PRODUCTION OF RICE HUSK ACTIVATED CARBON FOR IMPROVING URBAN DRY WEATHER FLOW QUALITY AT SUNGAI PINANG BASIN

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by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
BOD	Biological oxygen demand
CCD	Central composite design
CCD	Central composite design
COD	Chemical oxygen demand
DID	Department of Irrigation and Drainage
DOC	Dissolved organic carbon
DOE	Department of Environment
EA	Elemental analyzer
FTIR	Fourier Transformed Infrared
GAC	Granular activated carbon
IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
MTZ	Mass transfer zone
RSM	Response surface methodology
SEM	Scanning electron microscopy
TGA	Thermogravimetric analyzer
TTS	Total Suspended Solid
US	United State
USEPA	United States Environmental Protection Agency
WQI	Water Quality Index

PENGHASILAN KARBON TERAKTIF BERASASKAN SEKAM PADI UNTUK MEMPERBAIKI KUALITI AIR ALIRAN PERBANDARAN MUSIM KERING DI KAWASAN TADAHAN SUNGAI PINANG

ABSTRAK

Kajian ini mengkaji potensi sekam padi yang terdapat di Malaysia sebagai bahan asas untuk penghasilan karbon teraktif yang dapat digunakan untuk menyingkirkan bahan pencemar kuprum (II), zink (II) dan keperluan oksigen kimia dalam larutan akues. Bahan pencemar ini terdapat dengan kepekatan yang tinggi di kawasan tadahan Sungai Pinang terutamanya pada musim aliran kering. Dua jenis karbon teraktif telah dihasilkan iaitu melalui proses pengaktifan fizikal dan kimia. Keputusan yang terhasil daripada rekabentuk ujikaji mendapati suhu pengaktifan, tempoh pengaktifan dan nisbah jerap bahan kimia mempengaruhi berat karbon teraktif yang dihasilkan serta kebolehan menjerap bahan-bahan pencemar. Karbon teraktif yang dibangunkan adalah berliang meso dengan keluasan permukaan yang tinggi dan mempunyai purata saiz diameter liang lebih besar daripada 2.2 nm. Imbasan mikroskop elektron membuktikan kedua-dua karbon teraktif tersebut mempunyai struktur liang yang homogen. Analisis spektroskopi inframerah pengubahan Fourier mendapati terdapat pelbagai kumpulan berfungsi pada permukaan karbon teraktif. Kesan penjerapan bahan pencemar pada kepekatan awal (10-50 mg/L untuk kuprum (II) dan zink (II) dan 100-500 mg/L untuk keperluan oksigen kimia), tempoh sentuhan dan pH larutan, yang berbeza oleh karbon teraktif telah dikaji. Kajian penjerapan pada keseimbangan untuk semua bahan pencemar oleh karbon teraktif disesuaikan dengan isoterma Langmuir dan Freundlich. Didapati data-data analisis adalah lebih sesuai dengan model Freundlich. Data kinetik kemudiannya diuji dengan kajian pseudo aturan pertama dan pseudo aturan kedua. Semua kinetic penjerapan didapati mengikut pseudo aturan pertama kecuali kuprum (II) untuk karbon teraktif yang terhasil melalui pengaktifan kimia. Ujikaji turus dijalankan untuk mengkaji perlakuan takat bolos untuk bahan pencemar kuprum (II), zink (II) dan keperluan oksigen kimia oleh kedua-dua karbon teraktif. Didapati penjerapan maksimum untuk karbon teraktif yang terhasil melalui pengaktifan fizikal adalah 64.1, 55.0 dan 1204.0 mg/L pada kepekatan awal pada kepekatan awal kuprum, zink dan keperluan oksigen kimia masing-masing pada 10, 10 dan 500 mg/L pada aliran tetap 20 mL/min dengan ketinggian turus 3 cm. Kajian juga mendapati penjerapan maksimum kuprum (II), zink (II) dan keperluan oksigen kimia oleh karbon teraktif yang terhasil melalui pengaktifan kimia adalah masing-masing pada 75.3, 105.0 dan 2215.7 mg/g. Proses penjerapan disimulasikan menggunakan model empirik dan didapati model Thomas adalah bersesuaian untuk ujikaji ini. Rumusannya, kajian ini membuktikan bahawa sekam padi boleh ditransfomasikan kepada karbon teraktif yang dapat digunakan untuk merawat air yang tercemar.

PRODUCTION OF RICE HUSK ACTIVATED CARBON FOR IMPROVING URBAN DRY WEATHER FLOW QUALITY AT SUNGAI PINANG BASIN

ABSTRACT

This study investigates the potential use of rice husk that available in Malaysia, as the precursor for the preparation of activated carbon which can be applied for the removal of pollutants namely; copper (II), zinc (II) and chemical oxygen demand (COD) from aqueous solution. These pollutants exist at high level at Sungai Pinang basin, especially during dry weather flow season. Two types of activated carbons were prepared by physical (P-RHAC) and chemical (C-RHAC) activation. The experimental design results revealed that activation temperature, activation time and chemical impregnation ratio (IR) were important factors influencing the activated carbons yields and adsorption performance for pollutants. The activated carbons prepared were mesoporous with high surface area and average pore diameter larger than 2.2 nm. Scanning Electron Microscopy (SEM) analyses proved that the activated carbon samples demonstrated homogeneous type pore structures. Fourier Transform Infrared (FTIR) analyses revealed the presence of various functional groups on the activated carbon surfaces. The effects of pollutants adsorption at various initial concentration (10-50 mg/L for copper (II) and zinc (II) and 100-500 mg/L for COD), contact time and solution pH were studied. Adsorption equilibrium data for adsorption of all pollutants onto activated carbons were fitted to the Langmuir and Freundlich isotherm models. It was found that the data for all pollutants could best be represented by the Freundlich isotherm model. The kinetic data were tested with pseudo-first-order and pseudo-second-order models. The adsorption kinetic was observed to follow the pseudo-first-order model for the systems except for copper (II) removal using C-RHAC. The column experiments were carried out to investigate the breakthrough capacity of copper (II), zinc (II) and COD adsorption on P-RHAC and C-RHAC samples. The observed maximum uptake of copper (II), zinc (II) and COD onto P-RHAC was found to be 64.1, 55.0 and 1204.0 mg/g at initial concentration of 10, 10 and 500 mg/L, respectively at a constant flow rate and bed height of 20 mL/min and 3 cm. Meanwhile, the maximum uptake of copper (II), zinc (II) and COD onto C-RHAC was found to be 75.3, 105.0 and 2215.7 mg/g, respectively. The adsorption process was simulated using empirical models and it was found that Thomas model gives the best fit for this study. In sum, this study proves that the abundance rice husk could be transformed as activated carbon in which could be used to treat polluted water.

CHAPTER ONE

INTRODUCTION

1.1 Urbanization

Urbanization can be described as an increase in human population density coupled with increased energy use and extensive alteration of the landscape (McDonnell and Pickett, 1990). The impacts of urbanization extend over large areas eventhough the areal percentage of urban land inregional land-cover maps is typically quite small (Homer *et al.*, 2007). Impervious surfaces lead to higher amounts of runoff, increasing sediment and nutrient loads to surface waters, and these effects can be measured well downstream from where the built environment ends (Paul and Meyer, 2001).

Urbanized areas are defined as densely settled territories that contain 50,000 or more people. Urban clusters are smaller than urbanized areas, with population between 25,000 and 50,000 people. Densely settled territory is defined as core census block groups with population densities of 1000 peoples per square mile or more, and surrounding census blocks with population densities of 500 peoples per square mile or more. Urbanization is one of the key issues in China's economic development. Rapid urbanization has caused much pressure on energy, resources and environment. The emerging environmental issues attributed to urbanization, such as air pollution, water pollution, industrial pollution, traffic, vehicle-generated pollution, solidwaste and carbon emission are highly concerned as China continues developing.

Malaysia is presently going through a period of rapid development to fulfill a vision of a fully developed nation by 2020. The size of the urban areas has increased to accommodate increased urban population and the activities that power the economic engines for country's development. These developments have brought about several positive results such as economic improvements and alleviation of poverty. Nevertheless, inadequately controlled development has had significant adverse impact on the environment, such as flash flooding, erosion, mudflows and sedimentation, slope failure, water pollution and ecological damage, increased floatables and debris flow and depleting water resources. A sustainable response to the issue is urgently required. To address the problems, the Department of Irrigation and Drainage Malaysia (DID) has successfully prepared a new manual called *"Stormwater Management Manual for Malaysia"*. Based on the concept of source control, the new manual incorporates comprehensive planning and design procedure and guidelines for the controlling discharge and pollution has been implemented (DID, 2005).

1.2 Urban wastewater

Urbanization increases the population member quantity and urban life activities. This can dramatically bring about changes in runoff quality within catchments. Runoff in urbanized areas washes down contaminants accumulated on land surfaces into the drainage system before they are transported to receiving waters. Urban runoff may contain sediment and other polluting substances such as suspended solids, heavy metals (copper (II) and zinc (II)), nutrients, organic and bacteria. More frequent discharges can intensify channel erosion and increases sediment. Wastewater form residential, commercial and industrial areas causes foul smell, especially in the presence of garbage, and deteriorate the quality of storm water and polluted the existing rivers system or water receiver (DID, 2006).

1.3 Activated carbon adsorbent

Liquid phase adsorption using activated carbon has become one of the most popular methods for removal of various pollutants from wastewaters, owing to its efficiency in the removal of pollutants. Activated carbon adsorption has been known as one of the best available environmental control technologies (Moreno-Castilla, 2004). This adsorbent has the advantage of exhibiting high adsorption capacity due to its high specific surface area, adequate pore size distribution and relatively high mechanical strength (Mohanty *et al.*, 2005).

Despite their prolific usage, certain problems with the high costs of commercial activated carbon have limited their applications. The high production cost is mainly due to the expensive and non-renewable starting materials such as bituminous coal, lignite and petroleum coke, which is a major economic consideration. Therefore, this has prompted a growing research interest in the production of activated carbon from abundant renewable and low cost materials such as agricultural by-products.

Any carbonaceous material can be employed to obtain activated carbon. Biomass is produced from organic materials, either directly from plants or indirectly from industrial, commercial, domestic or agricultural by-products. Biomass falls into two main categories:

i) Woody biomass includes forest products, untreated wood products, energy crops and short rotation coppice, which are quick-growing trees like willow.

ii) Non-woody biomass includes animal waste, industrial and biodegradable municipal products from food processing and high energy crops.

One significant problem faced by the agricultural industries currently is the managing of the by-products and wastes produced. The disposal of the by-products in large quantity is difficult and expensive to the industries. However, if it is not attended properly, it will cause environmental pollution as well as harboring pests and diseases. This will result not only in wastage, but also severe economic set back to the industries and the country. Therefore, to make better use of these abundant agricultural by-products, they need to be utilised effectively to the point that they can be considered as valuable products that will serve as raw materials to support another industry. For this purpose, it is proposed to convert the negative value agricultural by-products into valuable products such as activated carbon. The use of agricultural wastes for the production of activated carbon is very attractive from the point of view of their contribution to decrease the cost of waste disposal, hence helping in environmental concern.

1.4 Problem statement

The expected increase of paddy production in Malaysia is expected to increase from the existing 2.4 million tonnes to 3.2 million tonnes in 2010 (BERNAS, 2006). At this stage, the waste-by-product that is rice husk will also increase dramatically. It is well known that most of the rice husk has no economic value and in fact cause a serious problem to local environment. Thus, finding an alternative and effective approach must be developed to utilize the rice husk as profitable materials.

Activated carbon adsorption has been proved to be superior as compared to other techniques for wastewater treatment due to its simplicity of design, high efficiency and ease of operation. However, the prolific use of commercial activated carbon is restricted by the high costs due to the use of non-renewable and expensive starting materials such as bituminous coal to produce the activated carbon. An attempt was made to prepare activated carbon from rice husk, which is a renewable, abundant and low cost precursor. Moreover, the use of rice husk represents a potential source of adsorbents which will contribute to solving the urban wastewater pollution problem in Malaysia. This will turn negative-value wastes into useful, value-added products, hence solving the waste disposal problem and secondly, the costs of activated carbon production will be reduced.

Sungai Pinang is an important river in state of Penang, Malaysia. The river flows through the town of Georgetown and forms one of the important features of the area. Despite its importance, the Sungai Pinang condition has degraded over the years in terms of pollution, river environment and ecosystem. Heavy metals pollutant in urban wastewater developed septic condition and harmful effects on human. Heavy metals such as zinc (II) and copper (II) are classified as priority pollutants. The presence of any of these metals in excessive quantities will interfere with many beneficial uses of water because of their toxicity; therefore, it is frequently desirable to measure and control the concentrations of these substances.

This study aims to investigate the feasibility of preparing mesoporous activated carbon from agricultural by-product abundantly available in Malaysia, namely rice husk for application in removing COD, zinc (II) and copper (II) from urban wastewater.

1.5 Research objectives

This research has four (4) objectives, which are follows:

(i) To prepare and characterize activated carbon from rice husk using physical activation and chemical activation.

(ii) To determine the optimum parameters for activated carbon preparation conditions by using response surface methodology.

(iii) To study the effect of adsorbate initial concentration, contact time, solution pH, isotherms and kinetics for removal of COD, zinc (II) and copper (II) onto activated carbon prepared using batch adsorption studies.

(iv) To establish the breakthrough curves of removal of COD, zinc (II) and copper (II) onto activated carbon prepared in fixed bed column.

1.6 Organisation of the thesis

There are altogether five chapters in this thesis. Chapter One (Introduction) presents an overview on the current scenario on urban wastewater pollution problem in the world and specifically in Malaysia and the needs to produce activated carbon from agricultural by-products abundantly available in Malaysia. The research objectives of the present study and the overall content of this thesis are summarized in the last section of this chapter.

Chapter Two (Literature Review) elaborates the quality of urban wastewater at different weather condition in particular river basin and important information on activated carbon adsorption technology for urban wastewater quality improvement as well as various precursors and activation methods used by previous researchers for preparation of activated carbon. Information on optimization of operating conditions for activated carbon preparation and characterization of activated carbon are also discussed in details. The last section explains the adsorption isotherms, kinetics and thermodynamics for batch adsorption system as well as the breakthrough characteristics of fixed-bed adsorption system.

Chapter Three (Materials and Methods) describes in detail all the materials and equipments used in the present study, including the experimental rig and schematic diagram. This is followed by the experimental procedure which includes activated carbon preparation, experimental design, model fitting and statistical analysis, activated carbon characterization and batch and fixed-bed adsorption studies.

Chapter Four (Results and Discussion) presents the results obtained from the experimental design used to prepare activated carbon from rice husk. The optimization results based on the pollutants removal as well as activated carbon yield are also presented and discussed. The batch adsorption studies of COD, zinc (II) and copper (II) onto the activated carbon followed by fixed-bed adsorption studies were included. Chapter Five (Conclusions and Recommendations) concludes the findings from the present research. The conclusions reflect the achievements of the listed objectives which were obtained throughout the study. Finally, recommendations for future research are listed.

CHAPTER 2

LITERATURE REVIEW

2.1 Water and life

Water is a precious resource, which we depend on for our live hood. Nearly 97% of the world's water is salty or undrinkable. Another 2% is locked in ice caps and glaciers. That leaves just 1% for all our humanity's needs for its agricultural, residential, industrial, community and personal needs. Good quality water is essential to maintain human life and to protect our natural eco-systems used from inland rivers, lakes and groundwater for drinking, horticulture, agriculture, industry, recreation and wetlands maintenance. More than 90% of our water supply comes from rivers and streams, which originate in our mountains and highland forests. With rapid development and increasing human populations, the requirements for water have increased together with greater demands for higher water capacity and quality. However, human activities have brought degradation of our water resources. These include the clearing of forests and natural vegetation for agriculture activities and timber harvesting and excessive use of fertilizers and pesticide with the development of agriculture plantations.

Urban developments such as residential, commercial and industrial have also resulted in the production and concentration of waste products, which end up as pollutants in the rivers. These will eventually lead to the deterioration of river water quality, particularly from point source pollutants. Discharge of untreated wastewater raw sewage and the disposal of the city effluent into the drain also could cause the degradation of our river water quality (Adinata *et al*., 2000).

2.2 Major types of urban water pollutants

Urban stormwater pollution and most pollution in combined sewer overflows originate from point diffuse sources. The processes controlling storm water quality, are rather complex, as shown in Figure 2.1. In contrast to point source pollution, such as industrial and municipal treatment plant outfalls, these sources of pollution are numerous and their contributions are difficult to quantify. Diffuse pollution is a hydrologic process that closely follows the statistic character of rainfall, and must be evaluated similarly (UNESCO, 1987). Urban storm water runoff may transport many undesirable pollutants. The pollutants present, and their concentrations, are a function of the degree of urbanization, the type of land use, the densities of automobile traffic and animal population, and the degree of air pollution before rainfall. Major pollutant types are classified as suspended sediments, oxygen-demanding substances, heavy metals, toxic organics, nutrients, bacteria, petroleum-based substances, acids and humic substances.

Domestic wasters have been identified as the dominant source of organic pollutants, pathogens and suspended solids, especially where waste is discharged directly to rivers, while livestock and agro-based industries have been identified as secondary sources. Effluents from a wide range of industries have been identified as sources of chemical pollution in urban catchments where most of the industrial areas are located. Table 2.1 describes the typical pollutants, sources and their impacts (DID, 2006).

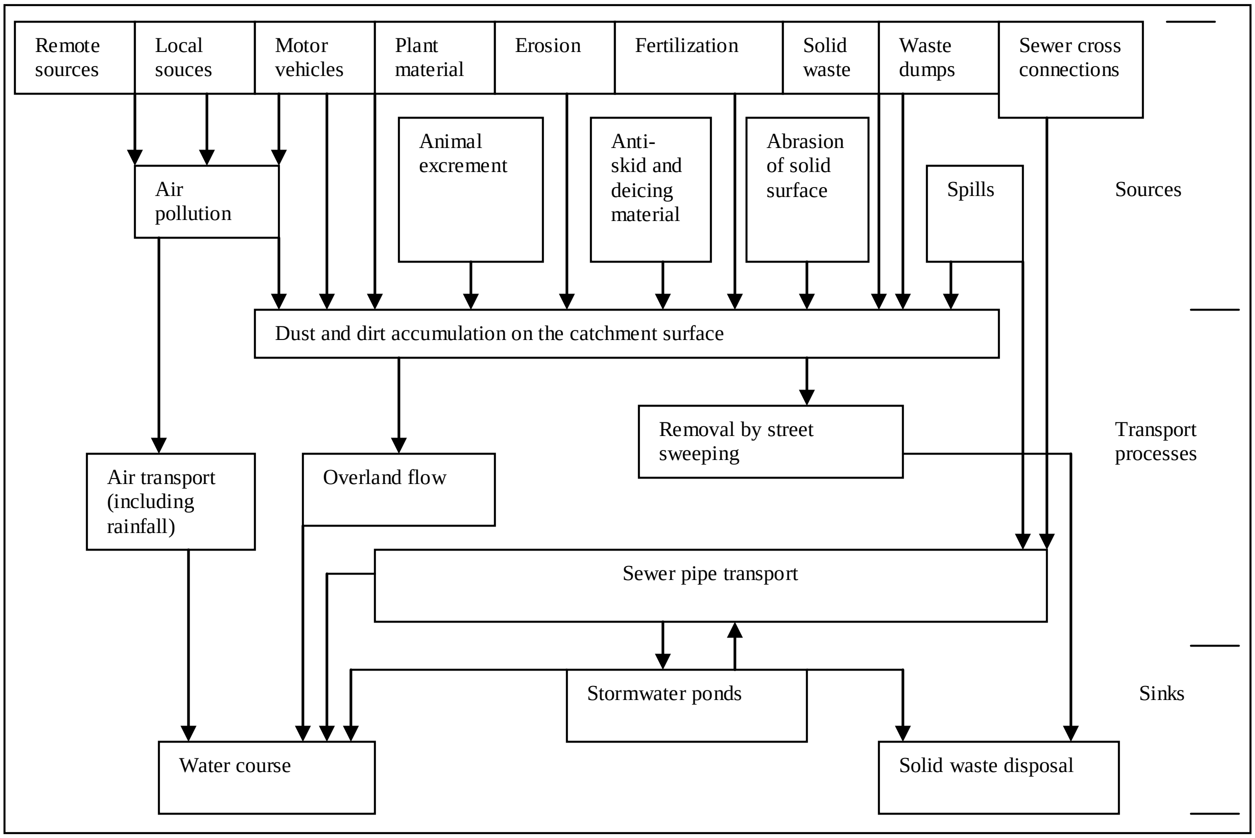

Figure 2.1: Sources of pollutants in stormwater and pollutant pathway (UNESCO, 1987)

2.3 Processes that generate urban pollutants

2.3.1 Atmospheric deposition

Atmospheric deposition is generally divided into wet and dry deposition. Wet deposition is closely related to the levels of atmospheric pollution by traffic, industrial and domestic heating, and other sources. Urban rainfall is generally acidic, with below 5 pH units. The elevated acidity of urban precipitation damages pavements, sewers, and other building materials. Particles are then washed off the surface by storm water. Dry atmospheric deposits are fine particles originating from a distance (fugitive dust) or locally (traffic on unpaved roads, construction and industrial) sources. Dust fall rates vary from region to region. Rural dust falls depend on soil condition; urban dust falls are more related to local air pollution (Alam *et al.*, 2009).

Table 2.1: Typical pollutants, sources and related impacts (DID, 2006).

Typical pollutants	Sources	Related impacts
Nutrients : Nitrogen, phosphorous	Urban runoff, animal waste, fertilizers, failing septic systems.	Algae growth; reduced clarity; lower dissolved oxygen; release of other pollutants
Oxygen consuming: BOD, COD, SOD.	Sullage, sewage, industrial wastewater, wet market.	Reduced dissolved oxygen in the river, fish kill
Solids; Sediment	Construction sites, other disturbed and/or-vegetated lands, eroding banks, road sanding, urban runoff.	Increased turbidity; reduced clarity; lower dissolved oxygen; deposition of sediments; smother aquatic habitat including spawning sites; sediment and benthic toxicity
Pathogens : Bacteria, viruses	Animal waste, urban runoff, failing septic systems.	Human health risks via drinking water supplies; contaminated shellfish growing areas and swimming beaches
Heavy Metals : Lead, copper, cadmium, zinc, mercury, chromium, aluminium	Industrial processes, normal wear of automobile brake lines and tires, automobile emissions.	Toxicity of water column and sediment: accumulation in aquatic species and through food chain
Hydrocarbons : Oil and grease, PAHs (Naphthalene, pyrenees)	Industrial processes, automobile wear, automobile emissions, automobile fluid leaks.	Toxicity of water column and sediment: accumulation in aquatic species and through food chain
Organic : Pesticides, PCBs, synthetic chemicals	Pesticides (herbicides, insecticides, fungicides, rodenticides), industrial processes	Toxicity of water column and sediment: bioaccumulation in aquatic species and through food chain

2.3.2 Erosion

Erosion of construction areas represents the largest source of sediments in urban runoff. Reported unit loads of sediment from urban construction sites ranged from 12 to

500 tonnes/half-year. Furthermore, building activities generate other pollutants such as chemicals from fertilizers and pesticides, petroleum products, construction chemicals (cleaning solvents, paints, acids and salts), and various solids. Grading exposes subsoil, increasing surface erosion due to storm water runoff. Erosion of urban lawns and park surfaces is usually low. Exceptions are open, unused lands, and construction sites. Soil is a source of suspended solids, organics, and pesticide pollution.

2.4 Urban development in Malaysia

Malaysia is presently going through a period of rapid development to fulfill a vision of fully developed nation by 2020. The size of the urban areas have been enlarged to accommodate increasing urban population and the activities that power the economic engines for the country's development. These developments have brought about several positive results such as economic improvements and alleviation of poverty. Nevertheless, inadequately controlled developments has had significant adverse impact on the environment, such as flash flooding, erosion, mudflows and sedimentation, slope failure, water pollution, ecological damage, increased floatable debris and depleting water resources.

Management of the quantity and quality of stormwater runoff urban areas is a complex task which has become an increasingly important environmental issue for urban communities. The increasing importance of urban stormwater management has been due to the increased environmental awareness of urban communities and recognition that urbanization of a catchment impacts on both quantity and quality of the aquatic environment. In point source pollution, pollutants are discharged from a concentrated and recognizable source while in non-point source pollution, water flows on the surface dissolving and washing away pollutants and soil sediment along its path and finally discharging into receiving waters. River pollution from non-point sources, such as agricultural activities and surface runoff is actually one of the major threats to surface and groundwater quality at the catchment scale. Agricultural water pollution is becoming a major concern not only in developed region such as the European Union but also in any developing countries. The intensification of agricultural practices, in particular the growing use of fertilizers and pesticides, and the specialization and concentration crop and livestock production, has had an increasing impact on water quality. Controlling water pollution from agricultural is made difficult by its particular nature. In most circumstances, agricultural pollution occurs over wide area, and its sources are diffuse and difficult to identify.

Concern for the quality of urban runoff originated when some engineers and researches observed that urban surface runoff accounted for most of the negative effects observed in rivers, lakes and other receiving waters downstream or within urban areas. These negative effects included acceleration in the erosion of river banks, devastation of river habitats and a decline in receiving water quality. It was also observed that discharge of a large storm event may shock the receiving water body many times greater than an ordinary sanitary effluent load (Alam et al., 2009).

2.4.1 Water quality status of the peninsular Malaysian rivers

A total of 120 river catchments covering an area of 654,708 km^2 for the whole country has been studied (DID, 2006). Table 2.2 shows the breakdown of major stations in various states.

Table 2.2: Breakdowns of major stations in various states (DID, 2006)

Area	Monitoring station	River catchment	Catchment area (km^2)
Peninsular Malaysia	750	77	166,378
Sabah	74	21	363,887
Sarawak	102	22	124,443
Total	926	120	654,708

In 2004, water samples were taken from 926 monitoring stations located in all the states of Malaysia. Figure 2.2 shows the water quality map of Peninsular Malaysia status. In summary, the overall quality status of the 120 Malaysian rivers in 2002 based upon water quality index (WQI) determination 9 rivers (8%) were found to be polluted, 53 rivers (44%) were slightly polluted while remaining 58 rivers (48%) are clean.

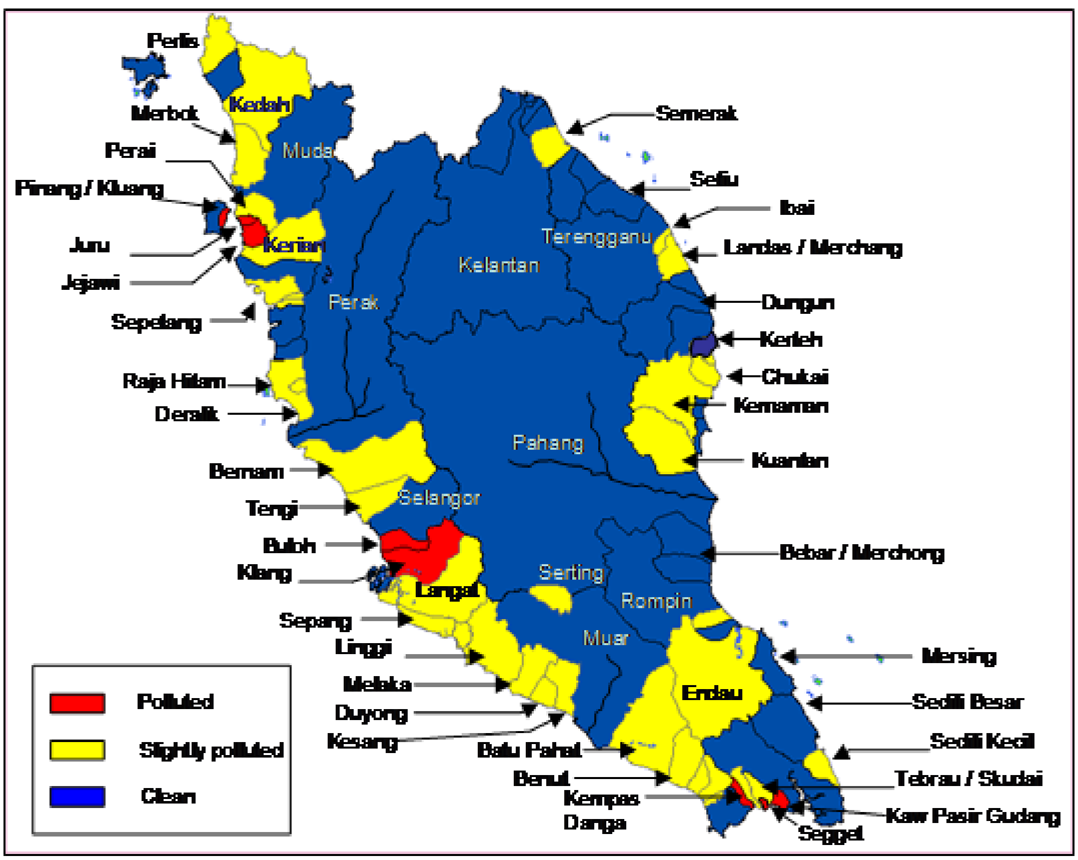

Figure 2.2: River water quality status for river basins of Peninsular Malaysia (DOE, 2002)

This shows that quality of urban flow is keep polluted and finally deteriorate nearby water receiver (river) and avoids any activities as it can be considered hazardous upon contact. It should be reiterated that the increasing level of pollutants in urban flow will remain an issue affecting our well being if proper attention is not given right at very source of the urban flow pollution problems. The development of adequate and economic local remediation are essential to remedy urban flow pollutions generated from urbanized area that to ensure our water resource and river environment do not deteriorate any further.

2.4.2 Urban weather flow quality

The Department of Environment (DOE) has established a uniform effluent discharge standard for the country (DOE, 2001). Standard A is stipulated for areas upstream of water intake area mean while Standard B applies for the other areas. The standard specifies the maximum concentration for 22 parameters and allowable range of pH value. From 22 parameters specified, 11 of them are considered as high toxicity. These elements are mercury, cadmium, chromium, hexavalent, arsenic, cyanide, lead, chromium, copper, manganese, nickel and tin.

Managing urban weather flow has been of primary concern for many municipalities as a means of improving receiving water quality and to meet water quality regulations (McPherson *et al.*, 2005). Dry weather urban runoff occurs without measurable precipitation, resulting from groundwater inflow, permitted discharge, and human activities including car washing, paddy irrigation, street washing, and construction activities involving water use. As such, urban storm runoff has been recognised as a prime cause of non-point source discharge such as heavy metals, polycyclic aromatic hydrocarbons, nutrients and other toxic compounds of anthropogenic origins (Characklis and Wiesner, 1997). Ho *et al.* (2003) found that the water quality in Hong Kong river was slightly better during the wet season because of the flushing effect of huge water flow.

Heavy metals lack transformation or decay mechanisms, and thus can accumulate in environmental media (e.g. sediment layers) or tissues of living organisms through the food chain, as a result, they become a potential pollutant source and deteriorate ecosystem integrity. In urban runoff, the main source of heavy metals is vehicle traffic and the metal species typically found include lead (Pb), zinc (Zn), iron (Fe), copper (Cu), cadmium (Cd), chromium (Cr) and nickel (Ni) (USEPA, 1995). Rivers are a dominant pathway for metals transport and trace metals may become significant pollutants of many small riverine systems. The existence of heavy metal in aquatic environments has led to serious concerns about their influence on plant and animal life.

Ecotoxicological effects of heavy metals are well understood and have been a global concern for environmentalists. Due to their accumulation through food chain and persistent in nature, it is necessary to remove toxic heavy metals from urban flow. Metals are non-biodegradable and have great environmental, public health and economic impacts. Beyond the permissible limits, they are generally toxic and some are even hazardous (Calace *et al.,* 2002). For example, zinc is considered as an essential element for life and act as a micronutrient when present in trace amounts. However too much zinc can be harmful to health. Zinc (II) is reported to be toxic beyond permissible limits. Symptoms of zinc toxicity include irritability, muscular stiffness, loss of appetite and nausea. The metal is further reported to be bioaccumulated into flora and fauna creating ecological problems. Zinc is present in high concentration in wastewater of pharmaceuticals, galvanizing, paints, pigments, insecticides, cosmetics, etc. that causes serious problem to the environment. Conventional technologies for the removal of heavy metal such as adsorption, electrolysis, ion exchange and reverse osmosis are often neither effective nor economical.

Numerous metals such as copper have toxic effects on human and environment (Taty-Costodes *et al.*, 2005). Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. Various technologies exist for the removal of such metals. They include filtration, chemical precipitation, ion exchange, adsorption using activated carbon, electrodeposition and membrane process. All these methods are generally expensive. A low-cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry. At present, there is a growing interest in using low-cost, commercially available materials for the adsorption of heavy metals.

Among the physico-chemical treatment process adsorption is found to be highly effective, cheap and easy to adapt. Activated carbon in most cases has been used as an adsorbent for reclamation of municipal and industrial wastewater for almost last few decades. But the high cost of activated carbon has inspired the investigators especially in developing countries like India to search for suitable low-cost adsorbents. As a result, recent research has focused on the development of cost effective alternatives using various natural sources and industrial wastes (Folke *et al.*,1997)

Metal nutritional requirements (Cu, Fe, etc.) differ substantially between species or elements, and optimum ranges of concentrations are generally narrow, severe unbalances on metal proportions caused by exposure to elevated concentrations can cause death for organisms (Power *et al.*, 1999). Other elements (Pb, Cd, Hg, etc.) exhibit extreme toxicity even at trace levels and do bioaccumulate, thus necessitating their constant monitoring. Determination of the total metal levels is useful for studies dealing with heavy metal pollution in some areas but does not provide enough information about their impact on the environment (Alonso *et al.*, 2004). During their transport, the trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena (Dassenakis *et al.*, 1997), which affect their behaviour and bioavailabilty. Regarding these processes, the dissolved organic carbon (DOC), originating from natural organic matter plays a key role.

Urban catchment is very flourishing with the attendant large volumes of highly contaminated effluent wastewater containing oils, suspended and dissolved solids, toxic, biodegradable and non-biodegradable matters and alkaline substance (Gao *et al.*, 1995) that poses serious environmental problems because of their color and high organic matter (Geogiou *et al.*, 2003). However, this existing wastewater treatment scheme is inadequate to produce treated wastewater that meets the local discharge limits, especially in terms of chemical oxygen demand (COD) (Dhass, 2008). Biological treatment process is generally efficient in biological oxygen demand (BOD), reduction and screening also addresses the suspended solids removal to a reasonable extent, but the dissolved non-biodegradable complex organic is a main challenge to the existing treatment units (Kumar *et al.*, 2008) Conventionally, adsorption processes using activated carbons are widely used to remove color and heavy metal pollutants from wastewaters. However, commercially available activated carbon is becoming too expensive. In the last few years, special emphasis has been placed on the preparation of activated carbons from several agricultural by-products due to the growing interest in low-cost activated carbons from renewable sources, especially for application in treatment of COD.

2.4.3 Existing treatment technologies for polluted urban flow

A number of different treatment and disposal or reuse alternatives are then developed and evaluated, and the best alternative is selected. It will therefore be helpful at this point to review the classification of the methods used for wastewater treatment as mentioned in Table 2.3 (Metcalf and Eddy, 1991). The contaminants in wastewater are removed by physical, chemical, and biological means. The individual methods usually are classified as physical unit operations, chemical unit processes, and biological unit processes. Although these operations and processes occur in a variety of combinations in treatment systems, it has been found advantageous to study their scientific basis separately because the principles involved do not change. Treatment methods in which the application of physical forces predominates are known as physical unit operations.

Treatment methods in which the removal of contaminants is brought about by biological activity are known as biological unit processes. Biological treatment is used primarily to remove the biodegradable organic substances (colloidal or dissolved) in wastewater. Basically, these substances are converted into gases that can escape to the atmosphere and into biological cell tissue that can be removed by settling. Biological treatment is also used to remove nutrients (nitrogen and phosphorus) in wastewater. With proper environmental control, wastewater can be treated biologically in most cases.

Table 2.3: Polluted urban flow treatment system

Contaminant	Treatment system
Suspended Solids	Screening and comminution
	Grit Removal
	Sedimentaion
	Filtration
	Flotation
	Chemical Polymer Addition
	Coagulation/Sedimentation
	Natural Systems (Land Treatment)
Biodegradable Organics	Activated sludge variations
	Fixed film reactor:trickling fliters
	Fixed film reactor:rotating biological contactors
	Lagoon variations
	Intermittent sand filtration
	Physical chemical systems
	Natural Systems
Volatile Organics	Air Stripping
	Off gas treatment
	Carbon adsorption
Pathogens	Chlorination
	Hypochlorination
	Bromine chloride
	Ozonation
	UV Radiation
	Natural Systems
Phosphorus	Metal salt addition
	Lime coagulation/sedimentation
	Biological Phosphorus Removal
	Biological-Chemical Phosphorus Removal
	Natural Systems

Source: Metcalf and Eddy, 1991

Treatment methods in which the removal or conversion of contaminants is brought about by the addition of chemicals or by other chemical reactions are known as chemical unit processes. Precipitation, adsorption, and disinfection are the most common examples used in wastewater treatment. In chemical precipitation, treatment is accomplished by producing a chemical precipitate that will settle. In most cases, the settled precipitate will contain both the constituents that may have reacted with the