Extraction And Stripping Of MethyleneBlue From Industrial Wastewater By Liquid-Liquid Extraction

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Abstract

Textile industries shouldpossess more dye contaminated effluents and it consumes high quantity of water. It must be treated or recycled before being discharged.   Present work gives a light of extraction, recovery of methylene blue.   It is a cationic dye; one of the most common used substance for dyeing cotton, wood, silk.Liquid- liquid extraction of methylene blue from textile wastewater using phenylpropiolic acid (extractant) in benzene has been studied at 27^0C.   While increasing the extractant concentration the percentage of extraction efficiency also increased. Loading capacity of dye has been found to be 3mg. The maximum stripping efficiency of dye from loaded organic dye was obtained using 1N H_2SO_4 as a stripping agent. The influencing parameters such as dye concentration, aqueous to organic phase ratio, organic to aqueous phase ratio, loading of dye, effect of diluent, effect of pH,carrierconcentration, stripping reagents have also been investigated. Under optimized conditions, real textile wastewater has been studied and the results are found to be satisfactory.

Keywords - *Wastewater,Extraction,Methylene blue, Diluent,Stripping agent.*

I. INTRODUCTION

The one of the most important industries in the last few decades was found to be a textile industry. It was broadcasted that more than 60% of the dyes world production was consumed by textile industries[1]. An increase in the volume and complexity of wastewater discharges to the environment have been resulted that the growth in textile industry and the changes in manufacturing processes[2].Textile wastewater possess a high chemical oxygen demand(COD) concentration, strong colour, large amount of suspended solids, broadly fluctuating pH, high temperature and low biodegradability caused by varying contaminates discharged into the environment, particularly aquatic environment[3].A large amount of liquid wastes that contain organic and inorganic compounds produced from the textile industries [4] and of them dyes are the most important one.   Thus one of the main sources of water pollution are dyes, which are used for colouring food, clothes, paper etc., At present it was estimated that, there are more than one lakh commercial dyes with a rough estimated production of 7×105 to 1×106 tons per year is produced world wide and 10 to15% of used dyes enter into the environment [5]. There are about 1000L of water is used for every 1000kg clothes processed in the dyeing section of textile industry and discharge of such coloured effluents imparts colour to the water bodies like rivers and lakes and interferes with its intended beneficial use [6].

Various industries use dyes extensively such as textile, rubber, paperetc., approximately15% of the dyes produced throughout the world are lost during the dyeing process [7].Today,the majority of dyes are synthetically produced. Dyes arecoloured substances and it has a capable of imparting their colour to other substances[8].Dyes usually have a synthetic origin and a complex aromatic molecular structure which makes them more stable and it was more difficult to biodegrade [9].

The major sources of dye wastewater discharge industries are, dyes production, textile preparation, dyeing and finishing plant. The textilewastewater often exhibits low biochemical oxygen demand (BOD) to chemical oxygen demand(COD) ratios, indicating the non-biodegradable nature of dyes[10].The chromophore responsible for colour and the auxochrome which can not only supplement the chromophore but also render the molecule soluble in water and enhanced affinity towards fiber are the key components of dye molecule[11]. Dye molecules can easily accumulate in living tissues and are resistant to light, chemical and other kind of exposure which can be considered as mutagens to human.Besides, it impedes light penetration, retardsphotosynthetic activity, inhibits the growth of biota and also has a tendency to

chelate with ions which produce micro toxicity[12]. For some dyes even less than 1 ppm is highly invisible and undesirable[13],and are visually detected and affect the aquatic life and food web even in low concentration[14]. These arecoloured compounds are not only aesthetically displeasing,but also inhibiting sunlight into the stream and affecting the photosynthetic reaction [15].

The biological processes often not effectiveenough to decolourise dyes of high photostability and physical /chemical processes not effective enoughto fully decompose the dye.   However, there are inherent problems with both the processes. Hence, the principle weakness of this processes are found to be the sludge generation and regeneration[16].

Methylene blue(MB)has been selected for the present study. It was discovered by caro in 1878. MB is the most important basic dye and it is chemically tetra methyl thioninium chloride and it dissociates in aqueous solution like electrolyte into methylene blue cation and the chloride ion [17]. Methylene blue ($C_{16}H_{18}N_3SCl$) is an aromatic heterocyclic compound. It has many applications such as laboratory reagent active pharmaceutical ingredient (API), biological stain etc.,[18]. MB is one of the most important and widely used cationic dyes in the textile and paper industries [19]. It appears asodourless, solid, dark green powder at room temperature. When it is dissolved in water it gives a blue solution. There are three molecules of water per molecule in the hydrated form of MB [20].It often served as model compound for removing organiccontaminantsand coloured bodies from aqueous solutions [21].

MB used as a model indicator for identifying the adsorption capacity of   adsorbents [22]. Its acute exposure can cause Heinz body formation, jaundice, quadriplegia, tissue necrosis in human [23, 24] nausea, profuse sweating, eye burns by direct contact, methemoglobinemia, mental confusion [25], cyanosis, convulsions, tachycardia, dyspynea, irritation to the skin and if ingested irritation to gastrointestinal track [26].

During the past few decades, several chemicals, physical and biological method are implemented to remove the dyes.   Processes like nanofiltration, colloidal gas aphrons, ultrasonic decomposition [27], Adsorption techniques using activated charcoal derived from different biomaterials are found enormous space in methylene blue removal[28].

Biological treatment is not effective due to low biodegradability of   the dyes and chemical techniques also cannot find as a suitable method due to the accumulation of concentrated sludge which itself possess a disposal problem [29].

The above method shows some sludge problems to remove the dyes. Hence alternative methods are required to remove the dyes from textile effluent. The Liquid-liquid extraction method was found to be a best method to remove the dyes. Liquid-liquid extraction (LLE) method is used for the purification enrichment separation and analysis of various compounds in mixtures. It is based on the principle that in a certain ratio a solute can distribute itself between two immiscible solvents.   Thus, the selection of both an extractant and a diluent determines equilibrium for a given system and the efficiency of extraction process depends on its mass transfer rate [30]. The main factors affecting LLE process are, organic to aqueous phase ratio, aqueous to organic phase ratio, extractant concentration, dye concentration, loading of dye, stripping reagent etc., to be discussed LLE methylene blue paper. In the present study, cationic dye namely, methylene blue using phenyl propiolic acid prepared in benzene as extractant was studied.   The dye extraction and stripping extracted dye were investigated and operating conditions were optimized.

II. EXPERIMENTAL

A. *MATERIALS*

Phenyl propiolicacid, Benzene,Methylene blue,Sulphuric acid,Xylene,Toluene, Hexane were obtained from Merck and of AR grade.

A UV-visible spectrometer (spekol 1200, Analytical Jena,Germany) was used to measure the absorbance of the dye and to establish its$\lambda_{max}$and its concentration .For agitation of solutions,a shaker was used. (IKA-KS 501).

Phenyl propiolic acid was used as extractant and dissolved in benzene. The dye solution was prepared in distilled water. H_2SO_4 is used as a stripping agent.

B.*PROCEDURE*

LIQUID-LIQUID EXTRACTION OF DYE
The organic solvent [(Phenyl propiolic acid + Benzene) (*V*o mL)] used for extractionwas added to the prepared aqueous dye solution (*V*a mL) and both the components were transferred into a glass-

stoppered bottle and the glass-stoppered bottle was shaken for known time in a shaker at 100 rpm. Then the solutiontransferred to a separating funnel. Sample of aqueous solutionat the bottomof the separating funnel was taken for absorbance measurement of dye. The wavelength of maximum absorption (λmax) for methylene blue was 650 nm. The experimental setup is shown in Fig.1. The distribution ratio (*D*) and percentage of extraction (*E*) were calculated as per the following equation[31]

$$D = \frac{[dye]_{org}}{[dye]_{aq}} \text{----------- (1)}$$

$$E = 100 \times \frac{[dye]_{aq}^{0} - [dye]_{aq}}{[dye]_{aq}^{0}} \text{--- (2)}$$

Where [dye]org is the dye concentration in the organic phase (mg/L), $[dye]_{aq}^{0}$ is the initial dye concentration of aqueous phase (mg/L), [dye]aq is the dye concentration of aqueous phase after extraction (mg/L).

In stripping, the loaded extractant (*V*o mL) and the aqueous strippant (acid solution) were added together into a glassstoppered bottle and shaken at 100 rpm then transferred the content to a separating funnel. The aqueous strippant was taken for dye concentration measurements
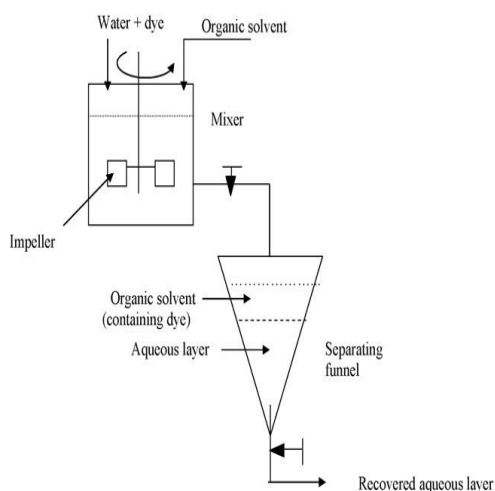

Fig.1 Schematic experimental setup for liquid-liquid extraction for removal of from aqueous solution

III. RESULTS AND DISCUSSION

A. THE EFFECT OF pH OF FEED PHASE
The effect ofpH of feed phase on the efficiency of dye extraction is studied and is shown in Figure.2. The pHof the feed phase maintained at pH 7± 0.1. The extraction efficiency of dye increased at pH 4.5 to 7 and extraction efficiency found about 35% to 80%. At higher pH (>7.0±0.1) percentage extraction efficiency is decreased from 99% to 58%. Hence further studies were carried out at pH 7± 0.1.
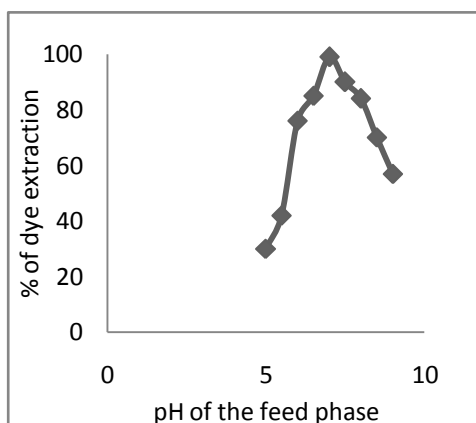

Fig.2.Effect of pH on the extraction of methylene blue(experimental conditions: volume of feed phase=10mL, volume of organic phase =10mL, extractant concentration= 1.1×10^{-1}M, Dye concentration= 10 ppm, Stripping time=5min)

B. SELECTION OF AN EXTRACTANT
The most suitable extractant was found to be phenyl propiolic acid to the experiment. Similarly three possible diluents were studied, namely benzene,toluene,xylene. The methylene blue was found to be a cationic dye andthe extraction takes place in presence of anionic extractant. The acidic extractant such as phenyl propiolic acid extracts substances by a cation-exchange mechanism, in which the hydrogen of the extractant is exchanged for desired ions. So the experiment shows more amount of dye beingextracted. Therefore phenyl propiolic acid was used as extractant in the subsequent tests.

C. INFLUENCE OF DILUENTS
The extraction carried out using different diluents for phenyl propiolic acid such as toluene,xylene,benzene,hexane from aqueous solution at pH 7± 0.1. phenyl propiolic acid solubility in hexane was very poor. In benzene and toluene, high extraction percentage of dye were obtained when compared to xylene(Table 1) shows the effect of diluent on dye extraction efficiency. Hence further studies benzene has chosen as a diluent.

Table 1
Effect of diluent on extraction efficiency

Diluents	Benzene	Toluene	Xylene	Hexane
Percentage of dye extraction	99.0	95.3	89.5	5.0

Extraction phase ratio 1:1

D. EFFECT OF EXTRACTANT CONCENTRATION

The extraction was first takes place in absence of the carrier and found that there was no extraction of methylene blue from the feed to organic phase. Phenyl propiolic acid which acts as a anionic carrier selected as a extractant. The effect of concentration of phenyl propiolic acid on extraction efficiency and distribution ratio(D) of the dye was investigated using phenyl propiolic acid of different concentration ranging from 0.01 to 0.4M.From Figure.3, It shows that percentage of extraction efficiency increased when increasing the concentration of extractant. Maximum extraction may found at 1.1×10^{-1}M

concentration of extractant.A further increase in the carrier concentration does not show any improvement in the extraction efficiency. Hence further studies were carried is 1.1×10^{-1}M phenyl propiolic acid as anextractant.
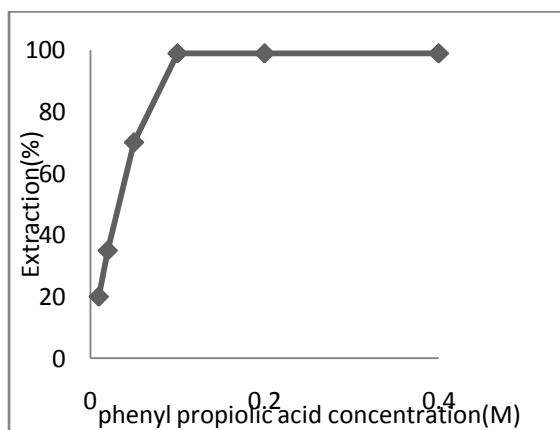
Fig.3.Effect of phenyl propiolic acid concentration (experimental conditions: Volume of feed phase=10mL, volume of organic phase=10mL, pH=7±0.1)

E. EFFECT OF DYE CONCENTRATION

The effect of initial dye concentration on the extraction efficiency of phenyl propiolic acid was tested. For carrier concentration 1.1×10^{-1}M, dye concentration ranging from 10ppm to 100ppm were tested. In 10ppm the extraction efficiency was more than 99.5%. Further increasing dye concentration from 20ppm to 100ppm, the percentage of dye extraction is decreasd.However, the absolute amount of dye extracted increased with increasing in dye concentration and is shown in Figure.4.
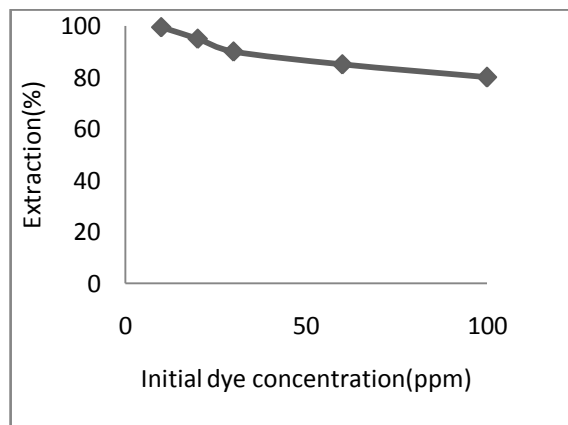
Fig.4.Effect of initial dye concentration (experimental conditions: volume of feed phase =10mL, volume of organic phase =10mL, pH=7± 0.1)

F. EFFECT OF EQUILIBRATION TIME

Effect of equilibration time on extraction efficiency was studied, which is the important parameter in the extraction process. A time interval of 0.5sec to 15mins has been chosen for methylene blue removal from aqueous solution at room temperature. From (Table2), After 3min 99.1% dye got extracted. After 5minutes it does not show any increment. This indicates that extraction process is fast one.After

5min, almost all dyes were transferred (99.1%) to the organic phase and hence an equilibration time of 5min is recommended.

Table 2
Effect of equilibration time

Time(min)	Extraction (%)
0.5	93.5
1	95.2
3	98.3
5	99.1
10	99.1
15	99.1

G. EFFECT OF TEMPERATURE

Figure.5. shows the effect of temp on extraction of dye from aqueous phase. From 20-28^{0}C the extraction rate remained unchanged at 99% from 20 to 28^{0}C. When the temperature raised from 28-60^{0}C the extraction rate decreased. Hence further studies were carried out at 27^{0}C.
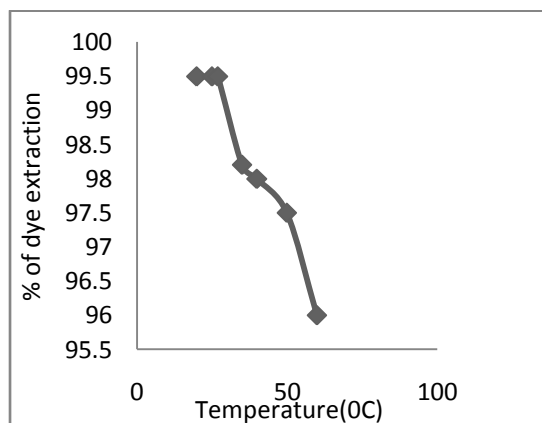

Fig.5.Effect of temperature (experimental conditions: volume of source   phase=10mL, volume of organic phase=10mL, extractant concentration=1.1×10^{-1} M, equilibration time=5min.)

H. EFFECT OF EXTRACTION PHASE RATIO (A/O Ratio)

The volume of aqueous to organic phase ratio were taken as 1:1, 2:1, 3:1, 4:1, 5:1 by keeping the organic phase volume as 10ml and found for percentage extraction efficiency. Figure.6clearly shows that at 1:1 ratio maximum percentage of removal was 99.12% which indicates that each carrier molecule may binds one dye molecule effectively. In other words, the lower ratio 1:1 yieldedhigh percentage removal of dye due to interaction of dye with organic.In 2:1, 3:1, 4:1, 5:1 ratio the extraction rate slowly decreases. Hence 1:1 aqueous to organic

phase ratio is taken as standard for the rest of investigation.
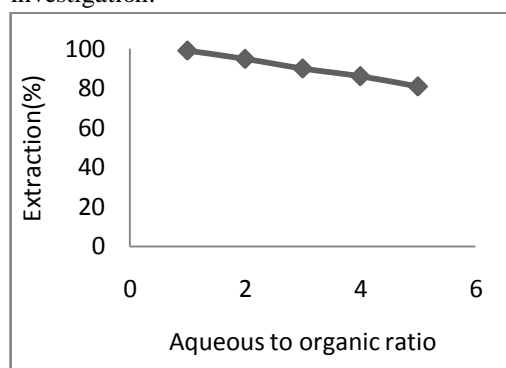

Fig.6.Effect of aqueous to organic ratio (experimental conditions : Volume of feed phase=10mL,volume of organic phase=10mL,extractant concentration=1.1×10^{-1}M ,pH=7±0.1)

I. LOADING OF DYE IN PHENYL PROPIOLIC ACID

Phenyl propiolic acid (1.1×10^{-1}M)in 10ml of benzene diluent was used for extraction at ambient temperature of 27^{0}C for 5minutes with equal volume of 10ml source phase and 10ml organic phase. After this in next phase the aqueous phase was analyzed for dye concentration after each stage of extraction and cumulative dye content transferred into organic phase was calculated. Then plot of cumulative dye content per1.1×10^{-1}M Phenyl Propiolic acid versus number of reuse times is shown in Figure.7.After each stage of dye extraction the aqueous phase (Raffinate)was removed followed by addition of 10ml of feed solution into loaded organic phase for the next stage. Two times it can be reused after that emulsion was noticed. This might be because of the extractant was unable to extract the dye from feed solution. The loading capacity of phenyl propiolic acid in benzene for extraction of dye from aqueous solution was 3mg of dye per 10ml of 1.1×10^{-1}M ofextractant.
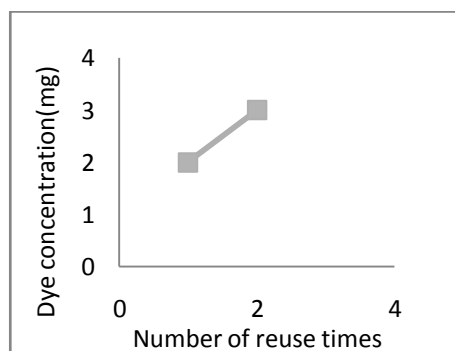
Fig.7.Loading of dye in phenyl propiolic acid (experimental Conditions: volume of source phase=10mL, volume of organic Phase=10mL, phenyl propiolic acid concentration=1.1×10^{-1}M, Equilibration time=5min)

J. EFFECT OF SALT CONCENTRATION

Textile industries contain salt like sodium chloride and sodium sulphate etc., To check the extraction efficiency with salts like sodium chloride, sodium sulphate of 1.0 to 3.0 g/L were tested and the percentage of extraction shown in (Table 3 and 4).It shows that the amount of salt did not much affect the extraction efficiency[32].

Table 3
Effect of sodium chloride

Concentration of Nacl (mg/L)	Extraction(%)
1000 2000 3000	99.12 99.14 99.23

Table 4
Effect of sodium sulphate

Concentration of Na_2So_4 (mg/L)	Extraction(%)
1000 2000 3000	99.01 99.03 99.16

K. EFFECT OF STRIPPING REAGENTS

It is very imperative to back extract the extracted dye from the organic phase and allow recycling of the organic solvent without loss of efficiency. Various inorganic acids such as Hcl, HNo₃, H_2SO_4 were used as stripping agent in this study. Sulphuric acid stripped the dye very well compared to other inorganic acids. It means that the presence of sulphuric acid in the stripping phase helped the dye by converting the dye hydrophilic moiety[33].The stripping in 1N H_2SO_4 occurs very well as compared to the 0.1N and 0.5N H_2SO_4.Hence 1N H_2SO_4 was found to be suitable for stripping of the extracted

dye. Thus 99% stripped within 5minutes. Further increase in the time does not improve stripping efficiency as presented in (Table 5)
Table 5
Effect of stripping agents onpercentage of dye stripping
Extraction phase ratio 1:1

L. EFFECT OF STRIPPING PHASE RATIO

Stripping agent	Percentage of stripping
HNo₃ (0.1N)	90.0
HNo₃ (0.5N)	91.2
HNo₃ (1.0N)	91.4
Hcl (0.1N)	93.1
Hcl (0.5N)	95.4
Hcl (1.0N)	95.4
H₂So₄ (0.1N)	95.0
H₂So₄ (0.5N)	97.4
H₂So₄ (1.0N)	99.0

The stripping (organic to aqueous) phase ratio is an important factor in the stripping process. The organic to aqueous phase ratio fixed at 1N H_2So_4 the stripping shows high extraction of 99%. The percentage of dye stripping increased with increasing phase ratio shown in Figure.8. The plot shows that 0/A ratio at 1/1 shows high % of dye stripped is 99.6 after that the efficiency of stripping will slowly decreases. Thus, a O/A phase ratio of 1/1 was maintained.
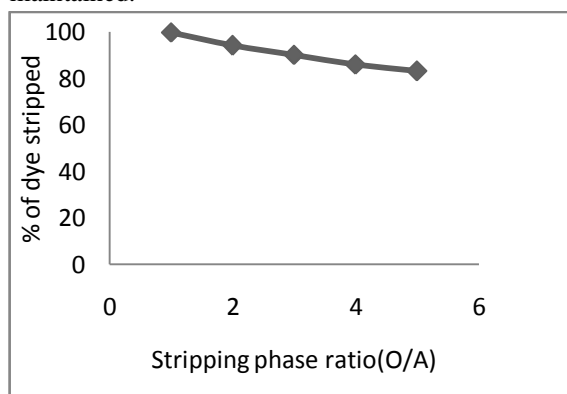

Fig.8. Effect of stripping phase ratio (experimental conditions: volume of source phase =10mL at pH=7, volume of organic phase=10mL,dye concentration=10mg /L, volume of stripping reagent=10mL)

M. EFFECT OF STRIPPINGCONTACT TIME

Table 6, Effect of stripping contact time on percentage of dye stripping

The stripping efficiency did not increase with increasing contact time in the range of 5-10minutes. This indicates the stripping was very fast and stripping reaction completed within 5minutes and 98% of dye was stripped from the loaded organic phase shown in (Table 6). When contact time was increased no further stripping was seen and hence the stripping contact time of 5min is recommended.

| Time(min)	Extraction(%)
2	97.0
4	97.5
5	98.0
7	98.0
10	98.0

N. MECHANISM FOR THE EXTRACTIONAND STRIPPING REACTIONS

The mechanism carried out so far showed that cationic dyes are extracted into phenyl propiolic acid under neutral condition and the extracted dye stripped into 1N H_2SO_4. One (Dye) molecule combines with one phenyl propiolic acid anion to form an ion pair as evident from 1:1 stoichiometry of the extracted complex. The reaction mechanismfor the extraction and stripping of the dye are shown the below equation .

Step I- Mechanism for extraction
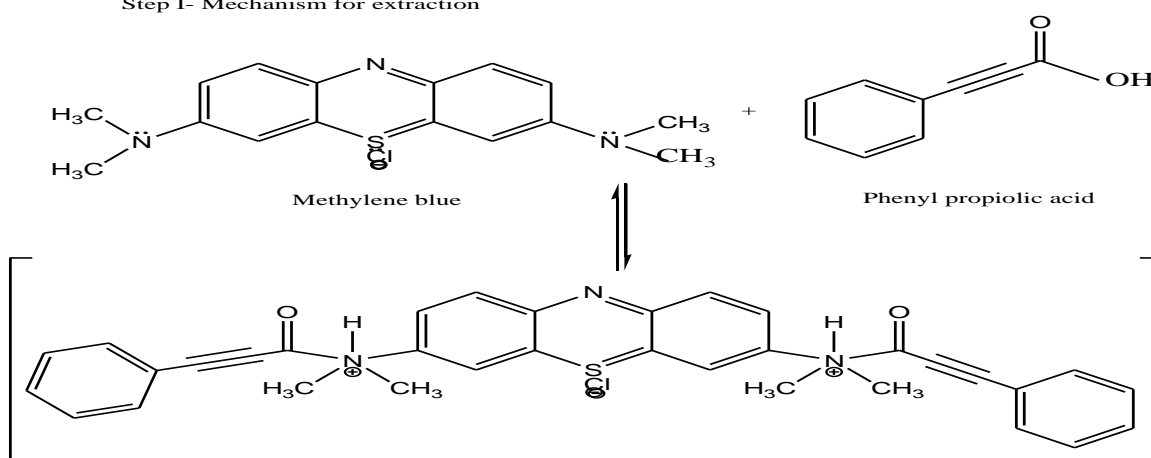
Step II Mechanism for stripping
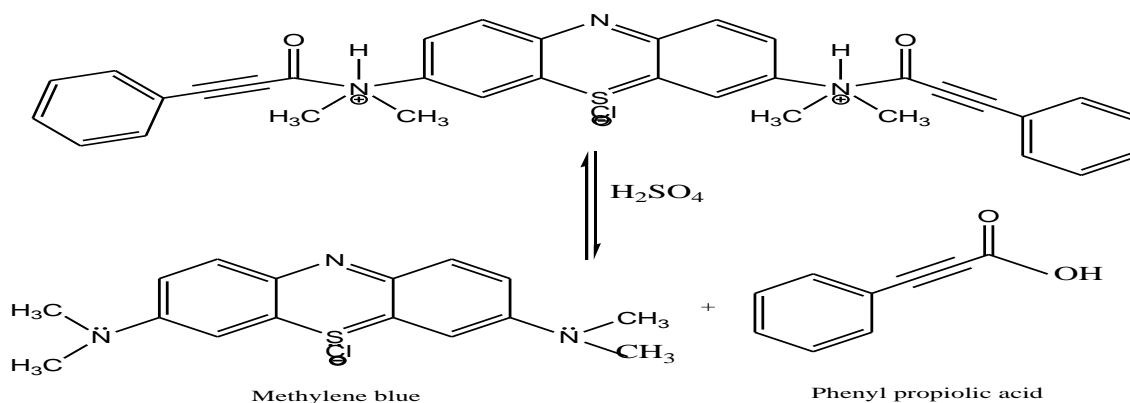
IV. CONCLUSION

The method presented offers a simple approach for selective extraction of cationic dye for removal and recovery from aqueous solution. The proposed flow chart shows the extraction of dye from industrial wastewater.

• Phenyl propiolic acid in benzene was able to extract more than 99% of cationic dye from aqueous solution in a short time.

• The extraction efficiency of dye was not affected in the presence of salts like NaCl and Na_2SO_4.

• The extraction phase ratio shows 99.1% of dye extraction.

• Stripping reaction was completed within 5min and 99% of the dye was stripped from loaded organic phase.

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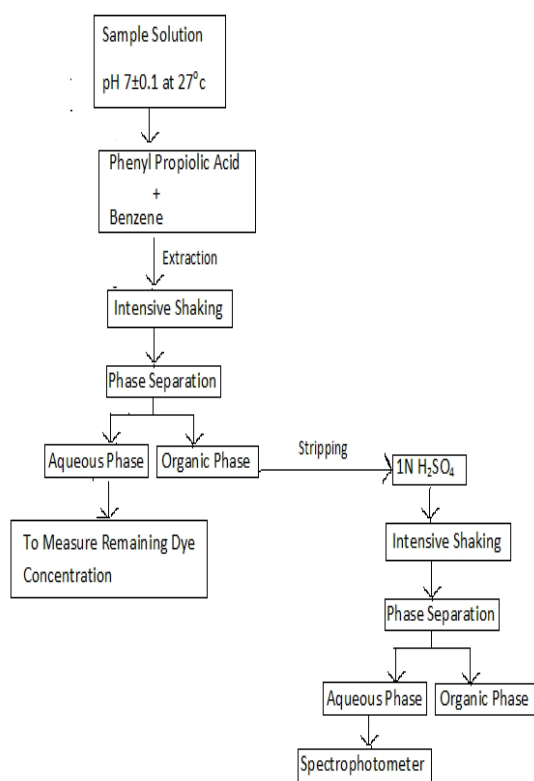
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