

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

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EFFECTIVE TREATMENT OF AMETRYN AND METOLACHLOR**

**by**

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## 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 Organization
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	(mg/g).(L/mg) <sup>1/n</sup>
$K_L$	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	-
$\Delta q$	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
$\epsilon_{\lambda}$	Molar absorptivity coefficient	-

# **PENGUNAAN TERBITAN TANAH LIAT SEMULAJADI UNTUK RAWATAN BERKESAN AMETRYE DAN METOLACHLOR**

## **ABSTRAK**

Satu kaedah baru bagi pengubahsuaian tanah liat semulajadi, montmorillonit 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 pembolehkan manipulasi telah dikaji menggunakan penjerap berkelompok dengan megubahsuaikan 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, Freundlich 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, menjuruskan penjerapan ametryn dan metolachlor 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 Brunauer-Emmet-Teller (BET) dari 2.12 ke 245.64 m<sup>2</sup>/g. Kajian morfologi menyokong anggapan bahawa interkalasi hexadecyltrimethylammonium 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,

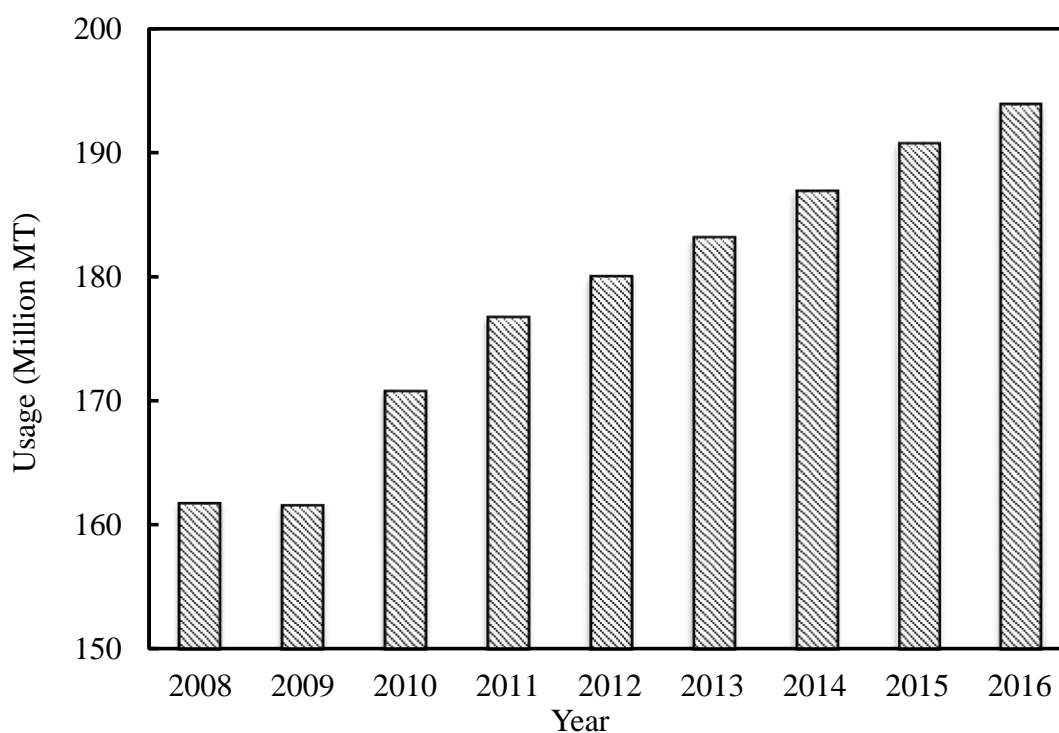
7.32-26.15 mg/g and 18.45-48.98 mg/g, respectively for HM, HNC, and AB. Equilibrium data was satisfactory fitted to the Langmuir isotherm model, while the adsorption kinetic was best described by the pseudo-second order model. Examination of the textural structure verified pore development, with a series of cavities distributed around the surface, with the Brunauer-Emmett-Teller (BET) surface areas ranging from 2.12 to 245.64 m<sup>2</sup>/g. Morphological study supported the presumption that the intercalation of hexadecyltrimethylammonium 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 lbs, 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  $> 283.2 \text{ m}^3/\text{s}$  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<sup>2</sup>.year, 191 ng/L and 5900 ng/m<sup>2</sup>.year, 106 ng/L and 5100 ng/m<sup>2</sup>.year, respectively. These polluted runoff would potentially affect the aquatic habitat, natural ecosystems, and clean drinking water resources (EPA, 1983).