UTILIZATION OF NATURAL CLAY DERIVATIVES FOR THE EFFECTIVE TREATMENT OF AMETRYN AND METOLACHLOR

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by

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TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: MATERIALS AND METHODS

CHAPTER FOUR: RESULTS AND DISCUSSION

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

APPENDICES

Appendix A1	List of chemicals and reagents
Appendix A2	List of instruments and apparatus applied in this work
Appendix B1	The effect of chemical impregnation ratio on the adsorptive uptake of metolachlor onto HM
Appendix B2	The effect of acid concentration on the adsorptive uptake of ametryn onto AM
Appendix C1	A summary of the preparation procedure of the clay derivatives
Appendix C2	A summary of the steps of the batch adsorption studies
Appendix D1	Zero-point-of charge determination of AB
Appendix D2	The plot of the non-linear Langmuir, Freundlich and Temkin isotherm models
Appendix D3	The plot of the (a) Pseudo-first order, (b) Pseudo-second order and (c) Elovich kinetic equations
Appendix E1	Fourier-Transform Infrared Spectrum of montmorillonite
Appendix E2	Fourier-Transform Infrared Spectrum of AM
Appendix E3	Fourier-Transform Infrared Spectrum of HM
Appendix E4	Fourier-Transform Infrared Spectrum of bentonite
Appendix E5	Fourier-Transform Infrared Spectrum of AB
Appendix E6	Fourier-Transform Infrared Spectrum of natural clay
Appendix E7	Fourier-Transform Infrared Spectrum of ANC
Appendix E8	Fourier-Transform Infrared Spectrum of HNC

LIST OF PUBLICATIONS AND AWARDS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

Symbol	**Description**
AB	Nitric acid modified bentonite
AOPs	Advanced oxidation processes
AM	Hydrochloric acid modified montmorillonite
ANC	Sulphuric acid modified natural clay
BET	Brunauer-Emmet-Teller
BSE	Back scattered electron
CEC	Cation exchange capacity
CR	Controlled-release
DDT	Dichlorodiphenyl trichloroethane
DNA	Deoxyribonucleic acid
EPA	Environmental Protection Agency
FAO	Food and Agricultural Oraganization
FTIR	Fourier-Transform Infrared
HDTMA	Hexadecyltrimethylammonium
HM	Hexadecyltrimethylammonium bromide modified montmorillonite
HNC	Hexadecyltrimethylammonium bromide modified natural clay
IR	Infrared
KBr	Potassium bromide
miRNA	Micro ribonucleic acid
NC	Natural clay
P	Peat

R	Aliphatic or aromatic hydrocarbon
SE	secondary electron
SEM	Scanning Electron Microscopy
UV	Ultraviolet
WHO	World Health Organization

LIST OF SYMBOLS

Symbol	**Description**	**Unit**
A	Temkin isotherm equilibrium binding constant	L/g
A_I	Absorbance	-
a	Initial sorption rate of Elovich kinetic model	mg/g h
B	Temkin isotherm constant	-
B_t	Boyd model constant	-
b	Elovich kinetic constant of activation energy for chemisorption	-
b_c	Path length of cell	cm
b_T	Temkin isotherm constant related to heat of sorption	J/mole
C	Solute concentration	mg/L
C_e	Herbicide concentration at equilibrium	mg/L
C_0	Initial herbicide concentration	mg/L
C_t	Herbicide concentration at time, t	mg/L
K_d	Soil adsorption coefficient	-
K_F	Freundlich isotherm constant	$(\mathrm{mg/g}).(\mathrm{L/mg})^{1/n}$
K_L	Energy of adsorption for Langmuir isotherm	L/g
K_oc	organic carbon-water partition coefficient	-
k_1	Pseudo-first order rate constant	1/h
k_2	Pseudo-second order constant	g/mg h
N	Number of data points	-
n	Adsorption intensity related to Freundlich constant	-
°C	Degree Celsius	-

pK_a	Acid dissociation constant	
P^-	Peat ion	-
P_0	Amount of equilibrium sites available on the peat	-
P_t	Amount of active sites occupied on the peat at time, *t*	-
pzc	Point-of-zero-charge	-
Q_0	Monolayer adsorption capacity	mg/g
q_e	Adsorption uptake at equilibrium	mg/g
q_t	Adsorption uptake at time *t*	mg/g
q_{cal}	Calculated adsorption capacity	mg/g
q_{exp}	Experimental adsorption capacity	mg/g
$q_{e,meas}$	Measured mean of adsorptive uptake	mg/g
$q_{e,calc}$	Calculated mean of adsorptive uptake	mg/g
$\overline{q_{e,calc}}$	Average mean of adsorptive uptake	mg/g
R	Gas constant	J/mole *K*
R_L	Separation factor	-
Δq	Normalized standard deviation	-
R	Adsorptive removal	%
R^2	Correlation coefficient	-
T	Absolute temperature	*K*
t	Time	h
$T^{1/2}$	Half life	-
V	Volume	L
W	Mass of adsorbent	g
ε_λ	Molar absorptivity coefficient	-

PENGGUNAAN TERBITAN TANAH LIAT SEMULAJADI UNTUK RAWATAN BERKESAN AMETRYE DAN METOLACHLOR

ABSTRAK

Satu kaedah baru bagi pengubahsuaian tanah liat semulajadi, montmorilonit dan bentonit kepada satu siri penjerap berfungsi melalui rawatan kimia telah dilaporkan. Penggunaannya untuk perawatan racun makhluk sekunder, ametryn dan metolachlor, yang selalu diaplikasikan untuk pengawalan serangga perosak, tumbuhan dan kulat telah dikaji. Pengubahsuaian tanah liat telah dijalankan dengan menggunakan rawatan asid dan hexadecyltrimethylammonium bromida (HDTMA), manakala pembolehubah manipulasi telah dikaji menggunakan penjerap berkelompok dengan megubahsuai kepekatan asal, masa sentuhan, dan larutan pH dengan menggunakan kajian kumpulan penjerap. Pemeriksaan ke atas ciri-ciri fizikal dan kimia termasuk morfologi permukaan, sifat-sifat struktur berlubang, permukaan kumpulan berfungsi, dan titik capaian arus sifar (pH_{zpc}) telah dianalisis. Data keseimbangan telah disimulasikan menggunakan model isotherma, Langmuir, Freundlic dan Temkin, manakala model kinetik ditetapkan menggunakan persamaan pseudo-first order, pseudo-second order dan Elovich. Hasil kajian menunjukkan prestasi yang signifikan dalam penyingkiran ametryn dan metolachlor. Penjerapan racun perosak didapati sangat dipengaruhi oleh larutan pH, menjurus penjerapan ametryn dan metalachlor kepada larutan berasid. Peningkatan kepekatan asal dari 25 mg/L kepada 150 mg/L dan 50 mg/L kepada 400 mg/L, menunjukkan peningkatan penjerapan ametryn dari 23.89-132.09 mg/g, 23.36-128.46 mg/g, 12.49- 50.12 mg/g, dan 24.88-148.91 mg/g, untuk montmorillonit, AM, ANC dan AB, manakala penjerapan metolachlor meningkat dari 7.23-38.69 mg/g, 7.32-26.15 mg/g dan 18.45-48.98 mg/g bagi HM, HNC dan AB, masing-masing Penjerapan data keseimbangan mematuhi model Langmuir, manakala model kinetik mengikut persamaan pseudo-second order. Pemeriksaan struktur tekstur mengesahkan pembentukan liang dengan siri berongga di sekitar permukaan, dengan peningkatan jarak kawasan permukaan Brunaeur-Emmet-Teller (BET) dari 2.12 ke 245.64 m^2/g. Kajian morfologi menyokong anggapan bahawa interkalasi hexadecyltrimethyammonium bromida (HDTMA) dan proses pengubahsuaian asid telah berjaya dicapai. Pengubahsuaian spektrum Fourier-Transform Infrared Spektroskopi menandakan pengubahsuaian dan pembangunan fungsi baru pada terbitan tanah liat. Hasil kajian mendapati terbitan tanah liat ini mempunyai potensi yang besar sebagai satu penyelesaian ekonomi dan teknik yang mudah untuk pemulihan berterusan air yang dicemari racun makhluk perosak.

UTILIZATION OF NATURAL CLAY DERIVATIVES FOR THE EFFECTIVE TREATMENT OF AMETRYN AND METOLACHLOR

ABSTRACT

A new route for the conversion of natural clay, montmorillonite and bentonite into a series of new functionalized adsorbents via simple chemical treatment has been presented. The unique application for the effective remediation of secondary pesticides, ametryn and metalachlor, widely applied for the control of nuisance insects, plants and fungi has been attempted. The clays were subjected to hexadecyltrimethylammonium bromide (HDTMA) and acid modifications, while the novel application was examined using batch adsorption experiments by varying the operational parameters, initial concentration, contact time, and solution pH. The physical and chemical characteristics including the surface morphology, pore structural properties, surface functional groups, and zero-point-of-charge (pH_{zpc}) were evaluated. Equilibrium data were simulated using the Langmuir, Freundlich and Temkin isotherm models, while the kinetic model was fitted to the pseudo-first order, pseudo-second order and Elovich kinetic equations. Result illustrated an encouraging performance towards the removal of ametryn and metolachlor. The adsorptive uptake of pesticides was found to be highly pH dependent, favouring the adsorption uptake of ametryn and metolachlor at the acidic condition. Increasing the initial concentrations from 25 mg/L to 150 mg/L, and 50 mg/L to 400 mg/L showed a greater adsorption uptake for ametryn of 23.89-132.09 mg/g, 23.36-128.46 mg/g, 12.49-50.12 mg/g, and 24.88-148.91 mg/g, for montmorillonite, AM and ANC, and AB, while the adsorption uptake of metolachlor increased from 7.23-38.69 mg/g, 7.32-26.15 mg/g and 18.45-48.98 mg/g, respectively for HM, HNC, and AB. Equilibrium data was satisfactory fitted to the Langmuir isotherm model, while the adsorption kinetic was best described by the pseudo-second order model. Examination of the textural structure verified pore development, with a series of cavities distributed around the surface, with the Brunauer-Emmett-Teller (BET) surface areas ranging from 2.12 to 245.64 m^2/g. Morphological study supported the presumption that the intercalation of hexadecyltrimetylammonium bromide (HDTMA) and acid modification process was successfully attained. Alteration of Fourier-transform infrared spectroscopy (FTIR) bands signified the modification and development of the new functionalities on the clay derivatives. The findings supported the great potential of these clay-derivatives as an economically advantageous solution and viable technique for the successive remediation of pesticides contaminated water.

CHAPTER ONE

INTRODUCTION

1.1 An overview on the contamination, health implications and treatment options of pesticide effluents

Pesticides is defined as a mixture of chemical substances, selectively applied against a specific group of pests or microbes in the agricultural field (Gavrilescu, 2005). Statistical data has shown that the global pesticides usage has increased from 162 to 194 million metric ton from 2008 to 2016 (Figure 1.1).

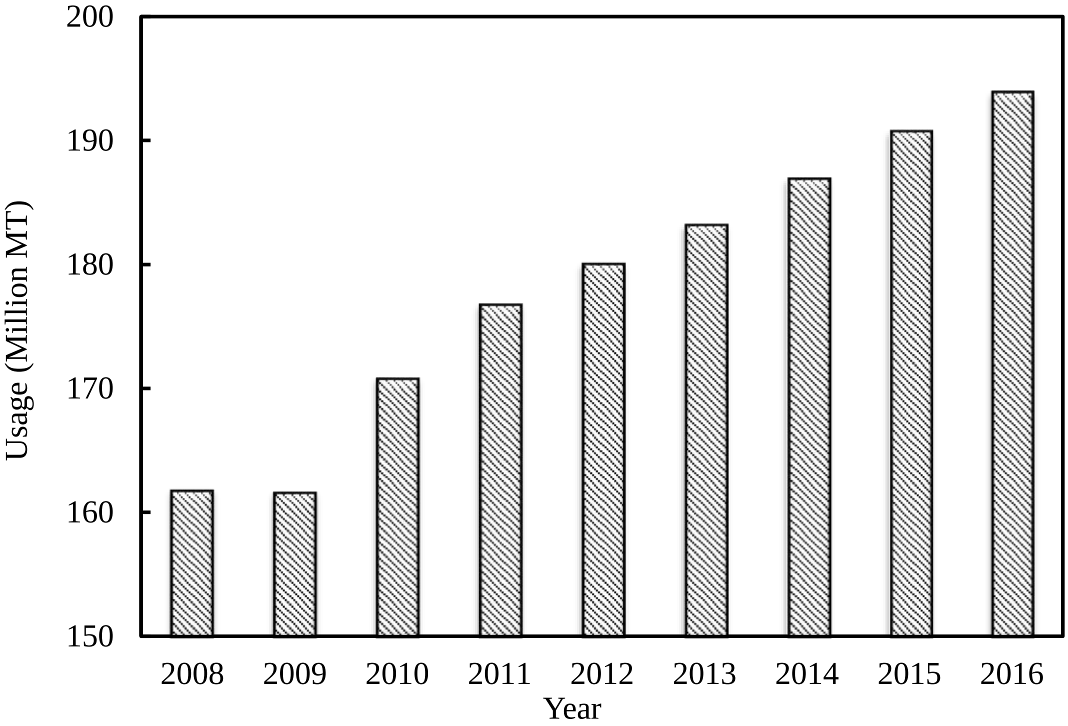

Figure 1.1: Global pesticides usage (Food and Agricultural Organization of United State, 2016)

Today, the indiscriminate discharge of organo-pesticide, ametryn, metolachlor and its metabolite into the surface water and marine coastal environment is dictated to be a primary concern by the environmental practitioners. The ubiquitous presence of ametryn and metolachlor, a second generation of herbicide in the ecosystems has attracted aesthetic concern, mainly ascribed to the highly mobile, unique toxic behaviour, and detrimental implications to the human health. Ametryn is a herbicide of the *s*-triazine family, with a chemical structure of the aromatic hexamer ring. It was firstly synthesized in 1962 (Gysin, 1962), and widely applied in the pre- and post-emergence control of broadleaf weeds and annual grasses (Tennant *et al*., 2001). The annual application of active ametryn is 380,000 libs, accounting 60% with corn, 20% with pineapple and 20% with sugarcane. The specific action of ametryn on plants is the inhibition of photosynthesis process, particularly at the photosystem II (PSII), leading to the blockage of electron transport by displacing plastoquinone from the unique binding site on the protein subunit, resulting in chlorosis (leaf yellowing) and tissue necrosis (Prade *et al*., 1998). On the contrary, metolachlor is a herbicide from the chloroacetanilide group that contains a chiral carbon atom, and usually exists as a pair of enantiomer. It was registered in 1976 for the general weed control in noncrop areas, and extended to the primary use for the plantation of corn and soybean. Metolachlor works through the inhibition of cell growth to prevent the synthesis of long chain fatty acids (protein synthesis).

These herbicides could be uptaken by the plant roots, and accumulate in the apical meristems to generate mutagenic and carcinogenic damages to the enzymatic systems and deoxyribonucleic acid (DNA) (Gichner *et al*., 1982). The biotransformation of these xenobiotics in plants could form the conjugates that are polymerized, and incorporated into the plant structural components in such a way that these reactive intermediates, active oxygen species or the final metabolites would produce detrimental impacts, and secondly, they could be conjugated and stored in plants (Higashi, 1988). These xenobiotic metabolites could induce oxidative stress, a promoter of the cellular pathway associated with the onset, or progress of a variety of diseases: atherosclerosis, cancer, psoriasis, Alzheimer, hypertension and heart-liver failure (Halliwell and Gutteridge, 2007; Veloso *et al*., 2013; Mostafalou and Abdollahi, 2013). During the reaction, the reactive species and these derivatives may attack lipids, proteins and nucleic acid molecules to cause metabolic alterations and cellular death.

Dormant seasonal applications of herbicides, specifically ametryn and metolachlor in conjunction with frequent rainfall may result in the generation of contaminated runoff and offsite environmental risks. A typical mechanism for the pesticides pollution is driven by the agricultural run-off during the storm events. The transient movement of these contaminants is highly dependent on the soil type, drainage, physical and chemical properties of the pesticides, and the changing weather (Wauchope, 1978; Brown and Hollis, 1996). Frank *et al*. (1982) have identified surface runoff as a predominant pathway for the discharge of pesticides into water streams from the 11 available watersheds in Ontario. Schiff and Sutula (2004) have reported that during the rain events, the flow may vary from < 0.03 to > 283.2 m^3/s in a matter of minutes per hours, to enhance the pesticide transport to the receiving waterways. According to Bucheli *et al*. (1998), the average concentration for the single rain event and total loads for triazines, acetamides and phenoxy acids were 903 ng/L and 13900 ng/m^2.year, 191 ng/L and 5900 ng/m^2.year, 106 ng/L and 5100 ng/m^2.year, respectively. These polluted runoff would potentially affect the aquatic habitat, natural ecosystems, and clean drinking water resources (EPA, 1983).