UNIVERSITI TEKNOLOGI MARA

PHARMACEUTICALS AS POTENTIAL CHEMICAL MARKERS IN WASTEWATER

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of the requirements for the degree of
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AUTHOR'S DECLARATION

I hereby declare that the work presented in this thesis was performed in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results on my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

This study evaluates the potential of common pharmaceuticals (acetaminophen, caffeine, carbamazepine, diclofenac, naproxen, ibuprofen and metoprolol) as chemical markers for domestic wastewater. After ingestion, these compounds pass through the human metabolism largely unaffected, are quantitatively excreted via urine and faeces. As the occurrences of pharmaceuticals in wastewater are considered low, a reliable, selective and sensitive analytical technique is required to concentrate and eliminate matrix effect, prior to chromatographic analysis. Therefore, in this study a simple and rapid tandem solid phase extraction (SPE) for the analysis of selected pharmaceuticals in wastewater was developed. Since the compounds are different in physico-chemical properties, no single SPE sorbent was able to retain and concentrate these compounds, thus coupling of two SPE cartridges in tandem was proposed. By connecting two SPE cartridges (C_{18} and Oasis HLB) in tandem with Oasis HLB on top of C_{18}, was able to simplify the SPE procedure using a single sample introduction step with the advantage of minimising amount of sample required and reducing analysis time. The washing and elution of compounds were done separately. Carbamazepine, diclofenac, naproxen and metoprolol were trapped in the Oasis HLB and eluted using methanol. Acetaminophen, caffeine and ibuprofen were trapped in the second cartridge (C_{18}) whereby ethyl acetate: acetone (1:1) was used to elute acetaminophen and caffeine, followed by second elution using methanol to elute ibuprofen. Separation of acetaminophen, caffeine, diclofenac and naproxen was done using high performance liquid chromatography-diode array detector (HPLC-DAD) with C_{18} column whereas separation of ibuprofen and metoprolol was done using high performance liquid chromatography-fluorescence detector (HPLC-FLD) with ODS-Hypersil column. The instrumental limits of detection ranged from 0.01 to 0.04 $\mu g\ L^{-1}$ and satisfactory recoveries were obtained between 76 % to 104 %. The calibration curves were linear from 0.1 to 5.0 $\mu g\ mL^{-1}$ with correlation coefficients (r^2) in the range of 0.995 to 0.999. The developed tandem SPE approach showed satisfactory precision. The method was applied to analyse pharmaceuticals in water samples from two wastewater treatment plants; Mawar wastewater treatment plant of Universiti Teknologi MARA (UiTM), Shah Alam and Indah Water wastewater treatment plant of Section 7, Shah Alam and the concentration of selected pharmaceuticals detected in these wastewater samples varied. The high concentration of caffeine (7.8-24.5 $\mu g\ mL^{-1}$) and acetaminophen (1.1-10.7 $\mu g\ mL^{-1}$) detected demonstrated the suitability of these compounds as quantitative chemical markers. In addition, periodical sampling (February 2012 – June 2012) of UiTM's wastewater treatment plant showed good correlation between concentration of caffeine and acetaminophen and students activities indicating the potential of these compounds as source specific chemical indicators.

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