THIN COATED ADSORBENT FOR THE REMOVAL OF CONTAMINANT OF EMERGING CONCERN

MUHAMAD SHARAFEE BIN SHAMSUDIN

UNIVERSITI SAINS MALAYSIA

2019

THIN COATED ADSORBENT FOR THE REMOVAL OF CONTAMINANT OF EMERGING CONCERN

by

MUHAMAD SHARAFEE BIN SHAMSUDIN

**Thesis submitted in fulfilment of the requirment
for the degree of
Master of Science**

January 2020

ACKNOWLEDGEMENT

In the name of ALLAH S.W.T, the most gracious and merciful. Alhamdulillahi robbil alamin, washolatu awassalam al asrofil anbiya I walmursalin wa ala alihi wa ashabihi ajmaiin, amma ba'du. First of all, I would like express my most thankful to ALLAH S.W.T. the Almighty. Second, let deliver sholawat and salam upon our prophet Muhammad S.A.W., who has brought us from darkness to the brightness, so we are always in the right way.

Special dedication to my beloved parent, Shamsudin Bin Abdul Aziz and Rohaya binti Abdullah and my siblings for their endless moral and financial support, then also them prays that made me become stronger to finish my research.

Besides, the biggest support which my backbone to my research, Associate Professor Dr. Suzylawati Ismail for all her knowledge guide and guidance, brilliant ideas, encouragements and supports throughout this research. I also feel grateful to have her in providing positive criticism, helps me to improve my analytical research, scientific-writing and presentation skills.Then, not forgotten to my colleagues, Syahida Farhan Azha, Shazlina Abd, Hamid, Faraziehan Senusi, Nuraffini Kamarulizam, Norlaila Mohammed Nor, Aiizat Ikhwan Abdul Jalil, Momina and Dr. Benjamin Jack Balliger for problem solver and guidance to me. Plus, to our all assistance engineer and staffs of for their cooperation and assistance.

Finally, thanks to Bridging Grant Universiti Sains Malaysia (304/PJKIMIA/6316498) for financial support for this research work. Thank you to Universiti Sains Malaysia, Engineering Campus for Providing research facilites.

MUHAMAD SHARAFEE SHAMSUDIN

TABLE OF CONTENTS

APPENDICES

LIST OF PUBLICATION

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATE

LIST OF SYMBOLS

C_0	Initial concentration (mg/L)
C_e	Concentration at equilibirum state (mg/L)
q_t	Adsorption capacity at time (mg/g)
q_e	Adsorption capacity at equilibrium state (mg/g)
$q_{e,max}$	Maximum adsorption capacity (mg/g)
$q_{e,cal}$	Calculated adsorption capacity (mg/g)
$q_{e,ave}$	Average adsorption capacity (mg/g)
K_L	Langmuir adsorption constant (L/mg)
K_F	Freundlich adsorption constant (mg/g)$(L/mg)^{1/n}$
n	The adsorption intensity
K_T	Temkin isotherm equilibrium binding constant (L/mg)
b	Constant related to the heat of adsorption (J/mol)
R	The universal gas constant (8.314 J/mol.K)
T	Temperature (K)
R^2	Correlation coefficient
K_1	Pseudo-first-order
K_2	Pseudo-second-order
ΔH^0	Enthalpy change (kJ/mol)
ΔS^0	Entropy change (J/mol.K)
ΔG^0	Gibb’s free energy (J/mol)

LIST OF ABBREVIATION

CEC	Contaminant of Emerging Concern
PHCP	Personal Health Care Product
COATER	Contaminant Emerging Remover
AC	Activated Carbon
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
FTIR	Fourier Transform Infrared
BET	Branauer Emmett Teller
ARE	Average Relative Error
pH_{sol}	pH solution
pKa	Negative log of the acid dissociation constant or Ka value
pH_{PZC}	pH point zero charge

PENJERAP TERSALUT NIPIS UNTUK PENYINGKIRAN BAHAN CEMAR BAHARU

ABTRAK

Di Malaysia, isu bahan cemar baharu (CEC) telah mendapat tumpuan baru-baru ini. Sulfamethoxazole dan Acetaminophen merupakan bahan cemar sasaran dalam kajian ini. Bahan cemar ini telah dikesan di loji rawatan kumbahan di Malaysia. Malangnya, kilang rawatan kumbahan tidak cukup berkesan untuk mengatasi bahan cemar ini. Oleh itu, dalam kajian ini, pendekatan baru yang menggunakan konsep penjerapan diperkenalkan. Pemilihan bahan penjerap yang berpotensi telah dilakukan untuk memilih penjerap yang sesuai untuk penjerap tersalut nipis. Karbon aktif telah dipilih sebagai penjerap berpotensi. Penyingkir bahan cemar baharu (COATER) digunakan untuk penjerapan sulfamethoxazole (SMX) dan acetaminophen (ACT) telah disiasat. COATER diformulasikan menggunakan Getah Neutral Pengoksida (ENR-50) dan poli (vinil) klorida (PVC) sebagai pengikat antara karbon aktif sebagai penjerap, kemudian disalut atas kain putih (substrat) menggunakan teknik memberus. 4 g karbon aktif ditambahkan ke dalam COATER (berat optima dalam kajian ini). Analisis pencirian menggunakan SEM-EDX, FTIR dan BET telah dilakukan. Keputusan analisis morfologi permukaan telah menunjukkan taburan dan lekatan karbon aktif jelas pada substrat. Melalui analisa unsur-unsur (EDX), unsur nitrogen telah dikesan pada COATER yang mewakili SMX dan ACT. Analisis FTIR telah mengesan pembentukan amida berlaku di antara COATER dan SMX. Kawasan permukaan dan jumlah liang COATER masing-masing adalah 64.3 m^2/g dan 0.07 cm^3/g. COATER telah dinilai melalui pelbagai parameter termasuk kepekatan awal, suhu, kadar pencampuran dan pH larutan. Kapasiti penjerapan meningkat dengan peningkatan kepekatan awal. Suhu optimum proses penjerapan ini ialah 30 °C. Keadaan pH optimum untuk SMX dan ACT pada pH sebenar (pH 4.80 untuk SMX) dan (pH 6.05 untuk ACT), yang memberikan penyingkiran tertinggi, 84.4% dan 45%, masing-masing. Hasil kajian keseimbangan dan kinetik menunjukkan bahawa model isoterma Langmuir dan pseudo-tertib-kedua, masing-masing, sesuai dengan penjerapan SMX dan ACT ke COATER. Kajian termodinamik menunjukkan bahawa penjerapan SMX dan ACT adalah eksotermik. Walau bagaimanapun, untuk kedua-dua bahan jerapan adalah baik dan spontan kerana nilai negatif ΔG^{o} diperoleh pada semua suhu.

THIN COATED ADSORBENT FOR THE REMOVAL OF CONTAMINANT OF EMERGING CONCERN

ABTRACT

In Malaysia, issues of Contaminant of Emerging Concern (CEC) have been recently highlighted. Sulfamethoxazole and Acetaminophen were targeted pollutant in this research. There are a large amount of these pollutants have been detected in sewage treatment plants in Malaysia. Unfortunately, sewage treatment plants are not effective enough to overcome these pollutant. Therefore, in this research study, a new approach applying adsorption concept is introduced. A screened of potential adsorbents have done to select the suitable adsorbent to be introduced into coated adsorbent (COATER). Activated carbon was chosen as potential adsorbent. Contaminant Emerging Remover (COATER) for adsorption of sulfamethoxazole (SMX) and acetaminophen (ACT) were investigated. The COATER is formulated using Epoxidized Neutral Rubber (ENR-50) and poly(vinyl) chloride (PVC) as binders with activated carbon as an adsorbent, then was coated on white cotton fabric (substrate) via brushing technique. 4 g of activated carbon added into COATER (optimum weight of this study). Characterization analysis using SEM-EDX, FTIR and BET were performed. The results of surface morphology analysis showed good distributed of activated carbon and clearly attached adsorbent onto the substrate. Through elements analysis (EDX, nitrogen element detected attached on COATER adsorption which represents SMX and ACT. FTIR analysis detected amide formation occurred between COATER and SMX. The surface area and pore volume of the COATER were 64.3 m^2/g and 0.07 cm^3/g respectively. The COATER was evaluated through varies parameters including initial concentrations, temperatures, mixing rate and pH of solution. The adsorption capacity increased with increasing initial concentration. The optimum temperature of this adsorption process was 30°C. The optimum pH condition for SMX and ACT at actual pH (pH 4.80 for SMX) and (pH 6.05 for ACT), which gave the highest removal, 84.4% and 45%, respectively. The result of equilibrium and kinetic studies indicated that Langmuir isotherm model and pseudo-second-order, respectively, are best-fitted with the adsorption of SMX and ACT onto COATER. The thermodynamic studies indicacted that SMX and ACT were favor to exothermic process. However, for both adsorbates the process were favorable and spontaneous due to the negative values of ΔG^{o} obtained at all temperatures.

CHAPTER 1

INTRODUCTION

1.1 Water and Pollutant

Seventy-one percent of the earth's surface is covered by water. Water may exist as saltwater for the ocean, rivers, lakes and underground. However, the ocean holds the majority of the earth water (98 %), with only 2 % existing as fresh (non-salty) water (Plessis, 2017). Water is useful in all kinds of business production such as industry, agriculture, transportation, energy and others (Grey and Sadoff, 2007). Moreover, water is an important element in maintaining life and is needed for the survival of all organisms (Siwar and Ahmed, 2014). Without access to water, any living organisms would be unable to survive. Humans can live three weeks without food, but humans cannot survive three or four days without water, because 60 % of the human body is composed of water, and it is required for every living cell in body to keep functioning. Besides, humans need water to flush waste from our bodies, maintaining body temperature through respiration and sweating, as well as a lubricant for our joints (Spector, 2018).

The rate of growth of global manufacturing and other industries are quite high, which subsequently affected the environment through the emission of air, water and soil pollution. Air pollution caused by the released gas and airborne particulates from industries contribute to climate change and harm human health. Soil also being polluted by industries disposing of waste that can make soils more acidic. This can affect plants health by restricting the amount of nutrition the plant receives. The existence of heavy metal, dyes, pharmaceutical waste other contaminants can cause water pollution. The pollution negatively impacts the quality of freshwater. Emission of these wastes into freshwater bodies can harm the ecosystem and human health, in addition to reducing the quality of freshwater sources.

Contaminants of Emerging Concern (CECs) are a class of pollutants that have been highlighted recently by researchers due to the harmful effect on the environment. CECs are the organic compound found in the wastewater solution and negatively affect aquatic life and human health at elevated concentrations. CECs encompasses many categories of pollutants, including personal health care products (PHCPs), pharmaceutical waste, food additive, wood preservative, laundry detergent, surfactants and other organic compounds. Pharmaceutical waste and personal health care are currently seen as a threat to the ecosystem and human health since it has the potential to cause significant ill effects once it starts to accumulate in the water bodies.

Pharmaceutical waste and PHCP can enter the environment by many pathways as shown in Figure 1.1. These substances largely from wastewater treatment, aquaculture treatment and leaking landfills (Price et al., 2010; Agency, 2016; Agency, 2018). Other exposure pathways exist, include emission from manufacturing industries, disposal of unused medicine to landfill and flushed down from the toilet bowl, irrigation with wastewater from hospital, veterinary medicine from hard surface in farmyards and disposal of carcasses of treatment animal (Boxall et al., 2012;Arsson, 2009;States, 2018). Up to 9 percent of medicine consumed by humans are excreted out from the body through urination, where it is then flushed down from the toilet and mixed with wastewater (Division, 2014).

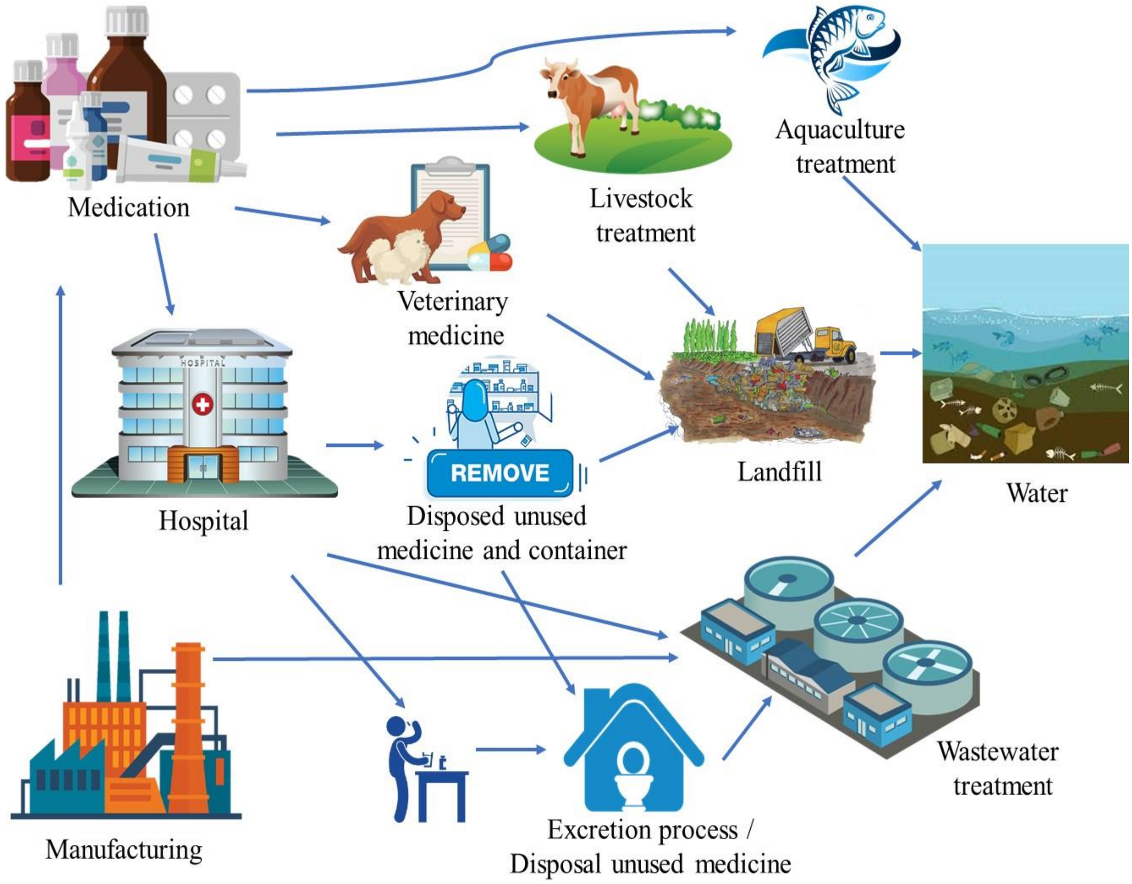

Figure 1.1 Pathway pharmaceutical waste and PHCP to the environment. (Adapted from (Arsson, 2009;Boxall et al., 2012;States, 2018))

As shown in Figure 1.1, it justifies the possible ways of pharmaceutical waste and PHCPs to the environment through previous literature studies. In Malaysia, Kualiti Alam Sdn. Bhd. is responsible for managing all the clinical wastes especially from hospitals and clinics. Pharmaceutical wastes and PHCPs are the wastes managed by Waste Management Center (WMC) under Environmental Quality (Scheduled Waste) Regulations 2005. Kualiti Alam Sdn. Bhd. used sterilisation system to dispose of the unused expired and contaminated medicines from hospital and clinic (Kualiti Alam, 2019). Sterilisation system is the process to eliminates transmissible agents from equipment, surface, food, biological culture or medication (Tetteh and Kaufmann, 2012). However, this management only been applied to the hospital and clinic but does not apply to personal residences, aquaculture activities and others, where incorrect disposal procedure occurs, largely through the sewage system. Unfortunately, sewage treatment plants do not have any specific treatment for pharmaceutical waste which can result in the waste being, discharged and distributed back to the resident.

Many studies have detected PHCPs and pharmaceutical waste in the environment at various locations around the world. An investigation carried out in the United States concerning pharmaceuticals and other organic contaminants in water sources reported that more than 30% of the 47 groundwater sites contained positive readings (Barnes et al. 2008). Besides that, according to researches conducted in Spain, United States, Switzerland and China, the antibiotic and analgesic substances are the most extensively studied in the literature. Investigation showed a high concentration of these substances was detected, within 10 µg/L to 1 mg/L (Sui et al. 2015).

A group of researchers from Universiti Teknologi Malaysia (UTM) under the Faculty of Civil Engineering has investigated the presence of pharmaceutical waste and personal health care products in sewage treatment plant in Johor, Malaysia (Yacob et al., 2017). Wastewater samples have been collected from five different types of sewage treatment plants and six pharmaceutical compounds are among the most dominant substances detected. The compound included acetaminophen, lincomycin, trimethoprim, sulfamethazine, sulfamethoxazole, clarithromycin, carbamazepine, ibuprofen and naproxen. As exhibited in Figure 1.2, the pharmaceutical products that contributed to the highest recorded concentrations were Acetaminophen (40,165 ng/L) and sulfamethoxazole (2,239 ng/L) (Yacob et al., 2017).

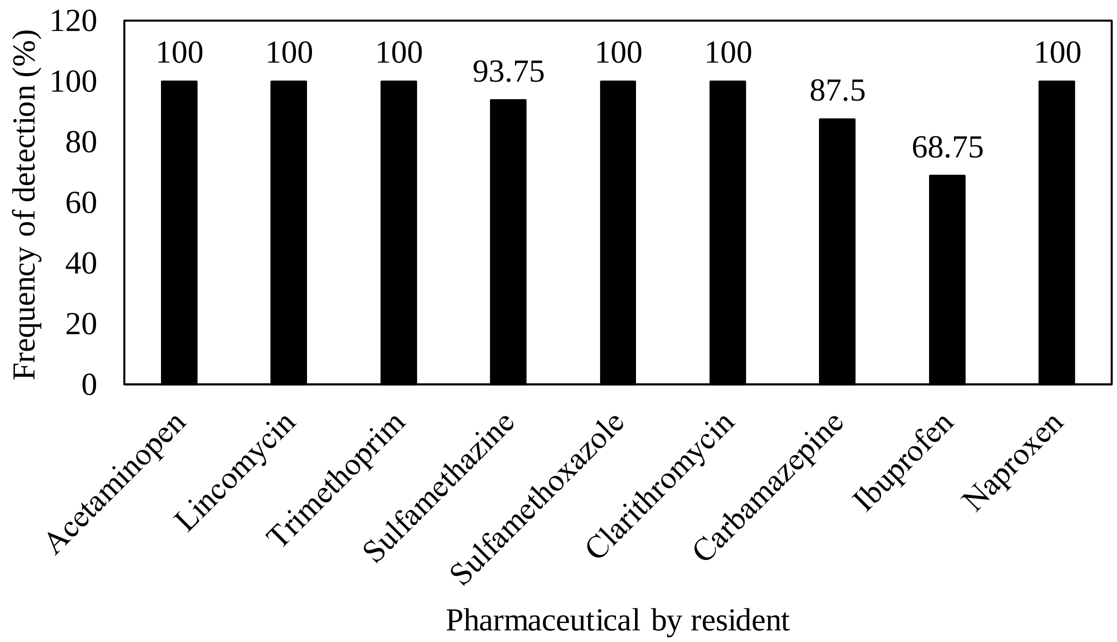

Figure 1.2 Frequency of detection of targeted pharmaceutical in sewage treatment plant (Yacob et al., 2017).

Even though these pollutants are found frequently in wastewater at low concentrations, the highest risk to aquatic life is through long term exposure which may lead to mutagenic and genotoxic effects. As a consequence, the compounds would drastically decrease the reproductive success of the affected aquatic life. The most critical effect that arises from the exposure of these compounds may cause damage to human liver and reproductive system, accumulate in tissues body and inhibition of cell proliferation (Patneedi and Prasadu, 2015).

1.2 Existing Treatment

As mentioned earlier, the disposal of unused or expired medicine from hospital or clinic has been disposed by Kualiti Alam Sdn. Bhd. through the sterilisation process. Unfortunately, the leached pharmaceutical waste and PHCPs to the sewage treatment plant and that may reach to water stream must go through wastewater treatment