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RE-SYNTHESIS OF MALACHITE GREEN

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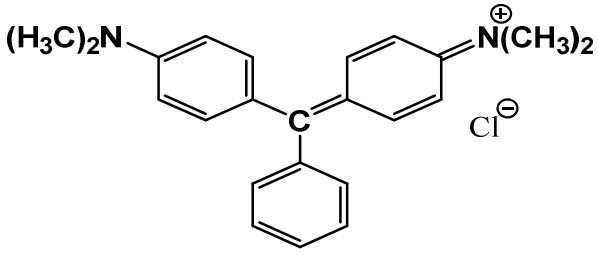
ABSTRACT

In this research work, we obtained a dye that is mainly used in the industry of textile it is also used in aquaculture as an antifungal, antiparasitic, antibacterial and therapeutic agent. For having a good yield we tried to design simple and better working conditions. It was determined the best conditions for the catalyst. By using $SnCl_4$ as a catalyst we had a better yield than other catalysts used before also the temperature at which reaction was carried out is low, and the time reaction is also short. Catalysts, solvent used in reaction, the molar ratio of reactants and the time reaction is done were the main parameters that leded to the establishment of optimal synthesis conditions.

INTRODUCTION

One of the vibrant and challenging zones that requires continuous research is the dyes industry. According to chemical structure and method of use (application) dyes can be classified. Based on chemical structure classification, triarylmethane is among the most important dyes. Both dyes triarylmethane, as well as leuco forms, are important compounds with various industrial, biological and analytical applications. These dyes also have wide usage of technological applications. Malachite green (Figure 1) is a cationic dye of triarylmethane that is used widely in the textile industry for giving dye to silk, cotton, wool, nylon and polyacrylonitrile fibers. [1] It is also used for giving dye to lacquers, tanneries, plastics, paper, food industry, and cellulose, as well it is used in dyes printing works, pharmaceutical, and cosmetics materials. [2] For manufacturing inks frequently malachite green dye is used. This dye due to possessing high efficacy against fish and roe, it is also used as a significant fungicide and antiseptic in fisheries and aquaculture. [3-5]



Malachite green

Figure 1 Malachite green dye structure (as chloride)

The study of literature presents different methods for making triarylmethane dyes including the nucleophilic reaction of arenes with triethyl orthoformate, oxidative coupling of aniline N, N- substitute with a metallic catalyst (palladium catalysts, etc.), triarylmethane can also be obtained microwave assisted synthesis. [6-9]. The reaction of aryl aldehydes with N, N-dimethylaniline is one of the most used methods for obtaining triarylmethane dyes. This reaction is commonly performed in the presence of Bronsted acids like H_2SO_4, HCl and methanesulfonic acid or Lewis acids such as $ZnCl_2$, montmorillonite K-10, and zeolites. [10]

The procedures that are presented in literature have disadvantages such as the use of corrosive acids in reaction, low yields, excess usage of solvent, severe reaction conditions, very long reaction time and difficulties in handling reagents. In some recent works catalysts such as copper (II), zirconium nitrate (IV), $SbCl_3$ have been successfully used for synthesizing triarylmethane dyes, [11-14]. In another work as a catalyst Bi $(NO_3)_3$ was used in the reaction that is carried out without solvent and results in desired products with good yields. [11]

As a result, development of simple methods for efficient synthesis of malachite green dye is an interesting challenge. Here in our present work, We studied benzaldehyde and N, N-dimethylaniline reaction in different reaction conditions (with solvent, solvent-free, reaction time). As solvents dichloromethane, ethanol and ethyl ether were tested. Our research showed that in the presence of $SnCl_4$, N, N-dimethylaniline reacts with benzaldehyde to produce adequate leucomalachite with good yield.

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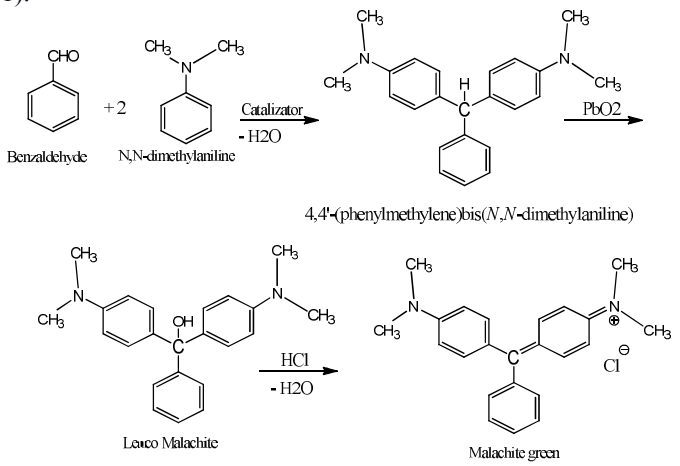
A new route that we described for obtaining the leucomalachite and malachite green dye is by using $SnCl_4$ as a catalyst. The condition in which we worked with solvent excellent results were obtained. The reaction for synthesis of leucomalachite and malachite green dye are shown in (Scheme 1).



Scheme 1 Reaction of synthesizing malachite green dye

MATERIALS AND METHODS

In this work, melting points were measured using a "Melting Point Meter" KRS-P1, Krüss Optronic GmbH, melting point apparatus and are uncorrected. The IR studies were carried on a Perkin Elmer FT-IR spectrophotometer-Spectrum 100. Benzaldehyde, N,N-dimethylaniline, hydrochloric acid, para toluenesulfonic acid, $SnCl_4$ and All chemicals that we used in our work were in reagent grade and they were used without further purification.

RESULTS AND DISCUSSION

In our research work, these syntheses were performed to find optimal conditions for benzaldehyde reaction with N, N-dimethylaniline in presence of various catalysts (compared to benzaldehyde in a concentration of 20% moles, in different molar ratios, solvents and reaction times) were used to achieving good yields of dye. The catalyst influence in the condensation of N, N-dimethylaniline with benzaldehyde in the presence of HCl, tin tetrachloride and p-toluenesulfonic acid, was observed. The reactants benzaldehyde: N, N-dimethylaniline were used is in the 1: 3 molar ratios. The was carried out is 115-120 ^{0}C temperature. We aim at this reaction to obtain the leucomalachite dye that oxidizes to malachite green dye. Malachite green was oxidizedusing lead oxide as oxidizing agent. In the result of 4 hours reaction time, the leucomalachite was obtained and the oxidation of leucomalachite to malchite green dye takes up to 2 hours to be completed, the overall reaction time was 6 hours. The results obtained and working conditions in synthesis are presented in Table I.

Table I Results and working conditions

Current Issue	Catalyst% moles	Yield%
1	HCl37%	62.33
2	APTS20%	66.71
3	$SnCl_4$20%	81.20

The abbreviations are: B =benzaldehyde; N,N,DMA = N, N-dimethylaniline, APTS = para toluenesulfonicacid.

Depending on the catalyst used in reaction to the variation of yield in the dye is represented in Figure 2 in a graph.

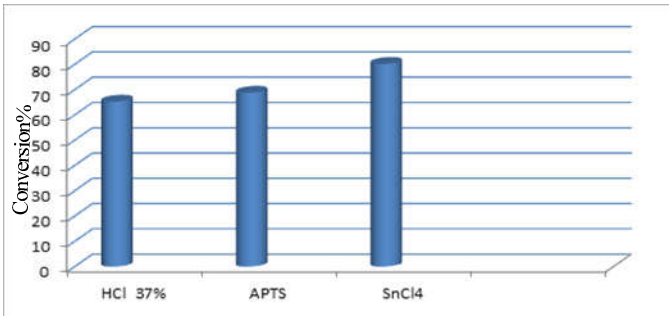


Figure 2 Yield variationdepending on thecatalyst of reaction

It is found that usage of tin chloride is a catalyst is efficient, in the synthesis of the malachite green respectively leucomalachite dyes, compared to using various acid catalysts that are obtained in higher yields. Influence of reactants on molar ratio in a reaction that occurs in the presence of $SnCl_4$ catalyst as a result of benzaldehyde condensation with N, N-dimethylaniline, reactants molar ratio influence over the yield in working with molar ratios of benzaldehyde: N, N-dimethylaniline 1: 2, 1 : 3, 1: 5 was observed. We worked with a molar ratio of the catalyst of 20% moles towards benzaldehyde.

The temperature at which reaction was preformed is 115-120 ^{0}C. Our aim in this work is to obtain leucomalachite which is subsequently oxidized to green malachite dye, using lead oxide as a catalyst the oxidation was carried out. The reaction took 4 hours to obtain leucomalachite and the oxidation of the leucoderived to malachite green dye was 2 hours. Reaction results and working conditions are shown in Table II.

Table II Reaction results and working conditions

Current Issue	Molar reportB :N,N DMA	Yield %
1	1:2	42.11
2	1:3	78.20
3	1:5	83.52

The abbreviations are: B = benzaldehyde; N,N DMA = N, N-dimethylaniline.

The graph in Figure 3 was drawn based on results obtained from the reaction which represents the yield variation of the dye depending on the variation of the ratio of reactants.

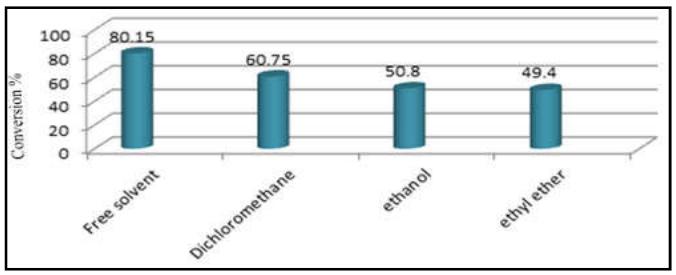


Figure 3 Yield variation depending on the ratio of reactants

It is found from experimental data, that an increase in the molar ratio of reactants (benzaldehyde: N, N-dimethylaniline) increases the malachite green dye yield. 1:3 molar ratio used in the other synthesis. This is because when we use a 1: 4 molar ratios of benzaldehyde: N, N-dimethylaniline of dye yield increase very less, only 2.5%. If the reaction is continued out with 1:5 molar ratio problems occur in removing the unreacted dimethylaniline. To observe the Influence of solvent in the reaction of obtaining leucomalachite the following solvents were used: dichloromethane, ethanol, and ethyl ether. 4 hours are required for the reaction to complete and 2 hours are required to oxidize leucomalachite using lead dioxide to obtain

malachite green dye. Compared to the reaction mixture the amount of solvent used is 30% (vol.). 1:3 molar ratio of benzaldehyde: N, N-dimethylaniline is used. The $SnCl_4$ catalyst amount used in all syntheses towards benzaldehyde is 20% moles. Related experimental data is shown in Table III.

Table III Reaction results and working conditions

Current Issue	Reaction Solvent	Yield %
1	Free solvent	80.15
2	dichloromethane	60.76
3	ethanol	50.80
4	Ethyl ether	49.40

In the laboratory syntheses, the values obtained are represented graphically in Figure 4

Figure 4 variation of yield in the synthesis of the leucomalachite depending on the solvent used.

As we can see from the graph that the best yields are obtained in solvent-free reaction conditions. When dichloromethane is used as a solvent yield is higher than (60%) invariants where ether or ethanol ether was used the yield lies around 50%. Influence of reaction time to synthesize the leucomalachite; the reaction time for obtaining the leucomalachite was observed to get an optimal time of reaction. The reaction time that was taken for observations is 1 hour, 2 hours, 4 hours and 8 hours. The conditions under which the synthesis was carried out are; benzaldehyde: N, N-dimethylaniline at 1: 3 molar ratio. The reaction temperature 115-120 ^{0}C. SnCl4 is used as the catalyst in the synthesis at a rate of 20% moles towards benzaldehyde. The reaction was continued without solvent and the oxidation time of leucomalachite in all cases was 2 hours. Table IV represents the working conditions and the results obtained.

Table IV Reaction results and working conditions

Current Issue	Reaction time(Hour)	Yield(%)
1	1	26.12
2	2	54.24
3	4	81.12
4	8	82.13

The results are shown in the graph in Figure 5.

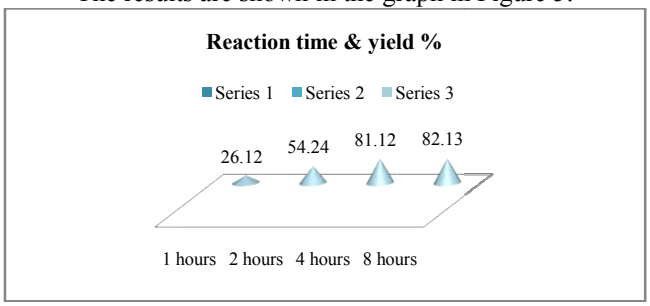


Figure 5 Depending on the reaction time yield variation of leucomalachite synthesis

As we can see from the graph the yield of leucomalachite in the synthesis can be increased with increasing reaction time. At 4 hours reaction time, 80.15% yield was obtained. If the reaction duration is increased twice the efficiency gets lower, leading to the idea that for a good yield in the synthesis of leucomalachite dye is 4 hours reaction time is enough. The refluxing time in the leucoderived synthesis refers to the time of reaction. Malachite green dye obtained after processing the raw product, the following experimental data was obtained; the Mp of dye was measured to be 138-139 ^{0}C and the IR spectrum obtained is represented in Figure 6.

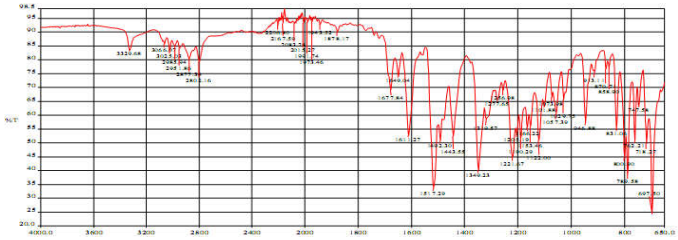


Figure 6 IR spectrum of malachite green dye

It was demonstrated that $SnCl_4$ is an efficient catalyst for the reaction of N, N-dimethylaniline with benzaldehyde compared with acid catalysts. Meanwhile, we determined the optimal conditions in the presence of this catalyst for the reaction. Using $SnCl_4$ as a catalyst in 20% moles compared with benzaldehyde, good yields of malachite green dye were obtained by taking 1: 3 molar ratios of benzaldehyde: N, N-dimethylaniline at a total reaction time of 6 hours. The temperature at which reaction is carried out is 115-120 ^{0}C without reaction solvent. our research on the synthesis of malachite green dye led to the determination of the optimum reaction conditions. The simple experimental procedure, reaction without solvent and good yields are the advantages of the present method [15].

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