POLYPYRROLE-MAGNETITE DISPERSIVE MICRO-SOLID PHASE EXTRACTION FOR THE DETERMINATION OF RHODAMINE 6G AND CRYSTAL VIOLET IN TEXTILE WASTEWATER

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A dissertation submitted in partial fulfillment of the
requirements for the award of the degree of
Master of Science in Chemistry

Faculty of Science
Universiti Teknologi Malaysia

APRIL 2017

To my beloved husband and mother

ACKNOWLEDGEMENT

Alhamdulillah I have managed to complete this research. I am greatly indebted to a number of people. First and foremost, I would like to express my deepest appreciation to my supervisors, Dr. Aemi Syazwani Abdul Keyon and Prof. Dr. Mohd Marsin Sanagi for their endless guidance throughout this research. Also, special thanks to my colleagues who sincerely helped me regardless of the time. I am really thankful for their priceless supervision and guidance, inspiring discussion and fruitful collaboration, all their invaluable hours to provide constructive critics, enthusiasm and continuous feedback. Without their continued support and patience, this dissertation would not have been the same as presented here.

In preparing this valuable piece of work, I also received much excellent encouragements, guidance and advices from Mr. Abdullah Ubaid Rahimi bin Che Mohd Rahim, my beloved husband who gave me all the necessary support needed for success, as such, I owe him a duty to be appreciative. This dissertation would not have been possible without warm love of my family, who had always supported me in breathless moments to happiness shelters despite of the distance. They showered me with love and compassion and enrich my life like no other. Therefore, this work is dedicated to them.

I would like to thank all the laboratory assistants and staffs for their enlightening companionship and encouragement of trudging through all the moments to complete this dissertation. May ALLAH rewards all of you with His blessing.

ABSTRACT

Polypyrrole-magnetite (PPy-Fe_3O_4) dispersive micro-solid phase extraction (PPy-Fe_3O_4-D-µ-SPE) method combined with ultraviolet-visible (UV-Vis) spectrophotometry was developed for the determination of the selected basic dyes in textile wastewater. PPy-Fe_3O_4 was used as adsorbent due to its stability and excellent conductivity as well as capable of adsorbing the studied dyes. Two basic dyes, Rhodamine 6G (Rh 6G) and Crystal Violet (CV) were chosen as model compounds. Several important D-µ-SPE parameters were evaluated and optimized including sample pH, amount of adsorbent, extraction time and type of desorption solvents. The optimum PPy-Fe_3O_4-D-µ-SPE conditions were sample solution pH 8, 60 mg of PPy-Fe_3O_4 adsorbent, 5 min of extraction time and acetonitrile as the desorption solvent. Under the optimized conditions, PPy-Fe_3O_4-D-µ-SPE method showed good linearity in the range of 0.05-7 mg/L with coefficient of determination $R^2 > 0.998$. The method showed good limit of detection (LOD) for the basic dyes (0.05 mg/L) and good analyte recoveries (97.4 to 111.3%) with relative standard deviations (RSD) < 10%. The developed method was successfully applied to the analysis of real textile wastewater where the concentration found was 1.03±7.9% mg/L and 1.13±4.6% mg/L for Rh 6G and CV respectively. From the result, it can be concluded that PPy-Fe_3O_4-D-µ-SPE method can be adopted for the extraction and analysis of trace level basic dyes in short time (total analysis time < 15 min).

ABSTRAK

Pengekstrakan fasa pepejal-mikro serakan ferum oksida bersalut polipirola (PPy-Fe_3O_4-D-μ-SPE) bergandingan dengan ultraviolet (UV-Vis) spektrofotometri telah dibangunkan bagi penentuan dua pewarna beralkali terpilih dalam air sisa tekstil. PPy-Fe_3O_4 telah digunakan sebagai penjerap disebabkan kestabilannya, mempunyai konduktiviti yang baik, luas permukaan yang tinggi dan juga mempunyai kebolehan untuk menjerap pewarna yang dianalisis. Dua pewarna bes, rodamin 6G (Rh 6G) dan kristal ungu (CV) telah dipilih sebagai sebatian model. Beberapa parameter yang penting telah dinilai dan dioptimumkan termasuk sampel pH, amaun penjerap, masa pengekstrakan dan jenis pelarut penyahjerapan. Keadaan optimum PPy-Fe_3O_4-D-μ-SPE ialah pH 8, 60 mg penjerap PPy-Fe_3O_4, masa pengekstrakan selama 5 min dan asetonitril sebagai pelarut penyahjerapan. Di bawah keadaan optimum, kaedah PPy-Fe_3O_4-D-μ-SPE menunjukkan kelinearan yang baik dalam julat 0.05-7.00 mg/L dengan pekali penentuan $R^2 > 0.998$. Kaedah ini menunjukkan had pengesanan (LOD) yang baik untuk pewarna beralkali yang dikaji (0.05 mg/L) dan pengembalian analit yang baik (97.4 to 111.3%) dengan sisihan piawai relative (RSD) < 10%. Kaedah yang dicadangkan telah berjaya diaplikasikan pada analisis sampel air sisa tekstil yang sebenar di mana kepekatan Rh 6G yang dikesan adalah 1.03±7.9% mg/L manakala CV mempunyai 1.13±4.6% mg/L. Dari hasil kajian ini, dapat dirumuskan bahawa kaedah PPy-Fe_3O_4-D-μ-SPE boleh digunakan dalam pengekstrakan dan analisis pewarna beralkali pada tahap yang rendah dalam masa yang singkat (jumlah masa analisis < 15 minit).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

PAHs	-	Polycyclic aromatic hydrocarbons
PCBs	-	Polychlorinated biphenyls
OPPs	-	Organophosphorus pesticides
OCPs	-	Organochlorine pesticides
Rh 6G	-	Rhodamine 6G
CV	-	Crystal Violet
D-µ-SPE	-	Dispersive micro-solid phase extraction
PPy-Fe_3O_4	-	Polypyrrole coated iron oxide
HPLC	-	High performance liquid chromatography
UV-Vis	-	Ultraviolet-visible
SPE	-	Solid phase extraction
FTIR	-	Fourier transform infrared
FESEM	-	Field emission scanning electron microscope
EDAX	-	Energy dispersive x-ray spectroscopy
XRD	-	x-ray diffraction
TGA	-	Thermogravimetric analysis
BET	-	Brunauer-Emmett-Teller
AC	-	Activated carbon
Fe_3O_4	-	Magnetite
γ-Fe_2O_3	-	Maghemite
PPy	-	Polypyrrole

LLE	-	Liquid-liquid extraction
µ-SPE	-	Micro-solid phase extraction
CNTs	-	Carbon nanotubes
Ag-SiO_2-PDPA	-	silver nanoparticles-doped silica-polydiphenylamine
TiO_2	-	Titanium dioxide
MWCNTs-PVA	-	multiwalled carbon nanotubes/polyvinyl alcohol cryogel composite
DEHP	-	di(2-ethylhexyl)phthalate
D-SPE	-	Dispersive solid phase extraction
CTAB	-	cetyltrimethylammonium bromide
zeolite NaY	-	sodium Y zeolite
NiZn:S	-	mixture of zinc acetate and nickel acetate with thioacetamide
MOF	-	metal-organic framework
MIL-101	-	Material Institute Lavoisier 101
MNPs	-	Magnetic nanoparticles
HKUST	-	Hong Kong University of Science and Technology
EU	-	European Union
TAM	-	triarylmethane
C.I	-	Colour index
M_w	-	Molecular weight
log K_{ow}	-	Octanol/water partition coefficient
N_2	-	Nitrogen gas
MeOH	-	Methanol
ACN	-	Acetonitrile
HEX	-	Hexane
$NaNO_3$	-	Sodium nitrate
NaOH	-	Sodium hydroxide
HNO_3	-	Nitric acid
pH_{ZPC}	-	pH of zero point of charge
HCl	-	Hydrochloric acid

rpm	-	Revolution per minute
ppm	-	Parts per million
LOD	-	Limit of detection
RSD	-	Relative standard deviation
K	-	Kelvin
IUPAC	-	International Union of Pure and Applied Chemistry
R^2	-	Coefficient of determination

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Environmental pollution has been a hot topic many years ago due to the release of hazardous materials into environment. Furthermore, they exist beyond the permitted limits. These hazardous materials are referring to environmental pollutants or contaminants that can be any substances occurring naturally or man-made including heavy metals (Li, Ma, van der Kuijp, Yuan, & Huang, 2014), polycyclic aromatic hydrocarbons (PAHs) (Gavrilescu, Demnerova, Aamand, Agathos, & Fava, 2015), polychlorinated biphenyls (PCBs) (Gavrilescu *et al*., 2015; Noguera-Oviedo & Aga, 2016), organophosphorus pesticides (OPPs), organochlorine pesticides (OCPs), triazines herbicides (Noguera-Oviedo & Aga, 2016), phenolic compounds (Deblonde, Cossu-Leguille, & Hartemann, 2011), triclosan (Dhillon, Kaur, Pulicharla, Brar, Cledon, Verma, & Surampalli, 2015), textile dyes (Ashfaq & Khatoon, 2014; Ribeiro & Umbuzeiro, 2014) and so on. Their presences are of concern because they possess high toxicity and pose threat to public health even at low concentration.

Therefore, the development of better analytical techniques always becomes the top priority in any qualitative and quantitative research study. This is important in order to study the properties of those pollutants such as physical state, oxidation state, complexation form and others, as well as to extract and preconcentrate them at trace level. Besides, monitoring activities for these contaminants in different food and environmental samples such as soil, air and water can also be done in order to avoid long term exposure. However, it is not easy to analyze unknown or known species at trace levels especially in complex environmental matrices.

Textile industry, for example in the process of batik painting, requires a large quantity of dyes and other chemicals, as well as large volume of water for washing. The problem lies when this industry discharges wastewater containing harmful dyes into the environment without appropriate treatment. This discharge of dyes has posed difficulty to be decolorized and decomposed biologically due to their resistant against the light exposure, water and many chemicals. The dyes in wastewater can increase not only environmental degradation like depletion of dissolved oxygen needed by marine life, loss of soil productivity, but also risks human illness for example the bad quality of drinking water for human consumption.

As this industry generates effluents containing large quantity of dyes into the environment, the waste is considered as pollutants due to their threats to public as such they consist of carcinogens like benzidine (Padhi, 2012). In addition, they have large variety of functional groups which contribute to their diverse properties. That is the reason the detection of these dyes becomes a major wastewater challenge. The highly undesirable presence of dyes at low concentration in wastewater is indeed a concern due to their toxicity, carcinogenic, and other harmful effects either to aquatic life or even human health for example bladder cancer in humans (Padhi, 2012).

The maximum concentration of dyes in water of more than 1 mg/L caused by untreated textile effluents can harm the public health (Carmen & Daniela, 2012). In addition, high concentrations of textile dyes in water bodies can prevent the re-oxygenation capacity of the receiving water and cut-off sunlight. Consequently, it would affect the biological activity in aquatic life and also the photosynthesis process of aquatic plants or algae (Carmen & Daniela, 2012). The targeted dyes to be analyzed are Rhodamine 6G (Rh 6G) and Crystal Violet (CV) because they are the commonly used basic dyes in the textile batik industry. Furthermore, they are readily available in the laboratory and not costly. Therefore, it is imperative to develop much simpler and low cost techniques. This technique is important not only due to its economical aspect but can also improve the quality of drinking water resources that have been contaminated with pathogens originating from wastewater.

During past decades, many conventional methods have been reported in dye analysis, yet they are high in cost and often less adaptable in wastewater containing dyes. A simple and economical technique known as dispersive micro-solid phase extraction (D-µ-SPE) is developed in this new application of dye analysis. Not only it is easy to operate, it is also effective as such the mode of its mechanism is an adsorption process. Importantly, since D-µ-SPE method requires the use of adsorbent, the economic aspect of the whole procedure including the search of less costly adsorbent material becomes the top priority especially in wastewater treatment.

Adsorption is known as an economical, effective and simple method to extract targeted species from aqueous matrix (Gupta, Ali, Saleh, Nayaka, & Agarwal, 2012) and commonly applicable in industry and laboratories for green extraction purposes. Many kinds of adsorbents have been developed for example natural materials like agro-waste products (Gupta & Suhas, 2009; Tran, Ngo, Guo, Zhang, Liang, Ton-That, & Zhang, 2015), clay (Srinivasan, 2011; Gupta & Suhas, 2009), biopolymer (Sanagi, Loh, Wan Ibrahim, Pourmand, Salisu, Ali, 2016; Tran *et al*., 2015), zeolite (Delkash, Bakhshayesh, & Kazemian, 2015), ion exchange resin (Bilal, Shah, Ashfaq, Gardazi, Tahir, Pervez, & Mahmood, 2013; Nagarale, Gohil, & Shahi, 2006), activated carbons (Sharma, Kaur, Sharma, & Sahore, 2011) and many more. Agro-waste products, clays and biopolymers are environmental friendly and can be found in large amount. However, they had low adsorption capacity (Sharma *et al*., 2011; Yang & Han, 2005) and insufficient stability data in real wastewater sample (Tran *et al*., 2015). As a result, some modification steps are required to overcome their drawbacks but still, the production cost is high depending on the modification conditions.

Zeolites, they have two kinds of them which are natural and synthetic zeolites. Natural zeolites can also be found in abundance and inexpensive price, but they had capability to degrade the water quality when they have low content of zeolite. They should not contain any water-soluble impurities in order to prevent contamination of water sample (Delkash *et al*., 2015). For synthetic zeolites, they are more expensive than the natural one but they have high efficiency and high cation exchange capacity. The recovery, enrichment as well as the removal of ionic pollutants can be performed by ion exchange resins but the problem with these adsorbents is when there is a change in concentration of ionic solutions, they have low selectivity, low mechanical stability and high degree of swellness or shrinkage (Nagarale *et al*., 2006). Activated carbon which is a commonly used adsorbent due to its efficiency and applicable to wide range of analyte adsorption, its usage could still be restricted due to economical consideration, poor regeneration ability and generation of large amount of greenhouse gases during its production stage (Shankar, 2008; Gupta & Suhas, 2009).

The main highlight of this study is the use of synthetic organic-inorganic hybrid based nanomaterials; polypyrrole-magnetite (PPy-Fe_3O_4) as adsorbent for the adsorption and desorption of textile dyes. The organic-inorganic hybrid-based adsorbent has gained attention in many separation studies for instance as adsorbents for water treatment purpose (Samiey, Cheng, & Wu, 2014), packing materials in high performance liquid chromatography (HPLC) column (Xiong, Yang, Huang, Jiang, Chen, Shen, & Chen, 2013) and others (Souza & Quadri, 2013). These are all because of their high selectivity, permeability, mechanical and chemical stability (Kango, Kalia, Celli, Njuguna, Habibie, & Kumara, 2013). They are also very flexible to adjust their structure and properties depending on the synthesis process and conditions they possess. Ultraviolet-visible (UV-Vis) spectrophotometer is a commonly used detection technique in dyes analysis and mostly available in most laboratories, thus, it is used in the current study.

1.2 Problem Statement

In Southeast Asia, textile industry especially batik production is very famous and the generation of dye wastewater indeed becomes a concern. This untreated wastewater can cause cancer and abnormalities (Koay, Ahamad, Nourouzi, Abdullah, & Choong, 2013). Furthermore, in Malaysia, a 2013 year statistic showed that the percentage of clean rivers was reduced by 1 % (Manan, Chai, & Samad, 2015). Likewise, there had been also a case in United States where the government had to spent around USD 76.6 billion to treat the children affected by this environmentally mediated diseases like prenatal methylmercury exposure, lead poisoning, childhood cancer, intellectual disability and other related diseases (Trasande & Liu, 2011). It showed that the emergence of these environmental pollutants is indeed harmful towards public health especially young generation by slowing down the development and learning ability of an individual. Besides, these water and air pollution problems can also lead to death (Prüss-Üstün, Bonjour, & Corvalán, 2008). Many conventional treatments had been done to treat wastewater for example oxidation, photo-degradation process and ozonation (Hozhabr Araghi & Entezari, 2015) but these methods have shortcomings of producing more toxic intermediates compared to the original compound. Adsorbents like agro-waste products, clays and biopolymers, they are environmentally friendly but they had low adsorption capacity and unstable in real wastewater samples. Therefore, advances in the analysis of wastewater make it possible to detect the dyes present in textile wastewater by employing adsorption process of newly developed solid phase extraction (SPE) technique termed D-µ-SPE. As D-µ-SPE method being developed with the introduction of better performance adsorbents, magnetic nanoparticles come in the interest of researchers due to their high surface area and easy separation from aqueous media using external magnet. The combination of organic and inorganic materials termed organic-inorganic hybrid-based nanocomposite is introduced as the studied adsorbent together with D-µ-SPE method as the heart of this study.

1.3 Aim and Objectives of Research

The aim of this study is to develop an improved microextraction method using organic-inorganic hybrid-based adsorbent for the determination of basic dyes from water sample. In order to achieve the aim, several objectives are proposed to:

i. Characterize previously prepared in-house polypyrrole-magnetite (PPy-Fe_3O_4) nanocomposite.
ii. Utilize the material as adsorbent in dispersive micro-solid phase extraction (D-µ-SPE) method for the extraction of Rhodamine 6G (Rh 6G) and Crystal Violet (CV) dyes.
iii. Optimize and validate the D-µ-SPE method for the analysis of dyes in water.
iv. Apply the developed D-µ-SPE method to the analysis of dyes in real wastewater sample from batik textile industry.

1.4 Scope of Research

This research focuses on the characterization of a new composite material, PPy-Fe_3O_4 to be utilized as adsorbent in D-µ-SPE method. For this study, in-house synthesized material (PPy-Fe_3O_4) is used as an adsorbent for the extraction of Rh 6G and CV. PPy-Fe_3O_4 nanocomposite is characterized using Fourier Transform Infrared (FTIR) spectroscopy, field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDAX), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and nitrogen adsorption analysis (BET), and its performance as D-µ-SPE adsorbent is investigated.

This study then focuses on the optimized D-μ-SPE procedure required where the parameters involved are sample pH, adsorbent mass, extraction time and type of desorption solvents. The analysis is carried out using UV-Vis spectrophotometer. It involves the mechanism of adsorption process as it is a suitable treatment option for organic contaminants (Pirkarami & Olya, 2014). The optimized and validated methods are then applied to analyze the targeted dyes in real wastewater sample from a batik factory in Kota Bharu, Kelantan.

1.5 Significance of Study

This study is very important to study the capabilities of the newly applied adsorbent in the extraction of the basic dyes in wastewater prior to their determination by UV-Vis spectrophotometer instrument. The adsorbent studied is thermally stable and can be reusable generally while the extraction technique used is environmentally friendly, faster and efficient. In addition, it is also expected that the developed low-cost and efficient technique will be a useful tool for the preconcentration of other analytes in various water samples.

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56

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