THE ENVIRONMENTAL FATE AND MOBILITY OF OESTROGENS INTO SOILS

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Engineering in Civil.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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ABSTRAK

Oestrogen merupakan gangguan endokrin terbesar di dalam alam sekitar yang menjadi satu kebimbangan. Oestrogen di laporkan sebagai kompound yang berpotensi untuk mengganggu alam sekitar. Oleh itu, kajian ini dijalankan untuk mengetahui lebih lanjut tentang kadar serapan oestrogen di dalam tanah yang berbeza, hubungan antara pekali air-oktanol dan pekali octanol-tanah bagi oestrogen semulajadi dan buatan dan juga kesan ke atas alam sekitar. Kajian ini dimulai dengan menyiasat jenis serapan dan faktor-faktor yang mempengaruhi kadar serapan oestrogens di dalam tanah. Kadar serapan oestrogen menunjukkan penyerapan yang tinggi dengan karbon organik, peningkatan kapasiti serapan adalah selari dengan karbon organik. Nilai K_{ow} dan K_{oc} digunakan untuk mengenalpasti pergerakan oestrogen di dalam tanah dan hasilnya, E2 dan EE2 dikategorikan dengan perlahan dan tiada pergerakan manakala E1 dikategorikan dengan sedikit pergerakan dan pergerakan yang perlahan. Nilai karbon organic memainkan peranan yang penting bagi mengetahui kadar serapan oestrogen di dalam tanah. Selain itu, faktor kadar serapan oestrogen turut dipengaruhi oleh kepelbagaian suhu dan pH. Analisis yang dijalankan membuktikan bahawa serapan oestrogen didalam tanah disebabakan oleh proses ‘physisorption’. Kesemua oestrogen menunjukkan ikatan yang lemah terhadap tanah disebabkan oleh kadar serapan oestrogen ke dalam tanah bergantung kepada ‘hydrophobicity’. Hubungan antara pekali air-oktanol (K_{ow}) dan pekali air-tanah (K_d) di tentukan berdasarkan kadar serapan antara oestrogen dan juga nilai bagi pekali air-oktanol (K_{ow}). Nilai log K_{ow} yang tinggi menunjukkan kurang pergerakan berlaku di dalam tanah. Hal ini menunjukkan ‘hydrophobicity’ bagi oestrogen memainkan peranan penting bagi proses serapannya didalam tanah. Akhirnya, hasil kajian ini juga menunjukkan perbezaan yang ketara antara nilai-nilai eksperimen dan nilai-nilai yang dihasilkan oleh model pengiraan, ‘Estimation Program Interface’ (EPISUITE). EPISUITE mengangarkan nilai yang berkurangan bagi log K_{ow} estrone (E1) tetapi nilai yang lebih besar bagi log K_{ow} 17 ß-estradiol (E2) dan 17α-ethnylestradiol (EE2). EPISUITE menganggarkan nilai yang lebih besar bagi oestrogen di dalam keadaan alam sekitar-tanah. Ini menunjukkan, apabila nilai berdasarkan kajian dimasukkan ke dalam model pengiraan, nilai menunjukkan perbezaan disebabkan oleh keadaan persekitaran yang berlaku. Oleh itu, kajian ini membuktikan bahawa walaupun model pengiraan digunakan, namun ia tidak menilai dengan tepat kesan terhadap persekitaran oleh bahan pencemar. Eksperimen tetap perlu dilakukan untuk mendapatkan pembahagian sebenar oestrogen dalam persekitaran.

ABSTRACT

The behaviour of oestrogens in the environment is of great concern due to the endocrine disruption potential. The occurrence of oestrogens is reported as the most potent compounds in the environment, thus this study was conducted to determine the sorption affinity of oestrogens in different types of soils, relationship with between octanol-water partition coefficient and soil-water partititon coefficient of natural and synthetic oestrogen and distribution of oestrogen in environment. The research started with the investigation of the sorption behaviour and factors that influences the sorption behaviour of oestrogens in different type of soils. The sorption behaviour of all oestrogens indicated high association with organic carbon of the soils as sorption capacity increased when organic carbon increased. The value of K_{ow} and K_{oc} used to classify the mobility of oestrogens into soils and as the result, while E2 and EE2 were classified as low to immobile and E1 was slight to low. The values of organic carbon plays an important role in adsorbing an amount of oestrogens in soils. The significant effect on oestrogens' sorption factors was observed in soils with varied temperature and pH. Based on the analysis, it was clear that the sorption mechanism of oestrogens into soils was physisorption. All the oestrogens indicated a weaker binding to all soils as sorption behaviour of oestrogens onto soils was dependent of their hydrophobicity. The relationship between octanol-water partitioning coefficient (K_{ow}) and soil-water partitioning coefficient (K_d) was being determine from the order of sorption among oestrogens was well correlated with their octanol-water partitioning coefficient (K_{ow}). The higher log K_{ow} values correlated to less mobile organic chemicals into soils. It is believed that hydrophobicity of oestrogens has play a major important role in regulating the sorption of oestrogens in soils. Finally, the result of this study also indicated a considerable difference between experimental values and values generated by the computational model, Estimation Program Interface (EPISUITE). The EPISUITE software underestimate the log K_{ow} value of estrone (E1) but overestimates log K_{ow} 17 ß-estradiol (E2) and 17α-ethnylestradiol (EE2). The result also shows that EPISUITE program was overestimated the oestrogens' partition in soils-environmental compartment. It can be concluded that by inputting the experimental values, the model changed remarkably and has given absolute values to the soil's ambient conditions. Thus, this study showed that although the computational model was indicative, it did not accurately assess the environmental impact of pollutant. The experiments need to be conducted to obtain the real partitioning of oestrogens in environment.

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LIST OF SYMBOLS

%	Percent
µg/g	Microgram per gram
µg/l	Microgram per litre
µm	Micro metre
cm	Centimetre
G	Gram
g/mol	Gram per mol
H	Hour
K	Kelvin
K_d	Soil water partition coefficient
K_F	Freundlich sorption coefficient
kg/l	Kilogram per litre
K_L	Langmuir sorption coefficient
km	Kilometre
K_{oc}	Organic carbon partition coefficient
K_{ow}	Octanol-water partition coefficient
K_P	Partition coefficient
l/d	Litre per day
l/kg	Litre per kilogram
l/mg	Litre per milligram
M	Molarity
m^3/mol	Cubic metre per mol
mg	Milligram
Mg/ha	Mega gram per hectare
mg/l	Milligram per litre
mg/m^3	Milligram per cubic metre
min^{-1}	Per minute
ml	Millilitre
ml/min	Milligram per minute
mm	Millimetre
mm Hg	Millimetre of mercury

mol/l	Mol per litre
mPa	Mega Pascal
ng/g	Nanogram per gram
ng/kg	Nanogram per kilogram
ng/l	Nanogram per litre
ng/m^3	Nanogram per cubic metre
Nm	Nano metre
^oC	Degree Celsius
Pa	Pascal
ppb	Part per billion
ppt	Part per thousand
rpm	Revolution per minute
Sw	Water solubility

LIST OF ABBREVIATIONS

AACC	American Association For Clinical Chemistry
ACN	Acetonitrile
ASTM	American Society Of Testing And Materials
BBP	Butyl-Benzene Phthalate
BCF	Bio Concentration Factor
BPA	Bisphenol A
BS	British Standard
CAFO	Concentrated Animal Feeding Operations
CAS	Chemical Abstracts Service
DBP	Dibutyl Phthalate
DDT	Dichlorodiphenyltrichloroethane
DMP	Dimethyl Phthalate
DNA	Deoxyribonucleic Acid
DOP	Dioctyl Phthalate
DT	Dissipation Times
E.coli	Eshericia Coli
E1	Estrone
E2	17β-Estradiol
E3	Estriol
EDCs	Endocrine Disrupting Compounds
EE2	17α-Ethynylestradiol
EEDs	Environmental Endocrine Disruptors
EFMs	Environmental Fate Models
EJF	Environmental Justice Foundation
EPA	Environmental Protection Act
EPISUITE	Estimation Program Interface
EREs	Oestrogen Responsive Elements
FMT	Free Malaysia Today
FOA	The Fiber Optic Association
GF/C	Glass Fiber Filter
HCL	Acid Hydrochloride

HMW	High Molecular Weight
HOC	Hydrophobic Organic Chemicals
HPLC	High Performance Liquid Chromatography
HRT	Hormone Replacement Therapy
LH	Luteinizing Hormone
LMW	Low Molecular Weight
LOD	Limit Of Detection
MCL	Maximum Contaminant Level
MeEE2	Mestranol
MeOH	Methanol
MEPH	Monoethylexyl Phthalate
NaCl	Sodium Chloride
NaOH	Natrium Hydroxide
NWHN	The National Women’s Health Network
OC	Organic Carbon
OECD	Organisation For Economic Co-Operation And Development
OM	Organic Matter
PCBs	Polychlorinated Biphenyl
PERs	Property Estimation Routine
RP-HPLC	Reverse Phase High Performance Liquid Chromatography
RSD	Relative Standard Deviation
SD	Standard Deviation
SHBG	Steroid Hormone-Binding Globulin
SPE	Solid Phase Extraction
SRC	Syracuse Research Corporation
SSA	Specific Surface Area
STPs	Sewerage Treatment Plants
TEBG	Testosterone-Oestrogen-Binding Globulin
UMP	Universiti Malaysia Pahang
USEPA	United State Environmental Protection Agency
UV	Ultraviolet
WHO	World Health Organization
WWTP’s	Waste Water Treatment Plants

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