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Removal of Violet C3R Dye from the Textile Dyeing Effluent using Selective Membrane Technology

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***Abstract:* - This study explores "Selective Liquid Membrane Technique" to recover or to remove dyes from textile wastewater using plant oils. The important parameters governing the extraction behaviour of dyes have been investigated such as pH of wastewater, temperature, mixing time, and type of plant oil. The experiment was carried out as laboratory procedures on VIOLET C3R dye with five plant oils (coconut, mustard, palm, sunflower and used cooking oil). The study revealed that the dye removal efficiency increased as the temperature was increased. Under low pH, the oil splits into two components and when shaken with the dye solution resulted in significant dye removal from the solution. When the dye solution was shaken with the oil under alkaline conditions, it formed a colloidal solution containing the oil plus the dye, and there separation was very difficult. However, the observed reduction in the absorbance under alkaline conditions can be attributed to the dye components losing some of their original color producing different colors that were not effectively measured at their respective wavelengths. The optimum conditions for the dye removal for various oils were at a pH of 2 and a temperature of 55 °C. The used cooking oil achieved the highest dye removal efficiency for Violet C3R dye (81.5%) followed by palm oil (78.36%).**

Keywords: Violet C3R, pH, removal efficiency

I. INTRODUCTION

Textile processing operations are considered an important part of the industrial sector in both developing and undeveloped countries. However, the textile industry is one of the most complex manufacturing industries. Various textile chemicals such as wetting agents, dyes, surfactants, fixing agents, softeners and other additives are used in wet processes (such as bleaching, dyeing and finishing) and as a result large volumes of highly polluted wastewater are produced. Dyes are widely used in textile industries for colouring fabric materials. One of the major problems concerning textile industries is the treatment and disposal of dye laden wastewater. The wastewater generated from the textile processing industries contains high amounts of suspended solids, dissolved solids, un-reacted dyestuffs (colour) and other auxiliary chemicals that are used in the various stages of dyeing and other processes. Wastewater effluents from textile plants cause major water pollution problems. Strong colour of the textile wastewater is the most serious problem of the textile waste effluent. It has been estimated that more than 700,000 tonnes of dyes are used annually of which over 15-20% are left in the effluent during the dyeing process. The presence of even small amount of dye in water (10–20 mg/L) is highly visible, aesthetically undesirable and affects the water transparency and in turns the photosynthetic activity in water bodies. In addition to colouring of the receiving water, dyes in the water bodies such as rivers and lakes also undergo chemical and biological changes that consume dissolved oxygen resulting in fish kills and the destruction of other aquatic organisms. Ground water systems are also affected by these pollutants because of leaching from the soil [11].

Textile dyeing effluents are also known to cause extreme variations of pH, dissolved oxygen (DO), temperature, chemical oxygen demand (COD) and dissolved salts of the receiving water bodies. Some dyes possess toxicity that is hazardous to aquatic life and posses serious health problems to human. Once the dye has contaminated the water, its removal by conventional wastewater treatment method is particularly difficult because many of the dyes are stable to light and oxidizing agents, and are resistant to aerobic bio - oxidation. Therefore, the removal of such dye from process effluent becomes environmentally important. Several methods have been tested for colour removal from industrial effluents to decrease their impact on the environment. These methods consist of various physical, chemical and biological processes. These include: adsorption, nanofiltration, colloidal gas aphrons, ultrasonic decomposition, electro coagulation, coagulation and precipitation, advanced chemical oxidation, electrochemical oxidation, photooxidation, predispersed solvent extraction, ozonation, supported liquid membrane, liquid-liquid extraction and aerobic and anaerobic biological processes.

The liquid membrane technique known as ''Supported Liquid Membrane'' (SLM) is a new technique used for treating wastewater. It has the advantage of achieving selective removal and concentration in single stage, thus having great potential for reducing cost significantly. SLM system has several advantages including: (a) low capital investment and operating cost, (b) low energy consumption, (c) minimal loss of extractant, (d) low liquid membrane Potential of Plant Oils as Liquid Membrane to Treat Textile Dyeing Effluents requirement and thus less amount of expensive extractants which offer good selectivity and (e) simple to operate and easy to scale up [6]. Traditionally, the colourimetric measurement technique has been used to evaluate the effectiveness of these various dye removal methods. In this technique, the absorbance of influent and effluent are measured at the appropriate wave length using spectrophotometer and the removal efficiency is determined. A standard calibration curve is usually determined at ambient conditions. However, for most of the dye removal methods the pH and temperature of the effluent vary within the ranges of 2-12 and 20-60 °C, respectively [2].

The aim of this study was to investigate the potential of using renewable, non toxic, natural plant oils as a liquid membrane for the removal of dye from textile wastewater. The specific objectives were: (a) To evaluate the effectiveness of five plant oils for dye removal, (b) To investigate the effects of pH on dye removal efficiency (c) To investigate the effects of Temperature on dye removal efficiency, (d) Analysis of variance using SPSS Software System.

II. MATERIALS AND METHODS

OILS: Four types of commercially available plant oils (coconut oil, mustard oil, sunflower oil, palm oil) were purchased from a local supermarket in Thrissur. Used cooking oil was obtained from a local restaurant in Pudukad. The viscosity of the fresh oil was given by the manufactories and is shown in Table 1.

Table 1: viscosity of oils.

OIL TYPE VISCOSITY	(mPas)
palm oil	0.106
sunflower oil	0.07
mustard oil	0.09
coconut oil	0.04

DYES: Cotton textile dye, Violet C3R was purchased from
"P.S.DEY CHEMICALS, MALAD, MUMBAI". The chemical structure is shown in figure 1.

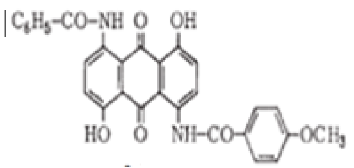

Fig 1 Chemical structure of dyes

REAGENTS AND EQUIPMENTS: The chemicals used in this study included sodium hydroxide (NaOH), sulphuric acid (H_2SO_4). The 98.6% NaOH and 98% H_2SO_4 were obtained from the environmental lab GEC Thrissur. Spectrophotometer 2202 was used for measuring the absorbance. The temperature variation was done by means of incubator. And the mixing was performed using magnetic stirrer.

STANDARD CURVE PREPARATION: To determine the concentration of the dye using colorimetric techniques, standard curve was developed from the standard solution of dye. The standard solution was prepared by dissolving 0.1 g of the dye in 1000 mL of distilled deionized water with pH of 7 and temperature 27 °C. Then, a set of 5 solutions with dye concentrations of 10, 20, 30, 40, 50 was prepared. The λmax was determined by scanning the specimen in spectrophotometer, and the obtained wavelength of Violet C3R- 550 nm Finally, the absorbance of the prepared solutions was measured (in triplicate) using a spectrophotometer shown in table 2. The absorbance was then plotted against the known dye concentrations (mg/L), the graph so obtained is shown in figure 2. A blank sample was used to zero the spectrophotometer.

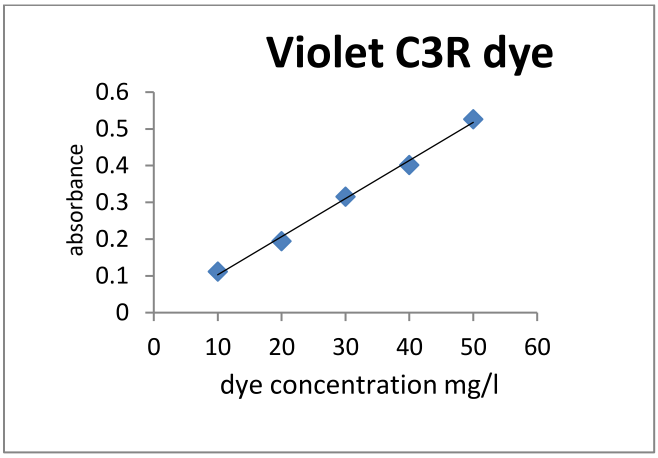

Fig 2 Standard curve

EXPERIMENTAL DESIGN: The effects of oil type, pH, temperature, mixing time, dye concentration and oil concentration on the removal of dye from textile wastewater were investigated. Five types of plant oil (coconut oil, mustard oil, sunflower oil, palm oil and used cooking oil), five levels of pH (2, 4,7,9 and 11) and five temperatures (15, 25, 35, 45 and 55 °C) were investigated. The experiments were designed as: five different pH, five temperatures, five oil types for 3 sample measurements, resulted in 375(3x5x5x5) treatments.

Table 2 : Absorbance of Dye for standard curve Preparation

Concentration (mg/l)	Absorbance
10	0.112
20	0.195
30	0.316
40	0.402
50	0.527

EXPERIMENTAL PROCEDURE: A volume of 500mL of each of the five solutions with pH 2, 4, 9, 11 was prepared. Synthetic dye wastewater was prepared by mixing 0.5 gram of dye in 500 mL of distilled deionised water with pH 7. Similarly dye wastewater with other four pH values was prepared separately. From each samples 100 ml was taken in 200ml Erlenmeyer flask and was kept in the incubator at 15°C until the temperature of the solution reach the desired temperature. The absorbance of each solution was observed using spectrophotometer. To a 30 ml test tube 10 ml of the sample maintained at 15°C was mixed thoroughly with 5 ml of vegetable oil by means of magnetic stirrer for 2 minutes.

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Then this mixture was transferred to small test tube which was then sealed and kept upside down in the incubator at the same temperature of 15°C until separation between the oil and the solution occurred. Absorbance of the treated dye solution was measured in spectrophotometer at the respective wavelength of the dye. The same procedure was repeated for all the oil types with the other pH and temperature. The analysis of variance was performed on the data obtained from the laboratory experiment. The percentage dye reduction was the dependent variable and independent variable was oil type, pH and temperature.

III. RESULTS AND DISCUSSIONS

The potential of five plant oils to be used as SLM was studied. The laboratory testing was performed on the dye wastewater. Treatment was done by varying temperature, pH and oil type. The effects of temperature and pH on the dye removal efficiency of different oils were tabulated as shown in table 3. These studies revealed that the dye wastewater can be treated by using plant oils as SLM. The results obtained shows that among the plant oil used maximum % of reduction was achieved by used cooking oil at a pH of 2 and 55°C temperature. Analysis of variance was performed on the dye removal efficiency data using the SPSS software and the results obtained are as shown in Table 4. The results showed that the type of oil, pH and temperature had significant effects on removal efficiency of the dye. The effect of pH was more pronounced than the type of oil and temperature and the five levels of pH were significantly different from one another at the 95% confidence level.

EFFECT OF OIL TYPE ON DYE REMOVAL EFFICIENCY

The results shown in Table 3 indicated that the used oil was the best suitable liquid membrane for removal of Violet C3R dye, with percentage reduction 81.59 %, followed by the palm with 78.36 %. The other oils achieved little over 60% removal efficiency. This higher removal efficiency of the used oil and palm oil may be due to their high viscosity as shown in Table 1. The other oils had a viscosity in the range of 0.04–0.09 mPas. The literature studies provide a good idea about how the dyes and oils nature is. The treatment mechanism behind the SLM technique is the ionic reaction taking place between the dye and oil. As general structure of all oils are similar but have some specific property of their own. One of the property is viscosity ie resistance to flow, which increases with the temperature. Results are shown in fig 3 to 7.

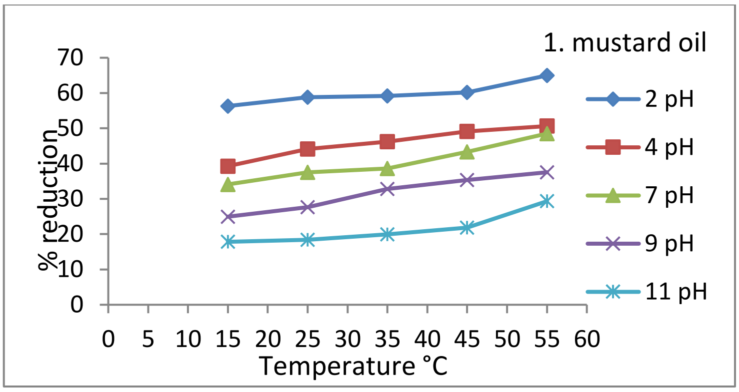

Fig 3: % dye reduction using mustard oil for violet dye

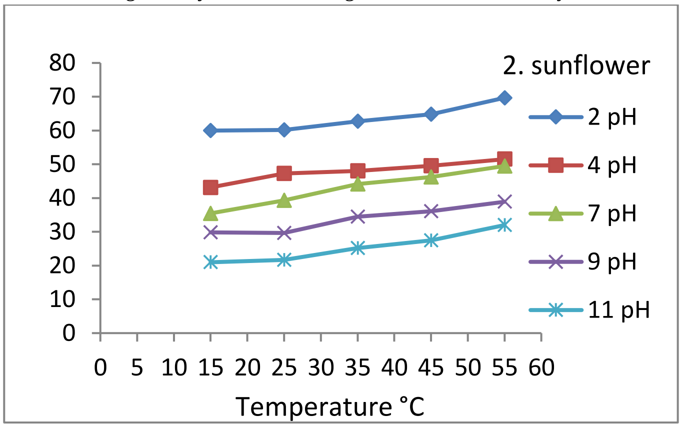

Fig 4: % dye reduction using sunflower oil for violet dye

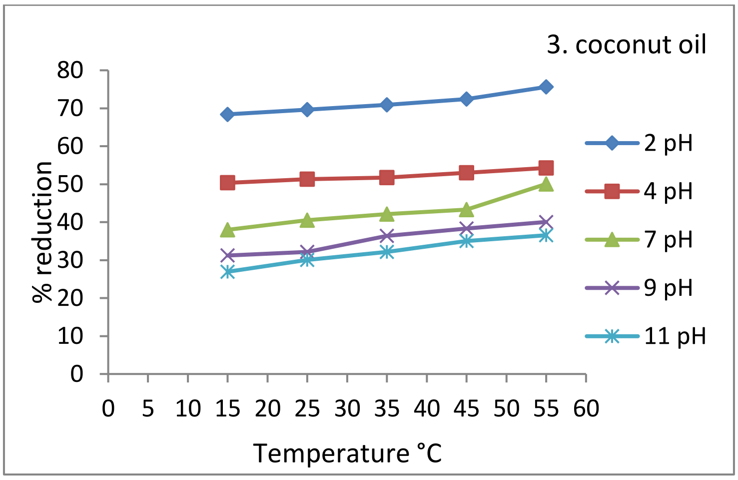

Fig 5: % dye reduction using coconut oil for violet dye

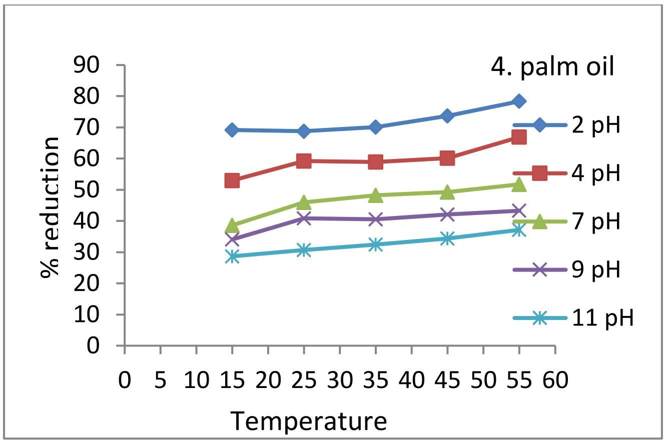

Fig 6: % dye reduction using palm oil for violet dye

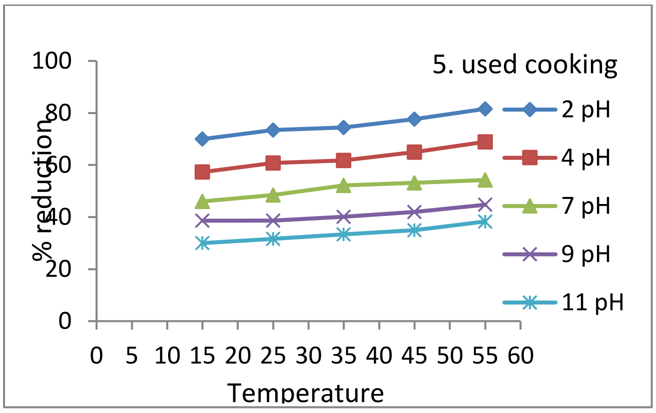

Fig 7: % dye reduction using used cooking oil for violet dye

EFFECT OF TEMPERATURE ON DYE REMOVAL EFFICIENCY

The results obtained from this study showed that the dye removal efficiency increased as the temperature increased for all oils and at all pH levels. Generally, the effect of temperature on rates of chemical reaction is important. Ordinarily, raising the temperature by 10 °C approximately doubles the rate of most but not all reactions. This is because the molecules are more likely to become sufficiently energy-rich to reach the required activation levels needed to undergo reactions by the increase in temperature.

EFFECT OF pH ON THE DYE REMOVAL EFFICIENCY

The dye removal efficiency was high at low pH condition comparing with high pH condition. Under low pH, the oil particle splits into two components diglyceride part and free fatty acid also with a release of hydrogen ion. The reaction mechanism under low pH was high which formed a cleared solution with oil hence it was easy to separate. When the dye solution was shaken with the oil under alkaline condition, it formed a colloidal solution containing the oil plus the dye, which was hardly separable. Hence low reduction percentage was observed, which may be due to the dye components losing some of their original color or producing different colors that were not effectively measured at their respective wavelengths[6].

OPTIMUM REMOVAL CONDITIONS

Most oils produced the highest removal efficiency at a pH of 2 and a temperature of 55 °C. The results also showed that the used cooking oil achieved the highest dye removal efficiency for Violet C3R (81.5 %) followed by palm oil (78.36 %) in table 4. The other oils achieved : Mustard oil (64.98%), Sunflower oil (69.67%) and Coconut oil (75.62%) this higher removal efficiency of used oil and palm oil may be due to their high viscosity. Viscosity has been used to assess chemical charges and characterize fluid textures. In vegetable oils, viscosity increases with the chain length of triglyceride fatty acids and decreases with the unsaturated fatty acid.

Table 4 : Optimum Removal Condition

Oil type	pH	Temperature(°C)	% Reduction
Mustard	2	55	64.98
Sunflower	2	55	69.67
Coconut	2	55	75.62
Palm	2	55	78.36
Used cooking oil	2	55	81.5

CONCLUSION

Dye removal from textile wastewater was achieved using plant oils (coconut, mustard, palm, sunflower and used cooking oil). The study revealed that the dye removal efficiency increased as the temperature of the medium increased. Under low pH, the oil splits into two components: diglyceride, free fatty acid and hydrogen ion. Reaction mechanism between the dye and oil under acidic condition is high and solution formed is clear to separate, resulting in percentage removal of dye. When the dye solution was shaken with the oil under alkaline conditions, it formed a colloidal solution containing the oil plus the dye, which was hardly separable. Hence low reduction percentage was observed, which may be due to the dye components losing some of their original color or producing different colors that were not effectively measured at their respective wavelengths.

The results also showed that the optimum conditions for the dye removal for various oils were at a pH of 2 and a temperature of 55 °C. The used cooking oil achieved the highest dye removal efficiency for violet (81.5%) followed by palm oil (78.36%). Analysis of variance was performed on the dye removal efficiency data using the SPSS software system The results showed that the type of oil, pH and temperature had significant effects on removal efficiency of the dye.

The potential of five oils to be used as liquid membranes in SLM technique was checked. And the output obtained shows that plant oils can be used to remove dye from wastewater. From the five oils the used cooking oil was the most efficient one, it is due to its high viscosity which got increased on cooking at high temperature. The

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study revealed that the dye removal efficiency was maximum by using used cooking oil because of its high vicosity as compared to others which enhances the reaction mechanism. And at high temperature of 55°C maximum dye reduction occurred because viscosity of oils increases according with the temperature and reaction mechanism speed up. Under low pH maximum percentage reduction occurred due to chemical reaction between dye and oil. Also the increase in mixing time favoured the reaction resulting in the increase of percentage dye reduction.

SCOPE OF STUDY

As the used oil is merely a waste coming from different restaurants which itself pollute the water can now be used as a liquid membrane for removal as well as recovery of dye from textile wastewater. Anyhow this study is not enough to make such conclusion but the positive results obtained can be referred for further studies. This study can be extended by setting up a pilot SLM treatment plant and testing for the same conditions. Also detailed study on oil property other than viscosity may be done for more clear results. Dyes of similar colour but different structure can also be studied to determine the structural significance.

Table 3 Percentage dye reduction achieved for Violet dye

oil type	tem/pH	2	4	7	9	11
mustard	15°C	56.32	39.29	34.12	24.97	17.84
	25°C	58.84	44.18	37.56	27.69	18.42
	35°C	59.17	46.23	38.64	32.86	19.96
	45°C	60.17	49.16	43.37	35.31	21.84
	55°C	64.98	50.63	48.51	37.54	29.34
sunflower	15°C	59.96	43.14	35.46	29.87	20.97
	25°C	60.13	47.26	39.29	29.65	21.64
	35°C	62.71	48.03	44.18	34.51	25.14
	45°C	64.75	49.5	46.23	36.06	27.42
	55°C	69.67	51.49	49.48	38.89	31.98
coconut	15°C	68.4	50.35	37.98	31.21	26.94
	25°C	69.65	51.29	40.53	32.18	30.06
	35°C	70.87	51.74	42.14	36.42	32.16
	45°C	72.41	52.98	43.28	38.35	35.07
	55°C	75.62	54.28	50.05	40.05	36.55
palm	15°C	69.17	52.98	38.61	34.07	28.67
	25°C	68.79	59.17	46.02	40.86	30.65
	35°C	70.14	58.94	48.26	40.57	32.47
	45°C	73.71	60.13	49.23	42.03	34.38
	55°C	78.36	66.89	51.74	43.28	37.14
Used oil	15°C	69.98	57.31	46.03	38.61	29.98
	25°C	73.41	60.74	48.51	38.64	31.64
	35°C	74.4	61.73	52.24	40.08	33.37
	45°C	77.61	64.94	53.17	41.98	34.91
	55°C	81.59	68.92	54.23	44.74	38.3

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