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EXTRACTION OF REMAZOL BRILLIANT ORANGE 3R FROM TEXTILE WASTEWATER USING TETRABUTYL AMMONIUM BROMIDE

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Abstract. Textile wastewater containing dyes is dangerous to the environment and affect mainly to some aquatic life. Their concentration must be reduced to acceptable levels before discharging into environment. In this research liquid-liquid extraction method is used to study on the recovery of Remazol Brilliant Orange 3R dye (orange 3R) from textile wastewater by using tetrabutyl ammonium bromide in dichloromethane. The parameter examined in this research were the effect of diluents, effect of pH, effect of extractant concentration, initial dye concentration and the suitable stripping agent to extract back the dye from organic phase. The result showed that almost 100% of 100 mgL^{-1} Orange 3R was extracted using 0.01 M tetrabutylammonium bromide (TBAB) and no significant affect of pH of feed phase solution on dye extraction. Extracted dye in the organic phase can be back extracted using salicylic acid in sodium hydroxide solution with ratio 1:1.

Keywords: Liquid-liquid extraction; reactive azo dye; Orange 3R; tetrabutyl ammonium bromide; textile wastewater

Abstrak. Air sisa buangan tekstil yang mengandungi pewarna adalah merbahaya kepada persekitaran dan mempengaruhi kehidupan akuatik. Kepekatan pewarna ini mestilah dikurangkan ke paras yang dibenarkan sebelum dibuang ke persekitaran. Dalam kajian ini, kaedah pengekstrakan cecair telah digunakan untuk mengkaji perolehan semula pewarna Remazol Brilliant Orange 3R daripada air sisa dengan menggunakan tetrabutilammonia bromida dalam diklorometana. Parameter yang dikaji adalah kesan pelarut, pH larutan, kepekatan pengekstrak, kepekatan awal pewarna dan egen pelucut yang sesuai untuk mengekstrak semula pewarna daripada fasa organik. Keputusan eksperimen menunjukkan hampir 100% daripada 100mgL^{-1} Remazol Brilliant Oren 3R telah diekstrak menggunakan 0.01 M tetrabutilammonia bromida (TBAB) dan tiada pengaruh pH larutan suapan yang ketara ke atas proses pengekstrakan pewarna. Pewarna yang telah diekstrak boleh diperolehi semula daripada larutan organik dengan menggunakan asid salisilik dalam larutan natrium hidroksida dengan nisbah 1:1.

Kata kunci: Pengekstrakan cecair; pewarna reaktif azo; oren 3R; tetrabutilammonia bromida; air sisa tektil

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1.0 INTRODUCTION

Textile industries are categorized as one of the major water consumers as it uses large volumes of water and chemicals for wet processing of textiles. Usually, reactive azo dyes are employed in the textile due to high stability, excellent colourfastness, and bright colour and ease application in industry. Azo dyes are characterized by the existence of nitrogen nitrogen double bond (-N=N-) and the presence of bright colour due to these azo bonds and associated chromospheres [1]. The reactive azo dyes-containing effluents from these industries have caused serious environment pollution because the presence of dyes in water is highly visible and affects their transparency and aesthetics even if the concentration of the dyes is low. Therefore, industrial effluents containing dyes must be treated before their discharge into the environment [2]. Reactive azo dyes also are recalcitrant to microbial degradation because they have complex aromatic molecular structures and the strong electron-withdrawing property of the azo groups is thought to protect against attack by oxygenates so that the conventional aerobic wastewater treatment processes usually cannot efficiently decolourize azo dye-contaminated effluents [3].

Several attempts have been made to treat such types of effluents for facilitating easy disposal, or to recover the chemicals and recycle the process water. As reported by Haghi [4], treatments for dye containing wastewater can be classified into three groups of physical, chemical and biological treatments. An anaerobic–aerobic treatment process based on mixed culture of bacteria isolated from textile dye effluent-contaminated soil was used to decolourize the reactive azo dyes Remazol Brilliant Orange 3R, Remazol Black B and Remazol Brilliant Violet 5R was investigated by Supaka *et al.* [5]. Red 3BS reactive dyes have been removed from aqueous solutions by sorption of ordered hexagonal and disordered mesoporous carbons [6]. Similarly, removal of reactive dye from textile batik industry using microfiltration membrane was proposed by Ahmad *et al.* [7]. Senthilkumar and Muthukumar [8] studied on decolourisation, toxicity and the possibility for recycling of treated water from acid dye effluents using ozone treatment. The ability of photoelectrocatalytic oxidation to degrade the commercially important copper–phtalocyanine dye, remazol turquoise blue 15 (RTB) was investigated [9].

Liquid-liquid extraction method is used for the purification, enrichment, separation and analysis of various compounds in mixtures. These are based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents. Therefore, the selection of both a diluent and an extractant determines the equilibrium for a given system and efficiency of the extraction process depends on its mass transfer rate [10].

The advantage of solvent extraction includes high through put, ease of automatic operation and of scale up, and high purification [11]. Other than liquid-liquid extraction method, various techniques are used to treat dye wastewater. Biological treatment is often the most economical alternative when compared with other physical and chemical processes [12]. However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation [13]. Besides, chemical methods include coagulation or flocculation combined with filtration, precipitation–flocculation with Fe (II)/Ca (OH)2, electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), and irradiation or electrochemical processes were investigate by previous researchers. However, the chemical methods are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use [14]. Physical method such as adsorption has been investigated by Hsu *et al.* [15] and Poots *et al.* [16]. These adsorption methods are capable of removing of dyes from concentrated wastewater. Regeneration of most of the adsorbents is difficult except for activated carbon. However, the adsorption treatment using activated carbon as adsorbent is quite expensive.

This paper will present the liquid-liquid extraction of reactive azo dyes (orange 3R) from simulated wastewater solution in the purpose of recovery high costly reactive dyes. Several parameters such as type of diluents, pH of solution, extractant concentration, initial dye concentration and type of stripping agents were studied.

2.0 MATERIALS AND METHODS

2.1 Materials

Remazol brilliant orange 3R was obtained from Perusahaan Nozi Batik, Kuala Terengganu, Tetrabutylammonium bromide (TBAB) and kerosene were obtained from Acros organics, xylene, n-dodecane, toluene, dichloromethane, chloroform, sodium carbonate, sulphuric acid were obtained from Merck KGaA, sodium hydroxide and thiourea were obtained from GCE laboratory chemicals, salicylic acid obtained from Ficher chemical and hydrochloric acid was obtained from J.I Baker. Spectrophotometer (Cole Parmer 1100 RS Spectrophotometer) was used to measure the absorbance of the dye. Sodium hydroxide and sulphuric acid were used for pH adjustment.

2.2 Experimental Procedures

The main purpose of interest was the amount of dye extracted. Therefore, the affecting parameters such as the effect of diluents, dye concentration, pH of solution extractant concentration and stripping agent were studied in this research. The extraction process was carried out by mixing an equal volume (10 mL) of aqueous solution of reactive dye and organic solution of TBAB in conical flask. The conical flasks were placed on a mechanical shaker for 18 hours and agitated at 320 rpm until equilibrium achieved. After equilibrium was established, the phases were separated using separating funnel. Sample of aqueous solution was taken for absorbance measurement of dye. The wavelength of maximum absorption for Remazol Brilliant Orange 3R dye (Orange 3R) was 492 nm. The distribution ratio (D) and percentage of extraction (%E) was calculated using the following equation.

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

$$E = 100 \times \frac{[dye]aq0 - [dye]aq}{[dye]aq0}$$

Where [dye]org is Dye concentration in the organic phase (mg/L), [dye]aq is Dye concentration of aqueous phase after extraction (mg/L) and [dye]aq0 is initial dye concentration of aqueous phase (mg/L).

In stripping process, the loaded organic phase and the aqueous stripping agent were added together into conical flask and shake for 18 hours at 320 rpm. Then, the mixture transferred into a separating funnel. The aqueous stripping agent was taken for dye concentration measurements.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Diluents

The effect of various diluents such as toluene, kerosene, n-dodecane, xylene, chloroform and dichloromethane on orange 3R dye were studied. The results show that the extraction of dye using toluene, kerosene, n-dodecane and xylene were about 50% -60% and almost 98% when using dichloromethane and chloroform as shown in Figure 1. This indicate that the polarity of diluents plays an important role in dye

extraction process. Using less polar diluents, the extraction of dye was low compared to high polar diluents. Highly polar solvent can strongly solvate ions that leads to faster ionization rates and higher rate of transfer. If the diluent is less polar, it does not solvate ions very strongly and cannot overcome the lattice energy of the solute. Therefore, both dichloromethane and chloroform give the high extraction percentages of dye. However, dichloromethane was chosen as diluent since the chloroform is more toxic and carcinogenic than dichloromethane [17].

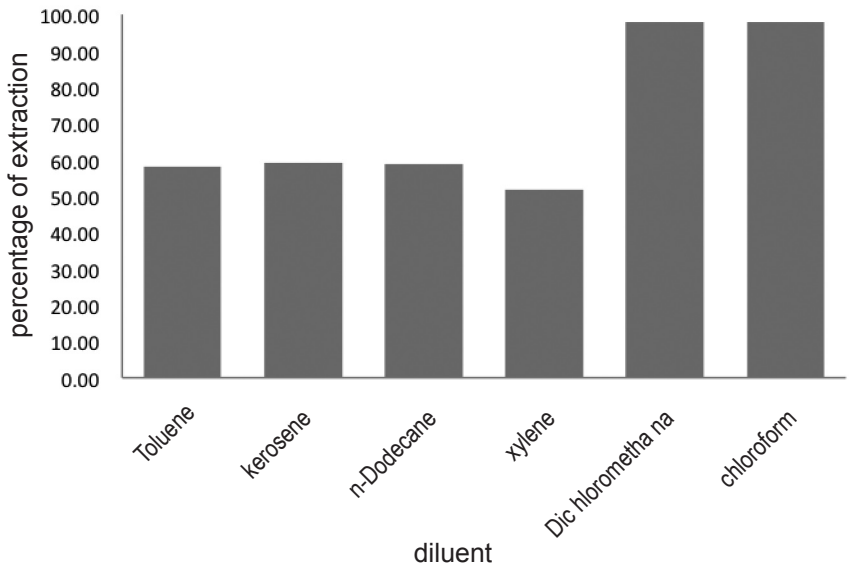

Figure 1 Effect of diluents on extraction (Experimental conditions: dye concentration= 100 ppm, aqueous to organic ratio = 1:1, [TBAB] = 0.1 M, Agitation time=18 hours, speed=320 rpm)

3.2 Effect of pH Solution

The effect of pH of waste solution on the efficiency of dye extraction was shown in Figure 2. The results show that only small increasing and decreasing of the dye extraction percentage when the pH were varied. Thus, the effect of the pH can be considered no effect on dye extraction. The percentage of dye extraction was about 98% . Thus, the further experiment to study the other parameters was carried out at pH 7 ± 0.1.

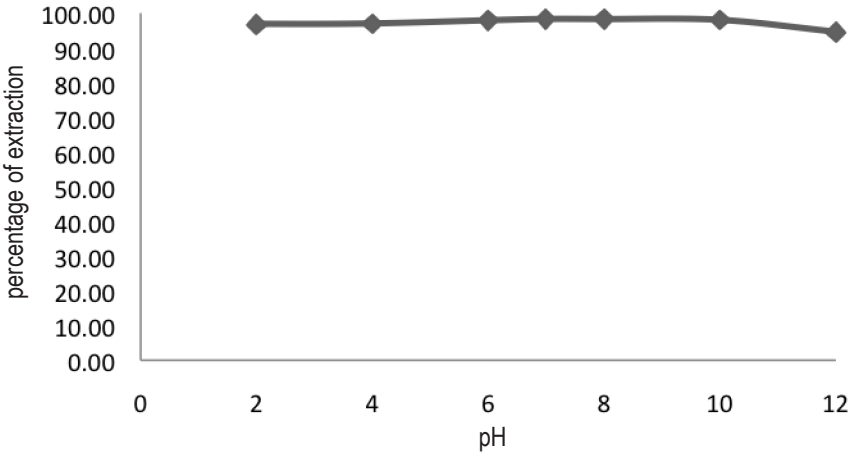

Figure 2 Effect of pH on extraction of dye (Experimental conditions: dye concentration= 100 ppm, aqueous to organic ratio = 1:1, [TBAB] = 0.1 M, Agitation time=18 hours, speed=320 rpm)

3.3 Effect of Extractant Concentration

The effect of TBAB concentration on dye extraction was next investigated in the concentration range of 1.0×10^{-3} to 2.0×10^{-1} M. Figure 3 shows that increasing the TBAB concentration, the efficiency of dye extraction also increased. The percentage of dye extraction seems plateau when the concentrations of TBAB are in the range of 0.05 to 0.2 M. In this range, almost 100% of dye was extracted. This is due to all the amount of dye was reacting to the TBAB since the amount of TBAB were kept increasing, meaning that the TBAB was in excess. Thus further study were carried out using 1.0×10^{-1} M TBAB concentration due to the economic factor since the TBAB is quite expensive.

The distribution ratio (D) of dye was calculated at different molar concentration of TBAB. The plot of log extracted dye versus log TBAB concentration (mgL^{-1}) was shown in Figure 4. As a result, a straight line is obtained with a slope value of 1.255 representing that dye to extractant concentration ratio was best at 1:1 and suggesting formation of 1:1 complex. It can be assumed that 1 mol of TBAB can best extract 1 mol of anionic dye. The positively charged tetrabutyl ammonium cation is necessary to extract the anionic dyes. The reaction between TBAB and dye is shown in Figure 5.

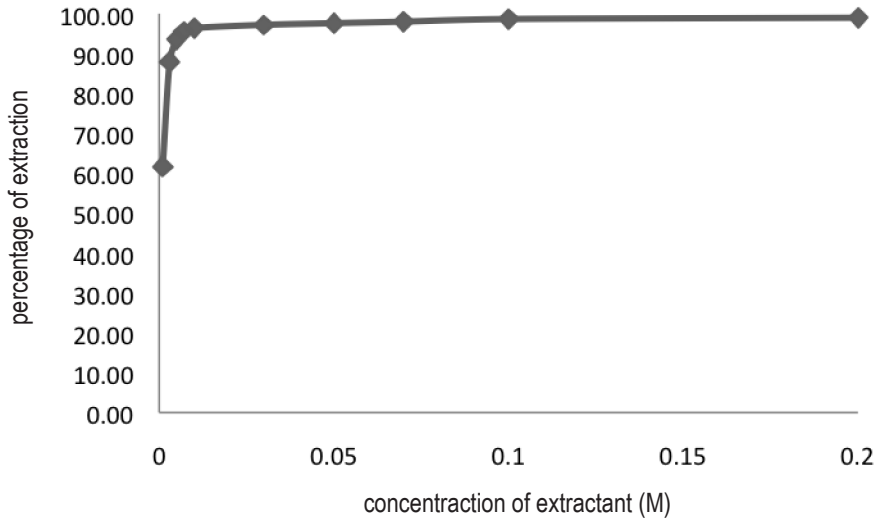

Figure 3 Effect of TBAB concentration on the extraction (Experimental conditions: dye concentration= 100 ppm, aqueous to organic ratio = 1:1, Agitation time=18 hours, speed=320 rpm)

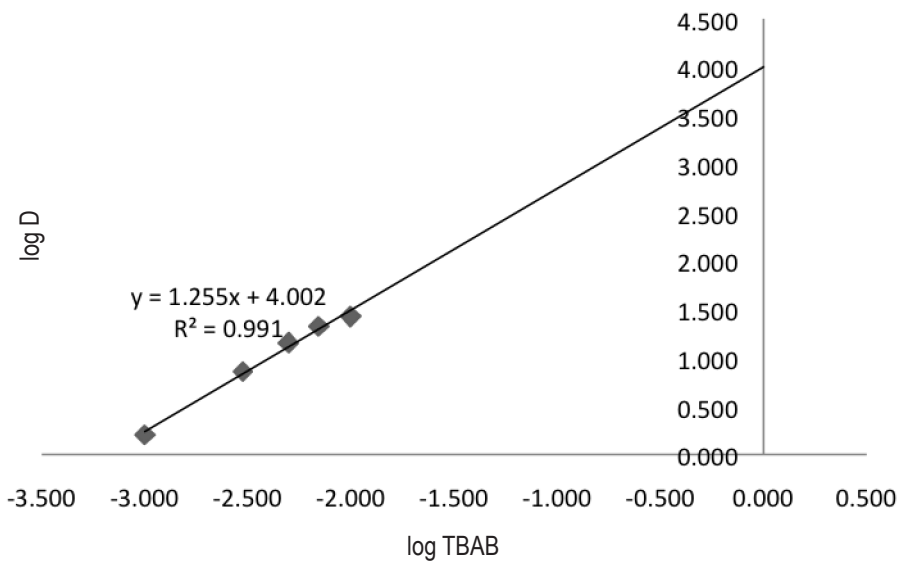

Figure 4 Distribution ratio (Experimental conditions: dye concentration= 100 ppm, aqueous to organic ratio = 1:1, Agitation time=18 hours, speed=320 rpm)

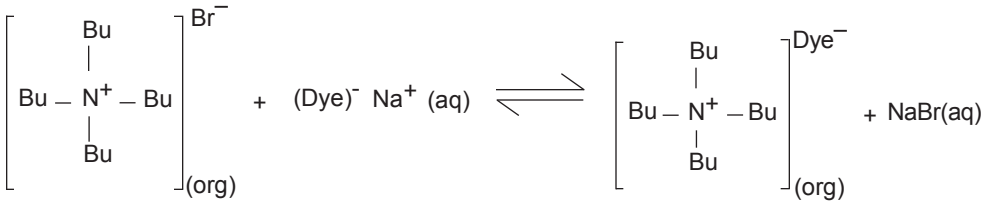

Figure 5 Reaction mechanisms of dye extraction

3.4 Effect of Dye Concentration

The effect of the initial dye concentrations on the extraction of dye was carried out. Figure 6 shows that the percentage of dye extraction decreased with increasing initial dye concentration. The result reveals that at 50 mg/L concentration of dye solution, almost 100% extraction was obtained. With further increase in dye concentration, the percentage of extraction of dye decreased. The extraction decrease because the amount of TBAB is not enough to react with the dye. In addition, from the previous result of this research, it can be assumed that 1 mol of TBAB can best extract 1 mol of anionic dye. Thus, the concentration should be increase when the concentration of dye increases.

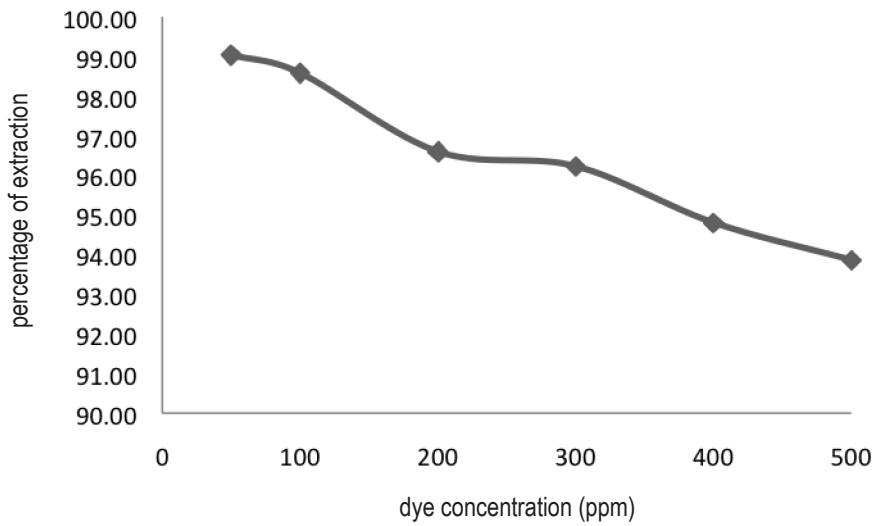

Figure 6 Effect of initial dye concentration on the extraction (Experimental conditions: dye concentration= 100 ppm, aqueous to organic ratio = 1:1, [TBAB] = 0.01 M, Agitation time=18 hours, speed=320 rpm)

3.5 Effect of Stripping Agent

Stripping agents used to back extract the dye from organic phase and allow the reuse the organic solvent without loss of efficiency. Several of stripping agents which were inorganic anions were used in this study such as HCl, H_2SO_4, Na_2CO3 and NaOH. The percentage of stripping for each stripping agent used is shown in the Table 1. Since the used of inorganic anions alone did not gave the high percentage of stripping, thus water insoluble salicylic acid added to the NaOH and Na_2CO3 while thiourea added to HCl, H_2SO_4. The result shows that the salicylic acid with NaOH stripped the dye better than others.

Table 1 Effect of stripping agent on extraction of dye (Experimental conditions: dye concentration= 100 ppm, aqueous to organic ratio = 1:1, [TBAB] = 0.1 M, Agitation time=18 hours, speed=320 rpm)

Stripping agent	%Stripping
1 M HCl	5.17
1 M H_2SO_4	3.78
1 M NaOH	33.76
1 M Na_2CO_3	3.07
1 M HCl + 0.5 M Thiourea	10.48
1 M H_2SO_4 + 0.5 M Thiourea	21.41
1 M Na_2CO_3 + 0.5 M S.A	53.29
1 M NaOH + 0.5 M S.A	59.18
1 M NaOH + 1.0 M S.A	81.44
1 M NaOH + 2.0 M S.A	58.75

HCl and H_2SO_4 give low percentage although thiourea was added to them because the hydrogen atom is more electronegative than the sodium atom. This is due to element with higher electronegative generally have more attraction for the bonding electron. In this research, dye is negatively charge and as a result, the sodium which is less electronegative atom will attract more to the dye. The concentration of salicylic acid (S.A.) dissolved in NaOH solution was varied in the range of 0.5 M-2 M while the concentration of NaOH was maintained at 1 M. Dye stripping was maximum which about 81.44% with 1:1 M ratio. Hence, salicylic acid in NaOH with 1:1 M ratio was chosen for stripping purpose. The reaction for stripping of the dye is shown in Figure 7.

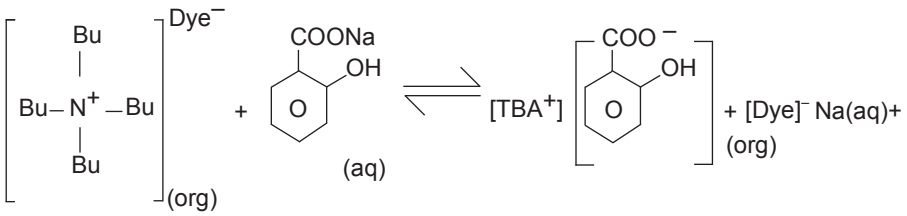

Figure 7 Reaction mechanisms for dye stripping

4.0 CONCLUSIONS

The conclusions of this study are dichloromethane is the suitable and effective solvent for the extraction of Remazol Brilliant Orange 3R dye in aqueous solution. Almost 100% of dye was extracted using TBAB and the potential stripping agent is Salicylic acids in NaOH solution with a ratio of NaOH to Salicylic acids is 1:1.

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REFERENCES

[1] Aksu, Z. 2005. Application of Biosorption for the Removal of Organic Pollutants: A Review. *Process Biochemistry.*140: 997–1026.

[2] Hao, O. J., H. Kim, and P. C. Chiang. 2000. Decolorization of Wastewater. *Criterion Review Environmental Science Technology.* 30: 449–505.

[3] Nigam, P., I. M. Banat, D. Singh, and R. Merchant. 1996. Microbial Process for the Decolourization of Textile Effluent Containing Azo, Diazo and Reactive Dyes. *Process Biochemistry*. 31: 435–442.

[4] Haghi, A. K. 2004. Removal of Dye from the Wastewater Produced by the Handmade Textile Industry. *Roumaine de Chimie.* 49(7): 657–660.

[5] Supaka, N., K. Juntongjin, S. Damronglerd, M. L. Delia, and P. Strehaiano. 2004. Microbial Decolorization of Reactive Azo Dyes in a Sequential Anaerobic–Aerobic System. *Chemical Engineering Journal.* 99: 169–176.

[6] Asouhidou, D. D., K. S. Triantafyllidis, N. K. Lazaridis, K. A. Matis, S. S. Kim, J. Thomas, T. J. Pinnavaia. 2009. Sorption of Reactive Dyes from Aqueous Solutions by Ordered Hexagonal and Disordered Mesoporous Carbons. *Journal of Microporous and Mesoporous Materials*. 117: 257–267.

[7] Ahmad, A. L., W. A. Harris, Syafiie, and B. S. Ooi. 2002. Removal of Dye from Wastewater of Textile Industry Using Membrane Technology. *Journal Technology of UTM*. 36: 31–44.

[8] Senthilkumar M. and M. Muthukumar. 2007. Studies on the Possibility of Recycling Reactive Dye Bath Effluent after Decolouration using Ozone. *Dyes and Pigments*. 72: 251–255.

[9] Osugi, M. E., G. A. Umbuzeir, F. J. V. Castro, and M. V. B Zanoni. 2006. Photoelectrocatalytic Oxidation of Remazol Turquoise Blue and Toxicological Assessment of its Oxidation Products. *Journal of Hazardous Materials*. 137: 871–877.

[10] Lee, D. W., W. H. Hong, and K. Y. Hwang. 2000. Removal of an Organic Dye from Water Using a Predispersed Solvent Extraction. *Separation Science Technology*. 25: 1951–1962.

[11] Yang, X. J., A. G. Fane, and K. Soldenhoff. 2003. Comparison of Liquid Membrane Processes for Metal Separations Permeability, Stability and Selectivity. *Industry Engineering Resources*. 42: 392–402.

[12] Mullan, G. M., C. Meehan, A. Conneely, N. Kirby, T. Robinson, P. Nigam, I. M. Banat, R. Marchant, and W. F. Smyth. 2001. Microbial Decolourisation and Degradation of Textile Dyes: Application. *Microbiology Biotechnology*. 56: 81–87.

[13] Bhattacharyya, K. G. and A. Sarma. 2003. Adsorption Characteristics of the dye, Brilliant Green, on Need Leaf Powder. *Dyes and Pigments*. 57: 211–222.

[14] Demirbas, A. 2009. Agricultural Based Activated Carbons for the Removal of Dyes from Aqueous Solutions: A review. *Journal of Hazardous Materials*. 167(1-3): 1–9.

[15] Hsu, Y., J. Chen, H. Yang, and J. Chen. 2001. Decolorization of Dyes Using Ozone in a Gas-Induced Reactor. *Journal of Industrial Chemical Engineering*. 47(1): 169–176.

[16] Poots, V. J. P., G. McKay, and J. J. Healy. 1976. The Removal of Acid Dyes from Effluent Using Natural Adsorbent. *Wood Water Resources*. 10: 1067–1070.

[17] Wade, L. G, Jr. 2006. *Organic Chemistry*. 6th ed. NJ: Prentice Hall.