UNIVERSITI TEKNOLOGI MARA

DEVELOPMENT OF ONLINE SOLID PHASE EXTRACTION LIQUID CHROMATOGRAPHY FOR THE ANALYSIS AND ASSESSMENT OF PHARMACEUTICALS IN SURFACE WATER AND WASTEWATER IN KLANG VALLEY

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ABSTRACT

The focus of this study was to develop an efficient and sensitive analytical method in analyzing pharmaceuticals in water. Solid phase extraction (SPE) is commonly applied for extraction of pharmaceuticals in water samples. However, SPE requires high volume of sample, up to 1000 mL to achieve desired analytical sensitivity, thus requires long analysis time. An improvement to conventional SPE, online solid phase extraction-liquid chromatography (online SPE-LC), has an advantage of minimizing sample volume and reducing analysis time by its automated SPE steps with direct injection into liquid chromatography. Using online SPE-LC, an aliquot of 10 mL water sample was injected directly into an autosampler and the analytes were preconcentrated on a Dionex Ion Pac AG14A SPE column. The eluted analytes were separated on a liquid chromatography column, Acclaim Polar Advantage II. The experimental parameters such as sample loading volume, SPE cleanup conditions and elution conditions were optimized. Response surface methodology (RSM) was employed to optimize SPE cleanup steps such as mobile phase composition and valve switching time. The optimized conditions were as following: 10mL of water sample was loaded onto SPE column with cleanup mobile phase of acetonitrile : 10 mM methanesulfonic acid (5:95;v/v) for 1 minute prior to column switching to connect the SPE column to the analytical column, whereby eluted analytes were transferred into the analytical column for separation for 4 minutes. Method validation showed good linearity with R^2>0.99. Recoveries evaluated using spiked samples at two concentrations (5 μg L^{-1} and 50 μg L^{-1}) ranged from 65 - 119 % with relative standard deviations lower than 12% and limits of detection were between 0.00-0.086 μg L^{-1}. The developed method was applied to influent, effluent and surface water of Klang wastewater treatment plants (WWTPs) and Klang River Basin. Acetaminophen, caffeine, ibuprofen and salicylic acid were the compounds frequently detected at concentrations up to 212.6 μg L^{-1}. Evaluation on the efficiency of WWTPs showed that caffeine, acetaminophen, ibuprofen and salicylic acid presented high removal efficiencies (>78%). The application of chemometric on selected pharmaceuticals provides valuable and promising techniques in determining potential chemical marker. Result from principal component analysis (PCA) with varimax rotation shows the sources contamination of acetaminophen and caffeine within the Klang River Basin were influenced by untreated wastewater. An environmental risk assessment by means of risk quotient (RQ) showed that most pharmaceuticals detected in the effluent wastewater and surface water categorized as low to medium risk. In the evaluation of possible chemical marker for wastewater contamination, acetaminophen and caffeine met the criteria of high frequency of detection and concentration. However, acetaminophen has the advantage of being source specific and was found to have good correlation to population. Despite the low concentrations of the selected pharmaceuticals in influents and surface water samples regular monitoring on these emerging pollutants should be conducted and the efficiency of the WWTP in removing the needs to be evaluated. Thus, the developed online SPE-LC method for the determination of pharmaceuticals in water would provide an efficient and fast approach for routine analysis.

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CHAPTER ONE
INTRODUCTION

1.1 Background of Study

Pharmaceuticals are known as emerging contaminants and their presence in the environment has become a global issue, as demonstrated by the increasing reports on their occurrence and effect on aquatic animals (Kummerova et al., 2016) and human health (Zenker et al., 2014). The consumption of pharmaceuticals increased over the years as the population increased. Pharmaceutical Services Division, Ministry of Health Malaysia have reported an increases in total utilization of medicines in Malaysia by 31.4% from 2011 to 2014 (PSD MOH, 2017).

The main sources of pharmaceuticals in the environment may come from industrial or disposal of human waste from municipals or hospitals into sewage wastewater treatment plants, where they may persist, partially or completely biodegrade during treatment. Therefore, the effluents that are discharged from these wastewater treatment plants may contribute to residues or traces of pharmaceuticals in the receiving water. Trace levels of pharmaceuticals that may be present in the environment normally varied within μg L^{-1} to ng L^{-1} concentration level. Hence, an efficient preparation method is important for better method sensitivity.

Sample preparation which include extraction and cleanup followed by analytical separation are usually focused in developing methods for the determination of pharmaceuticals in water. Recent technology in sample preparation and mass spectrometry detection permitted chemist to detect compounds at low concentration level. Solid phase extraction (SPE) is the most used method for extraction of pharmaceuticals in water samples. SPE procedure consists of four basic steps which include conditioning, sample adsorption, washing and elution. However, the extraction and cleanup of analytes in water samples using SPE is time consuming and requires high sample volume (up to 1 L) to achieve better sensitivity. Therefore, an improvement to conventional SPE, online solid phase extraction liquid chromatography (online SPE-LC) is getting more attention.