PREPARATION, CHARACTERIZATION AND ADSORPTION STUDIES OF CLAY AND CHITOSAN-BASED COMPOSITE ADSORBENTS FOR ACID, BASIC AND REACTIVE DYES

by

MANASE AUTA

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LIST OF ABBREVIATIONS

Symbol	**Description**
AB25	Acid blue 25
AB29	Acid blue 29
AC	Activated carbon
ANOVA	Analysis of variance
BB3	Basic blue 3
BB69	Basic blue 69
BET	Brunauer-Emmett-Teller
CBR	Cibacron red dye
CCB	Crosslinked chitosan beads
CCD	Central composite design
CD	Calcined dolomite
CEAC	Rice stalk activated carbon/chitosan composite
CH	Chitosan
DOE	Design of experiment
ECH	Epichlorohydrin
FPSLG	Functionalized paper sludge activated carbon
FTIR	Fourier transmission infrared
IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
LDF	London Dispersion Forces
MB	Methylene blue
MBC	Modified Ball clay
MHC	Modified Ipoh clay
MHC-CB	Modified Ipoh clay chitosan composite
MKKC	Modified Kuala Kangsar clay

MTZ	Mass transfer zone
MWT	Modified waste tea
Np	Number of points
PS	Paper sludge
PSLG	Paper sludge activated carbon
RBC	Raw Ball clay
RB19	Reactive blue 19
RD	Raw dolomite
RHC	Raw Ipoh clay
RKKC	Raw Kuala Kangsar clay
RO16	Reactive orange 16
Rpm	Revolution per minutes
RR222	Reactive red 222
RSM	Response surface methodology
RWT	Raw waste tea
SEM	Scanning electron spectroscopy
TGA	Thermogravimetric analysis
USA	United States of America
WT	Waste tea
WTAC	Waste tea activated carbon
WTAC-CCB	Waste tea activated carbon crosslinked chitosan beads
WTC	Waste tea carbon
XRF	X-Ray Fluorescence
Y	Response
Y_1	Percentage yield
Y_2	Percentage dye adsorption

LIST OF SYMBOL

Symbol	Description	Unit
a	Initial sorption rate for Elovich kinetic model	mg/g h
A_i	Absorbance	-
A_{RP}	Redlich-Peterson isotherm model constant	L/mg
b_o	Response model constant coefficients of design expert	-
b_T	Temkin constant related to heat of sorption	J/mol
B_t	Boyd model constant	-
B_{RP}	Redlich-Peterson isotherm model constant	$(L/mg)^g$
c	Solute or analyte concentration	mg/L
C_{ad}	Concentration adsorbed	mg/L
C_{bt}	Threshold concentration value	mg/L
C_d	Effluent sorbate concentration at minimum level	mg/L
C_e	Dye concentration at equilibrium	mg/L
C_{ex}	Column exhaustion point concentration	mg/L
C_i	Intraparticle diffusion model constant	mg/g
(C_t/C_o)	Normalized concentrations	-
$(C_t/C_o)_{exp}$	Experimental normalized concentration	-
$(C_t/C_o)_{cal}$	Theoretical normalized concentration	-
F	Fraction of solute adsorbed at time t	-
F_{AB}	Linear velocity of Adams-Bohart model	cm/min
g	Redlich-Peterson model component	-
ΔG	Gibbs free energy	kJ/mol
ΔH	Enthalpy change	kJ/mol
K_F	Freundlich isotherm constant	$(mg/g).(L/mg)^n$
K_L	Energy of adsorption for Langmuir isotherm	L/g

K_R	Redlich-Peterson isotherm constants	L/g
k_{AB}	Adams-Bohart adsorption rate constant	L/mg.min
k_{ip}	Diffusion rate constant	mg/g $h^{0.5}$
k_T	Temkin constant related equilibrium binding energy	L/mg
k_{Th}	Thomas constant	mL/min. mg
k_{YN}	Yoon-Nelson rate velocity constant	1/min
k_{PF}	Pseudo-first-order kinetic constant	1/h
k_{PS}	Pseudo-second-order kinetic constant	g/mg h
m	Mass of adsorbent	g
n	Adsorption intensity related to Freundlich isotherm	-
n_c	Number of center point	-
N_o	Saturation concentration	mg/L
N	Number of data points	-
p	Path length of cell	cm
q_e	Adsorption uptake at equilibrium	mg/g
q_m	Monolayer adsorption capacity related to Langmuir isotherm	mg/g
q_t	Adsorption uptake at time t	mg/g
q_{TH}	Thomas equilibrium uptake	mg/g
q_{cal}	Calculated adsorption capacity	mg/g
q_{exp}	Experimental adsorption capacity	mg/g
Q	Feed flow rate	mL/min
R	Gas constant	J/mol K
R^2	Correlation coefficients	-
ΔS	Entropy change	J/mol K
t	Time	min
t_{ex}	Effluent concentration after exhaustion at time t	min

t_{bt}	Effluent sorbate concentration at time t	min
T	Absolute temperature	K
V	Volume	L
W	Mass of adsorbent	g
Z	Adsorbent bed depth of Adams-Bohart model	cm

Greek letters

α	Distance of axial point from centre	cm
α_B	Bangham' equation constants	-
χ	Chi-square	-
τ	Time required for 50% of adsorbate breakthrough	min
λ	Wavelength	cm
θ	Fractional loading	-
ε	Molar absorptivity	L/mg cm

KAJIAN PENYEDIAAN, PENCIRIAN DAN PENJERAPAN BAGI PENJERAP TANAH LIAT DAN KOMPOSIT BERASASKAN CHITOSAN UNTUK PEWARNA ASID, BES DAN REAKTIF

ABSTRAK

Potensi sisa buangan boleh diperbaharui dan sumber mineral yang banyak di Malaysia telah digunakan untuk penyediaan perjerap bagi penjerapan pewarna daripada sisa air buangan sintetik. Karbon teraktif sisa teh (WTAC) dan karbon teraktif sisa enapcemar kertas (PSLG) yang dioptimumkan disediakan menggunakan kalium florida dan asetat sebagai agen pengaktifan manakala penjerap disediakan daripada dolomit, tanah liat Ipoh, tanah liat Kuala Kangsar dan tanah liat ball. Menerusi kalsinasi dan modifikasi menggunakan aluminum hidroksida dan asid sulfurik. Pembolehubah yang dioptimumkan adalah suhu pengaktifan, masa, nisbah kandungan kimia manakala respon adalah hasil dan penjerapan pewarna. Keadaan optimum untuk WTAC ialah 1.4 nisbah kandungan (IR), 120 min dan 800 ^{o}C manakala 0.95 IR, 105 min dan 810 ^{o}C dicapai untuk PSLG. Penjerap dicirikan menerusi analisis luas permukaan BET, mikroskopi elektron pengimbas, pengubahan Fourier infra merah, analisis elemen dan pendarkilau sinar-x imbasan untuk menentukan ciri fizikal dan kimia. Luas permukaan 2.97-854.25 m^{2}/g dan keporosan 0.003-0.516 cm^{3}/g dicapai. Eksperimen penjerapan tunggal, binari, kelompok dan kolum lapisan terbendalir tetap dijalankan. Sela 30-350 mg/L, 30-50 ^{o}C dan pH 2-12 diguna untuk mengkaji kesan kepekatan awal, suhu proses dan pH terhadap eksperimen penjerap berkelompok. Kesan kepekatan awal, tinggi lapisan terbendalir dan halaju aliran disiasat dalam kajian kolum lapisan terbendalir tetap. Garis lengkuk sesuhu keseimbangan dan data kinetik dimodelkan, mekanisma proses, termodinamik dan regenerasi untuk penjanaan berkelonpok. Model kinetic tertib kedua pseudo adalah yang terbaik untuk mewakili semua proses penjerapan. Penjerapan asid biru 25 oleh karbon sisa teh, reaktif oren 16 dan reaktif biru 19 oleh PSLG dan PSLG terubahsuai adalah eksotermik; manakala penjarapan MB dan asid biru 29 oleh WTAC, manik chitosan silang rangkai dan komposit chitosan WTAC adalah endotermik; garis langkuk sesuhu Langmuir paling sesuai menerangkan proses. Penjerapan MB tanah liat Ball, tanah liat Ball terubahsuai, tanah liat Ipoh, tanah liat Ipoh terubahsuai, tanah liat Kuala Kangsar dan tanah liat Kuala Kangsar terubahsuai paling sesuai di terangkan oleh model Redlich-Peterson dan endotermik termodinomiknya kecuali untuk RHC dan MHC merupakan eksotermik. Penjarapan 25.60-531-07 mg/g dan 25.01-683.46 mg/g direkodkan untuk kolum lapisan terbendalir tetap dan penjerapan berkelompok. Model Yoon-Nelson paling sesuai untuk menerangkan penjerapan MB kolum lapisan terbendalir tetap oleh komposit chitosan MHC, MB dan AB29 oleh WTAC-CCB. Keputusan regenerasi menunjukkan kejayaan penjerap untuk 5 kali kitaran penjerapan.

PREPARATION, CHARACTERIZATION AND ADSORPTION STUDIES OF CLAY AND CHITOSAN-BASED COMPOSITE ADSORBENTS FOR ACID, BASIC AND REACTIVE DYES

ABSTRACT

Potentials of abundant renewable waste and mineral resources in Malaysia were harnessed for preparation of adsorbents for adsorption of dyes from synthetic wastewaters. Optimized waste tea activated carbon (WTAC) and paper sludge activated carbon (PSLG) were prepared using potassium fluoride and acetate as new activating agents while other adsorbents were prepared from dolomite, Ipoh, Ball and Kuala Kangsar clays through calcinations and modification with aluminum hydroxide and sulphuric acid. The variables optimized were activation temperature and time, chemical impregnation ratio; and the responses were yield and dye adsorption. The optimal conditions for WTAC were 1.4:1 impregnation ratio (IR), 120 min and 800 ^{o}C while 0.95 IR, 105 min and 810 ^{o}C were obtained for PSLG. The adsorbents were characterized for BET surface area analysis, scanning electron microscopy, Fourier transform infrared, elemental analysis and X-ray fluorescence to determine their physical and chemical characteristics. The BET surface area of 2.97-854.25 m^{2}/g and porosity of 0.003-0.516 cm^{3}/g were obtained. A range of 30-350 mg/L, 30-50 ^{o}C and pH 2-12 were used to study the effect of initial concentration, process temperature and pH on the batch adsorption experiments. The effect of initial dye concentration, bed height and flow rate on breakthrough curves in fixed-bed column adsorption were investigated. Batch equilibrium isotherms and kinetics data were modeled, the mechanism of the process, thermodynamic and regeneration studies were evaluated. Pseudo-second-order best described all the adsorption processes. Adsorption of acid blue 25 by waste tea activated carbon, reactive orange 16 and reactive blue 19 by PSLG and functionalized PSLG were exothermic; while adsorption of methylene blue (MB) and acid blue 29 (AB29) by WTAC, crosslinked chitosan beads and WTAC chitosan composite (WTAC-CCB) was endothermic; Langmuir isotherm model best described the processes. The raw ball clay, modified ball clay, raw Ipoh clay, modified Ipoh clay (MHC), raw Kuala Kangsar clay and modified Kuala Kangsar clay adsorption of MB were best described by Redlich-Peterson model and were thermodynamically endothermic in nature except for RHC and MHC adsorbents adsorption process that were exothermic. Adsorption uptake of 25.60-531.07 mg/g and 25.01-683.46 mg/g were recorded for fixed-bed column and batch studies, respectively. Modeling of fixed-bed adsorption revealed Yoon-Nelson model as the best fitted model that described the adsorption of MB by MHC chitosan composite (MHC-CB), MB and AB29 by WTAC-CCB. The regeneration results revealed that the adsorbents were used successfully for five cycles of adsorption.

CHAPTER ONE

INTRODUCTION

1.1 Water and textile effluent

Water is essential to life. The organs of the human body, most tissues of animals and trees constitute approximately 55, 65 and 60% of water, respectively; but yet water availability and purity is still a global challenge. The fact that 71% of the planet surface is covered by water out of which fresh water is 2.5%, only less than 1% of this water is within human reach for consumption and this scarce commodity is not within the reach of a soaring population of 1.2 billion capita (Inglezakis and Poulopoulos, 2006). Various sources of this desideratum aside pipes have been streams, rivers, lakes, bore holes, rain and so on which are found in both developed and developing nations; yet the demand for fresh water outstrip its supply (Hurlimann et al., 2009). Conservation measures such as building of dams, reservoirs, digging of wells, desalination, collecting of rains and water recycling are gaining recognition.

Polluting water has adverse effects on humans and aquatic biota due to its implication in water supply for town and recreation (Carneiro et al., 2010). The pollutants in water may be conveyed from point or nonpoint sources. The point source pollution which often affects surface waters-rivers, lakes, seas are from chemical industries and anthropogenic activities. The point source varies in magnitude from dry cleaning and small scale business which may be small compared with large sources like textile, paper, petrochemical and cosmetics industries; industrial effluents are easily traceable due to their larger volumes and extent of pollution (Noble and Terry, 2004). Agricultural activities and landfill leachate constitute the nonpoint sources of water pollution which commonly affects ground waters. Pollution from such sources is controlled through minimization of activities of root-age (Ongley et al., 2010).

Malaysia, a developing nation diversifies in production of palm oil, paper making, textiles, furniture, electronics, and so on (Reinhardt, 2000). And thus, waste discharge from these industrial activities into numerous water streams results in severe pollution. Investigations on the use of large volumes of water in textile industry and composition of their effluents led the Association of Southeast Asian nations to declare this industry as a major source of wastewater, being about 22% of industrial wastewater in Malaysia (Jumasiah et al., 2005). It is also termed the most polluting source of waterwater among industrial sources (Khelifi et al., 2009). Large volumes of wastewater are disposed from different segmental stages during the operation of the textile industry (Kocabas et al., 2009). Typically, it is estimated that 40-65 L of effluent from textile industry are released for each kilogram of fabric produced, which constitutes the toxic dye pollutants (Ali et al., 2009; Mezohegyi et al., 2012). The as-disposed wastewater contains harmful dye substances which are recalcitrant to both removal and degradation and thereby jeopardizing the ecosystem (Hameed, 2009).

Malaysia also has a history of batik industry (homemade textile) that has been bequeathed from generations that thrives especially among people of the east coast of Peninsular Malaysia (Rashidi et al., 2012). The batik industry also contribute toward the generation of effluents as other textile plants. Depending on either hand drawn (using copper) or stamped batik, the method requires additional use of heavy metals. Batik industry in Malaysia is transforming from just outfits to some beautiful and artistic making of bags, curtains, cushion covers, slippers, curtains, Songket or cloth of gold used occasionally for weddings and so on (Hairuddin et al., 2012).

The economical benefits of modern textile and batik industries in Malaysia are immense however; Malaysian Environmental Regulation does not condone color from textile effluent. This is due to willingness demonstrated by Malaysian lawmakers to strengthen the environmental protection (Perry and Singh, 2001). More so, substances like dyes in wastewater are among the categories of pollutants that should not be overlooked (Dulman and Cucu-Man, 2009; Alam et al., 2009).

Textile effluent constituents include dyes (color), surfactants, chlorinated compounds, some recalcitrant organic compounds, heavy metals and other toxicants. This effluent is a menace and a threat to the entire ecosystem as it has carcinogenic and mutagenic effects on humans and its impediment to the photosynthesis of algae and aquatic plants due to the light absorption hindrance (Ahmad et al., 2009a). The dominance of some compounds in effluents over the others depends on the treatment process in the industry (Verma et al., 2012).

1.2 Textile Dye

Dyes are organic chemicals of chiefly synthetic origin, although some are also extracted from plants. They are classified chemically into two groups. Group one constitutes acid and metal-complex acid dyes (anionic), direct dyes (anionic), basic dyes (cationic) and disperse dyes (non-ionic); reactive and mordant (chrome) dyes are classified in group two categories (Gupta and Suhas, 2009). About 5-20 % of 700 000 metric tons of dyes produced annually from over 100 000 commercial dyes available are released into process water during textile production activities world wide (Tunç et al., 2009).

Anionic dyes are the acid, direct and reactive dyes which are negatively charged and are very soluble in water; each molecule of the dye contains at least one sulphonate (SO_3Na) group. Most of these dyes possess fused structure and some chemical components like anthraquinone, xanthenes, triphenylmethane and azine which make them more resistant to degradation. Typically, examples of dyes in this group include acid blue 29, acid blue 25, acid green 25, acid red 1, direct blue 71, direct blue 3, reactive orange 16 and reactive blue 19 (Carneiro et al., 2010). Reactive dyes undergo chemical reaction with the fibers making them covalently bonded to them; this gives excellent fastness to the material in question. In textile industries, they are the most widely used classes of dyes and are bright with every color of the visible spectrum from yellow to black (Xue et al., 2009). Reactive dyes high solubility in water makes them very difficult to eliminate in wastewater especially by other means other than adsorption (Baskaralingam et al., 2006).

Cationic dyes are basic dyes which predominantly have delocalized positive charges on their chromophore which are more concentrated on nitrogen (amino group) atoms (El Qada et al., 2008). Basic dyes are more toxic than anionic dyes (Qiao et al., 2009); examples of these dyes are methylene blue, basic blue 3, malachite green and so on. Methylene blue is a bluish famous dye which has wide applicability in textile industries, paper, hair coloration and for research. It is friendly to use but when inhaled, can make breathing difficult. Vomiting, diarrhea, nausea and burning sensation are experienced only when orally ingested. Its common usage has prompted many researches to find ways of effectively removing it from wastewater and reports of such researches have been captured in both original and review articles (Demirbas, 2009; Gupta and Suhas, 2009,; Rafatullah et al., 2010; Salleh et al., 2011).

The non-ionic dyes are mostly the disperse dyes which do not ionize in solution and some of them have the ability of bioaccumulation (Robinson et al., 2001). Disperse dyes are sparingly soluble in the water due absence of sulphonate groups in their molecules and are often found as dispersion in dye bath. The hydrophobic nature of these dyes makes them to be suitable for cellulose acetates, acrylic, nylon, synthetic polymer fibers. In this category examples of dyes are disperse blue 56, disperse red 72 and disperse yellow 54 (Carmen and Daniela, 2012).

1.3 Treatment of textile effluent

The challenge for developing mechanisms and processes for effective treatment of textile effluents has been the pill of research in the past decades with a view to preserving the environment from increasing anthropogenic abuse. Adsorption processes have outstripped other processes like membrane separation (Amini et al., 2011), photo-Fenton degradation (Ayodele et al., 2012), sonochemical degradation (Abbasi and Asl, 2008), electrochemical degradation (Fan et al., 2008), coagulation, among others due to its simplicity of applicability, effectiveness and universal nature which has earned it the best process in wastewater treatment method (Ali et al., 2012). It can be applied to remove both soluble and insoluble organic pollutants with about 99.9% efficiency, the immense research, development and successes recorded in its improvement in the past decades has now made it a major industrial separation technique (Richardson et al., 2002). There are numerous reports on the efficiency and efficacy of activated carbon as adsorbent in adsorption processes but the pricey nature of commercial activated carbon calls for search for alternatives or substitutes for the adsorbent (Al-Degs et al., 2009).

Malaysia and many part of the world are blessed with abundance of minerals and organic resources that are lying fallow and most often regarded and disposed off as wastes (El-Hendawy, 2005). These include agricultural biomass, clays, dolomite and sludge just to mention a few (Husain et al., 2003; Rozman et al., 2004). Research has shown that these materials can be converted into good adsorbents useful for effective treatment of dyes textile wastewater (Halim et al., 2012).

Adsorption process though predominantly a physical process has often exhibited chemisorptions capability depending on the forces involved. It entails both permeation and ion-exchange of dye molecules on the surface of the adsorbent from solution. Physical adsorption is non-specific (any adsorbate-adsorbent interaction) and takes place at enthalpy between 10 to 20 kJ/mol while specific chemisorptions occurs between enthalpy of 40 to 400 kJ/mol (Saha et al., 2010; Kołodyńska et al., 2012). Treatment of dye waterwater by adsorption process is influenced by factors such as adsorbent surface area, porosity, particle size, pH, contact time, temperature, surface chemistry and other physio-chemical factors (Al-Degs et al., 2009). Adsorption process is effective, easy to use, and its treated wastewater is reusable but the expensive commercial activated carbon used as adsorbent is its major disadvantage (Ahmad and Hameed, 2009).

Activated carbon is majorly an amorphous (with little microcrystalline structure) carbon material exhibiting high porosity and extended internal surface area. It can be prepared by either physical or chemical activation (or both) through pyrolysis of carbonaceous material in an inert atmosphere (Bansal and Goyal, 2005).

The preparation entails elimination of non-carbon materials such as sulfur, hydrogen, oxygen and nitrogen as vapor leaving mainly carbon atoms; before the completion of the activation process, the rearranged carbon atoms are developed into porous material with high and extended surface area (Rambabu et al., 2013). Activated carbons are obtained mainly in powder (small internal surface area) and granular (larger internal surface area) forms; which are associated with large and smaller pores, respectively. It has wide applicability which includes its use in wastewater treatment, pharmaceutical industries, paper and pulp mill, automobile industry, hydrometallurgy, medicine, food, oil industry and so on. Various alternative adsorbents have come to lime light to make the process economically friendly, these include sorbents prepared from renewable organic and inorganic materials (Bergaya and Lagaly, 2001; Deng et al., 2009).

Minerals are naturally occurring homogeneous inorganic solid substance having a definite chemical composition and characteristic crystalline structure, color and hardness. Clay minerals are generated as a result of hypothermal or weathering activities of rocks, which are classified majorly into kaolinite and montmorillonite. The classification is done with respect to the chemical composition of the clay materials. Kaolinite clays have an almost 1:1 (Si:Al) ratio of tetrahedral to octahedral sheets and montmorillonite has two silica tetrahedral sheets with one alumina sheet in-between them. Some other classes of clays exist but they are either sublet of the kaolinite or monmorillonite clays. The resultant charge of clays is usually negative which is as a result of substitution of Mg^{2+} for Al^{3+} and Al^{3+} for Si^{4+} in the octahedral and tetrahedral layers, respectively. Exchangeable cations such as K^+, Na^+, Ca^{2+} e.t.c. present in clay compensates for the negative charges (Mockovciakova and Olorinova, 2009; Jiang and Ashekuzzaman, 2012). Clay materials are acid treated or pillared for the purpose of enhancing the surface area, pore size, pore volume or modification of their surface chemistry; this modification transforms them into useful adsorbents for dye wastewater treatment (Jiang and Ashekuzzaman, 2012).

There are other mineral materials which are used for production of adsorbents materials, they include zeolite ($Na_2Al_2Si_3O_{10}\cdot 2H_2O$), sepiolite [($Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4\cdot 8H_2O$)], dolomite ($CaCO_3$. $MgCO_3$), gypsum ($CaSO_4\cdot 2H_2O$) and a host of others (Boucif et al., 2010; Zhang et al., 2011a). They are usually sourced naturally from the earth's crust and are often classified according to the active or dominant element in them.

Composite adsorbents consisting of separate interconnected part-compound materials through various methods with the aim of influencing the roughness, hydrophilicity, surface chemistry, surface energy, biocompatibility etc of the resulting adsorbent. Composite adsorbent has been produced with clay (Qiao et al., 2009), chitosan (Zhu et al., 2010b), activated carbons, organic and inorganic chemical compounds (Zhang et al., 2007b) and other wide varieties of materials. In fact inclusion of activated carbons with other materials to produce composite adsorbents has been found to improve its adsorption capabilities, selectivity and versatility (Mezohegyi et al., 2012).

1.4 Problem statement

Man’s quest for a better life through technological advancement has its own demerit to the ecosystem. Technological advancement mostly requires mimicking of natural phenomena synthetically in order to meet the global demand of the entire populace. Some of these technological processes results to direct or indirect pollution of the environment (Al-Rawajfeh et al., 2013).

Malaysia has diverse industries of which textile sector is notable (Ahmad and Hameed, 2009). The nature of operations in textile industries requires usage of large volumes of water which are often discharged into the environment at the end. Industrial textile effluents contain various degrees of harmful chemicals that have posed a global challenge of tackling and have initiated various researches to curb it (Ozmihci and Kargi, 2006; Ahmad and Hameed, 2010a). Adsorption technique through the usage of activated carbon is eminent in tackling this menace but the pricey nature of this adsorbent increases the cost of the process. Some few decades ago, cheaper, renewable and cosmopolitan precursors for activated carbon production have emanated through research as compared with the starting materials used for commercial activated carbon production (Ahmad and Hameed, 2009). More so, other substances such as chitosan, clays, sludge, and dolomite among others have been found to be useful as adsorbents in adsorption processes for tackling textile dyes effluents (Li et al., 2012).

The dependency of successful adsorptive separation on adsorbent quality and affordability has geared researchers into improving the development of good quality adsorbents from locally sourced materials as adsorbents of similar or comparable quality with commercial activated carbons. Emerging trends in research have shown that combination (grafting, chelation, impregnation, crosslinking, functionalization e.t.c.) of adsorptive materials with other substances tend to improve on their efficacy as adsorbents (Wan Ngah et al., 2011).

Malaysia is having the challenges of disposing waste generated from its abundant agricultural materials (Hameed et al., 2009a; Chiew and Shimada, 2013).

The need to harness potentials of these fallow materials and improve on the quality of the existing products is still grossly untapped. Valorization of these materials will bring economic benefits to the nation, help in tackling pollution problems through proper handling of wastes, alleviate pollution problems and promote Malaysia nation's contribution towards solving global pollution problem research wise (Foo and Hameed, 2009).

There is the need to investigate the use of diverse precursors, change method of preparation, introduce new activation agents, channel adsorbents for selective adsorption of pollutants and experiment the use of multicomponent adsorption systems as against single dye adsorption. The preparation methods of these adsorbents need to be optimized for high yield and adsorption capacity, and the adsorbents should be tested in both batch and continuous adsorption processes which are limitedly researched into (Smith et al., 2009).

Anionic and cationic dyes are among the major classes of dyes used regularly in textile industry and examples of these dyes include methylene blue, acid blue 29, acid blue 25, cibacron red dye, reactive orange 16 and reactive blue 19. Single and multi-component adsorption of dyes is important since most dye effluents have more than one dye. The adsorption performance of adsorbents using these processes will serve as a realistic solution to the natural textile effluent environmental pollution problems (Salleh et al., 2011; Labanda et al., 2011).

This research is aimed at preparing composite adsorbents, optimizing preparation parameters and functionalization of adsorbents from abundant precursors in Malaysia. The adsorbents developed will be used for adsorption of acid blue 25, acid blue 29, methylene blue, cibacron red, reactive orange 16 and reactive blue 19 from aqueous solution through batch and fixed-bed adsorption processes.

1.5 Research Objectives

This research is aimed at achieving the following objectives:

1. To optimize waste tea and paper sludge activated carbons preparation parameters (activating temperature, chemical impregnation ratio and activation time) using potassium acetate and fluoride as new activating agents; and functionalize the paper sludge activated carbon.

2. To develop adsorbents from dolomite, chitosan, Kuala Kangsar clay, Ball clay, and Ipoh clay materials.

3. To prepare chitosan-based composite adsorbents of the clay and activated carbon developed.

4. To evaluate the adsorption performance of the adsorbents prepared for acid blue 25, acid blue 29, methylene blue, basic blue 3, cibacron red, reactive orange 16 and reactive blue 19 dyes.

5. To characterize the precursors and adsorbents prepared for elemental analysis, proximate analysis, surface area and porosity distribution, Fourier-transform infrared spectroscopy, surface morphology and x-ray fluorescence.

6. To investigate the applicability of some dynamic models to the fixed-bed column adsorption data of methylene blue and acid blue 29 dyes on the chitosan-based clay and activated carbon prepared.

7. To study the regeneration of adsorbents prepared for repeated cycles of adsorption of acid blue 25, acid blue 29, methylene blue, basic blue 3, cibacron red, reactive orange 16 and reactive blue 19 dyes.

1.6 Scope of study

This research on treatment of reactive, acid and basic dye wastewater using chitosan, clay and activated based adsorbents and has the following scope:

The study consists of investigating the use of potassium acetate and fluoride as new activating agent for preparation of activated carbons from waste tea and paper sludge, use of raw waste tea (RWT), modified waste tea (MWT), calcined dolomite (CD), raw and modified ball, Ipoh and Kuala Kangsar clays as adsorbents. Chitosan based composites with waste tea activated carbon and modified Ipoh clay, and functionalization of paper sludge activated carbon with ethylenediamine will also be prepared. The efficacy of these adsorbents for adsorption of methylene blue (MB), basic blue 3 (BB3), cibacron red (CBR), acid blue 25 (AB25), acid blue 29 (AB29), reactive orange 16 (RO16) and reactive blue 19 (RB19) will be tested.

The precursors and adsorbents surface area, elemental analysis, proximate analysis, scanning electron microscopy, x-ray fluorescence and Fourier transform infrared spectroscopy characterization will be carried out.

The study covers single batch adsorption of MB, BB3, CBR, AB25, AB29, RO16 and RB19 on RWT, MWT, WTC, WTAC, WTAC-CCB, CCB, RBC, RHC, RKKC, MBC, MHC, MKKC, PSLG and FPSLG. And a mixture of RO16 and RB19 will be adsorbed on PSLG and FPSLG in the binary adsorption experiment. Fixed-bed column desorption of MB on MBC, MHC, MKKC, MHC-CB and WTAC-CCB and AB29 on WTAC-CCB will be examined.

Adsorption experiments will focus on investigating the effects of pH 2-12, inorganic salts (sodium chloride, sodium hydrogen carbonate and sodium sulfate) and initial solution control (30-350 mg/L).

Langmuir, Freundlich, Temkin and Redlich-Peterson isotherms models, pseudo-first-order, pseudo-second-order and Elovich kinetic models will be used to analyze the equilibrium and kinetics of the adsorption process. Gibbs free energy, enthalpy and entropy parameters will be determined to evaluate thermodynamics influence on the adsorption processes.

The fixed-bed column adsorption studies covers evaluating the effect of initial influent concentration, adsorbent bed height and influent flow rate on breakthrough curves. Modeling of fixed-bed column study will focus on investigating suitability of Adams-Bohart, Thomas and Yoon-Nelson models for adsorption of MB on MHC-CB and WTAC-CCB and AB29 on WTAC-CCB.

Regeneration of adsorbents used will be experimented for repetition of cycles of adsorption.

1.7 Thesis organization

The thesis is divided into six formations comprising of five chapters and a section for appendix, references and journal publications/conferences.

Chapter one presents the challenges faced with water pollution due to industrialization of Malaysia, and the potentials of the nation’s abundant resources to alleviate the menace economically and efficiently. Also, the problem statement, research objectives, scope of study and the organization of the entire thesis are outlined in this chapter.

Chapter two contains the literature review relaying information on various methods used in tackling dye wastewater with emphasis on adsorption from its fundamental principles. Advancement and challenges in the use of adsorption for dye wastewater treatment are discussed. Batch and fixed-bed column adsorption systems with their various forms of analysis such as isotherms, kinetics, mechanism, thermodynamics and fixed-bed column breakthrough curves are elaborated.

Chapter three comprises the materials and methods unit with detailed description of the experimental work carried out. The materials, equipment and methods used are presented in detail; preparation of various adsorbents used and their characterization procedures are discussed. The adsorbents prepared and adsorbate used for both the batch and fixed-bed column adsorption studies are expatiated. Adsorbent regeneration is discussed and a summary of the research activities is schematically presented in the form of a flow diagram.

Chapter four presents the collated results of chapter three experimental works and elaborated discussion. This includes detailed analysis of optimization data of waste tea and paper sludge activated carbons and characterization (Brunauer-Emmett-Teller, Fourier Transform Infrared spectrometry, thermogravimetric analysis, scanning electron microscopy, X-ray fluorescence, elemental analysis) of all the adsorbents used in this study. Effects of initial concentration, adsorption time, pH, temperature and salts on batch adsorption are discussed. Detailed analysis of isotherms, kinetics, mechanism and thermodynamics of the adsorption system is presented. Fixed-bed column adsorption breakthrough curves are discussed with respect to initial influent concentration, adsorbent bed depth and influent solution flow rate. Modeling of the fixed-bed adsorption systems using Adams-Bohart, Thomas and Yoon-Nelson models are presented. Desorption and regeneration result of the various adsorbents used is presented and discussed.

Chapter five presents conclusions and recommendations drawn from the study with respect to the objectives of this study.

The later section of the thesis contains the appendices, references and lastly, list of conferences and published journal articles emanating from this research.

CHAPTER TWO

LITERATURE REVIEW

This chapter presents a concise literature review of wastewater treatment technologies with emphasis on dye adsorption using different adsorbents. Some common factors that affect the preparation of activated carbons are also reviewed. Fundamental principles for collation and analysis of adsorption experimental data are highlighted. It also presents information on the merits of composites and functionalized adsorbents over mono-sorbents.

2.1 Pollution

The need to reconsider our approaches to controlling or solving pollution problems is eminent due to the alarming rate of pollution and its consequences on the ecosystem. Major forms of pollution include air, light, noise, personal, soil contamination, radioactive, thermal, water and visual. The interconnectivity between all forms of pollution calls for an integrated approach for absolute control of pollution menace even though they come in different forms and have different consequences (Ali et al., 2012).

2.1.1 Water Pollution

The presence in water of chemicals, particulate or bacterial matter that degrades its purity and quality leads to pollution of the water irrespective of the source (ocean, lakes, rivers and underground reservoirs). This action limits the availability of pure water for agricultural, domestic, industrial, public and other uses; therefore, protection of clean surface water has become a security issue as it is imperative for the custodian of natural resources (Cheng and Jia, 2010; Werner et al., 2012). Major culprits to water pollution are sectors that require clean water for their activities and the nature of such pollutants include domestic wastes, industrial effluents, agricultural wastes, radioactive wastes, oil spills, marine dumps, atmospheric depositions; this can be broadly classified into organic, inorganic, acid/base and radioactive pollutants. The textile industry effluent which predominantly constitutes inorganic dye substances is a major culprit (Ali and El-Mohamedy, 2012).

2.1.2 Effect of dye pollution on the environment

Tackling of dye wastewater is one of the most significant environmental sustainability measures that are globally acknowledged (Ali and El-Mohamedy, 2012). This is due to several sources that dye wastewater emanates which include industries such as cosmetics, paper and pulp, pharmaceuticals, electroplating, automobile, tanneries, textile among others. A very low concentration of dye substances in water is visible and impedes penetration of light which hinders photosynthesis activities of aquatic plants. Dye substances are known to have resistance to biodegradability and rather very stable in different weather conditions; half-life of hydrolyzed Reactive blue 19 dye is around 46 years at 25 ^{o}C, pH 7 (Carmen and Daniela, 2012). Exposure of these stable dye substances can cause cancer, jaundice, skin irritation, affects heartbeats, and other numerous health effects (Alver and Metin, 2012).

2.2 Dye wastewater treatment methods

Dye wastewater treatment entails application of known technology to upgrade or improve the quality of the wastewater. The science and engineering principles used to remediate dye pollutants from effluents through activities which have yielded some level of success but not without limitations that hinders their effectiveness and applicability, can be classified into physical, chemical and biological techniques. Since no particular technique is universally suitable in all pollutant removal, it is therefore crucial to understand the wastewater source, typical wastewater composition and the process of generating the waste within the facility so as to know the pretreatment ramifications as well as the method that will be suitable (Ali et al., 2012).

2.2.1 Biological Method

Biological dye wastewater treatment uses bacteria and some microorganisms through assimilation to remove pollutants. This technique has long been employed in wastewater treatment in the chemical industries. These bacteria have ability to provide the required energy needed for microbial metabolism and building block for cell synthesis through the use of diverse wastewater constituents. Through this metabolic activity, pollutants are removed as by products, raw materials for the metabolism and as generated products in chemical processing industries. This technique requires low capital and operating costs when compared with chemical and physical techniques, degrades or destroys organic pollutants and reduces aquatic toxicity. However, the method is ineffective in color removal, not flexible in operation and design, sensitive to diurnal and may require large areas of land for the operation (Fayidh et al., 2011).

2.2.2 Chemical Method

Chemical treatment method of treating dye wastewaters improves water quality through reactions which require certain chemicals (Sabur et al., 2012). Although the method is very effective in treating many industrial wastewater, the process (e.g. Coagulation, flocculation, neutralization) might generate waste (sludge) which will further pose a disposal problem. The need for some chemical reagents (chlorine, aluminum sulfate-alum, lime etc.) and energy for the reaction often incur costs in the process which makes it unattractive (Hassan et al., 2009).

2.2.3 Physical Method

Physical method of dye wastewater treatment consists of processes that do not require rigorous biological or chemical changes but predominantly physical phenomena to upgrade wastewater quality. Adsorption technique is one of the sure, steady, and easy to use processes that have meritoriously stood out in tackling dye pollutants in wastewater (Anbia et al., 2010; Li et al., 2011a). The advent of cheaper, effective and efficient adsorbents that can serve as an alternative to the pricey cosmopolitan commercial activated carbon which can be used without any pretreatment has made adsorption process the major industrial separation technique (Richardson et al., 2002; Crini, 2006).

2.3 Adsorption

Adsorption is a process of attracting and retaining or concentrating ions, atoms or molecules of a fluid to a solid surface. The substances concentrated on the surface are known as adsorbate (sorbate) while the solid surface is called adsorbent (sorbent). The adsorbate molecules are either from gas or liquid phase while the sorbent is in the solid phase (Ali et al., 2012). Adsorbents possess some forces on their discontinuity surface which are able to hold for some time diffused molecules in the fluid phase before adsorption is said to have occurred. The molecules or atoms naturally occurring on such surfaces have a tendency of attracting other molecules or atoms from the surrounding with the aid of their intrinsic force. London Dispersion Forces (LDF) are another type of Van der Waals force which exists between molecules, they are additive in nature and increases with the number of molecules. The LDF is short ranged and as such sensitive between adsorbate molecules and adsorbent surface. Activated carbon is said to have the strongest physical adsorption forces compared with any material known to mankind because it possesses this type of short range and additive LDF. The strength of this force or interaction dictates the ease or difficulty of adsorption or desorption of adsorbate for adsorbent recovery (regeneration) (Guļāns, 2012).

Adsorption process is now a major industrial separation technique as against its limited use as a physical - chemical process in the past four decades, this is due to the simplicity of the design, high efficiency, low cost, ease of operation and does not form harmful substances (Richardson et al., 2002; Arami et al., 2005; Crini, 2006). The sorption can be categorized as either physisorption or chemisorption depending on the nature of sorbate-sorbent forces of interaction. If van der Waals or electrostatic forces are responsible for the interaction, then the sorption process is physical. The polar nature of both sorbate and sorbent determines the attraction between them.

Physical adsorption supports layers of sorbate on the surface of a sorbent and is non-specific on sorbates, sensitive to temperature, reversible, kinetically fast and has low heat of adsorption (< 20 kJ/mol) which is equivalent to heats of condensation (2.1-20.9 kJ/mol) (Saha et al., 2010). When sorbate-sorbent interaction leads to a chemical reaction or formation of covalent bond, chemisorptions is said to have occurred. The formation of covalent bonds is due to the larger heat of adsorption (80-200 kJ/mol) involved and makes the process kinetically slower. The process only supports a layer (monolayer) of sorbate on adsorbent surface and is mostly irreversible (Chen and Chen, 2009; Awala and El Jamal, 2011).

2.4 Adsorbents

Adsorbent is the heart of adsorption system or the main active agent on which adsorption of fluid components occurs. The commonest shapes of commercial adsorbents are as spheres, pellets or granules of irregular shapes. Some characteristics or qualities of good adsorbents for dye adsorption includes large internal surface area, mechanical stability, kinetics, accessible pore size, adequate pore volume, selectivity, compatibility, ease of regeneration, affordability and availability (Ali et al., 2012).

2.4.1 Classification of dye adsorbent

Several adsorbents are used for adsorption of dye molecules and they can be classified as organic and inorganic according to their source material. Most inorganic materials such as some minerals and synthetic materials have been used as adsorbents with various levels of efficiency; examples of inorganic sorbents are: some oxides (CaO, MgO, ZnO), metal chlorides ($CaCl_2$), silicates ($MgSiO_3$), kieselguhr (diatomite), dolomite ($AB(CO_3)^2$ where A is either calcium, barium and/or strontium and the B is either iron, magnesium, zinc and/or manganese; sulphates ($CaSO_4$), clay (montmorillonite, kaoline), pillared clays and so on (Duffy et al., 2006). A summary of important commercial adsorbents and their areas of application are shown in Table 2.1.

2.4.2 Activated carbon

Activated carbon is an amorphous high porous carbonaceous material and an extended inter particulate surface area, possessing both hydrophilic surface functional groups and hydrophobic graphene layer making it useful for both adsorption and catalytic applications (Bansal and Goyal, 2005). Activated carbon is usually obtained in granules and powdered form but for some special applications; it can be produced in fibrous, spherical and even cloth forms.

Table 2.1 Important adsorbents from various materials (Noble and Terry, 2004; Bhatnagar and Sillanpää, 2010)

Adsorbent	**Application**
Activated carbon (hydrophilic and hydrophobic)	Removal of organic and inorganic pollutants in aqueous and gaseous phase.
Activated alumina (hydrophilic)	Drying of gas streams, organic solvents, transformer oils, removal of HCl from hydrogen, and has higher capacity than zeolite molecular sieves
Silica gel (hydrophilic)	Drying of gas streams, transformer oils and removal of hydrocarbon from gases; desiccant in packings, control of dew point in natural gas and double glazing
Zeolite molecular sieves (hydrophilic)	Removal of water from azeotropic mixtures, separation of air (oxygen), argon, normal from branched paraffin based on polarity and geometry (molecular size)

It can be produced in various pore sizes and surface area (300-1500 m^2/g) depending on the area of application. Bigger sorbate sizes and slower diffusion rates in liquid phase usually require larger pore size distribution while smaller pore size sorbent are used for gas phase applications. Activated carbon is prepared by partial combustion or pyrolysis of carbonaceous materials (wood, coal char, almond, coconut, or walnut shells etc.). Applications of activated carbon adsorbents are very versatile, these include industrial and wastewater treatment (Bhatnagar and Sillanpää, 2010), air pollution remediation (Chen et al., 2012), pharmaceuticals (Delgado et al., 2012), food processing (Nasehi et al., 2012), oil and gas industry (Ali et al., 2012), hydrometallurgy for recovery of gold, silver (Soleimani and Kaghazchi, 2008), and a list of others.

2.4.2(a) Preparation of activated carbon

Two main stages are involved during the preparation of activated carbon, they are carbonization and activation processes. The carbonization stage is aimed at alleviating the precursor of impurities so as to enhance the quality of the resulting char development during the activation process.

Carbonization

This involves removal of moisture content, volatile organic materials (alcohols, carboxylic acid, and phenol) or non carbon elements like sulfur, nitrogen, oxygen and hydrogen from the precursor through pyrolysis in an inert atmosphere or reducing gas (N_2, H_2). Heating of the furnace may be controlled for higher yield and better quality of char produced; from room temperature to 200 ^{o}C, then to 400-500 ^{o}C (Wereko-Brobby and Hagan, 1996; Lozano-Castelló et al., 2001; Yuen and Hameed, 2009). The resulting char undergoes irregular arrangement of its residual aromatic sheets resulting to interstices between the carbon materials. Some residual tarry materials which ideally should have been completely removed occupies this spaces created; this blockages often makes carbonized chars to have smaller pore sizes or become non porous (Bansal and Goyal, 2005).

Activation

This involves the conversion of carbon materials (char) into porous substance with increased surface area by clearing the char pore blockages through a gasification process in the presence of carbon dioxide or steam or activating agent or