUV-1800).

The mineralization of methylene blue was monitored by measuring the absorption intensity as a function of irradiation time whereas the degradation was monitored by measuring the absorbance on UV-Visible spectrophotometer (ShimadzuUV-1800).

The absorption maxima of the methylene blue have been found at the wavelength range 650-653 nm. Therefore, the degradation of the methylene blue was followed at the wavelength as a function of irradiation time with appropriate dilution. For each rate experiment, the degradation for the mineralization and decomposition of the model pollutants was

calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of absorbance of the methylene blue as a function of irradiation time, i.e. first order degradation kinetics. It was calculated in terms of mol L^{-1} min^{-1}.

Characterization
XRD Analysis

The crystal structure of $CaCrO_4$ formed by different methods is shown in figure 1. From XRD patterns and corresponding characteristics 2Θ value of diffraction peaks shows that the samples have tetragonal structure with space group I41/amd. The indexed results are in good agreement with JCPDS database card no. 75-0936.

The average particle size of crystallites was calculated from peak at half-width B using Scherer equation. The average particle size of CaC-US, CaC-RF and CaC-SS is near about 58 nm. This indicated that the particle size in nanometer range may be due to low temperature process which decreases the agglomerization.

Absorption Spectra

The main objective of this study is to develop a visible light active photocatalyst. The visible light absorption spectra of CaC-US, CaC-RF and CaC-SS are identical and absorb in visible range as shown in figure 2. The prepared samples have single absorption band confirmed that, the chromium is hexavalent not a trivalent.

Band gap energy

The UV/VIS diffuse reflectance spectroscopy method was used to estimate band gap energies of prepared samples. The minimum wavelength required to promote an electron depends upon the band gap energy E_{bg} of the photocatalyst as shown in figure 3 and is given by: $E_{bg} = 1240/\lambda$ eV

Where λ is wavelength in nanometer

Photoluminescence spectra

The photoluminescence emission spectra have been frequently used to examine the efficiency of charge carrier trapping, immigration, and transfer, and to understand the fate of electron-hole pairs in semiconductor particles [16]. PL emission spectrum with excitation wavelength at room temperature is as shown in figure 4. The main emission peak was attributed to the direct recombination of a conduction electron in Cr 3d orbital and a hole in hybrid valence band of O 2p and Ca 4d.

Photocatalytic Degradation

The photocatalytic activity of $CaCrO_4$ synthesized by different methods was evaluated by degradation of methylene blue under visible light irradiation; results are shown in Figure 5. The MB degradation percentage (16) was calculated at the irradiation time t min, the solution samples after centrifugal treatment were studied at 650-653 nm. The MB degradation percentage D.P (t) is calculated by

$D.P.\ (t) = (A_0-A_t)/A_0 X100\ \%$

The MB degradation by CaC-US is about 78%, CaC-RF is about 66%. While by CaC-SS is about 58% after 90 minute irradiation of visible light at 200 mg of photocatalyst, when MB concentration is 4 ppm. It was found that the self-photolysis degradation of MB was about 0% in the same condition. The temporal evaluation of spectral changes taking place during photo degradation of MB is as shown in Figure 5. The photocatalytic activity of $CaCrO_4$ was determined by the depletion of different concentrations of methylene blue dye in aqueous solution under visible radiation.

3. Results & Discussion

Photocatalysis is a powerful advanced oxidation process having many advantages over the other oxidation methods. It was observed that the degradation of methylene blue is more for CaC-US as compared with CaC –RF and CaC -SS. The degradation curves can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. For each experiment, the rate constant was calculated from the plot of natural logarithm of absorption intensity and dye concentration as a function of irradiation time. The degradation rate for the mineralization and decomposition was calculated using the formula given below,

$-dk[A]/dt = kc^n$

Where A=Absorbance

k= rate constant

c= concentration of MB

n=Order of reaction.

Blank experiments were carried out by irradiating aqueous solution of methylene blue in absence of photocatalyst, where no observable loss of methylene blue.Calcium chromate is known to be the semiconductor photocatalytic activity is non-toxic, relatively inexpensive and stable in aqueous solution. Certain reviews have been written regarding the mechanistic and kinetic details as well as the influence of experimental parameters. It has been demonstrated that degradation by photocatalysis can be more efficient than by other wet-oxidation techniques. We have tested the photocatalytic activity of three different photocatalysts prepared by different methods on the degradation kinetics of methylene blue. Figure 5 shows the degradation rate for the decomposition of methylene blue in the presence of different types of photocatalysts viz CaC-US, CaC -RF and CaC –SS.

It has been observed that the degradation of methylene blue proceeds much more in the presence of CaC -US as compared with CaC –RF and CaC -SS. Itconcluded that the catalyst prepared by ultrasonic method is more active than the other two catalysts. The differences in the photocatalytic activity of CaC -RF, CaC -SS and CaC US are likely to be due to differences in the BET-surface, impurities, lattice mismatches or density of hydroxyl groups on the catalyst's surface since they will affect the adsorption behavior of a pollutant or intermediate molecule and recombination rate of electron-hole pairs.

In all the following experiments, CaC -US was used as a photocatalyst since this material exhibited the highest overall activity for the degradation of methylene blue. By studying the dependence of the photocatalytic reaction rate on the substrate concentration is important from a mechanical and application point of view. The effect of substrate concentration on the degradation rate for the decomposition and mineralization of methylene blue was studied, as it is important from both the mechanistic and application point of view. As oxidation proceeds, less and less of the surface of the $CaCrO_4$ particle is covered as the pollutant is decomposed.Our results on the effect of the initial concentration on the degradation rate of methylene blue indicate that the degradation rate decreases as the substrate concentration increases. This may be due to the fact that as the initial concentrations of the dye increases, the colour of the irradiating mixture becomes more intense which prevents the light from entering the surface of the catalyst. Hence, the generations of relative amount of OH and O_2 on the surface of the catalyst do not increase as the intensity of light; illumination time and concentration of the catalyst are constant. Conversely, their concentrations will decrease with increase in concentration of the dye as the light photons are largely absorbed and prevented from reaching the catalyst surface by the dye molecules.As a result, on increasing the concentration of the dye, the degradation efficiency of the dye decreases.

The degradation rate for the mineralization and decomposition of methylene blue under investigation was found to decrease with the increase in catalyst concentration and remain almost constant above certain level. This can be explaining as fallows, as amount of catalyst is increased, the substrate molecules available are not sufficient. As the number of $CaCrO_4$ particles increases, i.e., although more area is available, for constant initial concentration of dye, the number of substrate molecules present in the solution is the same. Therefore, the additional catalyst powder does not engage in catalytic activity and the rate does not increase due to the increase in the amount of catalyst above a certain limit. The results agree with several previously reported studies.

Conclusion

$CaCrO_4$ as photocatalyst can efficiently catalyze the photo mineralization of textile dye like methylene blue in the presence of visible light and oxygen. The degradation rate by CaC-US is more as compare with CaC-RF and CaC-SS. The observations of this investigation clearly show the importance of selecting the optimal degradation parameters to achieve high degradation rates, which are essential for any practical use of the photocatalytic oxidation process.The best degradation condition depends strongly on the nature of pollutant. The investigations were conducted at the laboratory scale in order to determine the optimal degradation condition and further studies are required.

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Figures:

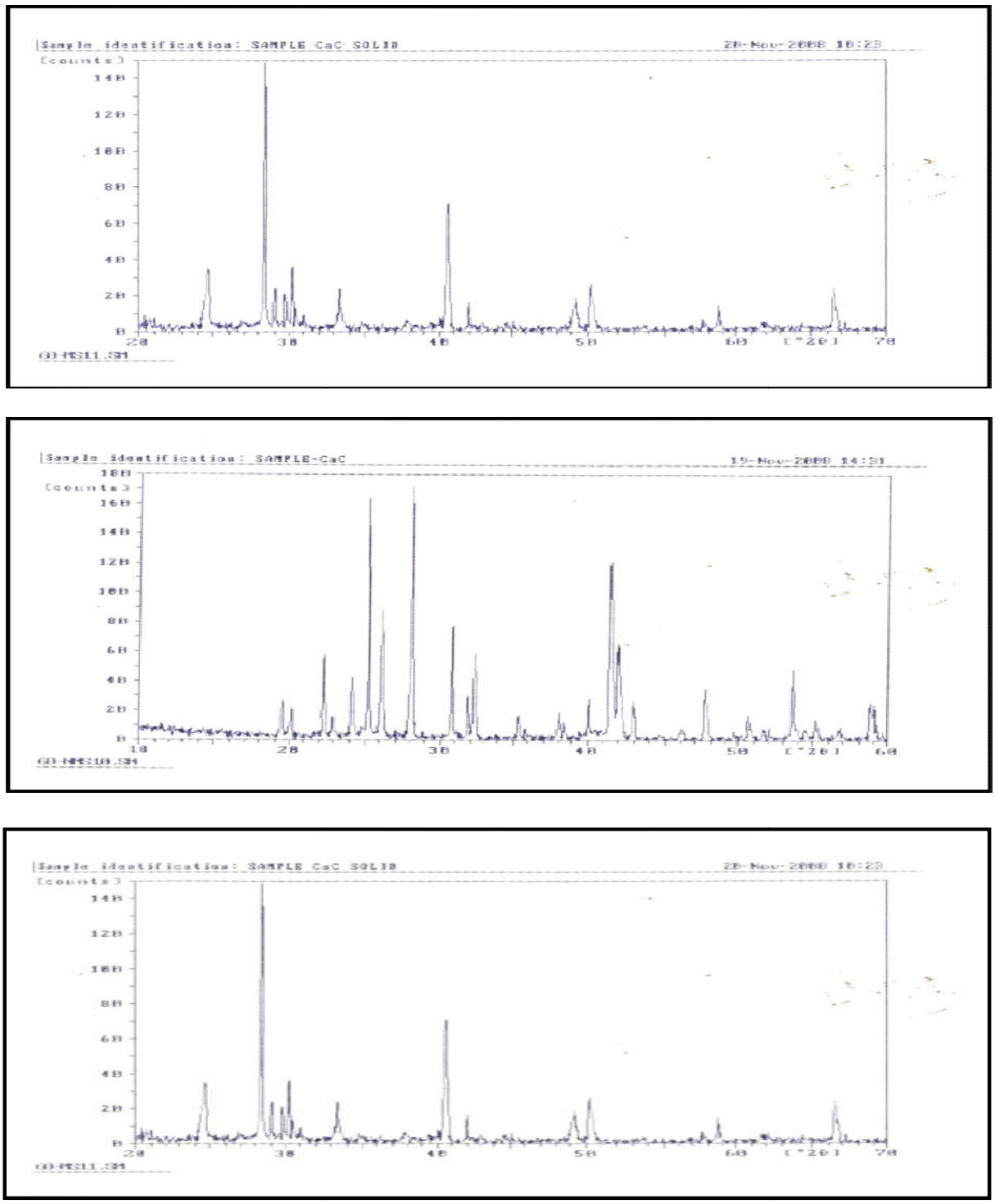

Figure 1: XRD spectra of $CaCrO_4$ synthesize with US, RF and SS methods.

Figure 2: The visible light absorption spectra of CaC-RF & CaC-SS are identical and absorb in visible region

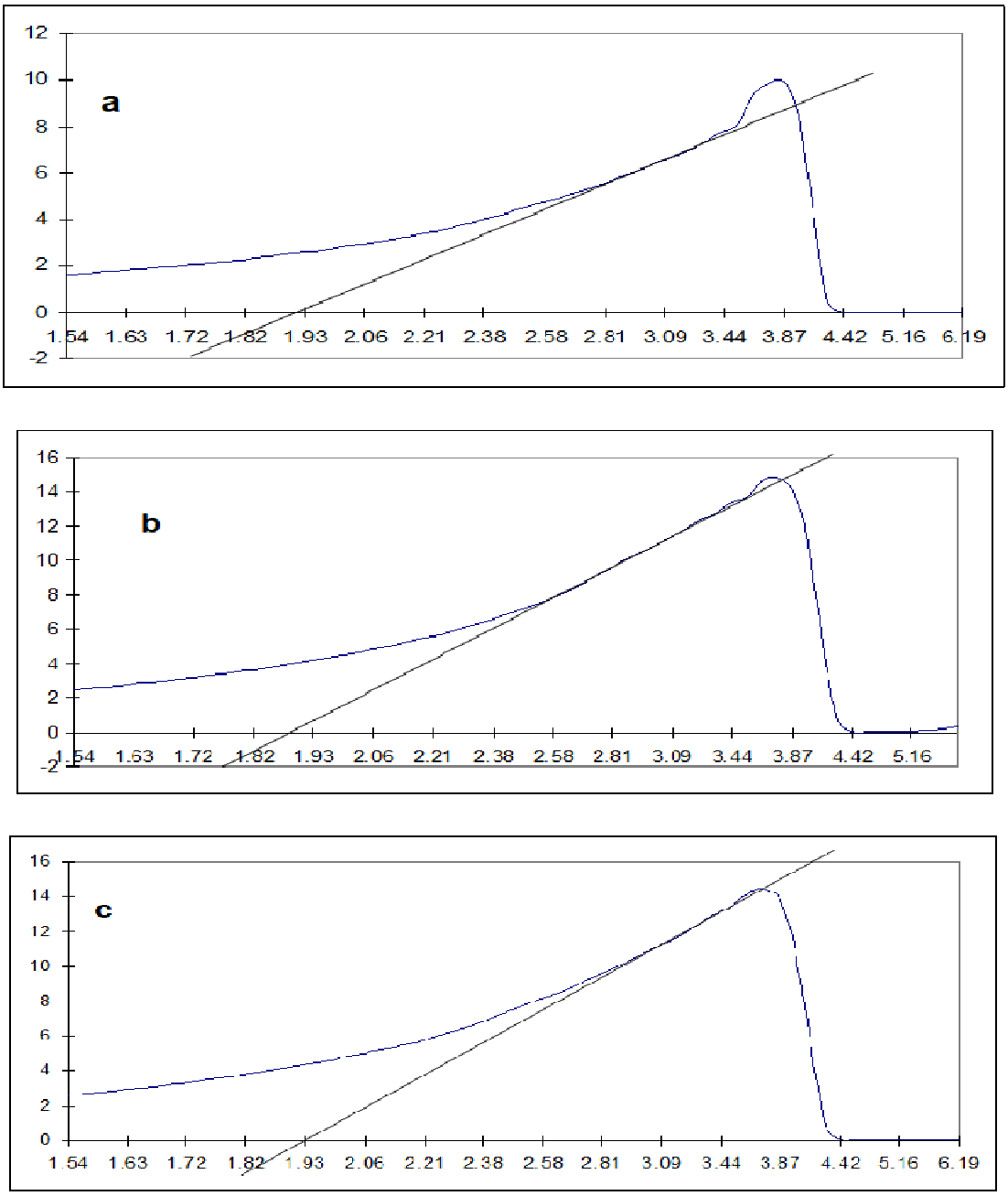

Figure 3: shows (αEbg)2 versus Ebg for band gap transition, where α is the absorption coefficient and Ebg is the photon energy.The value of Ebg extrapolated to α=0 gives an absorption energy, which corresponds to a band gap energy 1.93 eV.

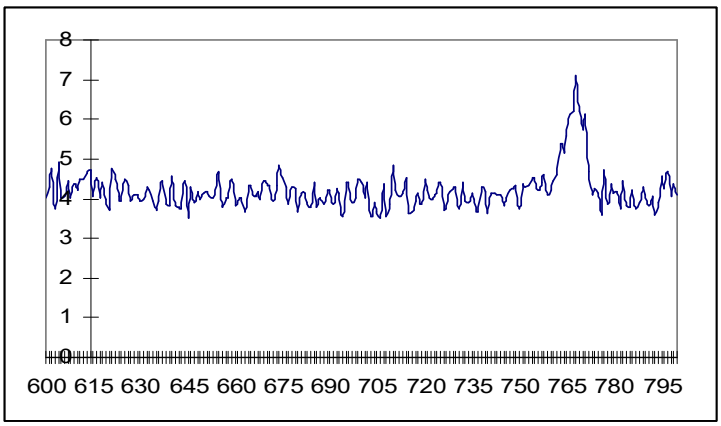

Figure 4: Photoluminescence spectra of CaC-US

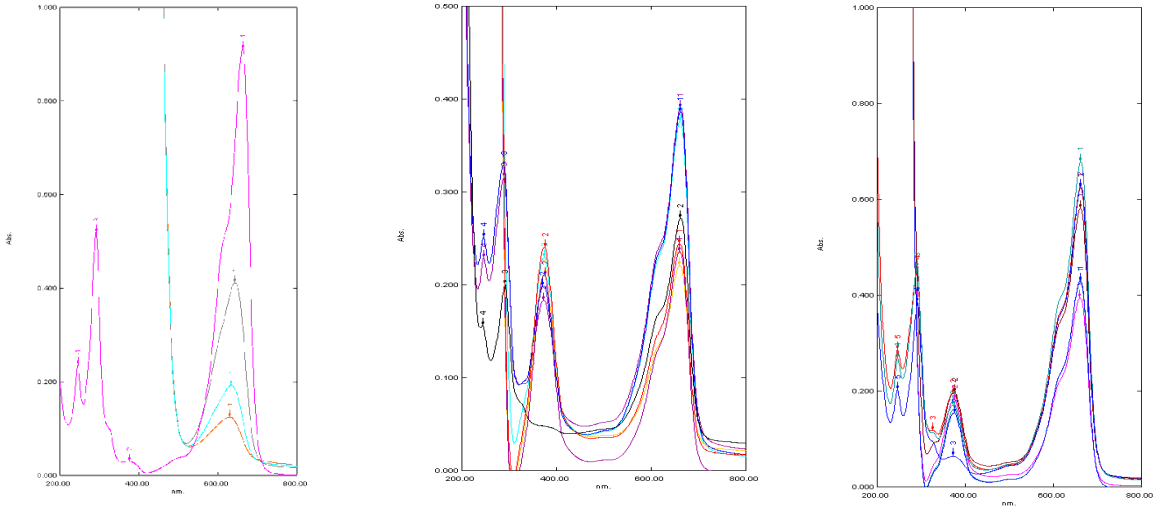

Figure 5:Comparison of degradation rate for the mineralisation and decomposition of methylene blue in present of different calcium chromate. Experimental Conditions: Concentration of Methylene blue (4ppm), Volume 100ml, pH=5.6, Catalyst (200mg).

BIODEGRADATION OF TEXTILE DYE ORANGE F2R BY *BACILLUS CEREUS OFR-1* - AN ECO-FRIENDLY APPROACH

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ABSTRACT

Textile industries utilize enormous amounts of dyestuffs for coloring the fabric. The unused large numbers of dyestuffs are discharged along with textile effluents which pose serious threats to the environment. Traditional effluent treatment methods are unable to remove these dyes from the environment. Hence biological degradation of textile dyes is now the most preferred method. The textile dye Orange F2R is commonly used in textile industries. In the present study, a new bacterial strain was exploited for biodegradation of Orange F2R dye which was isolated from acclimatized samples and primarily designated as OFR-1. The morphological, biochemical, and 16s rRNA identification revealed that OFR-1 as Bacillus cereus OFR-1. Various physicochemical cultural conditions used for degradation of Orange F2R dye by Bacillus cereus OFR-1 were: Temperature 37^{0}C, pH 7.0, inoculum size 1%, dye concentration 800 ppm in nutrient media. Glucose and Yeast extract were proved excellent carbon and nitrogen source. These all studies showed 98% of dye decolourization which was confirmed by spectrophotometer.

Keywords: *Biodegradation, decolourization, Orange F2R, Bacillus cereus OFR-1.*

Introduction

The world's first synthetic dye was commercially and successfully discovered by William Henry Perkin in 1856. At the end of the 19th century, more than 10000 synthetic dyes were discovered and utilized in textile industries (Robinson et al., 2001). In the current scenario the growth of textile industries is proportionate to the use of synthetic dyestuffs, which contribute to the rise in environmental pollution due to textile effluent (Pandey et al., 2007). The generation and nature of textile effluent depend on the various manufacturing operations in textile industries during the alteration of fiber to textile fabric (Dhanve et al., 2008).The textile effluent is characterized by high values of Temperature, pH, BOD, COD, harmful chemicals, and heavy metals due to processing strategies and types of dyes used for processing (Banat et al., 1996). Near about 2, 80,000 tons of dyes are discharged along with textile effluent per year (Jin et al., 2007). Azo dyes contain -N=N- (azo bond), are the major group of synthetic dyes and are widely found synthetic dyes which are discharged in the environment (Chang et al., 2001b; Saratale et al., 2009b). Due to presence of the one or more azo bonds (-N=N-) in chemical structure, azo dyes absorb light in the visible wavelength (Chang and Kuo, 2000). Due to complex chemical structure, 90% of azo dyes persist after treatment and enter in the environment (Pierce, 1994). These untreated dyes and their metabolites pose a serious threat to the environment and are carcinogenic, toxic, and mutagenic (Fang et al., 2004; Asad et al., 2007). Improper release of azo dyes and their intermediates are perilous to aquatic life which reduce the penetration of sunlight in water and so reduce the amount of dissolved oxygen, photosynthetic activity, and water quality which badly affect on the life of aquatic flora and fauna and pose a serious environmental threat (Vandevivere et al., 1998) hence the development of effective treatment against this pollutants has been carried out (Lucas and Peres, 2006; Neamtu et al., 2002). Moreover, presence of azodyes in effluents increases BOD (Biological Oxygen Demand), COD (Chemical Oxygen Demand), TOC (Total Organic Carbon) (Saratale et al., 2009b). Various types of microorganisms such as bacteria, actinomycetes, fungi, algae, and yeasts can degrade wide variety of dyes through aerobic, anaerobic, sequential aerobic-anaerobic treatment. Hence the key objectives of the present research work were to degrade harmful textile azo dye Orange F2R by bacteria isolated from acclimatized samples. Identification studies revealed that a potent bacterium was *Bacillus cereus*. Maximum decolourization was achieved by optimizing various parameters. Analysis of degraded metabolites of dye was carried out by FTIR techniques.

Materials and Methods

Soil and Water Samples: Soil and water samples were collected from the nearby area of textile effluent discharge, Effluent treatment plant.

Textile dye: Orange F2Rwas purchased from Sigma Aldrich (USA) having an analytical grade (λ max- 494 nm)**.** Its formula weight is 1034.264876. It doesn't form precipitation with hard water or even with acid.

Acclimatization of Soil and Water samples

Collected soil and water samples were mixed properly and homogenized. These samples were added with increasing concentration of dye to acclimatize the microflora for one month period. One gram acclimatized sample was serially diluted and used for isolation of dye decolorizing bacteria.

Isolation, Screening, and Identification of dye decolorizing bacteria

Isolation of dye decolorizing bacteria was carried out on nutrient agar plates by using acclimatized samples. Isolated colonies were screened using nutrient agar containing 100 ppm dye concentration. Colonies showing zone of decolourization were further screened in nutrient broth containing the same dye at the same concentration. The bacterial isolate showing maximum decolourization of broth was selected and designated as OFR-1 and used for further study. Primarily the isolate was identified by Morphological and Biochemical tests as per Bergey's manual. Organism was identified by 16S rRNA sequencing.

Dye Decolourization Experiments

Effect of Temperature and pH on dye decolourization

The effect of different temperatures on the dye decolourization ability of OFR-1 was studied by inoculating the organism in a 30 ml sterile nutrient broth containing 100 ppm dye concentration. The tubes were kept at various temperatures (Room temperature, 37^0C, 45^0C, 55^0C, and 65^0C) for 24 hours. To study the effect of different pH, the isolate was inoculated in a 30 ml sterile nutrient medium containing 100 ppm dye concentration having pH in the range of 6 to 10. Tubes were kept for incubation for 24 hours at 37^0C.

Effect of dye concentration and Inoculum size on dye decolourization

To examine the effect of dye concentration, the tubes containing 30 ml sterile nutrient broth were inoculated with OFR-1. The tubes were added with various concentrations of Orange F2R in the range of 100 ppm to 1000 ppm and kept for incubation at 37^0C for 24 hours. Further, the effect of inoculum size was also studied. 30 ml sterile nutrient broth containing 100 ppm dye concentration was inoculated with 1%, 2%, 3%, and 4% inoculum size of the bacterial isolate OFR-1. Tubes were kept for incubation at 37^0C for 24 hours.

Effect of Carbon and Nitrogen sources on dye decolourization

To study the effect of Carbon and Nitrogen sources on dye decolourization, the selected isolate was inoculated in a 30 ml sterile Minimal medium having 100 ppm of dye concentration and 1% of different Carbon and Nitrogen sources such as Glucose, Sucrose, Starch, Peptone, Yeast extract, and Meat extract. The tubes were kept for incubation at optimum temperature and pH for 24 hours. The decolourization was then supervised spectrophotometrically.

Percent decolourization Assay

The percent decolourization of dye was determined by comparing the initial absorbance and final absorbance of dye after decolourization at its maximum absorbance wavelength (λ max) by spectrophotometer (Systronics-106 model) and calculated by using the following formula.

$$\textbf{\% decolourization} = \frac{\text{Initial Absorbance} - \text{Final Absorbance}}{\text{Initial Absorbance}} \times 100$$

Analytical Studies
FTIR Analysis

Extraction of dye degraded products was carried out by the equal volume of Dichloromethane (DMC). These extracted metabolites were analyzed by FTIR (Perkin Elmer Spectrum 65) and compared with standard dye.

Results

Isolation, Screening, and Identification of dye decolorizing bacteria

Total 14 bacterial isolates were isolated from acclimatized soil samples out of this 1 isolate were observed as potent Orange F2R decolorizing bacterium. It was primarily designated as OFR-1 and further Morphological, Biochemical (Table 1, Table 2 and Table 3) and Molecular Identification (16s rRNA sequencing) revealed that the isolate was *Bacillus cereus OFR-1*. The construction of dendrograms and phylogenetic calculations were done by MEGA 4.0 software with NJ (Neighbor-Joining) methods. Phylogenic Analysis is showed in Figure 1.

Table1: Morphological characteristics of OFR-1

Size (mm)	Shape	Colour	Margin	Elevation	Consistency	Opacity	Gram nature	Shape	Motility
2	Circular	Colorless/dull	Undulate	Raised	Smooth	Opaque	Gram Positive	Rods	Motile

Table 2: Biochemical characteristics of OFR-1

Utilization of						Hydrolysis of		
Glucose	Fructose	Sucrose	Mannitol	Lactose	Maltose	Casein	Starch	Gelatine
A, G	A, G	+	-	-	A, G	+	+	-

A= Acid G=Gas

Table 3: Biochemical characteristics of OFR-1

Enzyme Activity			Indole	Methyl red	Voges-Proskauer	Citrate utilization	Nitrate reduction
Catalase	Urease	Oxidase					
+	+	-	-	-	+	+	-

'-' = Negative test; '+' = Positive test.

Molecular identification

The construction of phylogeny was done by searching DDBJ BLAST. On the basis of 16s rRNA sequencing , organism was identified as of *Bacillus cereus OFR-1.*

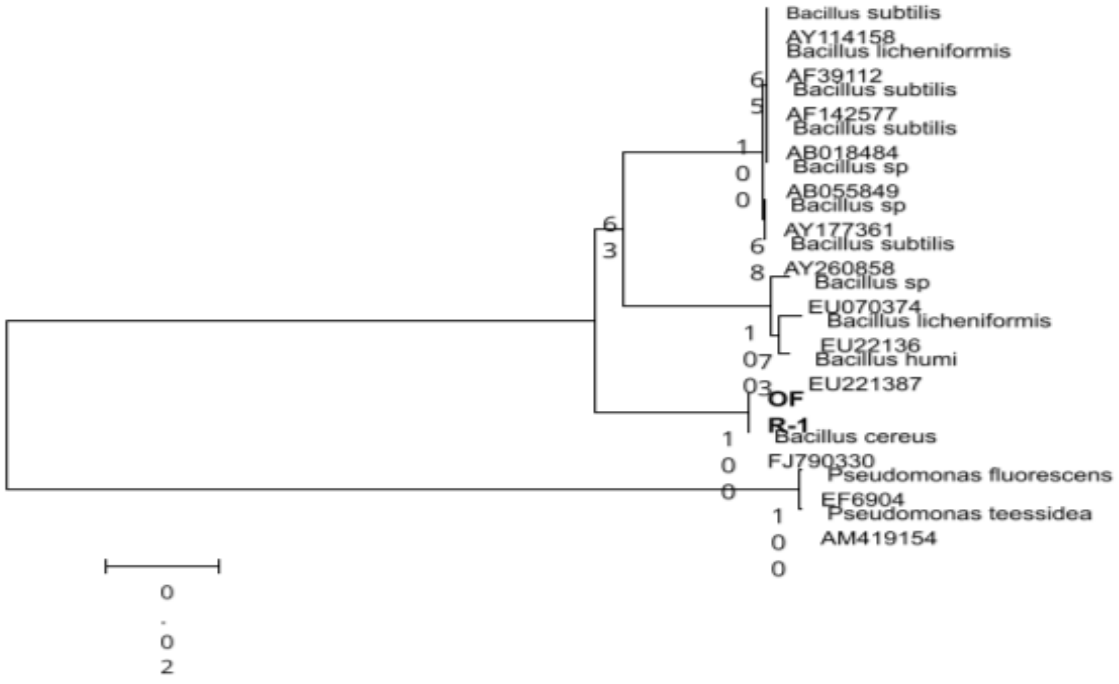


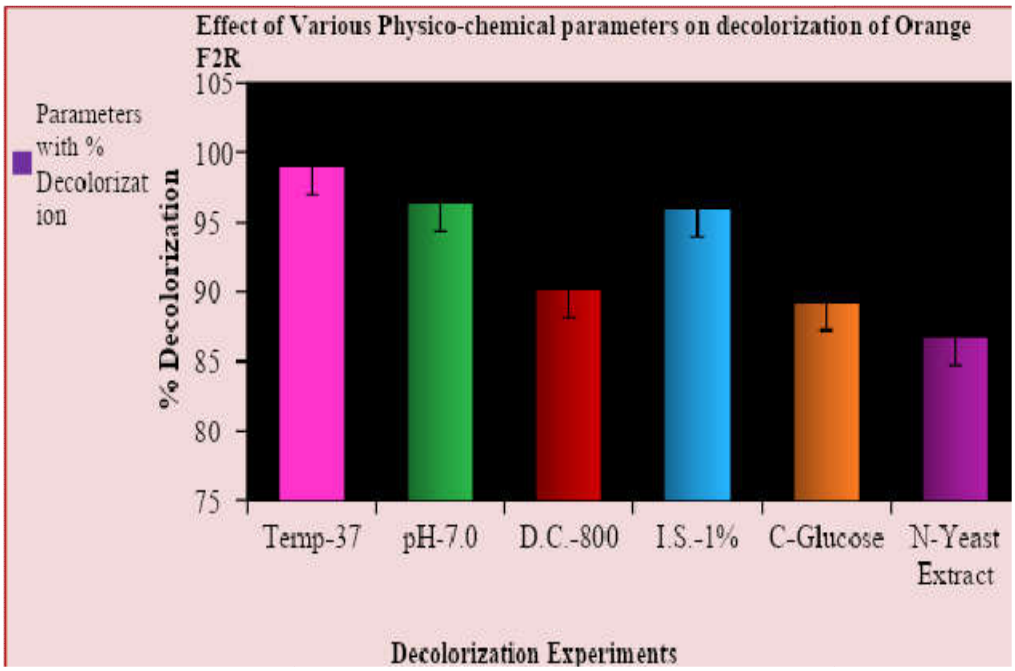
Figure 1: Phylogenetic Tree of OFR-1. The 16S rRNA sequence showing relationships among OFR-1 and closest type strain species of *Bacillus cereus.*

Decolourization Experiments

Effect of Temperature and pH on dye decolourization

It was observed that the isolate OFR-1showed maximum decolourization at temperature range Room temperature to 45^0C, specifically at 37^0C (98.99%). The maximum decolourization was observed at 8.0 – 10.0 pH, specifically at pH 7.0 (96.31%) (Figure 2).

Figure 2: Effect of various physic-chemical parameters on decolourization of Orange F2R by *Bacillus cereus OFR-1* within 24 hours.



Where- Temp-Temperature; **D.C.-** Dye Concentration; **I.S.-** Inoculum Size; **C-** Carbon source; **N**- Nitrogen Source.

Effect of dye concentration and Inoculum size on dye decolourization

It was observed that the promising isolate was able to decolorize Orange F2R up to 800 ppm very efficiently (90.12%). Above 800 ppm, the dye decolourization rate was decreased. The promising isolate was studied for dye decolourization ability in various concentrations *viz.* 1%, 2%, 3% and 4% in 30 ml Nutrient broth containing 100ppm Orange F2R concentration. It was found that the isolate showed the highest decolourization (95.89%) when added in 1% concentration (Figure 2).

Effect of Carbon and Nitrogen sources on dye decolourization

OFR-1 showed 89.23% decolourization of dye when the medium was added with 1% Glucose as compared to Starch and Sucrose while it showed 86.73% decolourization with Yeast Extract (Figure 2).

Analytical Studies

FTIR (Fourier Transform Infrared Spectroscopy) analysis

The FTIR spectrum of standard (Original) dye was compared with the spectrum of treated dye. FTIR spectrum of original dye showed a peak at 3413.54 cm^{-1} indicates intramolecular hydrogen bonding of Aromatic O-H and –OH stretching. The degradation metabolites of Orange F2R exhibited peaks at 3328.60 cm^{-1} denotes a weak bond of N-H stretching for Secondary amines. This spectrum of metabolites formed after degradation of Orange F2R dye by *Bacillus cereus OFR-1* indicates dye was degraded and there was formation of alkyl chloride, secondary amines. The new peaks formed in by-product and some peaks disappeared from the original dye indicating degradation of dye (Figure 3 and Figure 4).

Figure 3: FTIR spectra for Standard (Original) Orange F2R dye

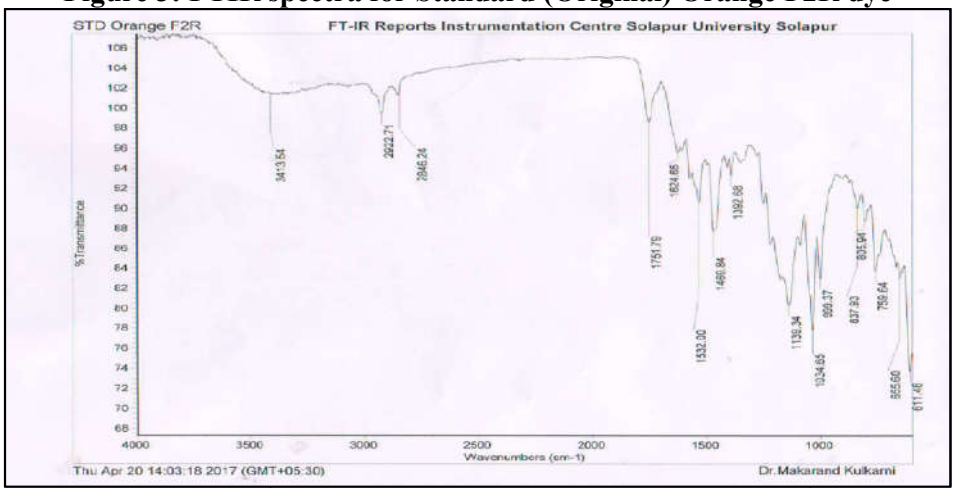
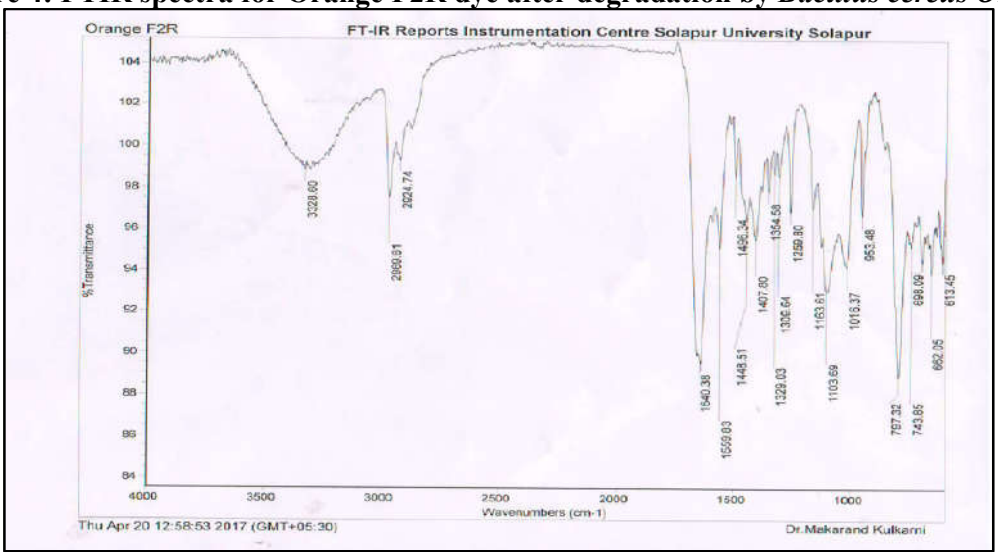


Figure 4: FTIR spectra for Orange F2R dye after degradation by *Bacillus cereus OFR-1*



Discussion

The extrinsic factors as pH, Temperature, inoculum concentration, dye structure, and concentration have a substantial impact on the uptake of dye for microbial metabolism (Krishnan et al., 2016). The optimization studies exhibited that *Bacillus cereus OFR-1* showed highest decolourization at pH 7.0 (neutral pH) (96.31%) and 37^{0}C temperature (98.99%) when added with 1% inoculum size (95.89%) in presence of up to 800ppm dye concentration (90.12%). These reports were strongly in accordance with the reports revealed by Geetha *et al.* (2016), who suggested the decolourization of dye Alizarin Red S by *Escherichia coli* and *Pseudomonas sp.* They found that when the medium was optimized with 1% Glucose, 1% Peptone, temperature 37^{0}C, pH 7.0, dye concentration 500mg/l and a combination of 50 immobilized bacterial cells, 1% Glucose, 1% Peptone in 100 ml of Minimal salt medium, these bacteria showed highest decolourization rate as 78.04% by *Escherichia coli* and 69.17% by *Pseudomonas sp.* It was also reported that if pH increased from 3.0 to 7.0, the decolourization efficiency of isolate also gets increased and maximum at pH 7.0. At the temperature range 25^{0}C to 35^{0}C there was maximum decolourization and the optimum temperature was 35^{0}C (Walaa, 2016). These results were exactly similar to the present research work. Dye concentration and bacterial growth are inversely proportional to each other. As the dye concentration increased, the bacterial growth and eventually percent dye decolourization also get decreased. Decrease in

color removal ability may be toxic nature of dye for bacteria by inhibiting metabolic activities. Generally, one or more Sulphonic acid groups are present on aromatic rings of azo dyes which inhibit the growth of microorganisms may be like detergents (Chen et al., 2003). The isolate was able to decolorize the dye Orange F2R up to 800 ppm concentration while increasing dye concentration ceased the growth of *Bacillus cereus OFR-1.* Same results were also revealed earlier (Renganathan et al., 2006)

Dyes are said to be deficient in carbon source hence they are very difficult to microbial degradation without supplement of additional carbon source in the medium which acts as co-metabolite (Khan and Mathur, 2015) and nitrogen source (Tony et al., 2009). Nitrogen sources contain a source of electron donors which helps in the reduction of azo dyes (Das et al., 2009). The rate of biodegradation gets enhanced in presence of carbon and nitrogen sources. It was observed that *Bacillus cereus OFR-1*showed the highest decolourization of Orange F2R in presence of 1% glucose as carbon source 1% Yeast Extract as nitrogen source.

Conclusion

The potent isolate *Bacillus cereus OFR-1*was isolated from acclimatized soil samples and identified by 16s rRNA sequencing. It is revealed that a single bacterium can tolerate and consequently decolorize toxic and higher concentrations of dye. After various experiments finally it can be concluded that this promising isolate can be exploited for the bioremediation and detoxification of harmful textile azo dye Orange F2R and also for bioremediation of textile effluent which is a cost-effective approach and will lead to green technology.

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