



Recovery and Reuse of Methylene Blue from Aqueous Solution Using Phenol as Carrier

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Textile industries consume a large quantity of water and generate highly dye contaminated effluents. Textile wastewaters have to be treated or recycled before being discharged. Present work gives a light of extraction, recovery and reuse of methylene blue (MB) a cationic dye; one of the most commonly used substance for dyeing cotton, wood, silk *etc.*, using liquid-liquid extraction method. Even though methylene blue is not only strongly hazardous, it shows some health problems like increased heart rate on acute exposure, shock, vomiting, Heinz body formation, *etc.* Extraction of methylene blue was carried out using phenol and xylene as carrier and diluent respectively in this work. It was found that extraction increased by increasing the pH of the feed solution and concentration of the carrier. The extracted dye was stripped using acetic acid and found stripping efficiency, increased with increase of acid concentration. More than 99 % dye was extracted with 0.9 mol of phenol and extracted dye was stripped 99 % with 8 N acetic acid. Factors like initial dye concentration, temperature, contact time, the effect of pH, aqueous to organic phase ratio, various stripping agents and different diluents were investigated. Stripped dye and used carrier were reused. FT-IR technique was used to check the reusability of stripped dye.

Keywords: Methylene blue, Acetic acid, Phenol, Xylene, Carrier, Extraction, Stripping.

INTRODUCTION

Of the waters covering 70 % of the earth's surface, only 3 % is fresh and only 0.4 % is actually available to us. This fresh water is spread all over the world in water bodies like ponds, rivers, lakes, wells and underground bodies. Due to unlimited use and greedy approach, level of fresh water dropped fatal and became contaminated also. So compared to the total population, this remaining quantity is very less. With a projected 2/3 of the world's population living in water stressed areas by 2030, water scarcity is an issue that cannot be ignored. Therefore, for the remaining water, people have to fight. Some scholars even predicted that third World war will be for fresh water [1]. So save water to save the planet and the mankind, is what nature wants from us.

Textile industries produce large amounts of liquid wastes that contain organic and inorganic compounds [2] and of them dyes are the most important one. Dyes, which are used for colouring clothes, paper, plastic, food, rubber, cosmetics, *etc.*, are one of the main sources of water pollution. It was estimated that at present, there are more than one lakh commercial dyes

with a rough estimated production of 7×10^5 to 1×10^6 tons per year is produced worldwide and 10 to 15 % of used dyes enter into the environment [3]. In the dyeing section of a textile industry, about 1000 L of water is used for every 1000 kg clothes processed and discharge of such coloured effluents imparts colour to the water bodies like rivers and lakes and interferes with its intended beneficial use [4]. In most of the developing countries dye wastewater is discharged directly into fresh water bodies without any treatment due to its technological and economic limitations [5]. Dyes usually have synthetic origin and a complex aromatic molecular structure which makes them more stable and more difficult to biodegrade [6]. Dye molecule comprises of two key components, the chromophore responsible for colour and the auxochrome which can not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity towards fiber [7]. For some dyes even less than 1 ppm is highly invisible and undesirable [8] and even in low concentration are visually detected and affect aquatic life and food web [9]. These coloured compounds are not only aesthetically displeasing, but also

inhibiting sunlight into the stream and affecting the photosynthetic reaction [10]. The textile wastewater often exhibits low biochemical oxygen demand (BOD) to chemical oxygen demand (COD) ratios, indicating the non-biodegradable nature of dyes [11]. Dye molecules are resistant to light, chemical and other kind of exposure which can be considered as mutagens to human and can easily accumulate in the living tissue. Besides, it impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate with ions which produce microtoxicity [12].

Methylene blue (MB), the most important basic dye, was discovered by Caro in 1878. Methylene blue is chemically tetra methyl thioninium chloride and it dissociates in aqueous solution like electrolyte into methylene blue cation and the chloride ion [13]. Methylene blue is one of the most important and widely used cationic dyes in the textile and paper industries [14]. It is often served as model compound for removing organic contaminants and coloured bodies from aqueous solutions [15]. It is also used as a model indicator for identifying the adsorption capacity of adsorbents [16]. Methylene blue is also used in microbiology, surgery, diagnosis and as a sensitizer in photo-oxidation of organic pollutants [17].

Methylene blue ($C_{16}H_{18}N_3S$) is an aromatic heterocyclic compound. Besides being dye, it has many applications such as an active pharmaceutical ingredient (API), biological stain, laboratory reagent, *etc.* [18]. At room temperature it appears as a solid, odorless, dark green powder. It yields a blue solution when it is dissolved in water. The hydrated form of methylene blue has three molecules of water per molecule. It is commonly used for dyeing wool, cotton, wood, paper, temporary hair colourant and coating for paper sock [19,20]. Even though it is not strongly hazardous, it shows some health problems. A dosage of 7 mg/Kg of methylene blue will cause increased heart rate, shock, vomiting and 2-4 mg/Kg dosage will make hemolytic anemia and skin desquamation in infants. 20-80 mg/Kg causes hypotension and bluish colour skin similar to cyanosis [21]. Its acute exposure can cause Heinz body formation, jaundice, quadriplegia, tissue necrosis in human [22,23] nausea, profuse sweating, eye burns by direct contact, methemoglobinemia, mental confusion, [24] cyanosis, convulsions, tachycardia, dyspnea, irritation to the skin and if ingested irritation to gastrointestinal track [25].

During the past few decades, several chemicals, physical and biological methods are implemented to remove the dyes. Processes like nano filtration, colloidal gas aphanes, ultrasonic decomposition [26], electrochemical degradation, electrochemical oxidation, ozonation, ion exchange method, integrated chemical-biological degradation [27], photo-Fenton oxidation [28] photocatalysis, solar photo-Fenton and biological processes, Fenton biological treatment scheme, bulk liquid membrane technology, liquid membrane technology, sonochemical degradation, solvent extraction method, coagulation *etc.* [29] Adsorption techniques using activated charcoal derived from different biomaterials are found enormous space in the methylene blue removal. Wide varieties of activated carbons are produced by various researchers from food sludge [30], oil palm empty fruit bunch [31], eucalyptus bark [32], oil palm wood [33], bamboo [34], coir pith [35] *etc.* Beside these low

cost biomass materials also used by many researchers. Beer brewery waste [36], algal biomass [37], pretreated walnut shell [38], cotton stalk, cotton waste and cotton dust [39], lotus leaf [26] *etc.* are some of the biomasses used. Studies revealed that methylene blue can also be removed and recycled using graphene oxides as an adsorbent [40]. These methods have their own advantages and disadvantages. Since most of the dyes made up of complex aromatic molecular structure and have synthetic origin, 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 poses a disposal problem [41]. In the case of adsorption technique, in spite of their good efficiency and applicability for adsorbing a wide variety of materials, their use can sometimes be restricted due to economic consideration and regeneration is expensive and involve adsorbent loss as well as efficiency [42].

Liquid-liquid extraction (LLE) method is used for purification, enrichment, separation and analysis of various compounds in a mixture. It is based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents, one of which is usually water (aqueous phase) and the other an organic solvent (organic phase) [43]. Extractant determines the equilibrium of a given system and the efficiency of the extraction process depends on its mass transfer [44]. Since the solvent extraction method gives high throughput, ease of automatic operation and of scale up and high purification [45], this method is adopted for the present study.

This study deals with the separation of methylene blue from wastewater using phenol as a carrier and xylene, a less toxic and economical solvent when compared to others diluents [41], as diluent. The dye extraction and stripping of extracted dye were investigated and optimal conditions were tested. Reusability of stripped dye and organic phase also checked.

EXPERIMENTAL

Methylene blue (98 %), phenol (99 %), sodium hydroxide (97 %), sulphuric acid (95-98 %), acetic acid (99 %), hydrochloric acid (35 %), nitric acid (70 %), sodium chloride (99.5 %), sodium sulphate (99 %), xylene (99 %), benzene (99.5 %), toluene (99.5 %), isoamyl alcohol (98 %), dichloromethane (99 %), chloroform (99 %), *etc.* were obtained from Merck and of AR grade. Feed solution of methylene blue is prepared by dissolving 0.1 g in 100 mL distilled 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. Phenol was used as an extractant and dissolved in xylene. Acetic acid was used as stripping agent, sodium hydroxide and sulfuric acid were used to adjust the pH of the feed solution. The effect of salts was checked using sodium chloride and sodium sulphate.

For measuring the pH of an aqueous solution pH meter (ELICO India) was used and to check the UV measurements of the dye concentration in the raffinate and in striped solution, UV spectrophotometer (ELICO SL159 UV spectrophotometer, India) also used. For agitation of the solution, a mechanical stirrer (REMI 1MLH, India) was utilized. FT-IR spectrophotometer provided by Shimadzu used for FT-IR spectroscopic analysis.

Extraction method: Extraction experiments were conducted as follows. 25 mL (100 mg/L) of feed phase solution containing dye and 25 mL (0.9 M/L) organic phase was taken in a glass stoppered bottle. The pH of the aqueous dye solution was adjusted using 2 N NaOH and 1 N H₂SO₄.

After adjusting the pH, the glass stoppered bottle was shaken at 100 rpm for 5 min in a shaker and transferred into a separating funnel and left to separate. The raffinate was collected for measuring the remaining dye concentration in the solution. The wavelength of maximum adsorption (λ_{max}) for methylene blue was 660 nm. The distribution ratio (D) and percentage of extraction (E) was calculated as per the given equations [46].

$$D = \frac{[\text{dye}]_{\text{org}}}{[\text{dye}]_{\text{aq}}}$$

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

where $[\text{dye}]_{\text{org}}$; concentration in the organic phase (mg/L); $[\text{dye}]_{\text{aq}0}$; is the initial dye concentration of the aqueous phase (mg/L); $[\text{dye}]_{\text{aq}}$; is the dye concentration of aqueous phase after extraction (mg/L).

Stripping method: In stripping, the loaded extractant and the aqueous strippant (acid solution) were shaken at 100 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.

The extraction process and stripping process were repeated by adding inorganic salt like NaCl and Na₂SO₄ to study the effect of salt in the extraction process.

FT-IR technique: The quality and consistency of the liquids in extraction were determined by Fourier transform infrared (FT-IR) method [10]. The analysis of FT-IR was carried out for the samples taken from all phases after extraction, stripping and raw dye. Fig. 6 represents the spectral curves with the absorption peaks at specific intensities for the samples taken from organic phase after extraction, aqueous phase after stripping and of raw dye respectively.

RESULTS AND DISCUSSION

Influence of pH of feed phase: pH is an important factor to be studied, for being the textile effluents are containing different alkalis and acids. The effect of pH of the feed phase on the efficiency of dye extraction is studied and shown in Fig. 1. pH of the feed phase of different concentrations was maintained between pH 7 and 14 to check the extraction efficiency at different pH. The pH was adjusted using 2 N NaOH and 1 N H₂SO₄. Extraction of cationic dye methylene blue from the aqueous solution was studied using 0.9 mol/L phenol at 1: aqueous to organic phase (A/O) ratio in the initial pH range from 7 to 14 ± 0.1 and the dye concentration of 30 mg/L. It was found that extraction efficiency, increased when pH increased from 7 to 11.5. At pH 11.5 the extraction showed a maximum of 99.12 %. Similar extraction behaviour with variation in feed pH has been reported in the literature [29]. Above pH 11.5 extraction efficiency decreased and the colour started to change. So the pH 11.5 selected as the optimal condition for maximum extraction.

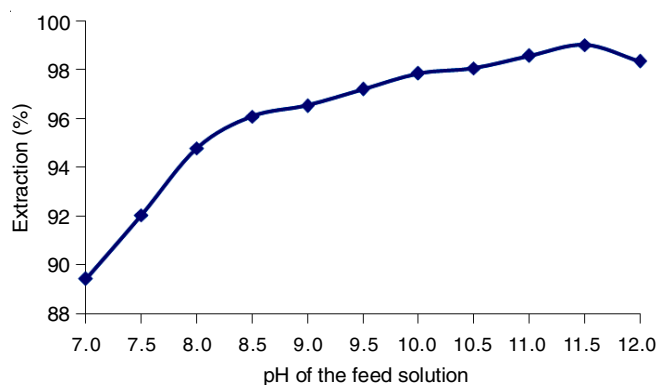


Fig. 1. Effect of pH on the extraction of methylene blue (experimental conditions: volume of feed phase = 25 mL, volume of organic phase = 25 mL, extractant concentration 0.9 M)

It may be explained that at low pH, phenoxide ion may be protonated and this phenomenon hindered the adsorption of basic dye due to competition for adsorption between dye cations and protons. When the initial pH increased, phenoxide ion may have become more stable, which provided more binding sites for the positively charged dye cations due to electrostatic attraction.

Influence of carrier concentration: Extraction was first carried out in the absence of the carrier and was found that there was no extraction of methylene blue from the feed to the organic phase. So, some kinds of carrier were tested. Here, phenol which can acts as an anionic carrier has been selected. The effect of concentration of phenol on the extraction efficiency and the distribution ratio (D) of the dye was investigated using phenol of different concentrations ranging from 0.1-1.0 M. The result given in Fig. 2 shows that at 0.9 M, 99.12 % extraction is completed and therefore 0.9 M is taken as the carrier concentration for the rest of the investigation. A further increase in the carrier concentration did not show any improvement in the extraction efficiency.

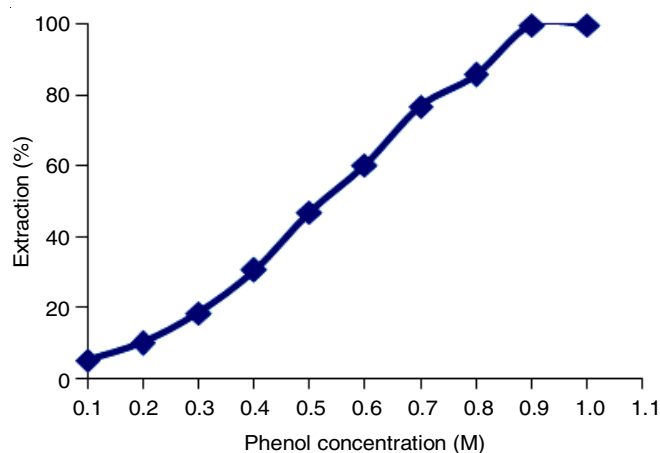


Fig. 2. Effect of phenol concentration (experimental conditions: volume of feed phase = 25 mL, volume of organic phase = 25 mL, pH 11.5)

Influence of diluents: The extraction is carried out using different diluents for phenol. Lighter diluents like xylene, benzene, toluene, hexane, isoamyl alcohol (Table-1) and denser diluents like dichloro methane, carbon tetrachloride and chloroform (Table-2) were tested. Except hexane all other diluents

TABLE-1
EFFECT OF LIGHTER DILUENTS

S. No.	Lighter diluents	Extraction (%)
1	Xylene	99.12
2	Benzene	98.33
3	Toluene	98.95
4	Hexane	10.00
5	Isoamyl alcohol	97.26

TABLE-2
EFFECT OF DENSER DILUENTS

S. No.	Denser diluents	Extraction (%)
1	Dichloro methane	98.10
2	Chloroform	98.93
3	Carbon tetra chloride	99.05

showed more than 98 % extraction capacity of phenol at pH of 11.5. In hexane phenol showed no miscibility. Since xylene is less harmful than other diluents, it is selected as diluent for phenol [47].

Influence of dye concentration: The effect of initial dye concentration on the extraction efficiency of phenol was tested. For carrier concentration of 0.9 M, dye concentrations ranging from 10 ppm to 100 ppm were tested. In 10 ppm and 30 ppm extraction efficiency was almost same and was more than 99 % and above 30 ppm efficiency decreased [48]. Hence 30 ppm is chosen for further investigation since textile effluents contain a higher dye concentration (Fig. 3).

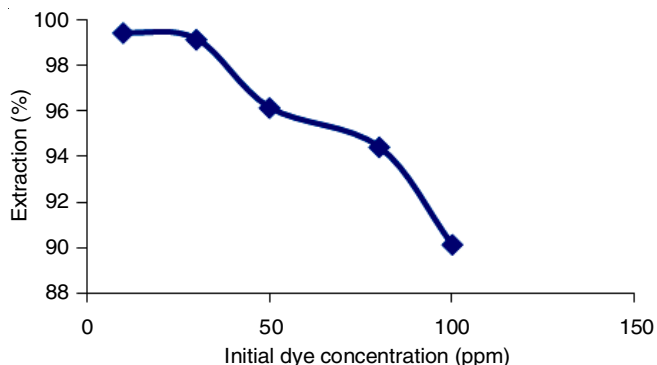


Fig. 3. Effect of initial dye concentration (experimental conditions: volume of feed phase = 25 mL, volume of organic phase = 25 mL, pH 11.5)

Influence of temperature: Effect of temperature on extraction efficiency was studied. Fig. 4 shows that the extraction increased as temperature raised and reached the maximum at 80 °C. This enhancement in efficiency can be interpreted by the improving of the diffusion of species, which transported through liquid membrane, due to the reduction of the membrane viscosity [49]. When the temperature was raised above 80 °C the extraction decreased drastically. This is probably due to the evaporation of the solvent or it can also be due to a lower complexation at higher temperatures [50].

Influence of contact time: Experiments were performed to investigate the effect of contact time, which is an important parameter in the extraction process. A time interval of 30 s to 10 min is chosen for methylene blue removal from aqueous solution at room temperature. Extraction increased as time went on and 99.12 % dye got extracted within 5 min. After 5

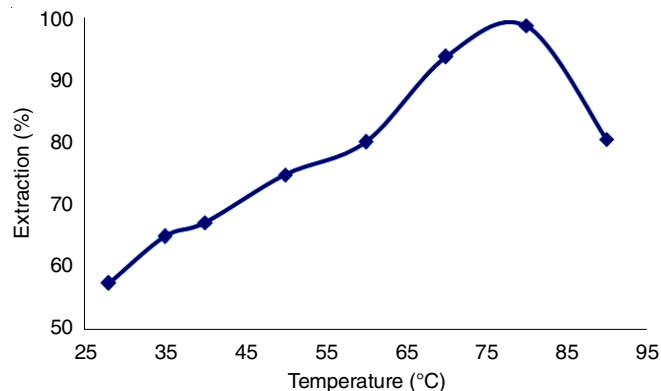


Fig. 4. Effect of temperature (experimental conditions: volume of feed phase = 25 mL, volume of organic phase = 25 mL, extractant concentration 0.5 M and pH 11.5)

min further increment did not report. This indicates that the extraction process is a fast one. Similar findings are reported in literature also [12]. So the optimum condition for equilibrium was taken as 5 min. for the rest of the investigation (Table-3).

TABLE-3

S. No.	Time (min)	Extraction (%)
1	0.5	92.02
2	1	95.56
3	2	97.62
4	5	99.12
5	10	99.12
6	15	99.12

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 the organic phase volume as 10 mL and investigated for extraction efficiency. The result shown in the Fig. 5 clearly shows that for 5:1 efficiency decreased from 99.12 to 82.7 %. At 1:1 extraction of 99.12 % indicates that each carrier molecule may binds one dye molecules effectively. So 1:1 aqueous to organic ratio is taken as the standard for the rest of the investigation.

Influence of salt concentration: Effluent streams from textile industries usually contain high amounts of salt like

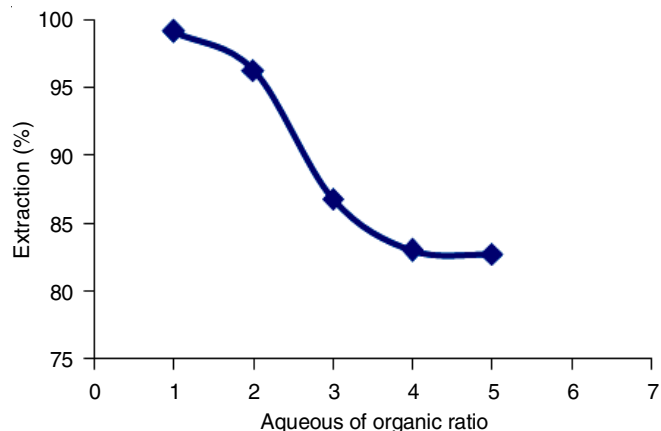


Fig. 5. Effect of aqueous to organic ratio (experimental conditions: volume of feed phase = 25 mL, volume of organic phase = 25 mL, extractant concentration 0.9 M)

sodium chloride and sodium sulphate, *etc.* [42]. To check the extraction efficiency with salt, sodium chloride and sodium sulphate of 1.0 to 5.0 g/L were tested and the findings are listed in Tables 4 and 5. It is concluded that the amount of salt did not much affect the extraction efficiency [31].

S. No.	Concentration of NaCl (mg/L)	Extraction (%)
1	1000	99.02
2	2000	99.08
3	3000	99.10
4	4000	99.12
5	5000	99.13

S. No.	Concentration of Na ₂ SO ₄ (mg/L)	Extraction (%)
1	1000	99.01
2	2000	99.03
3	3000	99.04
4	4000	99.07
5	5000	99.12

Stripping studies: Extracted methylene blue was subjected to react with different mineral acids as well as organic acids. Mineral acids like sulphuric acid, nitric acid, hydrochloric acid were tested. Organic acids tested were oxalic acid and acetic acid. All the acids were tested within the range of 1 to 6 N. Since acetic acid showed an increase in stripping efficiency it was tested up to 8 N. For sulphuric acid of 1 N, 2 N and 4 N stripping was 32, 41.25 and 48 %, respectively. Nitric acid did not show stripping property up to 4 N, and at 6 N it was about 22 %. For hydrochloric acid, 0, 5 and 8.7 % were stripping capacity at a concentration of 1, 2 and 4 N, respectively. Acetic acid only showed a maximum stripping capacity and it were 30.1 % for 1 N, 41.37 % for 2 N, 63.2 % for 4 N and 82.45 % for 6 N. At 8 N concentrations it was found that stripping was more than 99 %. Since acetic acid is less or moderately harmful [51] than mineral acids the finding was important. Table-6 gives the different stripping abilities of above mentioned acids.

S. No.	Acid	Conc.	Extraction (%)
1	H ₂ SO ₄	6 N	48.70
2	HNO ₃	6 N	22.00
3	HCl	6 N	8.70
4	CH ₃ COOH	6 N	82.45
5	CH ₃ COOH	8 N	99.00

Reusability of stripped dye: Since methylene blue has shown some adverse effect to mankind, it was quite interesting to show the reusability of the dye and thereby reduce the chemicals consumption and cost of production also.

From the FT-IR spectrum (Fig. 6), it is clear that, theoretically stripped dye can be reused since the functional groups present in the raw dye is present in stripped dye also. Stripped dye, which can be reused can also be re extracted.

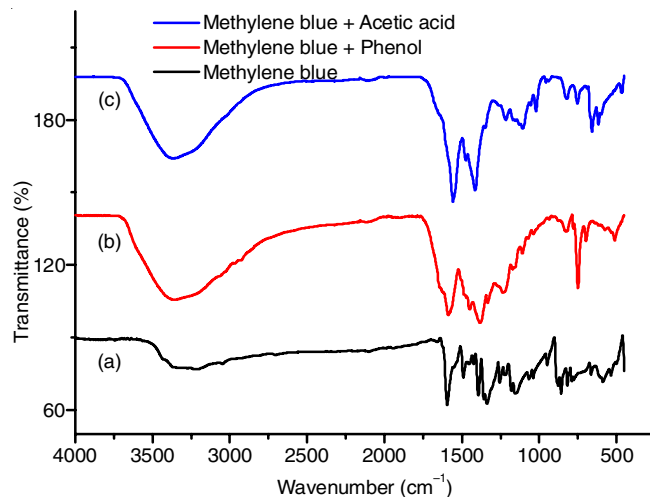


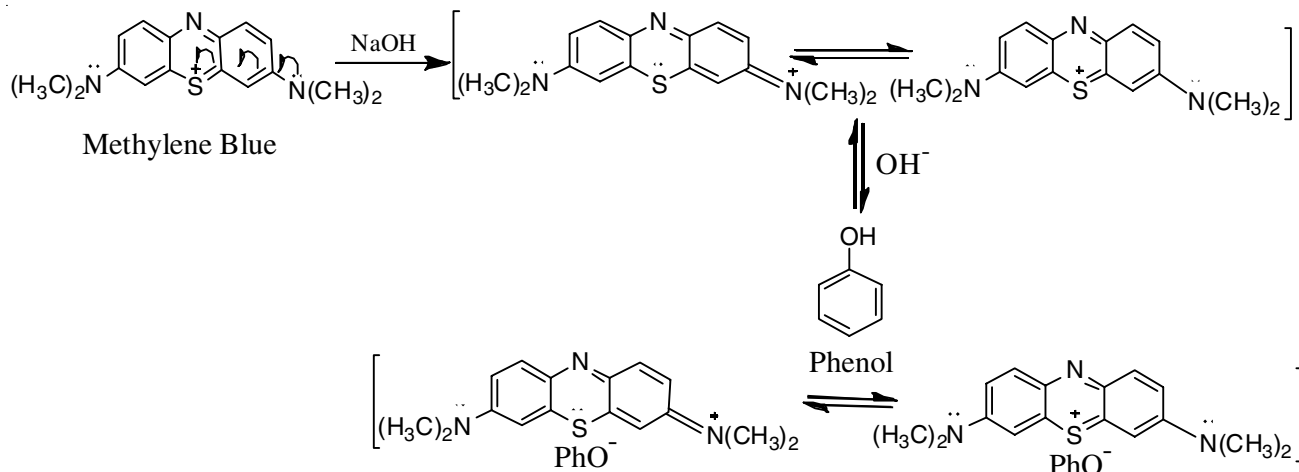
Fig. 6. (a) IR spectrum raw dye (b) IR spectrum of extracted dye (c) IR spectrum of stripped dye

Reusability of used organic phase: Reusability of used organic phase was also tested and the result is shown in the Table-7. The stripped organic phase can be reused for more than ten times without much variation in carrier efficiency [31]. After the 10th run, extraction shows much decrease and it may be due to the loss of some of the phenol molecules while stripping.

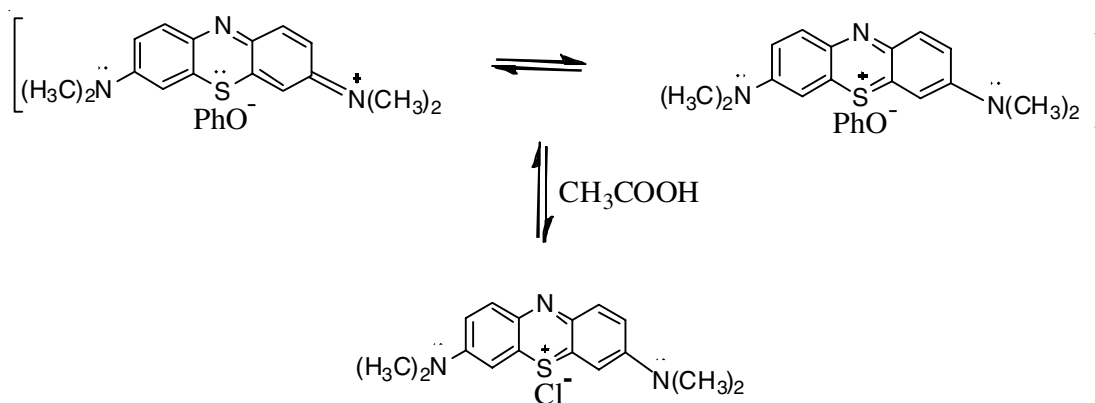
FT-IR spectral analysis: FT-IR spectra have been used for determining the specific functional groups or chemical bonds that exist in a compound. The presence of a peak at a specific wave number would indicate the presence of a specific chemical bond. Fig. 6 shows the IR spectra of normal methylene blue, extracted methylene blue and stripped methylene blue, respectively. Fig-6 (a) shows the following important peaks for raw methylene blue. The stretching frequency at 2924 cm⁻¹ corresponds to the -CH_{3(Terminal)} group and 2810 cm⁻¹ indicates the -C_(Het)-N(CH₃)₂ in raw methylene blue dye. -N⁺-(CH₃)₂ which is formed by the resonance gives a peak at 1643 cm⁻¹. A frequency of 1550 cm⁻¹ corresponds the C-N and C-C bonds and 1373 cm⁻¹ corresponds to -CH_{3(asym)} group. A high peak around 1348 cm⁻¹ is the most important indication. The Presence of this peak clearly shows the existence of C=S⁺ which indicates that methylene blue exists as ionic in nature in aqueous solution. Vibrational bands at 1204-800 cm⁻¹ is the characteristics of C-S-C, C-H, C-C and C-H_(out of plane) respectively. The above mentioned vibrational bands are in good agreement with the theoretical values of methylene blue [52].

The presence of a new stretching frequency around 1309-1290 cm⁻¹ corresponds to phenoxide ion (PhO⁻) [53] and moreover lowering of the frequency of C-S-C bond (from 1100 to 1030 cm⁻¹) indicates the interaction of phenol with methylene

No. of times	1	2	3	4	5	6	7	8	9	10	11
Extraction (%)	99.1	99.1	98.9	98.7	98.5	98.4	98.4	98.3	98.3	98.0	85.0



Scheme-I: Mechanism of extraction process



Scheme-II: Mechanism of stripping process

blue (Fig. 6b). It is inferred that the phenol is effectively worked as a carrier for methylene blue extraction.

Absence of an intense peak in a region of 1309-1290 cm⁻¹ indicates that phenol has been removed from the extracted dye. The most important finding is the presence of a new peak at 1735 cm⁻¹, the vibrational frequency of -CH₃COO⁻ (Fig. 6c). Interaction of acetic acid is confirmed by the lowering of the frequency of C-S-C bond (from 1030 to 1013 cm⁻¹), which indicates that acetic acid worked as a strippant for the removal of methylene blue dye from phenol (Fig. 6c).

Proposed mechanism for extraction and stripping:

Based on the above discussed spectral analysis, we proposed a mechanism (Schemes I and II) for the recovery and reuse of methylene blue using phenol as a carrier [54].

Conclusion

Methylene blue was successfully extracted, recovered and reused using phenol as carrier and xylene as diluent. Extraction showed a maximum value of 99.12 % with an initial dye concentration of 30 ppm, pH of 11.5 and carrier concentration of 0.9 M. Normal temperature, inorganic salt and equilibrium time showed the least effect on the extraction. The extracted dye was separated using 8 N acetic acid. Stripped dye and organic phase were reused and which make the investigation fruitful and effective. From the FT-IR spectra it was clear that phenol acted as an effective carrier and acetic acid as an effective strippant.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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