

SYNERGISTIC FORMULATION FOR REACTIVE DYES EXTRACTION
USING BENIGN BASED EMULSION LIQUID MEMBRANE

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Specially dedicated to my beloved parents, family members, supervisor and friends. Your endless love, support and prayers make it possible.

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ABSTRACT

Dye loaded in the wastewater is considered as a pollutant due to its toxicity and carcinogenic effect. Hence, the removal of dyes from wastewater is highly demanded. There are many methods introduced for the extraction of dyes but they consume high energy and chemicals. Emulsion liquid membrane (ELM) extraction is one of the promising techniques to simultaneously extract and recover solute from wastewater solution. However, it has some drawbacks such as slow extraction rate, low loading capacity and use of non-friendly based diluent. In this research, emulsion liquid membrane was studied as an alternative method to extract and recover the dye from wastewater. The aims of this study are to formulate a synergistic extractant liquid membrane on extraction of dye (Orange 3R) using palm oil as a diluent, to study the mechanism of Orange 3R extraction and stripping process and optimization of ELM extraction of Orange 3R. The liquid membrane formulation was investigated on the selection of the extractant and synergist extractant using liquid-liquid extraction process. The mechanism of extraction and stripping process was determined by selection of extractant and synergist extractant concentration, extraction kinetic of dyes and selection of stripping agents and its concentration using liquid-liquid extraction process. ELM process was optimized using response surface methodology for four parameters which were surfactant concentration, treat ratio, agitation speed, and extraction time. The important parameter affecting the recovery process of dye which is initial feed concentration was investigated. Results showed that the liquid membrane formulation was determined using Tricaprylmethylammonium Chloride (Aliquat 336) as an extractant and Di-(2-ethylhexyl)phosphoric acid (D2EHPA) as a synergist extractant. The extraction and stripping process was performed at 0.08 M D2EHPA, 0.1 M Aliquat 336, and 0.1 M NaOH, where 86 and 100% of dyes has been extracted and stripped respectively in liquid-liquid extraction process. The optimum condition for ELM extraction performance was achieved at 3.2 % (w/v) of surfactant concentration (Span 80), 12000 rpm of homogenizer speed, 12 minutes of extraction time, 1:9.8 of treat ratio, and 413 rpm of agitation speed. At this condition, 90 % of dye was extracted and 28% was stripped. Almost 10 times of wastewater volume can be treated by a single volume of emulsion liquid membrane. Therefore, ELM process is a promising technology to separate dye from wastewater while solving environmental problems simultaneously.

ABSTRAK

Pencelup yang terdapat di dalam air sisa dianggap sebagai bahan pencemar disebabkan ketoksikan dan kesan karsinogeniknya. Oleh itu, penyingkiran pencelup dari air sisa adalah sangat diperlukan. Terdapat banyak kaedah yang diperkenalkan untuk pengekstrakan pencelup tetapi ia menggunakan tenaga yang tinggi dan bahan kimia yang banyak. Pengekstrakan emulsi membran cecair (ELM) adalah salah satu teknik yang berkebolehan untuk mengekstrak dan memperoleh bahan larut dari air sisa secara serentak. Walaubagaimanapun, ia mempunyai beberapa kelemahan seperti kadar pengekstrakan yang perlahan, muatan beban yang rendah dan menggunakan pelarut yang tidak mesra alam sekitar. Dalam kajian ini ELM telah dikaji sebagai kaedah alternatif untuk mengekstrak dan memperoleh pencelup dari air sisa. Tujuan kajian ini adalah untuk memformulasi membran cecair ekstrak bersinergi untuk mengekstrak pencelup (Orange 3R) menggunakan minyak kelapa sawit sebagai bahan pelarut, mengkaji mekanisma pengekstrakan Orange 3R dan proses pelucutan, dan pengoptimuman ELM bagi pengekstrakan Orange 3R. Formulasi membran cecair diselidik ke atas pemilihan ekstrak dan ekstrak bersinergi menggunakan proses pengekstrakan cecair-cecair. Mekanisma pengekstrakan dan proses pelucutan ditentukan oleh pemilihan kepekatan ekstrak dan ekstrak bersinergi, kinetik pengekstrakan pencelup dan pemilihan agen pelucutan dan kepekatannya menggunakan proses pengekstrakan cecair-cecair. ELM dioptimumkan menggunakan kaedah tindakbalas permukaan bagi empat pembolehubah iaitu kepekatan surfaktan, nisbah rawatan, kelajuan pengaduk, dan masa pengekstrakan. Pembolehubah penting yang mempengaruhi proses perolehan pencelup iaitu kepekatan air sisa awal telah disiasat. Keputusan menunjukkan bahawa formulasi membran cecair adalah dengan menggunakan tricaprilmetilammonium klorida (Aliquat 336) sebagai ekstrak dan asid di-(2-etilheksil)fosforik asid (D2EHPA) sebagai ekstrak bersinergi. Mekanisma dan proses pelucutan dicapai pada 0.08 M D2EHPA, 0.1 M Aliquat 336, dan 0.1 M NaOH, di mana 86 dan 100% pencelup masing-masing telah diekstrak dan dilucutkan dalam proses pengekstrakan cecair-cecair. Keadaan optimum untuk prestasi pengekstrakan ELM dicapai pada 3.2% (w/v) kepekatan surfactant (Span 80), 12000 rpm kelajuan penghomonogen, 12 minit masa pengekstrakan, nisbah rawatan 1:9.8, dan 413 rpm kelajuan pengaduk. Pada keadaan ini, 90% pencelup telah diekstrak dan 28% telah dilucutkan. Hampir 10 kali jumlah air sisa boleh dirawat dengan satu isipadu emulsi membran cecair. Oleh itu, proses ELM merupakan teknologi yang berkebolehan untuk memisahkan pencelup dari air sisa buangan disamping pada masa yang sama dapat menyelesaikan masalah alam sekitar.

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LIST OF ABBREVIATIONS

Aliquat 336	-	Tricaprylmethylammonium Chloride
ANOVA	-	Analysis of Variance
BLM	-	Bulk Liquid Membrane
BBD	-	Box-Behnken Design
D	-	Distribution
D2EHPA	-	Di-(2-ethylhexyl)phosphoric Acid
DF	-	Degree of Freedom
DOE	-	Design of Experiment
ELM	-	Emulsion Liquid Membrane
F	-	Fisher
HLB	-	Hydrophile-lipophile Balance
LLE	-	Liquid-liquid Extraction
MS	-	Mean Square
NaHCO	-	Sodium Bicarbonate
NaOH	-	Sodium Hydroxide
NaCl	-	Sodium Chloride
Na ₂ CO ₃	-	Sodium Carbonate
O/W	-	Oil in Water
RSM	-	Response Surface Methodology
SS	-	Sum-Square
SC	-	Synergistic Coefficient
Span 80	-	Sorbitan Monooleate
SLM	-	Supported Liquid Membrane
TDA	-	Tridodecylamine

TOA	-	Trioctylamine
TOPO	-	Tri-n-octylphosphine Oxide
TBP	-	Tributylphosphate
TDA	-	Tridodecylamine
UV	-	Ultra-Violet
W/O/W	-	Water in Oil in Water
W/O	-	Water in Oil

LIST OF SYMBOLS

M	-	Molar
rpm	-	Rotation per minutes
w/v	-	Weight per volume
Ppm	-	Part per million
g/mL	-	Gram per milliliter
mg/l	-	Milligram per liter
nm	-	Nanometer
mL	-	Milliliter
min	-	Minutes
hr	-	Hour
TR	-	Treat ratio
°C	-	Degree celcius
cm ⁻¹	-	Per centimeter
[]	-	Concentration
μ	-	Viscosity
%	-	Percentage
C _t	-	Concentration of dye at time t
C _{int}	-	Concentration of dye at initial state respectively
k _{eq}	-	Equilibrium constant

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Currently, the world faces critical environmental issues. The main reasons of these issues are rapid growing population, fast growth of industrial development and urbanization. There are various sources that contaminate the water such as domestic and industrial effluents. Industrial waste effluent is a major source for this problem and need to be discharged properly. One of the major sources of wastewater is from the textile industry.

Wastewater containing dyes from the textile industry is considered a pollutant to the environment due to the carcinogenic effect and toxicity. These effluents will cause harmful effect on water quality that will increase in colour, intensity, toxicity and turbidity. It has been predicted that more than 100,000 types of commercial dyes including reactive dyes are produced with over 7×10^5 tons produced yearly (Bahloul *et al.*, 2016). Reactive dyes are soluble in aqueous solution and form complexes that possess a remarkable electro-catalytic property. Normally, 4% of the reactive dyes in the textile industry are lost (Bahloul *et al.*, 2013). This is the main concern about the abnormal colouration that has been discharged to the environment which will cause a reduction of photosynthesis on algal and aquatic plants due to limited transmittance of light into water bodies.

There are many methods of dye treatment in wastewater that include physical treatment, chemical treatment and microbiological methods (Forgacs *et al.*, 2004). Although physical technology can be used for the extraction of reactive dyes from aqueous solution like adsorption on activated charcoal, precipitation by alum, ozonation, and electrolysis, it has a drawback of generating a secondary pollution by creating a large amount of sludge (Kabra *et al.*, 2011), quite expensive and have limited their application (Ahmad and Rahman, 2011). Many biological technologies especially on bioremediation methods have been applied on extraction of dyes from textile effluent. Bioremediation is the used of living organism for cleaning the contaminated sites. Previous study shows that many microorganisms are capable of degrading textiles dyes including fungi (Parshetti *et al.*, 2006), yeast (Jadhav and Govindwar, 2006), algae (Daneshvar *et al.*, 2007) and bacteria (Tamboli *et al.*, 2010). The disadvantages of these methods are only focused on the extraction of dye but not to recovered them. Therefore, they produce a secondary pollution.

At the present time, liquid membrane technology is one of the promising methods for separation of specific solute in variety of mixtures. There are three types of liquid membrane which are supported liquid membrane (SLM), bulk liquid membrane (BLM) and emulsion liquid membrane (ELM). Among the techniques, ELM offers some benefits such as low cost, low energy used due to its recycling usage and a high interfacial area resulting in enhancement of mass transfer rate (Peng *et al.*, 2012). The advantages of ELM are the extraction and recovery occur in a one stage process that make product can be separated and concentrated simultaneously. This also has been proved by several researchers on high efficiency of extraction and recovery of various solute from wastewater such as chromium (Othman *et al.*, 2016), tungsten (Lende and Kulkarni, 2015), cadmium (Zeng *et al.*, 2016), acetic acid (Lee, 2015), dyes (Liu *et al.*, 2016), phenol (Othman *et al.*, 2016), palladium (Noah *et al.*, 2015) and rare earth (Zhang *et al.*, 2016). The uniqueness of this system is that it is a simultaneous extraction and recovery in single step process, that separate and concentrate the product in a one step process. However, the main disadvantage of this method is the emulsion instability for longer extraction time. In order to solve the problem and for a faster extraction, a new formulation of liquid membrane need to be explored to overcome the problem.

1.2 Problem Statement

Dye in the textile effluents is a major pollutant due to the toxicity and carcinogenic effect. Even though dyes are considered as a pollutant, dyes are also a valuable chemical in the textile industry and it is a crucial to treat the dye waste water. There are many methods on the extraction of dye in textile industry such as biological (Daneshvar *et al.*, 2007), liquid-liquid extraction, steam distillation, adsorption and chemical oxidation (Villegas *et al.*, 2016). These conventional methods have its own drawbacks such as high operating cost, produces secondary pollutant and time consuming. At the present time, liquid membrane technology especially ELM technique is expected to be the promising method to encounter the disadvantages of conventional methods.

ELM is a combination of two systems which are extraction and stripping process occurred simultaneously in a single stage process. The extractant will extract the solute from the feed phase and form a complex in the liquid membrane phase and diffuse to the interphase of stripping and liquid membrane phase. ELM provides many advantages such as low concentration of chemical used, high surface area for mass transfer, very selective to the targeted solute and low-cost process. Therefore, the ELM was chosen as the great technology to replace the conventional methods on extraction and recovery of dyes in this study. Several researchers attempted on the extraction of dye using ELM process such as the extraction of Methylene Blue (Bahloul *et al.*, 2013b), Congo Red (Dâas and Hamdaoui, 2010), Acid Yellow 99 (Bahloul *et al.*, 2016), Cristal Violet (Agarwal *et al.*, 2010) and Red3BS (Othman *et al.*, 2011). Despite of the advantages, ELM has some problems with the extraction rate and stability that make it unable to be commercialized for industrial purposes.

The extraction rate is associated with the liquid membrane (LM) formulation which is the most important step in ELM process. Suitable extractant, diluent and stripping agent should be chosen to formulate LM for extraction and recovery of dyes. Many previous studies used various petroleum based diluents such as heptane (Chanukya and Rastogi, 2013; Dâas and Hamdaoui, 2010), pentanol (Mokhtari and

Pourabdollah, 2013), hexane (Bahloul *et al.*, 2013b) and kerosene (Masu *et al.*, 2005; Othman *et al.*, 2011; Peng *et al.*, 2012) in LM formulation. Petroleum based LM is non-environmental friendly and can cause other pollutions. Therefore, green based LM such as palm oil and coconut oil has been prove as a potential diluent in many research such as in the extraction of chromium (Othman *et al.*, 2016), Direct Yellow 27 (Melo *et al.*, 2015) and Astacyl Golden Yellow (Muthuraman and Palanivelu, 2006).

On the other hand, the extractant plays the most important role in LM formulation. Various single extractants have been used for extraction of anionic, neutral and cationic species of dyes. However, single extractant has suffered from some drawbacks such as slow phase separations and tiny loading capacity (Zhang *et al.*, 2016a). Therefore, a new formulation was developed by mixing the extractants (synergistic extractant) and this system has been applied on numerous extraction of metal and it has been proven that by using the synergistic extractant the extraction efficiency was increased and reduced the extraction time (Wannachod *et al.*, 2016). According to the finding, a synergistic extractant is expected to be used as an alternative formulation in ELM process for extraction of basic dyes from wastewater.

1.3 Objectives

The main objective of this research is to study the possibility of using a synergistic extractant in ELM system to extract dyes from the wastewater. In summary, the objectives of this research are:

- i. To determine a synergistic liquid membrane formulation for Orange 3R dye extraction using Liquid-liquid Extraction (LLE) process.
- ii. To investigate the mechanism of Orange 3R extraction and stripping process.
- iii. To optimize the extraction of Orange 3R dye in Emulsion Liquid Membrane (ELM) process using RSM.

1.4 Scopes of the Study

In order to achieve the first objective, a liquid membrane formulation has been obtained by using synergistic extractant for the extraction of Orange 3R from the simulated wastewater. The extraction of dyes has been carried out by using a liquid-liquid extraction process. Palm oil has been set as a diluent. Various types of extractant and synergist extractants has been investigated on the performance of extracting dyes. The parameters that has been studied were selection of extractant and synergist extractant.

The mechanism of the Orange 3R extraction process has been carried out by manipulating numerous parameters such as effect of extractant concentration, effect of synergistic concentration and extraction kinetic of dye. Meanwhile, for the stripping process, the parameters studied was stripping agent selection and stripping agent concentration.

The performance of Orange 3R extraction in ELM process has been studied by manipulating several parameters which are treat ratio (1:1-1:10), agitation speed (150-450 rpm), Span 80 concentration (1-7 %w/v) and extraction time (1-15 min) in the second objectives. The optimization of the extraction of Orange 3R dye performance has been designed using design of experiment (DOE) and optimized using RSM method. Four parameters have been chosen such as treat ratio, agitation speed, Span 80 concentration and extraction time to the respond of dye extraction performance.

1.5 Significance of Study

According to the environmental and economic problems, it is important to remove and recover reactive dyes from textile industry wastewater. Liquid membrane technology especially ELM process shows a promising method for separation of organic and metal extraction. ELM process is a promising method that can give a high

efficiency due to the advantages of the process such as simple operations, low operational cost, less chemicals used, large mass transfer area was and the extraction and stripping process occurred simultaneously. So, it is a great technology to overcome the disadvantages of the existing conventional treatment. However, ELM process draws some disadvantages on extraction rate and instability of emulsion. In this research, a synergistic extractant is used to formulate the liquid membrane phase to increase the extraction rate. Meanwhile, Span 80 as a surfactant are used in the ELM process was optimized to overcome the swelling and breakage problem.

1.6 Thesis Outline

This thesis consists of 5 chapters. In Chapter One, the research background, problem statement, research objective, research scope and significance of study are introduced. The details of researches related to liquid membrane technology including the types, characteristics, current and future development of liquid membrane technology are reviewed in Chapter Two. Also, the details of researches related to the dyes wastewater and their conventional alternatives in extracting and recovering are reviewed in this chapter. Chapter Three explains the materials used and methodology involved to conduct the study while all the results of the finding will be discussed in Chapter Four. Conclusion and recommendation are discussed in Chapter Five.

REFERENCES

- Abbassian, K., & Kargari, A. (2016). Modification of membrane formulation for stabilization of emulsion liquid membrane for extraction of phenol from aqueous solutions. *Journal of Environmental Chemical Engineering*, 4(4), 3926–3933.
- Agarwal, A. K., Das, C., & De, S. (2010). Modeling of extraction of dyes and their mixtures from aqueous solution using emulsion liquid membrane. *Journal of Membrane Science*, 360(1–2), 190–201.
- Ahamd, A. L., Harris, W. A., Syafiee, & Seng, O. B. (2007). Removal of Dye From Wastewater of Textile Industry Using Membrane Technology. *Jurnal Teknologi*, 36(F), 31–44.
- Ahmad, A. L., Buddin, M. M. H. S., & Ooi, B. S. (2015). Extraction of Cd (II) Ions by Emulsion Liquid Membrane (ELM) Using Aliquat 336 as Carrier, *American Journal of Chemistry*, 5(3A), 1–6.
- Ahmad, M. A., & Rahman, N. K. (2011). Equilibrium, kinetics and thermodynamic of Remazol Brilliant Orange 3R dye adsorption on coffee husk-based activated carbon. *Chemical Engineering Journal*, 170(1), 154–161.
- Al-Kdasi, A., Idris, A., Saed, K., & Guan, C. T. (2004). Treatment of Textile Wastewater By Advanced Oxidation Processes – a Review. *Global NEST Journal*, 6(3), 222–230.
- Allègre, C., Moulin, P., Maisseu, M., & Charbit, F. (2006). Treatment and reuse of reactive dyeing effluents. *Journal of Membrane Science*, 269(1–2), 15–34.
- Alventosa-deLara, E., Barredo-Damas, S., Alcaina-Miranda, M. I., & Iborra-Clar, M. I. (2012). Ultrafiltration technology with a ceramic membrane for reactive dye removal: Optimization of membrane performance. *Journal of Hazardous Materials*, 209–210, 492–500.

- Amin, S. N. A., & Wan Omar, W. N. N., (2011). *Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. Biomass and Bioenergy*, 35, 1329-1338.
- Amini, M., Arami, M., Mahmoodi, N. M., & Akbari, A. (2011). Dye removal from colored textile wastewater using acrylic grafted nanomembrane. *Desalination*, 267(1), 107–113.
- Anand, K., & Elangovan, S. (2017). Optimizing the ultrasonic inserting parameters to achieve maximum pull – Out strength using response surface methodology and genetic algorithm integration technique. *Measurement*, 99, 145–154.
- Andrade, F., & Elizalde, M. P. (2016). Synergistic Extraction of Ni (II) by Mixtures of LIX 860 and Bis (2 - Ethylhexyl) Phosphoric Acid, Solvent Extraction and Ion Exchange, 23,85-99.
- Anitha, M., Ambare, D. N., Singh, D. K., Singh, H., & Mohapatra, P. K. (2015). Extraction of neodymium from nitric acid feed solutions using an emulsion liquid membrane containing TOPO and DNPPA as the carrier extractants. *Chemical Engineering Research and Design*, 98, 89–95.
- Anjaneyulu, Y., Sreedhara Chary, N., & Samuel Suman Raj, D. (2005). Decolourization of industrial effluents - Available methods and emerging technologies - A review. *Reviews in Environmental Science and Biotechnology*, 4(4), 245–273.
- Azizitorghabeh, A., Rashchi, F., Babakhani, A., & Noori, M. (2017). Synergistic extraction and separation of Fe(III) and Zn(II) using TBP and D2EHPA. *Separation Science and Technology*, 52(3), 476–486.
- Babu, B. R., Parande, a K., Raghu, S., & Kumar, T. P. (2007). Cotton Textile Processing : Waste Generation and Effluent Treatment. *The Journal of Cotton Science*, 153(11:141), 141–153.
- Bahloul, L., Bendebane, F., Djenouhat, M., Meradi, H., & Ismail, F. (2016). Effects and optimization of operating parameters of anionic dye extraction from an aqueous solution using an emulsified liquid membrane: Application of designs of experiments. *Journal of the Taiwan Institute of Chemical Engineers*, 59, 26–32.
- Bahloul, L., Ismail, F., & Samar, M. E. H. (2013). Extraction and desextraction of a cationic dye using an emulsified liquid membrane in an aqueous solution. *Energy Procedia*, 36, 1232–1240.

- Belkhouche, N. E., Didi, M. A., & Villemin, D. (2016). Separation of Nickel and Copper by Solvent Extraction Using Di - 2 Ethylhexylphosphoric Acid - Based Synergistic Mixture, *Solvent Extraction and Ion Exchange*, 23, 677-693
- Benyahia, N., Belkhouche, N., & Jönsson, J. Å. (2014). A comparative study of experimental optimization and response surface methodology of Bi(III) extraction by emulsion organophosphorus liquid membrane. *Journal of Environmental Chemical Engineering*, 2(3), 1756–1766.
- Bertea, A. & Bertea, A.P. (2008). Decolorisation and recycling of textile wastewater (in Romanian), Performantica Ed, ISBN 978-973-730-465-0, Iasi, Romania
- Bhatti, I., Qureshi, K., Kamarudin, K. S. N., Bazmi, A. A., Bhutto, A. W., Ahmad, F., & Lee, M. (2016). Innovative method to prepare a stable emulsion liquid membrane for high CO₂ absorption and its performance evaluation for a natural gas feed in a rotating disk contactor. *Journal of Natural Gas Science and Engineering*, 34, 716–732.
- Biswas, S., Pathak, P. N., & Roy, S. B. (2012). Carrier facilitated transport of uranium across supported liquid membrane using dinonyl phenyl phosphoric acid and its mixture with neutral donors. *Desalination*, 290, 74–82.
- Biswas, S., Pathak, P. N., Singh, D. K., Roy, S. B., & Manchanda, V. K. (2010). Synergistic extraction of uranium with mixtures of PC88A and neutral oxodonors. *Journal of Radioanalytical and Nuclear Chemistry*, 284(1), 13–19.
- Bruice, P. Y. (2006). *Essential Organic Chemistry* (1st ed.). Upper Saddle River, N. J.: Pearson Prentice Hall.
- Caporaso, N., Genovese, A., Burke, R., Barry-Ryan, C., & Sacchi, R. (2016). *Effect of olive mill wastewater phenolic extract, whey protein isolate and xanthan gum on the behaviour of olive O/W emulsions using response surface methodology*. *Food Hydrocolloids*, 61, 66-76.
- Carmen, Z., & Daniela, S. (2012). Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview, *Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update*, Dr. Tomasz Puzyn (Ed.)
- Chakraborty, M., Bhattacharya, C., & Datta, S. (2010). Chapter 4 - Emulsion Liquid Membranes: Definitions and Classification, Theories, Module Design, Applications, New Directions and Perspectives A2 - Kislik, Vladimir S. BT - Liquid Membranes (pp. 141–199). Amsterdam: Elsevier.

- Chang, S. H., Teng, T. T., & Ismail, N. (2010). Extraction of Cu(II) from aqueous solutions by vegetable oil-based organic solvents. *Journal of Hazardous Materials*, 181(1–3), 868–872.
- Chanukya, B. S., Kumar, M., & Rastogi, N. K. (2013). Optimization of lactic acid pertraction using liquid emulsion membranes by response surface methodology. *Separation and Purification Technology*, 111, 1–8.
- Chanukya, B. S., & Rastogi, N. K. (2013). Extraction of alcohol from wine and color extracts using liquid emulsion membrane. *Separation and Purification Technology*, 105, 41–47.
- Choppin, G. R., & Morgenstern, A. (2000). Thermodynamics of Solvent Extraction. *Solvent Extraction and Ion Exchange*, 18(6), 1029–1049.
- Dâas, A., & Hamdaoui, O. (2010). Extraction of anionic dye from aqueous solutions by emulsion liquid membrane. *Journal of Hazardous Materials*, 178(1–3), 973–981.
- Daneshvar, N., Ayazloo, M., Khataee, A. R., & Pourhassan, M. (2007). Biological decolorization of dye solution containing Malachite Green by microalgae *Cosmarium* sp. *Bioresource Technology*, 98(6), 1176–1182.
- Darvishi, D., Haghshenas, D. F., Alamdari, E. K., Sadrnezhad, S. K., & Halali, M. (2005). Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA. *Hydrometallurgy*, 77(3–4), 227–238.
- Das, C., Rungta, M., Arya, G., DasGupta, S., & De, S. (2008a). Removal of dyes and their mixtures from aqueous solution using liquid emulsion membrane. *Journal of Hazardous Materials*, 159(2–3), 365–371.
- Das, C., Rungta, M., Arya, G., DasGupta, S., & De, S. (2008b). Removal of dyes and their mixtures from aqueous solution using liquid emulsion membrane. *Journal of Hazardous Materials*, 159(2–3), 365–371.
- Dehmlow, E.V. and Dehmlow, S.S. (1993) Phase Transfer Catalysis. 3rd Edition, VCH, New York.
- Djenouhat, M., Hamdaoui, O., Chiha, M., & Samar, M. H. (2008). Ultrasonication-assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane. Part 2. Permeation and stripping. *Separation and Purification Technology*, 63(1), 231–238.

- Santos, D. A. B., Cervantes, F. J., & van Lier, J. B. (2004). Azo dye reduction by thermophilic anaerobic granular sludge, and the impact of the redox mediator anthraquinone-2,6-disulfonate (AQDS) on the reductive biochemical transformation. *Applied Microbiology and Biotechnology*, 64(1), 62–69.
- Elisangela, F., Andrea, Z., Fabio, D. G., de Menezes Cristiano, R., Regina, D. L., & Artur, C.-P. (2009). Biodegradation of textile azo dyes by a facultative *Staphylococcus arlettae* strain VN-11 using a sequential microaerophilic/aerobic process. *International Biodeterioration & Biodegradation*, 63(3), 280–288.
- Ertugay, N., & Acar, F. N. (2013). Removal of COD and color from Direct Blue 71 azo dye wastewater by Fenton's oxidation: Kinetic study. *Arabian Journal of Chemistry*, 10, S1158-S1163.
- Fernandes, A., Pacheco, M. J., Ciríaco, L., & Lopes, A. (2015). Review on the electrochemical processes for the treatment of sanitary landfill leachates: Present and future. *Applied Catalysis B: Environmental*, 176–177, 183–200.
- Fettouche, S., Tahiri, M., Madhouni, R., & Cherkaoui, O. (2015). Removal of reactive dyes from aqueous solution by adsorption onto Alfa fibers powder. *Journal of Materials and Environmental Science*, 6(1), 129–137.
- Fiamegos, Y. C., & Stalikas, C. D. (2005). Phase-transfer catalysis in analytical chemistry. *Analytica Chimica Acta*, 550(1–2), 1–12.
- Firmino, P. I. M., da Silva, M. E. R., Cervantes, F. J., & dos Santos, A. B. (2010). Colour removal of dyes from synthetic and real textile wastewaters in one- and two-stage anaerobic systems. *Bioresource Technology*, 101(20), 7773–7779.
- Forgacs, E., Cserháti, T., & Oros, G. (2004). Removal of synthetic dyes from wastewaters: A review. *Environment International*, 30(7), 953–971.
- Fouad, E. A. (2009). Separation of copper from aqueous sulfate solutions by mixtures of Cyanex 301 and LIX ® 984N. *Journal of Hazardous Material*, 166, 720–727.
- Frankenfeld, J. W., Cahn, R. P., & Li, N. N. (1981). Extraction of Copper by Liquid Membranes. *Separation Science and Technology*, 16(4), 385–402.
- Gadhawe, A. (2014). Determination of Hydrophilic-Lipophilic Balance Value. *International Journal of Science and Research*, 3(4), 573–575.
- Gasser, M. S., El-Hefny, N. E., & Daoud, J. A. (2008). Extraction of Co(II) from aqueous solution using emulsion liquid membrane. *Journal of Hazardous Materials*, 151(2–3), 610–615.

- Georgin, J., Dotto, G. L., Mazutti, M. A., & Foletto, E. L. (2016). Preparation of activated carbon from peanut shell by conventional pyrolysis and microwave irradiation-pyrolysis to remove organic dyes from aqueous solutions. *Journal of Environmental Chemical Engineering*, 4(1), 266–275.
- Ghoreishi, S. M., & Haghghi, R. (2003). Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent. *Chemical Engineering Journal*, 95(1–3), 163–169.
- Gong, H., Jin, Z., Wang, X., & Wang, K. (2015). Membrane fouling controlled by coagulation/adsorption during direct sewage membrane filtration (DSMF) for organic matter concentration. *Journal of Environmental Sciences (China)*, 32(July), 1–7.
- Goyal, R. K., Jayakumar, N. S., & Hashim, M. A. (2011). A comparative study of experimental optimization and response surface optimization of Cr removal by emulsion ionic liquid membrane. *Journal of Hazardous Materials*, 195, 383–390.
- Griffin, W. C. (1949). Classification of surface-active agents by “HLB.” *Journal of the Society of Cosmetic Chemists*, 1(5), 311–326.
- Guo, Z., Dong, J., Su, H., Cai, R., & Ma, X. (2015). Stability and performance study of newly developed emulsion prepared with polymeric rubber emulsifier and using the emulsion for nicotine extraction. *Separation and Purification Technology*, 156, 617–624.
- Gupta, A., Zhao, R., Novak, J. T., & Douglas Goldsmith, C. (2014). Application of Fenton’s reagent as a polishing step for removal of UV quenching organic constituents in biologically treated landfill leachates. *Chemosphere*, 105, 82–86.
- Gupta, V. K., & Suhas. (2009). Application of low-cost adsorbents for dye removal – A review. *Journal of Environmental Management*, 90(8), 2313–2342.
- Haaland, P. D. (1991). Experimental Design in Biotechnology. *Drying Technology*, 9(3), 817.
- Harruddin, N., Othman, N., Lim Ee Sin, A., & Raja Sulaiman, R. N. (2015). Selective removal and recovery of Black B reactive dye from simulated textile wastewater using the supported liquid membrane process. *Environmental Technology*, 36(3), 271–280.
- Hayworth, H. C., Ho, W. S., Burns, W. A., & Li, N. N. (1983). Extraction of Uranium from Wet Process Phosphoric Acid by Liquid Membranes. *Separation Science and Technology*, 18(6), 493–521.

- Ho, W. S. W., & Sirkar, K. K. (1992). *Membrane Handbook*. Boston, MA: Springer US.
- Homsirikamol, C., Sunsandee, N., Pancharoen, U., & Nootong, K. (2016). Synergistic extraction of amoxicillin from aqueous solution by using binary mixtures of Aliquat 336, D2EHPA and TBP. *Separation and Purification Technology*, *162*, 30–36.
- Huang, S.-M., Kuo, C.-H., Chen, C.-A., Liu, Y.-C., & Shieh, C.-J. (2017). RSM and ANN modeling-based optimization approach for the development of ultrasound-assisted liposome encapsulation of piceid. *Ultrasonics Sonochemistry*, *36*, 112–122.
- Jadhav, J. P., & Govindwar, S. P. (2006). Biotransformation of malachite green by *Saccharomyces cerevisiae* MTCC 463. *Yeast*, *23*, 4.
- Jakubowska, A. (2010). Interactions of different counterions with cationic and anionic surfactants. *Journal of colloid and interface science*, *346*, 398-404.
- Jiao, H., Peng, W., Zhao, J., & Xu, C. (2013). Extraction performance of bisphenol A from aqueous solutions by emulsion liquid membrane using response surface methodology. *Desalination*, *313*, 36–43.
- Jiao, J., Rhodes, D. G., & Burgess, D. J. (2002). Multiple Emulsion Stability: Pressure Balance and Interfacial Film Strength. *Journal of Colloid and Interface Science*, *250*(2), 444–450.
- Kabra, A. N., Khandare, R. V., Waghmode, T. R., & Govindwar, S. P. (2011). Differential fate of metabolism of a sulfonated azo dye Remazol Orange 3R by plants *Aster amellus* Linn., *Glandularia pulchella* (Sweet) Tronc. and their consortium. *Journal of Hazardous Materials*, *190*(1–3), 424–431.
- Kaci, M., Meziani, S., Arab-Tehrany, E., Gillet, G., Desjardins-Lavis, I., & Desobry, S. (2014). Emulsification by high frequency ultrasound using piezoelectric transducer: Formation and stability of emulsifier free emulsion. *Ultrasonics Sonochemistry*, *21*(3), 1010–1017.
- Kaith, B. S., Sharma, K., Kumar, V., Kalia, S., & Swart, H. C. (2014). Fabrication and characterization of gum ghatti-polymethacrylic acid based electrically conductive hydrogels. *Synthetic Metals*, *187*(1), 61–67.
- Kamiński, W., & Kwapiński, W. (2000). Applicability of Liquid Membranes in Environmental Protection. *Polish Journal of Environmental Studies*, *9*(1), 37–43.

- Kargari, A., Kaghazchi, T., & Soleimani, M. (2004). Role of emulsifier in the extraction of gold (III) ions from aqueous solutions using the emulsion liquid membrane technique. *Desalination*, 162(1–3), 237–247.
- Karimi, R. F. and Bjorkegren, S. (2012). A Study of the Heavy Metal Extraction Process using Emulsion Liquid Membranes. Master, Chalmers University of Technology, Sweden
- Kibami, D., Pongener, C., Rao, K. S., & Sinha, D. (2017). Surface characterization and adsorption studies of *Bambusa vulgaris*-a low cost adsorbent. *Journal of Materials and Environmental Science*, 8(7), 2494–2505.
- Kiernan, J. a. (2015). Classification and naming of dyes, stains and fluorochromes. *Biotechnic & Histochemistry: Official Publication of the Biological Stain Commission*, 76, 261–278.
- Kim, J. S., Han, K. S., Kim, S. J., Kim, S.-D., Lee, J.-Y., Han, C., & Rajesh Kumar, J. (2016). Synergistic extraction of uranium from Korean black shale ore leach liquors using amine with phosphorous based extractant systems. *Journal of Radioanalytical and Nuclear Chemistry*, 307(2), 843–854.
- Körbahti, B. K., Artut, K., Geçgel, C., & Özer, A. (2011). Electrochemical decolorization of textile dyes and removal of metal ions from textile dye and metal ion binary mixtures. *Chemical Engineering Journal*, 173(3), 677–688.
- Kulkarni, P. S. (2003). Recovery of uranium(VI) from acidic wastes using tri-n-octylphosphine oxide and sodium carbonate based liquid membranes. *Chemical Engineering Journal*, 92(1–3), 209–214.
- Kulkarni, P. S., Mukhopadhyay, S., Bellary, M. P., & Ghosh, S. K. (2002). Studies on membrane stability and recovery of uranium (VI) from aqueous solutions using a liquid emulsion membrane process. *Hydrometallurgy*, 64(1), 49–58.
- Kumar Goyal, R., Natesan, J., & Hashim, M. (2011). *Chromium removal by emulsion liquid membrane using [BMIM] +[NTf 2] – as stabilizer and TOMAC as extractant. Desalination*, 278, 50-56.
- Kumbasar, R. A. (2010). Selective extraction of chromium (VI) from multicomponent acidic solutions by emulsion liquid membranes using tributylphosphate as carrier. *Journal of Hazardous Materials*, 178(1–3), 875—882.
- Kwiatkowski, J. F. (2011). *Activated Carbon: Classifications, Properties and Applications*. Nova Science Publishers.

- Le-Clech, P., Chen, V., & Fane, T. A. G. (2006). Fouling in membrane bioreactors used in wastewater treatment. *Journal of Membrane Science*, 284(1–2), 17–53.
- Lee, S. C. (2015). Removal of acetic acid from simulated hemicellulosic hydrolysates by emulsion liquid membrane with organophosphorus extractants. *Bioresource Technology*, 192, 340–345.
- Lende, A. B., & Kulkarni, P. S. (2015). Selective recovery of tungsten from printed circuit board recycling unit wastewater by using emulsion liquid membrane process. *Journal of Water Process Engineering*, 8, 75–81.
- Li, N. N. (1978). *Facilitated transport through liquid membranes — an extended abstract*. *Journal of Membrane Science*, 3, 265–269.
- Lin, S. H., Pan, C. L., & Leu, H. G. (2002). Equilibrium and mass transfer characteristics of 2-chlorophenol removal from aqueous solution by liquid membrane. *Chemical Engineering Journal*, 87(2), 163–169.
- Liu, M., Chen, Q., Lu, K., Huang, W., Lü, Z., Zhou, C., and Gao, C. (2017). High efficient removal of dyes from aqueous solution through nanofiltration using diethanolamine-modified polyamide thin-film composite membrane. *Separation and Purification Technology*, 173, 135–143.
- Lu-ting, P. A. N. (2006). Extraction of Amino-J Acid from Waste-water by Emulsion Liquid Membrane, *The Chinese Journal of Process Engineering*, 6, 5.
- Lv, G., Wang, F., Cai, W., & Zhang, X. (2014). Characterization of the addition of lipophilic Span 80 to the hydrophilic Tween 80-stabilized emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 447, 8–13.
- Manu, B., & Chaudhari, S. (2002). Anaerobic decolorisation of simulated textile wastewater containing azo dyes. *Bioresource Technology*, 82(3), 225–231.
- Manzak, A., & Tutkun, O. (2005). Extraction of Citric Acid Through an Emulsion Liquid Membrane Containing Aliquat 336 as Carrier. *Separation Science and Technology*, 39(10), 2497–2512.
- Martinez-Porchas, M., Martinez-Cordova, L. R., Lopez-Elias, J. A., & Porchas-Cornejo, M. A. (2014). Bioremediation of Aquaculture Effluents. *Microbial Biodegradation and Bioremediation, Elsevier Insights*, 542–555.
- Masu, S., Botau, D., & Manea, F. (2005). Application of emulsion liquid membrane technique for MB R 12 Red reactive dye-containing simulated wastewater treatment. *Chemical Bulletin*, 50(64), 1–2.

- Mattioli, D., Florio, L. De, Giordano, A., Tarantini, M., Enea, S., Centexbel, I. D. V. (2005). Efficient use of water in the textile finishing industry. *E-Water*, 1, 1–18.
- Melo, R. P. F., Barros Neto, E. L., Moura, M. C. P. A., Castro Dantas, T. N., Dantas Neto, A. A., & Oliveira, H. N. M. (2015). Removal of direct Yellow 27 dye using animal fat and vegetable oil-based surfactant. *Journal of Water Process Engineering*, 7, 196–202.
- Mezohegyi, G., van der Zee, F. P., Font, J., Fortuny, A., & Fabregat, A. (2012). Towards advanced aqueous dye removal processes: A short review on the versatile role of activated carbon. *Journal of Environmental Management*, 102, 148–164.
- Mokhtari, B., & Pourabdollah, K. (2013). Emulsion liquid membrane for selective extraction of bismuth from nitrate medium. *Korean Journal of Chemical Engineering*, 30(7), 1458–1465.
- Mokhtari, B., & Pourabdollah, K. (2015). Emulsion liquid membrane for selective extraction of Bi(III). *Chinese Journal of Chemical Engineering*, 23(4), 641–645.
- Mortaheb, H. R., Amini, M. H., Sadeghian, F., Mokhtarani, B., & Daneshyar, H. (2008). Study on a new surfactant for removal of phenol from wastewater by emulsion liquid membrane. *Journal of Hazardous Materials*, 160(2–3), 582–588.
- Murali, V., Ong, S. A., Ho, L. N., & Wong, Y. S. (2013). Evaluation of integrated anaerobic-aerobic biofilm reactor for degradation of azo dye methyl orange. *Bioresource Technology*, 143, 104–111.
- Muthuraman, G., & Palanivelu, K. (2006). Transport of textile dye in vegetable oils based supported liquid membrane. *Dyes and Pigments*, 70(2), 99–104.
- Muthuraman, G., & Teng, T. T. (2009). Extraction and recovery of rhodamine B, methyl violet and methylene blue from industrial wastewater using D2EHPA as an extractant. *Journal of Industrial and Engineering Chemistry*, 15(6), 841–846.
- Muthuraman, G., Teng, T. T., Leh, C. P., & Norli, I. (2009). Extraction and recovery of methylene blue from industrial wastewater using benzoic acid as an extractant. *Journal of Hazardous Materials*, 163(1), 363–369.
- Najm, I. N., Snoeyink, V. L., Lykins, Benjamin W., J., & Adams, J. Q. (1991). Using Powdered Activated Carbon: A Critical Review. *Journal (American Water Works Association)*, 83(1), 65–76.

- Ng, Y. S., Jayakumar, N. S., & Hashim, M. A. (2010). Performance evaluation of organic emulsion liquid membrane on phenol removal. *Journal of Hazardous Materials*, 184(1–3), 255–260.
- Nigam, P., Armour, G., Banat, I. M., Singh, D., & Marchant, R. (2000). Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues. *Bioresource Technology*, 72(3), 219–226.
- Noah, N. F. M., Othman, N., & Jusoh, N. (2015). Highly selective transport of palladium from electroplating wastewater using emulsion liquid membrane process. *Journal of the Taiwan Institute of Chemical Engineers*, 64, 134–141.
- Nosuhi, M., & Nezamzadeh-Ejhieh, A. (2017). High catalytic activity of Fe(II)-clinoptilolite nanoparticules for indirect voltammetric determination of dichromate: Experimental design by response surface methodology (RSM). *Electrochimica Acta*, 223, 47–62.
- Ooi, Z. Y., Harruddin, N., & Othman, N. (2015). Recovery of kraft lignin from pulping wastewater via emulsion liquid membrane process. *Biotechnology Progress*, 31(5), 1305–1314.
- Othman, N., Noah, N. F. M., Harruddin, N., Abdullah, N. A., & Bachok, S. K. (2014). Selective extraction of palladium from simulated liquid waste solution by emulsion liquid membrane process using D2EHPA as a mobile carrier. *Jurnal Teknologi (Sciences and Engineering)*, 69(9), 1–4.
- Othman, N., Noah, N. F. M., Poh, K. W., & Yi, O. Z. (2016). High Performance of Chromium Recovery from Aqueous Waste Solution Using Mixture of Palm-oil in Emulsion Liquid Membrane. *Procedia Engineering*, 148(6), 765–773.
- Othman, N., Noah, N. F. M., Shu, L. Y., Ooi, Z.-Y., Jusoh, N., Idroas, M., & Goto, M. (2016). Easy removing of phenol from wastewater using vegetable oil-based organic solvent in emulsion liquid membrane process. *Chinese Journal of Chemical Engineering*. 25, 45-52.
- Othman, N., Sulaiman, R. N. R., Rahman, H. A., Noah, N. F. M., Jusoh, N., & Idroas, M. (2018). Simultaneous extraction and enrichment of reactive dye using green emulsion liquid membrane system. *Environmental Technology*, In press.
- Othman, N., Zailani, S. N., & Mili, N. (2011). Recovery of synthetic dye from simulated wastewater using emulsion liquid membrane process containing tri-dodecyl amine as a mobile carrier. *Journal of Hazardous Materials*, 198, 103–112.

- Park, Y., Skelland, A. H. P., Forney, L. J., & Kim, J. H. (2006). Removal of phenol and substituted phenols by newly developed emulsion liquid membrane process. *Water Research*, 40(9), 1763–1772.
- Parshetti, G., Kalme, S., Saratale, G., & Govindwar, S. (2006). Biodegradation of malachite green by *Kocuria rosea* MTCC 1532. *Acta Chimica Slovenica*, 53(4), 492–498.
- Peng, W., Jiao, H., Shi, H., & Xu, C. (2012). The application of emulsion liquid membrane process and heat-induced demulsification for removal of pyridine from aqueous solutions. *Desalination*, 286, 372–378.
- Problems, P. (2016). Kinetics of Chromium (Iii) Transport Through the Double-Carrier, *Physicochemical Problems of Mineral Processing*, 52(1), 87–97.
- Punzi, M., Anbalagan, A., Aragão Börner, R., Svensson, B.-M., Jonstrup, M., & Mattiasson, B. (2015). Degradation of a textile azo dye using biological treatment followed by photo-Fenton oxidation: Evaluation of toxicity and microbial community structure. *Chemical Engineering Journal*, 270, 290–299.
- Quan, X., Chen, S., Su, J., Chen, J., & Chen, G. (2004). Synergetic degradation of 2,4-D by integrated photo- and electrochemical catalysis on a Pt doped TiO₂/Ti electrode. *Separation and Purification Technology*, 34(1–3), 73–79.
- Rajewski, J., & Religa, P. (2016). Synergistic extraction and separation of chromium(III) from acidic solution with a double-carrier supported liquid membrane. *Journal of Molecular Liquids*, 218, 309–315.
- Ruppert, M., Draxler, J., & Marr, R. (1988). Liquid-Membrane-Permeation and Its Experiences in Pilot-Plant and Industrial Scale. *Separation Science and Technology*, 23(12–13), 1659–1666.
- Sain, R. S., Ray, S., & Basu, S. (2014). Synergism in Solvent Extraction and Solvent Extraction Kinetics. *Journal of Chemical , Biological and Physical Sciences*, 4(4), 3156-3181.
- Scholler, C., Chaudhuri, J. B., & Pyle, D. L. (1993). Emulsion liquid membrane extraction of lactic acid from aqueous solutions and fermentation broth. *Biotechnology and Bioengineering*, 42(1), 50–58.
- Shamsuddin, N., Das, D. B., & Starov, V. M. (2015). Filtration of natural organic matter using ultrafiltration membranes for drinking water purposes: Circular cross-flow compared with stirred dead end flow. *Chemical Engineering Journal*, 276, 331–339.

- Shea, J. J. (1998). *Surfactants And Polymers In Aqueous Solutions. IEEE Electrical Insulation Magazine*, 14, 1-471.
- Singh, S. K., Dhama, P. S., Dakshinamoorthy, A., Sundersanan, M., Kumar, S., Dhama, P. S., Sundersanan, M. (2009). Studies on the Recovery of Uranium from Phosphoric Acid Medium Using Synergistic Mixture of 2-Ethyl Hexyl Hydrogen 2-Ethyl Hexyl Phosphonate and Octyl(phenyl)-N,N-diisobutyl Carbamoyl Methyl Phosphine Oxide. *Separation Sciences and Technology*, 44 (2), 491-505.
- Soloman, P. A., Basha, C. A., Velan, M., Ramamurthi, V., Koteeswaran, K., & Balasubramanian, N. (2009). Electrochemical degradation of Remazol Black B Dye effluent. *Clean - Soil, Air, Water*, 37(11), 889–900.
- Solomons, T. W. G. and Fryhle, C. B. (2011). *Organic Chemistry* (10th ed.). Asia: John Wiley & Sons (Asia) Pte Ltd.
- Spagni, A., Grilli, S., Casu, S., & Mattioli, D. (2010). Treatment of a simulated textile wastewater containing the azo-dye reactive orange 16 in an anaerobic-biofilm anoxic-aerobic membrane bioreactor. *International Biodeterioration & Biodegradation*, 64(7), 676–681.
- Starks, C. M. (1971). Phase-transfer catalysis. I. Heterogeneous reactions involving anion transfer by quaternary ammonium and phosphonium salts. *Journal of the American Chemical Society*, 93(1), 195–199.
- Strzelbicki, J., & Charewicz, W. (1980). The liquid surfactant membrane separation of copper, cobalt and nickel from multicomponent aqueous solutions. *Hydrometallurgy*, 5(2–3), 243–254.
- Sukriti, Sharma, J., Chadha, A. S., Pruthi, V., Anand, P., Bhatia, J., & Kaith, B. S. (2017). Sequestration of dyes from artificially prepared textile effluent using RSM-CCD optimized hybrid backbone based adsorbent-kinetic and equilibrium studies. *Journal of Environmental Management*, 190, 176–187.
- Tamboli, D. P., Kurade, M. B., Waghmode, T. R., Joshi, S. M., & Govindwar, S. P. (2010). Exploring the ability of *Sphingobacterium* sp. ATM to degrade textile dye Direct Blue GLL, mixture of dyes and textile effluent and production of polyhydroxyhexadecanoic acid using waste biomass generated after dye degradation. *Journal of Hazardous Materials*, 182(1–3), 169–176.
- Tehrani-Bagha, A. R., Mahmoodi, N. M., & Menger, F. M. (2010). Degradation of a persistent organic dye from colored textile wastewater by ozonation. *Desalination*, 260(1–3), 34–38.

- Villegas, L. G. C., Mashhadi, N., Chen, M., Mukherjee, D., Taylor, K. E., & Biswas, N. (2016). A Short Review of Techniques for Phenol Removal from Wastewater. *Current Pollution Reports*, 157–167.
- Wang, G., Deng, Y., Xu, X., He, X., Zhao, Y., Zou, Y., and Yue, J. (2016). Optimization of air jet impingement drying of okara using response surface methodology. *Food Control*, 59, 743–749.
- Wannachod, T., Wongsawa, T., Ramakul, P., & Pancharoen, U. (2016). The synergistic extraction of uranium ions from monazite leach solution via HFSLM and its mass transfer. *Journal of Industrial and Engineering Chemistry* 33, 246–254.
- Welham, A. (2000). *The theory of dyeing (and the secret of life)*. *Journal of the Society of Dyers and Colourists*, 116, 140-143.
- Wojciechowski, K., Kucharek, M., & Buffle, J. (2008). Mechanism of Cu(II) transport through permeation liquid membranes using azacrown ether and fatty acid as carrier. *Journal of Membrane Science*, 314(1–2), 152–162.
- World-Bank. (2007). Environmental , Health , and Safety Guidelines for Textile Manufacturing. *International Finance Corperation*, 1, 1–20.
- Xuan-cai, D., Fu-quan, X., Study of the swelling phenomena of liquid surfactant membranes, *Journal of Membrane Science*, 59, 183-188 (1991).
- Zaharia, C., Suteu, D., Muresan, A., Muresan, R., & Popescu, A. (2009). Textile Wastewater Treatment By Homogeneous Oxidation With Hydrogen Peroxide. *Romania, Environmental Engineering and Management Journal*, 8(6), 1359–1369.
- Zaheri, P., Abolghasemi, H., & Ghannadi, M. (2015). Chemical Engineering and Processing : Process Intensi fi cation Intensi fi cation of Europium extraction through a supported liquid membrane using mixture of D2EHPA and Cyanex272 as carrier. *Chemical Engineering & Processing: Process Intensification*, 92, 18–24.
- Zeng, L., Zhang, Y., Liu, Q., Yang, L., Xiao, J., Liu, X., & Yang, Y. (2016). Determination of mass transfer coefficient for continuous removal of cadmium by emulsion liquid membrane in a modified rotating disc contactor. *Chemical Engineering Journal*, 289, 452–462.

- Zhang, G., Chen, D., Zhao, W., Zhao, H., Wang, L., Wang, W., & Qi, T. (2016a). A novel D2EHPA-based synergistic extraction system for the recovery of chromium (III). *Chemical Engineering Journal*, 302, 233–238.
- Zhang, G., Chen, D., Zhao, W., Zhao, H., Wang, L., Wang, W., & Qi, T. (2016b). A novel D2EHPA-based synergistic extraction system for the recovery of chromium (III). *Chemical Engineering Journal*, 302, 233–238.
- Zhang, L., Chen, Q., Kang, C., Ma, X., & Yang, Z. (2016). Rare earth extraction from wet process phosphoric acid by emulsion liquid membrane. *Journal of Rare Earths*, 34(7), 717–723.
- Zou, D., Jin, Y., Li, J., Cao, Y., & Li, X. (2017). Emulsification solvent extraction of phosphoric acid by tri-n-butyl phosphate using a high-speed shearing machine. *Separation and Purification Technology*, 172, 242–250.