

Potential of Plant Oils as Liquid Membrane to Treat Textile Dyeing Effluents

Hima M U¹, K.J. Sosamony²

¹Dept. of Civil Engg., IES College of engineering, Thrissur, Kerala, India

²Dept. of Civil Engg., GEC, Thrissur, Kerala, India

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 BLUE M R 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 or 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 blue dye (77.08%) followed by palm oil (73.34%).

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 poses 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 aphanes, 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 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

A. 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
mustard oil	0.09
sunflower oil	0.07
coconut oil	0.04

B. Dyes

Cotton textile dye, Blue M R was purchased from “P.S.DEY CHEMICALS, MALAD, MUMBAI”. The chemical structure is shown in figure 1.

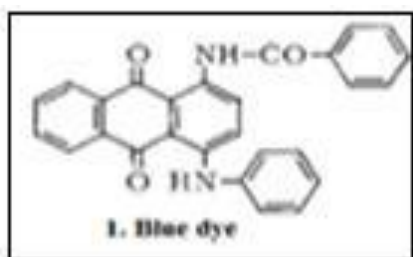


Fig 1 Chemical structure of dyes

C. Reagents And Equipments

The chemicals used in this study included sodium hydroxide (NaOH), sulphuric acid (H2SO4). The 98.6% NaOH and 98% H2SO4 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.

D. 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 λ_{max} was determined by scanning the specimen in spectrophotometer, and the obtained wavelength for blue M R was 662.4 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.

E. 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 three dyes for standard curve preparation

Concentration (mg/l)	absorbance
10	0.164
20	0.314
30	0.461
40	0.589
50	0.732

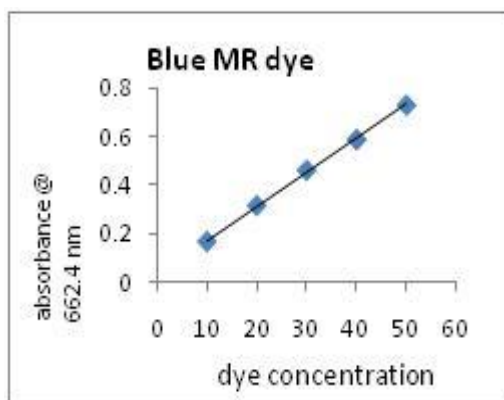


Fig 2. Standard curve for blue dye

F. 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. 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 were 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.

the best suitable liquid membrane for removal of Blue MR dye, with percentage reduction 77.08%, followed by the palm with 73.34%. 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.

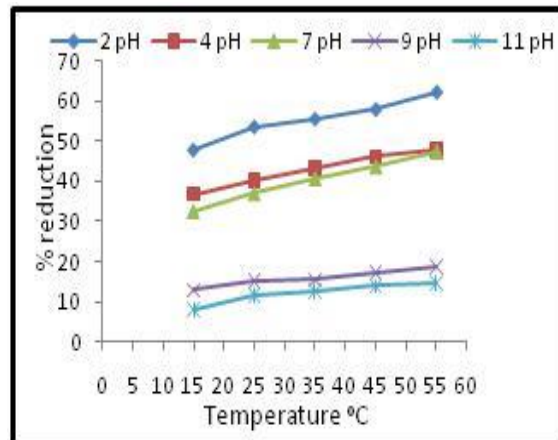


Fig 3. Effect of pH and temperature on percentage reduction using mustard oil.

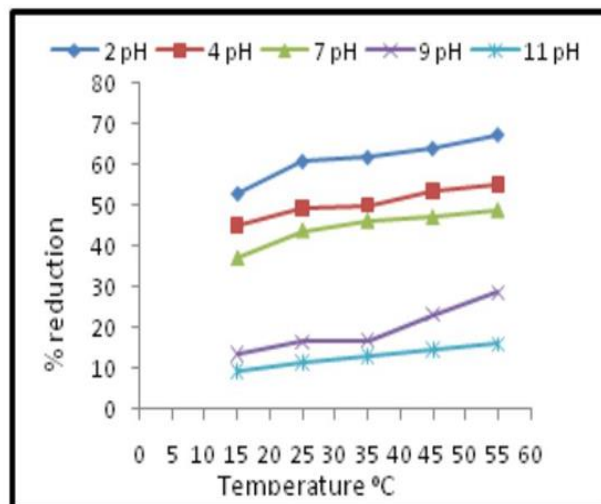


Fig 4. Effect of pH and Temperature on percentage reduction using sunflower oil.

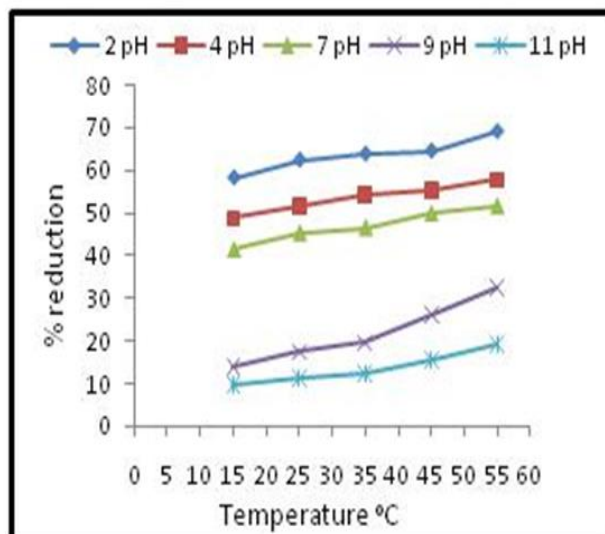


Fig 5. Effect of pH and temperature on percentage reduction using coconut oil

Table 3 percentage dye reduction using plant oils at different pH and temperature

Oil type	Tem/p H	2	4	7	9	11
mustard	15	47.96	36.83	32.6	12.85	7.98
	25	53.65	40.19	37.01	14.96	11.38
	35	55.57	43.29	40.63	15.43	12.74
	45	57.89	46.03	43.51	17.15	13.89
	55	62.14	47.88	47.24	18.68	14.77
Sunflower	15	52.81	44.99	37.08	13.41	9.27
	25	60.78	49.25	43.8	16.47	11.43
	35	61.8	50.08	46.18	16.98	13.04
	45	64.01	53.46	47.02	23.26	14.61
	55	67.4	55.18	48.71	28.6	15.98
coconut	15	58.2	48.73	41.43	13.91	9.68
	25	62.35	51.78	45.33	17.43	11.38
	35	63.79	54.33	46.52	19.52	12.52
	45	64.52	55.42	49.91	25.98	15.46
	55	69.1	57.72	51.61	32.48	19.19
palm	15	63.16	49.24	44.12	25.81	13.24
	25	64.01	52.29	45.67	30.05	14.07
	35	65.38	55.69	46.52	29.98	17.41
	45	70.63	56.54	49.41	34.13	19.48
	55	73.34	60.78	54.9	35.87	23.43
Used oil	15	63.16	50.59	46.69	25.81	17.82
	25	67.4	53.48	50.96	30.73	19.69
	35	68.25	56.03	51.78	32.43	20.54
	45	71.65	57.56	55.18	36.84	22.07
	55	77.08	63.33	56.88	41.26	25.62

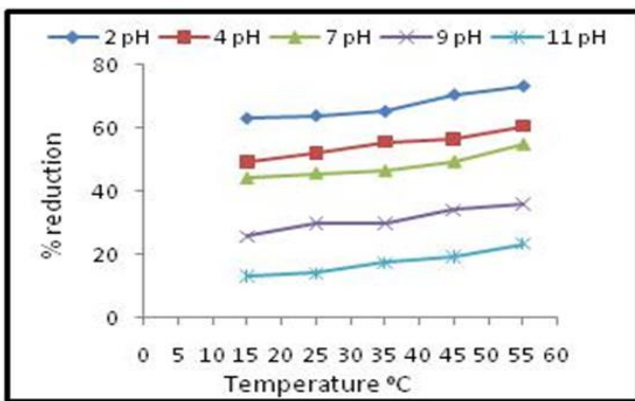


Fig 6. Effect of pH and temperature on percentage reduction using palm oil.

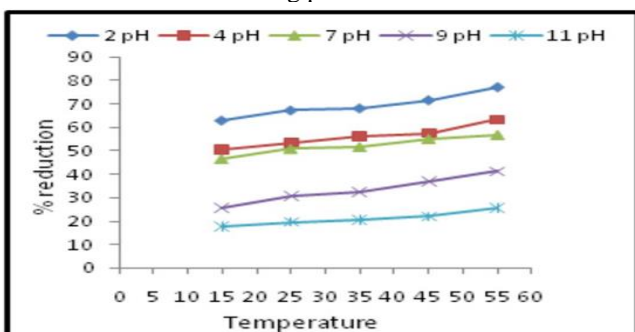


Fig 7. Effect of pH and temperature on percentage reduction using used cooking oil.

A. 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.

B. 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].

C. 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 blue dye (77.08%) followed by palm oil (73.34%) in table 4. The other oils achieved : Mustard oil (62.14), Sunflower oil (67.40) and Coconut oil (69.10) 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	pH	Temp.	%reduction
mustard	2	55	62.14
sunflower	2	55	67.4
Coconut	2	55	69.1
palm	2	55	73.34
Used cooking oil	2	55	77.08

E. Results of Analysis of Variance Using SPSS

Analysis of variance was performed on the dye removal efficiency data using the SPSS system (version 19) as shown in Table 5. The results showed that the type of oil, pH and temperature had significant effects on removal efficiency of the dye ($P=0.0001$). There were also significant interactions between the parameters ($P=0.0001$). The effect of pH was more pronounced than the type of oil and temperature.

Table 5 : ANOVA result using SPSS

Source	Sum of Squares	df	Mean Square	F	P
O	7968.211	4	1992.053	52586.658	.0001
P	117669.793	4	29417.448	776568.447	.0001
T	5515.592	4	1378.898	36400.463	.0001
O * P	1051.711	16	65.732	1735.206	.0001
O * T	64.904	16	4.057	107.084	.0001
P * T	181.989	16	11.374	300.262	.0001
O * P * T	407.072	64	6.361	167.906	.0001
Error	9.470	250	.038		
Total	132868.742	374			

IV. 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 77.08% followed by palm oil 73.34%. 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 study revealed that the dye removal efficiency was maximum by using used cooking oil because of its high viscosity 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.

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 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.

ACKNOWLEDGMENT

I express my sincere thanks to Smt. K.J. Sosamany, project guide, assistant professor, Department of Civil Engineering, for her valuable advice and guidance. I also express my heartfelt thanks to Shri. Vijayan. P, Head of the Department, Smt Jayakumari.V (Staff Co-ordinator), Dept. Of Civil Engineering, for their cooperation and assistance. I would also like to thank Smt. Shahida, Lab Chemist for her valuable guidance throughout the project. I would like to thank Smt. Julie Chandra C.S, Assistant professor, Department of Chemical Engineering for her suggestions about the reaction mechanism involved in the project. I would also like to thank staff of our library- reference section, and my friends for their support. Finally, and most

of all, I would like to thank my parents for their eternal support and encouragement.

References

- [1].A.E. Ghaly, “Decolorization of Remazol Brilliant Blue Dye Effluent by Advanced Photo Oxidation Process (H₂O₂/UV system)” American Journal of Applied Sciences, Dec 2007, PP 1054-1062.
- [2] A.G. Souza, “Effect of heating and cooling on rheological parameters of edible vegetable oils.” J. Food Eng., March 2005, Vol. 67, PP 401-405.
- [3]A.L. Ahmad, “Micellar-enhanced ultrafiltration for removal of reactive dyes from an aqueous solution” Desalination, Sept-2006, Vol. 19, PP 153–161.
- [4]A.M. Neplenbroek, “Nitrate removal using supported liquid membranes: transport” mechanism Journal of Membrane Science, May 1992, Vol. 67, PP 107-119.
- [5]A.S. Mahmoud, “Influence of Temperature and pH on the Stability and Colorimetric Measurement of Textile Dyes” American Journal of Environmental Sciences, June 2007, Vol. 4, PP 205-218.
- [6]E.V.Veliev, “Application of Diffusion Model for Adsorption of Azo Reactive Dye on Pumice.” J. Environ. Stud., March 2006, Vol.15 , PP 347-353.
- [7]Fountain, C.W., “Viscosity of common seed and vegetable oils.” J. Chem. Edu., June 1997, Vol.74, PP 224-227.
- [8]G. Muthuraman “Use of vegetable oil in supported liquid membrane for the transport of Rhodamine B” Desalination, Jan 2009, Vol.249, PP 1062– 1066.
- [9]Janani Narayanan, “Recovery of acetic acid by supported liquid membrane using vegetable oils as liquid membrane” Indian Journal Of Chemical Technology, May 2008, Vol. 15, PP-266-270.
- [10]Katayon saed, “Treatment of textile wastewater by advanced oxidation processes – a review.” Global Nest: the Int. J., Feb 2004, Vol. 6, PP 222-230.
- [11]Lisha Kurup, “Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using hen feathers.” Journal of Hazardous Materials, Vol-14, March 2007, PP 243– 248.
- [12]Mi-Hwa Baek, “Removal of Malachite Green from aqueous solution using degreased coffee bean” Journal of Hazardous Materials , July 2009, PP 820–828.
- [13]M.S. Brooks, “Removal of Dye from Textile Wastewater Using Plant Oils Under Different pH and Temperature Conditions” American Journal of Environmental Sciences vol 4, July 2007, PP 205-218.
- [14]Muhammad Ridwan Fahmi, “Characteristic of Colour and COD Removal of Azo Dye by Advanced Oxidation Process and Biological Treatment” IPCBEE , July 2011, vol.18 , PP 13-18.
- [15]M.S.Brooks, “Decolorization of Remazol Brilliant Blue Dye Effluent by Advanced Photo Oxidation Process” American Journal of Applied Sciences, June 2007, vol-12, PP-1054-1062.
- [16]N. Othman, “Liquid-liquid extraction of Black B Dye from Liquid waste solution using tridodecylamine” journal of environmental sciences and technology, July 2011, Vol. 3 PP-324-331.
- [17]N.M. Kocherginsky, “Recent advances in supported liquid membrane technology” Separation and Purification Technology , Jan 2007, Vol. 53, PP 171–177.
- [18]P.Pandit, “Removal of Ionic Dyes from Water by Solvent Extraction Using Reverse Micelles” Environ. Sci. Technol. 2004, 38, 2435-2442
- [19]Rajesh Kannan, “Equilibrium and Kinetic Studies on Sorption of Malachite Green using Hydrilla Verticillata Biomass” Int. J. Environ. Res., March 2010, Vol-4, PP 817-824.
- [20]R. Jayaraj, “Removal of Congo red Dye from Aqueous solution using Acid Activated Eco- Friendly Low Cost Carbon prepared from marine algae Valoria bryopsis” J. Chem. Pharm. Res., July 2011, Vol-3, PP:389-396.
- [21]Reyad A.S. “Experimental study and modeling of basic dye sorption by diatomaceous clay” Applied Clay Science, April 2003, PP 111 – 120.
- [22]S.A. Avlonitis, “Simulated cotton dye effluents treatment and reuse by nanofiltration” Desalination , Dec 2008, PP 259–267.
- [23]Siew-Teng Ong, “ Dye Waste Treatment” Water , Feb 2011, Vol. 3, PP 157-176.
- [24]Sohail Noor, “Different techniques recently used for the treatment of textile dyeing effluents.” J.Chem.Soc. Aug 2010, Vol. 32, PP 115-124. [25]Sung Wook Won, “Adsorption performance and mechanism in binding of Reactive Red 4 by coke waste” Journal of Hazardous Materials , May 2006, Vol-138, PP 370–377.
- [26]S.W. Puasa, “Micellar-enhanced ultrafiltration for removal of reactive dyes from an aqueous solution” Desalination , March 2005, PP 153–161. [27]Tabrez A Khan, “Removal of some basic dyes from artificial textile wastewater by adsorption on Akash Kinari coal”, Journal of scientific & industrial research, April 2004, Vol. 63, PP 355-364.
- [28]T.A. Albanis, “Removal of dyes from aqueous solutions by adsorption on mixtures of fly ash and soil in batch and

column techniques” Global Nest: the Int. J. Vol. 2, No 3, march 2000, PP 237-244.

[29]U.A. Atay,“Removal of methylene blue by using biosolid” global nest Journal, Vol. 8, march 2006, pp 113-120.

[30]Zhemin Shen,“Degradation of dye solution by an activated carbon fiber electrode electrolysis system” Journal of Hazardous Materials , Feb 2001, PP 107–116.

AUTHORS

1. Hima M U, M Tech in Environmental Engineering, IES College of engineering, email id: hima.radish@gmail.com
2. K.J. Sosamony, M Tech in environmental engineering, GEC thrissur:

Correspondence Author – Hima M U, M Tech in Environmental Engineering, IES College of engineering, email id: hima.radish@gmail.com, contact number: 7560839608