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# Effective Extraction And Recovery of Malachite Green from Wastewater using Orthochloro Benzoic Acid

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**Abstract:** Textile industries consume a large quantity of water and generate highly dye contaminated effluents. Textile wastewater has to be treated in order to be recycled in the process or to meet legislative requirements before being discharged. Malachite green (MG), used extensively for dyeing silk, wool, jute, leather, ceramics, cotton and is also widely used in aquaculture as a parasiticide and in food, health, and other industries for one or the other purposes. It controls fungal attacks, protozoan infections and some other diseases caused by helminths on a wide variety of fish and other aquatic organisms. However, the dye has generated much concern regarding its use, due to its reported toxic effects. It has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenecity and respiratory toxicity. Present study gives a light of effective extraction and recovery of Malachite green using orthochloro benzoic acid by liquid-liquid extraction method. Experimental conditions like initial dye concentration, temperature, equilibrium time, effect of pH, aqueous to organic phase ratio, various stripping agents and different diluents were investigated. Investigation suggested that, dye concentration of 30ppm, carrier concentration of 0.15M and 11.5 pH of the feed solution etc. are the optimal conditions for the maximum extraction. Xylene was selected as solvent for its less toxicity. Present study showed a maximum 98.67% of dye extraction for the above experimental conditions. Extracted dye was recovered using 6.5 M acetic acid solution with a 99.04 % efficiency.
**Key Words:** Malachite Green, Ortho chloro benzoic acid, Acetic acid,Extraction, Carrier, Stripping.

## Introduction

Water which is a basic need of all living things is filled about 75 % of earth. Due to the over usage and greedy encroachment of water bodies,potable water level still goes on decreasing day by day.Among various industries, textile industry is equally considered as an intensive water consuming activity besides utilizing a large amount of chemicals and dyes.Thereforewater resources need to be conserved and the industrial effluent is to be recycled. So the concept of reuse, recycle and reduce have been very well conceived by industries, efforts in this direction need to be accelerated[1]. In 21st century, numerous numbers of synthetic dyes are being used in various industries such as textile, leather,paper, printing, food, cosmetics, paint, pigments, petroleum, rubber, plastic, pesticide and pharmaceutical industry for different purposesbecause of their ease and cost effectiveness

in synthesis, firmness, high stability to light, temperature, detergent and microbial attack and variety in colour compared with natural dyes[2]

Approximately 12% of synthetic dyes are lost during manufacturing and processing operations and 20% of these lost dyes enter the industrial wastewaters .Textile industries consume two thirds of the dyes manufactured. During textile processing, up to 50% of the dyes are lost after the dyeing process due to poor interaction between dye molecules and fibre of fabrics and about 10–15% of them are discharged in to the effluents. Hence, considerable amounts of dyes cometo effluent stream and pollute the waters. However, wastewater containing dyes are very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light, heat and oxidizing agents[3].Present work dealt with the removal of dye malachite green (MG) from waste water.MG is extensively used in textile industries for dyeing, in food industry as a food colouring agent, food additive, and a medical disinfectant and anthelmintic.Also used in aquacultures and animal husbandry as an antifungal, anti-bacterial,anti-parasitical therapeutic agent[4]. However, malachite green has now become a highly controversial compound due to the risks it poses to the consumers of treated fish5[5] including its effects on the immune system, reproductive system and its genotoxic and carcinogenic properties. It can cause severe effects on nervous system, reproductive system, liver, brain and kidney[6]

MG which is a triphenylmethane dyes biodegradation due to presence of nitrogen in their back bone (generate carcinogenic, genotoxic,mutagenic and teratogenic problems) is a difficult task[7]. Malachite green is reduced to leucomalachite green in the tissues and then to primary and secondary arylamines. Research conducted in rats in USA revealed that derivatives of malachite green like malachite green chloride or leucomalachite green caused slight increases in a few types of tumors: cancers of the thyroid gland, liver, and mammary gland in females exposed to malachite green chloride; of the thyroid gland and testes in males exposed to leucomalachite green; and of the thyroid gland and liver of females exposed to leucomalachite green[8]

During the past few decades several chemical, physical and biological methods are implemented to remove the dyes from waste water. Processes like nano filtration, colloidal gas aphrons, ultrasonic decomposition[9]electro chemical degradation, electro chemical oxidation, ozonation, ion exchange method, integrated chemical biological degradation[10], photocatalysis, solar photo-fentonand biological processes, Fenton biological treatments scheme, bulk liquid membrane technology, liquid membrane technology, sonochemical degradation, solvent extraction method, coagulation etc.

Dye pollutants are generally resistant to biological degradation and a number of chemical and physical processes such as chemical precipitation, coagulation, electrocoagulation[11].Physical methods such as precipitation, flocculation or adsorption using bone char and activated charcoal do not degrade the pollutants but only transfer them from the liquid phase to the solid phase, thus causing secondary pollution or requiring regeneration that is a costly and time-consuming process. Chemical methods including oxidative degradation by chlorine, hydrogen peroxide and ozone, reductive degradation by sodium hydrosulfite, photocatalysis and electrochemical treatment require high dosage of chemicals and produce large quantity of sludge, and thus have been proved to be expensive.Moreover, the resulting by-products by chemical degradationmay be coloured themselves or/and even toxic. Biodegradation (aerobic or anaerobic) of dyes is cost effective, environmental friendly and does not produce large quantities of sludge,but it is very selective and thus not suitable for most dyes. For most of these decolorization methods the expensive dyes cannot be recovered because of the destruction of dyes. Obviously, thenon-destructive techniques seem to be more attractive since therecovered dyes are more valuable than that of the purified water[12].Solvent extraction method is another effective way to remove dyes from wastewater. Many researches are reported regarding solvent extraction method. Since the solvent extraction method gives high through put, ease of automatic operation and of scale up and high purification[13], this method is adopted in this present study. In this paper we explore the idea of solvent extraction of MG using orthochloro benzoic acid as carrier.

## Experimental

### Reagents

Malachite Green,orthochloro benzoic acid (99%), Sodium Hydroxide(97%), Sulphuric Acid(95-98%), Acetic Acid(99%), Hydrochloric Acid(35%), Nitric Acid(99%),+Sodium Chloride 99.5(99.5%) Sodium Sulphate (99%), Xylene(99),Benzene(99.5%), Toluene (99.5%) Chloroform(99%)etc. were obtained from Merck and of AR grade. Feed solution of Malachite Green is prepared by dissolving in distilled water and made up to 100ml. Orthochloro benzoic acid was used as extractant and dissolved in xylene. Acetic acid was used as

stripping agent and sodium hydroxide and sulphuric acid were used to adjust the pH of the feed solution. The effect of salts was checked using Sodium Chloride and Sodium Sulphate.

**Apparatus**

pH meter(Elico India) was used to measure the pH of aqueous solution. For UV measurements for the dye concentration in the raffinate and striped solution, UV spectrophoto meter (ELICO SL159 UV Spectrophotometr, India) also used. For agitation of solution a mechanical stirrer (REMI 1MLH, India) was utilized.

**Procedure**

**Preparation of cationic dye solutions**

The cationic dye used in the present study is malachite green, in commercial purity, which was purchased from Merck Chemicals, Mumbai, India, and used without further purification. The stock solution of 100mg/L was prepared by dissolving an appropriate amount of MG in 1L of deionized water. The working solutions were prepared by diluting the stock solution with distilled water in accurate proportions to give the required different initial concentrations namely 10, 30, 50, 80, and 100 ppm.

**Extraction method**

Extraction experiments were conducted as follows. A feed phase solution containing dye 25ml (100mg/L) and organic phase 25ml (0.15M/L) were taken in a glass stoppered bottle.The pH of the aqueous dye solution was adjusted using 2N Sodium Hydroxide and 1N Sulphuric Acid. After adjusting the pH the glass stoppered bottle was shaken at100 rpm for 5 min in a shaker, and transferred in to a separating funnel and left to separate. The raffinate was collected for measuring the remaining dye concentration in the solution. The wave length of maximum adsorption ($\lambda_{max}$) for MG was 618nm. The distribution ratio (D) and percentage of extraction (E) were calculated as per the given equations[14].

$D = [dye]_{org} / [dye]_{aq}$

$E = 100x\ [dye]_{aq0}-[dye]_{aq}/[dye]_{aq0}$

Where $[dye]_{org:}$,concentration in the organic phase (mg/L);$[dye]_{aq0}$ is the initial dye concentration of the aqueous phase (mg/L);$[dye]_{aq}$ is the dye concentration of aqueous phase after extraction (mg/L).

The extraction process repeated by adding inorganic salt like NaCl and $Na_2SO_4$ to study the effect of salt in extraction process.

**Stripping *method***

In stripping, the loaded extractant and the aqueous strippant (acetic acid solution) were shaken at100 rpm for 5 min in a shaker and added the content to a separating funnel. The separated aqueous strippant was taken for measuring the dye concentration.

## Results and Discussion

**Influence of diluents**

The extraction is carried out using different diluents for orthochloro benzoic acid. Solvents like xylene, toluene, benzene, hexane etc.(Table-1) were tested. Except hexane and toluene all other diluents showed more than 97% extraction capacity for orthochloro benzoic acid at pH of 11.5. Since xylene is less harmful than other diluents, it is selected as diluent for orthochlorobenzoic acid[15].

**Table-1**

| Sl. No. | Lighter diluents | % of extraction |
|---|---|---|
| 1 | Xylene | 98.67 |
| 2 | Benzene | 98.33 |
| 3 | Toluene | 0 |
| 4 | Hexane | 0 |
| 5 | Chloroform | 99.02 |

**Influence of pH of Feed phase**

Since textile effluents are containing different alkalis and acids, the pH of the colorant-containing wastewater is one of the important parameter affecting the extraction process. Effect of pH on the feed phase is studied and is shown in fig.2.It can be seen that dye adsorption was unfavourable at pH >7. Since acidic condition is not favour the extraction, pH of the feed phase was maintained between pH 7 and 14 to check the extraction efficiency at different pH .The pH was adjusted using 2N Sodium Hydroxide and 1N Sulphuric Acid. Extraction increased as pH increased from 7 and maximum value attained at pH value 11.5.After 11.5 extraction did not show particular change. Lower adsorption of MG at acidic pH is may be due to the presence of the excess $H^+$ions which are competing with dye cations. It is known that pH can affect the structural stability of MG and consequently its colour intensity .The decrease of extraction after 11.5 may be due to the structural changes of MG molecules at high pH[16]

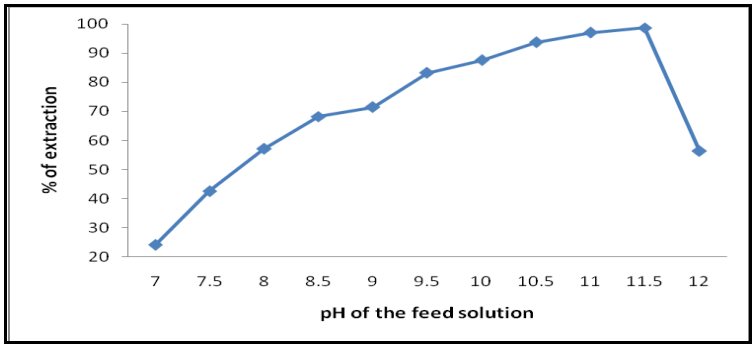


**Fig.2- Effect of pH on the extraction of Malachite Green (experimental conditions: volume of feed phase = 25 ml, volume of organic phase = 25 ml, extractant concentration 0.15 M)**

**Influence of Dye concentration**

The effect of initial dye concentration on the extraction efficiency was tested. For carrier concentration of 0.15 M, dye concentrations ranging from 10 ppm to 100 ppm were tested. In10ppm and 30 ppm extraction efficiency was almost same and was more than 98% and above 30ppm efficiency decreased. 30ppm is chosen for further investigation since textile effluents contains higher dye concentration. The data were shown in fig.4.

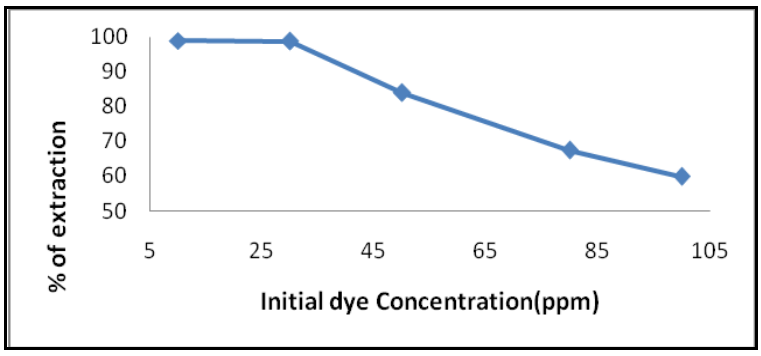


**Fig.4-Effect of dye concentration (experimental conditions: volume of feed Phase = 25 ml, volume of organic phase = 25 ml, pH 11.5)**

**Influence of carrier concentration**

Effect of carrier dosage was studied by adding different carrier concentration (0.05M-0.25 M) into flasks containing 25 ml of 100 mg $L^{-1}$ malachite green solutions. The pH of the solutions was preadjusted to 11.5 according to the result of the study on effect of pH. Flasks were shaken at 100 rpm. Result shown in the fig.3 clearly tells that extraction efficiency of the orthochloro benzoic acid is increased from 0.05M and reached the maximum at 0. 15M and further increase in concentration did make any difference in extraction.

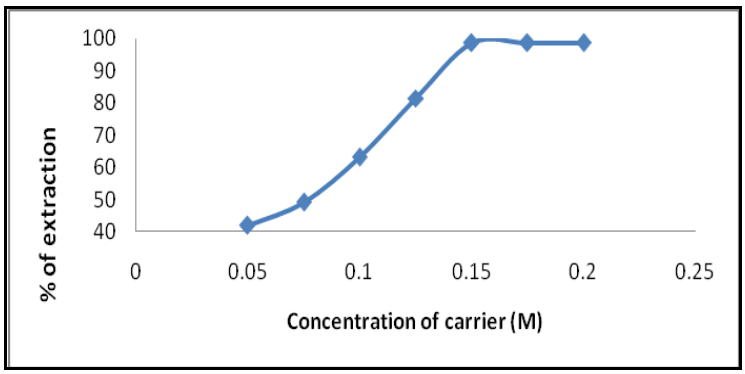


**Fig.3- Effect of concentration of orthochloro benzoic acid (experimentalconditions: volume of feed Phase = 25 ml, volume of organic phase= 25 ml, pH 11.5)**

**Influence of contact time**

The contact time for maximum extraction was determined in the initial extraction experiments, which were monitored at 5 min interval for 40 min. Since maximum extractionwas achieved within the first 5 min (Table2), this was used for all further experiments. The maximum dyeremoval rate was found to be 98.67%.

**Table.2-Effect of Contact time**

| Sl.No | Time in min. | % 0f Extraction |
|---|---|---|
| 1 | 0.5 | 37.24 |
| 2 | 1 | 78.89 |
| 3 | 2 | 87.36 |
| 4 | 5 | 98.67 |
| 5 | 10 | 98.67 |

**Influence of temperature**

Effect of temperature on extraction efficiency was studied.fig.5shows that extraction increased as temperature raised and reached the maximum at a temperature of $80^0$C.Further increase in temperature didnot show any change in extraction.

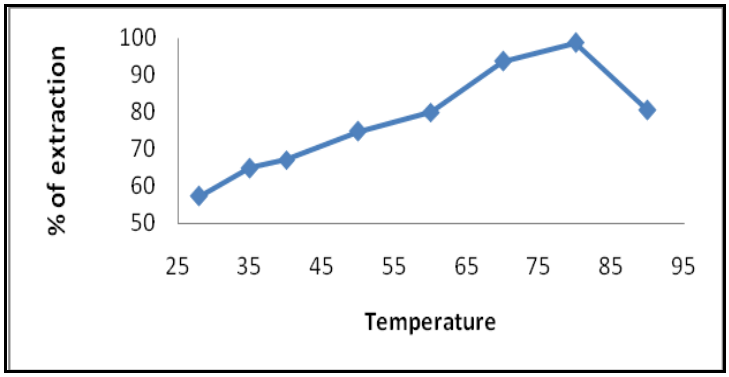


**Fig.5- Effect of temperature (experimental conditions: volume of feed phase = 25 ml, volume of organic phase = 25ml,extractant concentration 0.15 M and pH 11.5)**

**Influence of aqueous to organic phase ratio**.

The phase volume ratios of aqueous to organic phase were taken as 1:1,2:1,3:1,4:1 and 5:1 keeping organic phase volume as 25ml and investigated for extraction efficiency. Result shown in the fig.6clearly shows that for 5: l efficiency decreased from98.86% to 72.74%. At ratio 1:1 extraction showed 98.67% and therefore 1:1 is taken as standard A/O ratio.

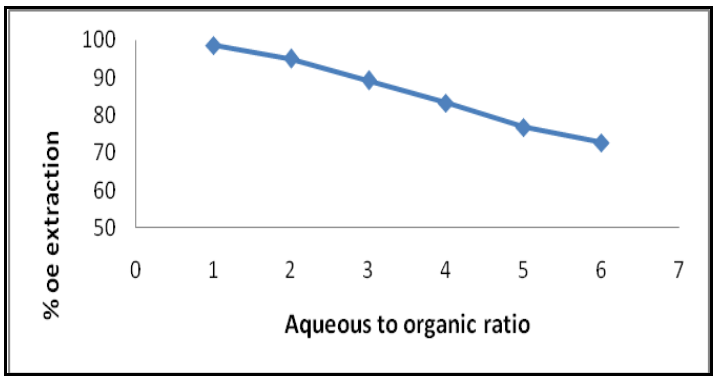


**Fig.6-Effect ofaqueoustoorganicratio(experimentalconditions:volume of feed phase = 25 ml, volume of organic phase =25ml,extractant concentration 0.15 M and pH 11.5)**

**Influence of salts concentration**

Effluent streams from textile industries usually contains high amount of salt like Sodium Chloride and Sodium Sulphate etc[16]. To check the extraction efficiency with salt, Sodium Chloride and Sodium Sulphate of 1g/L to 5g/L were tested and findings are listed in Table-3 and Table4. From the result we can conclude that amount of salt did not affect greatly the extraction efficiency.

**Table.3-Effect of Sodium Chloride**

| Sl.No. | Concentration of NaCl (mg/L) | %of extraction |
|---|---|---|
| 1 | 1000 | 98.67 |
| 2 | 2000 | 98.60 |
| 3 | 3000 | 98.32 |
| 4 | 4000 | 98.12 |
| 5 | 5000 | 98.01 |

**Table.4-Effect of Sodium Sulphate**

| Sl. No | Concentration of $Na_2SO_4$ (mg/L) | % of extraction |
|---|---|---|
| 1 | 1000 | 98.67 |
| 2 | 2000 | 98.67 |
| 3 | 3000 | 98.12 |
| 4 | 4000 | 98.12 |
| 5 | 5000 | 98.04 |

**Stripping Studies**

Extracted Malachite green was subjected to react with different mineral acids as well as organic acids. Mineral acids like sulphuric acid, hydrochloric acid, nitric acid were tested. Organic acids tested were oxalic acid and acetic acid. Except acetic acid and oxalic acid allother acids tested did not show any extraction tendency. Acetic acid showed a maximum stripping valueof 99.20% at a concentration of 6.5M.The values are given in Table 5.

**Table.5- Effect of Acids in Stripping**

| Sl.No | Acid | Concentration | % of Extraction |
|---|---|---|---|
| 1 | H2SO4 | 6N | 0 |
| 2 | HNO3 | 6N | 0 |
| 3 | HCl | 6N | 0 |
| 4 | H2C2O4 | 2N | 32.74 |
| 5 | CH3COOH | 6 N | 95.14 |
| 6 | CH3COOH | 6.5N | 99.04 |

**Reusability of used xylene**

Since all chemicals show some adverse effect to mankind, it was quite interesting to show the reusability of xylene and thereby reduce the chemicals consumption and cost of production also. Xylene was tested for successive 10 extraction experiments using 0.15M orthochloro benzoic acid and result is shown in Table6.

**Table.6- % of extraction using used xylene**

| No. of times | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| % of Extraction | 98.67 | 98.63 | 97.25 | 97.02 | 95.92 | 93.54 | 90.4 | 88.3 | 87.3 | 84 |

## Conclusion

Present study concluded that Malachite Green can be extracted and recovered effectively using orthochloro benzoic acid in xylene.Some factors such as pH, time, temperature and dosage were found to affect the percentage of extraction. Maximum extraction of 98.67 was shown at pH 11.5 and 0.15M of carrier concentration. It was seen that inorganic salt like sodium chloride did not affect the extraction badly. Extracted dye was recovered from the solution using 6.5N acetic acid. Organicphase(xylene) was re used and which make the investigation fruitful and effective.To check the reusability of dye, further study is to be needed.

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