ACTIVATED CARBON-LIMESTONE-ALGINATE (ALA) BEADS FOR THE REMOVAL OF COLOUR AND TURBIDITY FROM KERIAN RIVER WATER

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ABSTRAK

Kajian ini memberi tumpuan kepada penggunaan karbon aktif (AC), batu kapur (LS) dan alginat dalam merawat air sungai Kerian. Nisbah campuran terbaik (AC: LS) 3:7 telah diadaptasi berdasarkan kajian terdahulu untuk menghasilkan penjerap komposit untuk menghilangkan warna dan kekeruhan dan diikuti dengan regenerasi penjerap komposit yang telah digunakan. Faktor dos penjerap, masa sentuhan dan kelajuan agitasi diambil kira dalam proses pengoptimuman demi mendapatkan nilai maksimum untuk menghilangkan warna dan kekeruhan air sungai. Oleh itu, penjerap komposit berjaya menyingkirkan warna sebanyak 94.15% dan 90.92% kekeruhan dengan menggunakan tetapan dos penjerap optimum 23.14 g, kelajuan kilat 114rpm dan masa sentuhan 71 minit. Model penjerapan kinetik dan isoterma untuk penjerap komposit juga telah ditentukan. Hasilnya menunjukkan bahawa kapasiti penjerapan maksimum satu penyerap komposit lapisan untuk warna dan kekeruhan adalah 17.857 PtCo/g dan 8.078 NTU/g, masing-masing. Sementara itu, model penjerapan kinetik menggambarkan kesesuaian penggunaan pseudo tertib kedua. Isoterm Freundlich sesuai untuk data penjerapan keseimbangan. Penjanaan semula penjerap dilakukan oleh kaedah pencuci pelarut menggunakan metanol tetapi malangnya penyingkiran warna dan kekeruhan air sungai tidak berjaya kerana ia membawa kepada nilai negatif.

ABSTRACT

This study focused on the usage of activated carbon (AC), limestone (LS) and alginates in treating the Kerian river water. Therefore, the best mix ratio (AC: LS) 3:7 has been adapted based on the previous study to produced composite adsorbent for removal of colour and turbidity and followed by regeneration of the used composite adsorbent. Factor of adsorbent dosage, contact time and shaking speed were considered for optimization processes to get maximum value for the removal of colour and turbidity of the river water. As a result, the composite adsorbent manages to remove 94.15% colour and 90.92% turbidity by using optimum adsorbent dosage settings of 23.14 g, shaking speed of 114rpm and contact time of 71min. Kinetic and isotherm adsorption model for composite adsorbent were also determined. The result shows that the maximum adsorption capacity of one layer composite adsorbent for colour and turbidity are 17.857 PtCo/g and 8.078 NTU/g, respectively. Meanwhile, the kinetic adsorption model describes the suitability of the use of pseudo-second order. Freundlich isotherm is suitable for equilibrium adsorption data. Regeneration of adsorbent is done by solvent wash method by using methanol but unfortunately the removal of colour and turbidity of river water was not successful which it brings negative value.

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LIST OF ABBREVIATIONS

AC	Activated carbon
AG	Alginate
ALA	Activated carbon-Limestone-Alginate
BET	Brunauer-Emmett-Teller
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DOE	Department of Environmental
EDX	Energy dispersive x-ray
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granular activated carbon
GLS	Granular Limestone
INWQS	Interim National Water Quality Standards for Malaysia
IUPAC	International Union of Pure and Applied Chemistry
LS	Limestone
MB	Methylene blue
MPN	Most probable number
MOH	Ministry of Health Malaysia
NOM	Natural organic matter
NSDWQ	National Standard for Drinking Water Quality for Malaysia
NWQS	National Water Quality Standards for Malaysia
PAC	Powdered activated carbon

SEM	Scanning Electron Microscopy
TDS	Total dissolved solid
TOC	Total organic carbon
WHO	World Health Organization
WQI	Water Quality Index

NOMENCLATURES

As	Arsenic
Ca^{2+}	Calcium(II) ion
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
Cd	Cadmium
Cd^{3+}	Cadmium(III) ion
Cr	Chromium
Cr^{3+}	Chromium(III) ion
Cu^{2+}	Copper(II) ion
E. coli	Escherichia coli
Fe	Iron
Fe^{3+}	Iron(III) ion
$FeCl_3$	Iron trichloride
Hg	Mercury
$MgCO_3$	Magnesium carbonate
MgO	Magnesium oxide
Mn	Manganese
Ni^{2+}	Nickel(II) ion
NH_3-N	Ammoniacal nitrogen

Pb	Lead
Pb^{2+}	Lead(II) ion
$TiCl_4$	Titanium tetrachloride
Zn^{2+}	Zinc(II) ion

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Safe water is essential for human life because each person requires at least 20 to 50 litres of clean and safe water a day for drinking, cooking and simply keeping themselves clean (National Academy of Sciences, 2008). Rivers definitely play a very significant role in providing water resources and many functions for the survival of natural and human systems.

Since the number of polluted rivers are increasing, the availability of good quality raw water is also decreasing. The quality of the river water is degraded by point sources (sewage, sullage, industrial effluent, etc) and non-point sources pollutants (urban and rural runoff) (Abdullah and Zaki, 2018). In 2013 in Selangor, seven districts consist of more than one million consumers were affected by water disruptions. It was due to the diesel tanker spillage in Selangor River 10 km from the intake area of a water plant and resulting to the shutdown of four treatment plants. These four plants produce 2.67 billion liters of water daily, meeting 57% of water demand in Selangor, Kuala Lumpur and Putrajaya (Sira Habibu and K. Ruban, 2013).

Meantime, the rapid growth of population leads to the growing demand of water usage for drinking, irrigation, municipal and industrial development. By the year 2020, the water demand is projected to reach 20 billion m^3 as demand is increasing 4% annually. Since rivers contribute 97% of fresh water resource, this is a signal that water supply would have to be treated extensively in future (Kailasam, 2011). Due to that, it is vital to search a suitable method to treat river water. Rivers in Malaysia were degraded due to poor management and public apathy. Thus, the quality of river water must be preserved and monitored properly as it might be degraded due to human activities as well as urbanization.

There are many water treatment methods have been done in order to treat polluted rivers from various types of pollutants. These methods include centrifugation, filtration, membrane processing, sedimentation, disinfection, crystallization, gravity separation, precipitation, flotation, oxidation, evaporation, coagulation, distillation, solvent extraction, ion exchange, electrolysis, adsorption, etc (Ali, 2012). However, adsorption has being the most significant separation technique that has wider application for the removal of heavy metals, organic and inorganic micropollutants from water due to its operation that is easy to handle and large selection of adsorbents available (Mohammed et al., 2014). Thus, in this experimental study, new composite adsorbent was used to remove physical parameters which are colour and turbidity that exist in river water through adsorption process.

1.2 Problem Statement

Due to an increasing demand from a growing population and climate change, it is important to manage the water resources efficiently to prevent water shortage. The increasing trend of the polluted rivers percentage in Malaysia also contributes to the shortage problem of the water resources which fully dependent with treated fresh water from the main resources such as river or groundwater. Furthermore, a drastic increase in population and economic activity density make it more difficult to meet the increasing demand for treated and raw water (Pillay and Vijaindren, 2016).

There are many methods of water treatment such as ozonation (Akbar, Aziz et al., 2015), advanced oxidation process (Fahmi et al., 2011), coagulation (Ramavandi, 2014) and adsorption (Agnihotri & Singhal, 2017) that have been effectively considered for the removal of various pollutants from water. All of them has their own advantages and disadvantages regarding their cost, environmental impact and productiveness. One of the most favourable methods in treating the river water is through adsorption process.

Literatures on the colour and turbidity removal from river water are not well studied especially with limestone-activated carbon-alginate composite adsorbent even there are a quite number of articles on the removal of colour and turbidity using adsorption process. Most of the studies discussed about the removal of heavy metals and dyes from synthetic solution and wastewater. At the same time, some adsorbents do not work well for certain pollutants. Previous studies reported that turbidity was removed by adsorbent materials derived from various plants, gravel and charcoal. Meanwhile, colour and dye were removed by composite adsorbent or alginate bead.

In this experimental study, adsorption process using a new composite adsorbent was applied to remove colour and turbidity in the river water. The single use of activated carbon and limestone in water treatment is not always very promising. Hence, these two are combined to make an effective composite adsorbent which is activated carbon-limestone-alginate (ALA) beads for the removal of colour and turbidity by applying adsorption process.

1.3 Objectives

The objectives in this study are:

1. To determine the characteristics of composite adsorbent, which is activated carbon-limestone-alginate bead.
2. To analyze the removal efficiency of colour and turbidity by using the composite adsorbent.
3. To study the adsorption isotherm and adsorption kinetic and regeneration capability.

1.4 Scope of Work

The focus of this study is to treat river water by using composite adsorbent and utilize the river water as a source of drinking water. First, to identify the parameters present in the river water sample, the characteristics of the river water sample need to be studied. After tested all the parameters, the results were compared with the guideline of Drinking Water Quality Standard by Ministry of Health Malaysia (MOH) such as pH, temperature, colour, turbidity and chemical oxygen demand (COD) while the parameters chosen for treatment were colour and turbidity.

Next, the composite adsorbents were prepared by mixing activated carbon and limestone by using alginate as a binder. The adsorbents will be tested towards parameters removal from river water treatment by batch-studies to determine the optimum adsorbent dosage, shaking speed and contact time. After that, adsorption isotherms and adsorption kinetics were studied in order to verify the adsorption mechanism and kinetic features of composite adsorbent.

For characterization of the composite adsorbents, they were tested using Autosorb Quantachrome for BET surface area, pore size and pore volume, scanning electron microscope (SEM) and fourier transform infrared spectroscopy (FTIR) to determine its adsorptive characteristics. Lastly, the composite adsorbent will be regenerate and recover from solutions after adsorption by using methanol.

1.5 Dissertation Outline

The thesis has been categorized into specific chapters for better viewing and understanding of the study. This dissertation consists of five chapters.

Chapter 1: Introduction – this chapter gives an introduction on river water treatment being the alternative solution to solve the water scarcity and water pollution, followed by the problem statement to identify, and understand why this research was carried out and its relevance to current times followed by the objectives of this research in order to set the desired target of work and finally the justification of this research.

Chapter 2: Literature review – this chapter includes the review of previous studies of the water treatment technologies and adsorbent materials used. This chapter also explains the details on the isotherms and kinetics model and regeneration study.

Chapter 3: Methodology – this chapter presents the experimental works and procedures for batch experiments in optimization study. Other than that, this chapter also describes about materials and equipment used, procedures of the experiment and precautions taken throughout completing the treatment process.

Chapter 4: Results and Discussions – this part provides the results and discussions of the study and summary of the findings from the river water treatment using composite adsorbent of the two parameters involved in this study. All the data are presented in the form of tables and graphs.

Chapter 5: Conclusions and Recommendations – this chapter explains the major findings of the research objectives. Some recommendations are discussed based on the results obtained for related studies in the future. Finally, all the related sources of information that have been used in this study are clearly stated in the references.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Globally, the world appears besieged by water stress. However, experts have deduced that the main problem is not water scarcity but poor management which is precipitating a crisis (Biswas and Tortajada, 2011). Corresponding to the continual deterioration of water quality on a global basis is the degradation at the country level, especially in developing countries. Rivers are vital for nature and human society and so the river water quality is a crucial factor in river management that involving all stakeholders ranging from government to the private sector. The major river management issues are all linked to water quality because poor river water quality will severely affect the water supply.

Many studies have been conducted in river water treatment to treat water and reduce the concentration of pollutants as well as avoiding from ground and surface water pollution. The researches that have been carried out mostly concentrate on physical and chemical treatment. Hence, this literature review will discuss about river water techniques done by other researchers, especially on adsorption as it is the focus of this study. Other aspects such as river water in Malaysia and pollution of river water in Malaysia also will be discussed in this chapter.

This chapter includes several sections which is benefit of river water, pollution of river water in Malaysia, water treatment, adsorption mechanisms, types of adsorbent, adsorption isotherms and kinetics and regeneration of composite adsorbent in the second, third, fourth, fifth, sixth, seventh and eighth section, respectively.

2.2 Benefit of river water

A river is defined as a natural stream of water flowing in a channel into the sea, lake or other water bodies. It is dynamic, disturbance-driven ecosystems where the flow is responsible for structuring aquatic and riparian zone (Murchie et al., 2008). A river is much more than water flowing to the sea. Its ever-shifting bed and banks and the groundwater below, are all important parts of the river. Even the meadows, marshes, forests and backwaters of its floodplain are part of a river. A river flows downhill together with sediments, dissolved minerals, organic matters, heavy metals and dead animals (McCully, 1996). The soil moisture and aquifers which are located underground hold the water content where the fresh water is found. Groundwater can feed the streams and keeps a river flowing even when there is no rainfall (Deming, 2005).

Rivers are sources of life, providing water supply for the people, irrigation for agriculture, cheap and efficient transportation, rich sources of food, hydro-electric power and as well as water use for industries. Rivers also are the natural habitats for streamline and aquatic flora and fauna, and the river surroundings support a rich biodiversity of life forms. All of us know that water is needed in all aspects of life and an adequate supply of good quality water is important for our well-being. Without water, development would also not be possible because it is a common factor that cuts across all sectors of development. Ensuring that this crucial resource is well managed is critical and, in this case, maintaining the health of rivers is important to continue enjoying the benefits and services they provide.

In addition, this water supply is also distributed to the consumers for daily use, especially as drinking water. The increasing of river water pollution leads to the higher concentrations of the existing pollutants and consequently, it decreases water quantity as the good quality water available for use decreases. Hence, water treatment costs are higher due to the presence of new pollutants in rivers. In the past, conventional treatment system which includes coagulation and flocculation, screening, sand filtration, fluoridation and disinfection (chlorination) was employed to treat raw surface water. Unfortunately, the pollutants might enter the distribution and supply network and this kind of system is not suitable to remove the pollutants.

2.3 Pollution of river water in Malaysia

Water pollution can be defined as changes in water either physically, chemically or biologically that disrupt the benefits of water usage causing extreme danger to health and public safety as well as to animals and plants. Water pollution sources basically are from point sources such as discharges from industrial and sewage treatment plant and non-point sources such as surface water runoffs from the housing, commercialization, agriculture land use, industrial and others. Basic natural causes of water pollution are high mobility of water in the hydrologic cycle, water acting as a universal solvent, dumping ground for human wastes and irresponsible dumping of highly toxic industrial waste. These will lead to the destruction of aquatic life, threatening of human life, harming wildlife and have the potential of breaking the life chain also impairing industrial operations (Environmental Quality Council, 2003).

Thus, Water Quality Index (WQI) is used to evaluate the status of river water quality and the corresponding suitability in terms of water uses according to the National

Water Quality Standards for Malaysia (NWQS). According to the WQI, the status of water quality is divided into three categories, which are clean, slightly polluted and polluted. The river water quality trend in Malaysia of different category from 2005 to 2016 is shown in Figure2.1. The river water quality in terms of WQI was decreased in 2016. Out of 477 rivers monitored by the DOE, the percentage of clean rivers has decreased to 47% in 2016 compared to 58% in the previous year. Meanwhile, the percentage of the polluted river has increased from 7% to 10% in 2016 as shown in the Figure 2.1 below.

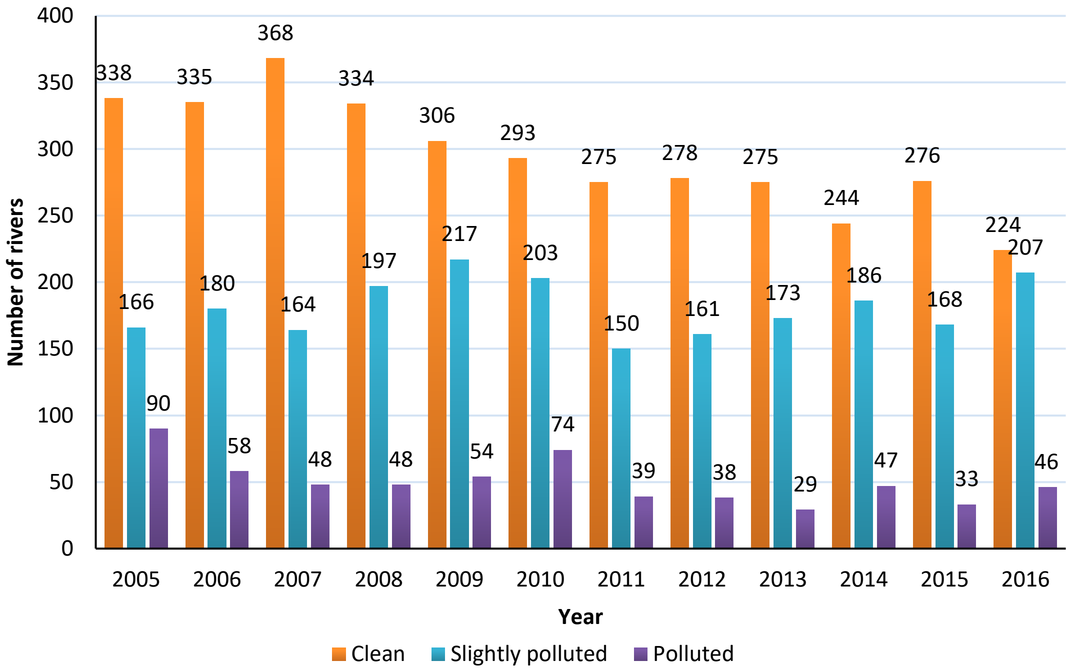

Figure 2.1: River water quality trend under different category from 2005 to 2016 (DOE, 2017)

Deterioration of water quality will lead to extinction of ecological system and biodiversity, coverage of oil and dangerous substances on surface water and rocks in the river and declining health rate due to polluted river. High concentration of colour and turbidity also will reduce aesthetic value of the river and affecting tourism industry.

Hence, related parties should prevent direct waste disposal to any drainage and rivers, establish love the river attitude, soil erosion prevention via Sustainable Development and generate collaboration from all parties on river protection. People also need to report any untreated illegal discharges from factories and industrial premises (Environmental Quality Council, 2003). In addition, appropriate river water treatments need to be conducted in order to reduce the amount of pollutants such as coagulation, advanced oxidation process, ozonation and adsorption.

2.4 Water treatment

River water treatment is known as the process of removing contaminants from flowing or stagnant river water including physio-chemical treatment of water with the combination of conventional and advance treatment process to produce an environmentally safe and pure water suitable for drinking and multiple uses in domestic, institution and industrial application. Screening, centrifugation, filtration, membrane processing (micro-, ultra-, and nanofiltration, reverse osmosis), sedimentation, disinfection, crystallization, gravity separation, precipitation, flotation, oxidation, evaporation, coagulation, distillation, solvent extraction, ion exchange, electrolysis, adsorption and electrodialysis are the methods have been created and used for the removal of pollutants from polluted water (Ali, 2012). Due to their high operational and capital costs, these methods have been investigated to be circumscribed. Reverse osmosis and ion exchange are interesting methods since the pollutant values can be regained along with the removal of the waste product (Mishra et al., 2009). However, the cost of water treatment by reverse osmosis, ion exchange, electrodialysis and electrolysis are higher than adsorption (Ali, 2014).

Coagulation is the process of reducing or neutralizing the negative charge on suspended particles or zeta potential and this allows the van der Waals force of attraction to stimulate initial aggregation of colloidal and fine suspended materials to form microflock. In order to maximize its effectiveness, rapid, high energy mixing is necessary to ensure the coagulant is fully mixed into the process flow. The coagulation process occurs very fast, in a matter of fractions of a second (Hosseini et al., 2008). The normal procedure of jar test can be conducted to initially find the best performing coagulant and dose rate and to determine the optimum PH and temperature for the chosen coagulant and dose rate as well. Performance is usually judged on turbidity and then on colour removal. Jar tests can also be used to compare the usefulness of different coagulant aids. Hosseini et al. (2008) investigated that coagulation with aluminium sulphate and ferric chloride is an effective method to clarify raw water by reducing the turbidity and will lead to lower treatment costs for industries. Pollutant removal efficiency at various coagulant doses and pH was determined. Ferric chloride produced better results than aluminium sulphate in lowering the turbidity, but poly electrics should be used to produce more decrease in turbidity. Poly electrics with ferric chloride have more effect in omitting turbidity in comparison to alum also decrease in coagulant dosage when using coagulant aid is perceptible. The efficiency of the coagulation of raw water is highly dependent on the control of PH and coagulant dose within an optimum range. The result shows that clarification process can be used in wastewater treatment and reduces the operational cost too.

When new water treatment technologies are invented, membrane filtration has become a mainstream technology that competes effectively with rapid granular filtration. In membrane processes, membrane serves as a driving force to separate the pollutants from water and wastewater (Van Der Bruggen et al., 2003). However, fouling can cause difficulties in membrane technology for water treatment. fabricated a novel nanofiltration (NF)-like GO surface deposited poly(amide-imide)–polyethyleneimine (PAI–PEI) hollow fiber membrane via an instant dip-coating method. The results showed that a better performance with up to 86% higher pure water permeability is observed when compared with only PEI cross-linked hollow fiber membrane of similar selectivit (Goh et al., 2015).

Ozonation process is an advanced oxidation process (AOP) that has been found to be effective in drinking and groundwater treatment (Kedir et al., 2016). This process is based on the use of ozone gas, which is a strong oxidizing agent. It involves the presence of multiple reagents in the water known as hydroxyl radical, which act as a strong oxidizing agent to eliminate a wide variety of organics, inorganics and microbiological, taste and odor problems (Akbar et al., 2015). Kedir et al. (2016) studied the methyl tertiary butyl ether (MTBE) degradation in water with chlorine-based advanced oxidation process (AOP). They found that by using free chlorine as a chemical oxidant in combination with low-pressure (LP) and medium-pressure (MP) mercury lamps, more than 99% of MTBE was degraded in deionized water within 15–30 min at pH 5 and 7, respectively. Chlorine-based AOP could be a promising technique for treating water contaminated with MTBE (Kedir et al., 2016). Besides, there is also a study that has been carried out to investigate the removal of acid red 88 (AR88) by means of electro-Fenton which involved oxidation by hydroxyl radicals. This study was able to remove 87% of initial TOC values of 0.25 mM AR88 solution (Özcan and Gençten, 2016). Both studies show the potential uses of oxidation that can be applied in treating water pollutants.

Adsorption is a surface phenomenon in which the pollutants accumulate on any solid surface. In water treatment, the pollutants are called adsorbates and any solid phase are called adsorbent. Water treatment by adsorption technology is optimized by various factors such as nature of adsorbent and adsorbates, concentration of adsorbate, pH, contact time, adsorbent dosage, particle size of adsorbent, temperature and the presence of other pollutants. In this technology, equilibrium is developed when an adsorbent in contact with the polluted water and the amounts of pollutants adsorbed become constant at this point. The relationship between adsorbed amount of a pollutant on adsorbent at equilibrium and a given temperature is known as an “adsorption isotherm.” Various models are used to analyze adsorption data such as Langmuir, Freundlich, Dubinin-Kaganer-Radushkevich, Harkin-Jura, and Temkin. The efficiency of water treatment can be evaluated by calculating the values of the parameters of these models. The adsorption process is first optimized in batch mode followed by its application at the column structures (Ali, 2014). Until now, adsorption has been found to be more versatile and superior to other techniques for wastewater treatment that covers from starting ease of operation, cost, design simplicity, insensitivity to toxic substances and almost complete removal of dyes, even from concentrated solutions (Foo and Hameed, 2010).

In Malaysia, Kamaruddin (2015) have demonstrated that the use of carbon-mineral composite which included activated carbon, limestone and polyvinyl alcohol was able to remove various pollutants from Kerian River. They found that the removal of turbidity, color, total suspended solid (TSS), iron and manganese were 91.86%, 93.44%, 91.27%, 98.49% and 98.18%, respectively. They concluded that the composite material has a good potential for future application and adsorption will be a good technology of water treatment soon. A lot of works has been done on the removal of different pollutants from water by using adsorption batch study. Initially, AC was widely used for the removal of pollutants from water, which has been replaced by some effective and low-cost adsorbents (Pirilä, 2015). Meanwhile composite adsorbent has been explored by researchers nowadays due to its improvement on pollutant removal in water. The modification made by composite adsorbent does not affect significantly its pore structure and it increases the adsorption capacity, which means that it improves the composite adsorbent functional characteristics.

2.5 Factors contributing adsorption batch test

Various studies have evaluated the factors that contributed to the adsorption process. The operating factors that have been identified are the effect of adsorbent dosage, contact time and the shaking speed. The contributions of these operating factors are further discussed in Section 2.5.1, 2.5.2 and 2.5.3.

2.5.1 Effect of adsorbent dosage

Several studies on the effect of adsorbent dosage in adsorption process are shown in Table 2.1 which shows that the adsorbent dosage is one of the crucial operating factors in order to determine the capacity of an adsorbent for a given adsorbent amount at the operating conditions. Based on reviews made as shown in Table 2.1, for a greater removal of pollutants, higher amount of adsorbent dosage needed to provide more adsorption sites of the adsorbent. However, when the adsorption reached equilibrium, the removal of pollutants decreased due to the lack number of adsorption sites through the adsorption reaction (Yagub et al., 2014).

Table 2.1: Review of studies regarding the effect of adsorbent dosage

Pollutants	Types of adsorbent	Adsorbent dosage	Findings	References
COD, color and Cu(II) from cotton dyeing wastewater	Coconut shell activated carbon (CSAC)	2 – 8 g/L	Increasing dosage of CSAC gradually increases the removal percentage of COD, color and Cu (II).	(Kamaruddin, 2015)
Fluoride from groundwater	Gypsi-ferous limestone (GLS)	1 – 20 g/L	The increase in the percent of adsorption with the adsorbent dosage is due to the availability of more adsorption sites at a higher adsorbent mass. Then, the amount of fluoride adsorbed decreased was possibly due to the lower ratio of fluoride ions to the available active binding sites.	(Fufa et al., 2014)
Acid orange 7 (AO7) from textile dye	Activated carbon	0.5 - 1.5 g/L	Increasing adsorbent dosage led to increasing the decolorization efficiency (%) of AO7 from 59.96 to 89.40% due to the increased available surface area.	(Noorimotlagh et al., 2014)
COD from wastewater	Bentonite	0.2 - 1.2 g	The removal of COD increased with increasing the adsorbent dosage.	(Abdullah et al., 2013)
Cd from aqueous solution	Nanocomposite (Silica aerogel activated carbon)	0.02 – 0.5 g	The removal percentage of cadmium increased by increasing the amount of adsorbent from 0.02 in 0.10 g and fixed at greater amount.	(Givianrad et al., 2013)

2.5.2 Effect of contact time

To remove the water pollutants, previous studies have investigated the effect of contact time. Table 2.2 shows the review on several studies investigating the effect of contact time on the adsorption reaction. From Table 2.2, it can be concluded that mostly the removal of pollutants increased rapidly at the initial stage due to the larger available adsorption sites on the surface of the adsorbents. Rigorous mixing and longer solid–liquid contact cause better interaction between the media and the leachate. More active surface area of media is exposed to the adsorbate by continuous shaking (Aziz et al., 2011). Then, the removals gradually slow after reaching the equilibrium state as the surface of the adsorbents were nearly saturated with pollutants and the water pollutants traverse farther and deeper into the pores of the adsorbent showing the reactions were continued in slow rate. Consequently, the adsorption rate and driving force of water pollutants decreased.

Table 2.2: Review of studies regarding the effect of contact time

Pollutants	Types of adsorbent	Contact time	Findings	References
Methylene blue	Volcanic ash (VA)	15 minutes	Optimum contact time to adsorb methylene blue and reach equilibrium was for 15 minutes. After that, its ability has decreased and would not up again.	(Said et al., 2014)
Acid orange 7 (AO7) from textile dye	Activated carbon	30 minutes	The amount of adsorbed AO7 was drastically increased with increasing contact time. Then, it was gradually increased with increasing contact time from 30 to 60 min, respectively.	(Noorimotlagh et al., 2014)

Cd from aqueous solution	Nanocompo-site (Silica-aerogel activated carbon)	90 minutes	The removal of Cd is increasing as the contact time increase. The maximum removal of Cd at 90 minutes was 60%.	(Givianrad et al., 2013)
Permethrin pesticide from water	Chitosan-ZnO nanoparticle-s (CS-ZnONPs)	90 minutes	The pesticide adsorption was fast at initial stages and then slowed down near the equilibrium. This phenomenon was due to the availability of many vacant surface sites for adsorption during the initial stage. After that, other vacant surface sites were difficult to be adsorbed due to repulsive forces between the adsorbate molecules on the adsorbent.	(Moradi Dehaghi et al., 2014)
Ni2+ and Pb2+ in aqueous solution	Chitosan-activated charcoal	180 minutes	Adsorption increased with increase in contact time before equilibrium was attained.	(Odoemelam et al., 2015)
Fluoride from ground-water	Gypsiferous limestone (GLS)	12 hours	The steep portion, for contact time from 0.5 to 12 h within which steady increase in the percentage of adsorption was observed and the last flat part for contact time from 12 to 24 h within which fluoride adsorption percentage significantly approached constant.	(Fufa et al., 2014)

2.5.3 Effect of shaking speed

The optimum shaking speed was determined by varying the shaking speeds. Several studies on the effect of shaking speed in adsorption process are shown in Table 2.3. Basically, the adsorption increases simultaneously with the agitation speed at the beginning of adsorption. Increase in shaking speed causes better surface contact between the adsorbent and the aqueous solution, thus enhanced the sorption rate (Sabir Hussain et al., 2011). In addition, removal efficiencies are greater at high shaking speed and shaking time. This adsorption behaviour occurs since initial kinetic energy of the adsorbents and pollutant molecules increase as the shaking speed increase. However, based on Table 2.3, a research by Daud et al. (2017) shows that at the beginning of adsorption of COD from leachate solution by the cockle shells (CS), the rate of adsorption increases simultaneously with the agitation speed. After reaching 150 rpm, the adsorption dissipates even with a further increase in the shaking speed. Therefore, the adsorption may have attained equilibrium at 150 rpm (28%), such that no further improvement can be attained. Consequently, the probability of interaction between the molecules and the adsorbent becomes significant. Hence, the amount of adsorbate increases until it reaches the equilibrium state. The adsorption diminishes even with the increasing shaking speed after reaching the equilibrium state. To be concluded, the optimum shaking time, settling time and shaking speed will give maximum reduction of pollutants.

Table 2.3: Review of studies regarding the effect of shaking speed

Pollutants	Types of adsorbent	Shaking speed	Findings	References
Orthophosphate (PO4-P)	Granular activated carbon (GAC) & Limestone (LS)	350 rpm	Limestone has potential to remove approximately 90% orthophosphate at higher shaking speed ranging between 300 and 400 rpm.	(Sabir Hussain et al., 2011)
Heavy metals Fe^{2+}, Pb^{2+}, and Cu^{2+}	Olive stone activated carbon (OSAC)	200 rpm	OSAC efficiently removed 99.39% Fe^{2+}, 99.32% Pb^{2+}, and 99.24% Cu^{2+} with 200 rpm shaking speed.	(Alslaibi et al., 2013)

Colour, COD, iron, ammoniacal nitrogen	Activated carbon, zeolite	350 rpm	More than 95% of colour, 90% of COD, 95% of iron and 55% of ammoniacal nitrogen was removed by activated carbon, while more than 75% of colour, 50% of COD, 95% of iron and 90% of ammoniacal nitrogen was removed by zeolite.	(Aziz et al., 2011)
Colour, COD, iron, ammoniacal nitrogen	Activated carebon, mixed media (activated carbon and limestone)	350 rpm	More than 95% of colour, 90% of COD, 95% of iron and 55% of ammoniacal nitrogen were removed using activated carbon while 86% of colour and COD, 95% of iron and 48% of ammoniacal nitrogen were removed using a mixed media (mixture ratio of activated carbon and limestone 15:25 by volume)	(Foul et al., 2009)
COD from leachate solution	Cockle shell (CS)	150 rpm	At the beginning of adsorption, the adsorption increases simultaneously with the agitation speed. After reaching 150 rpm, the adsorption dissipates even with a further increase in the shaking speed. Therefore, the adsorption may have attained equilibrium at 150 rpm (28%), such that no further improvement can be attained.	(Daud et al., 2017)

2.6 Types of adsorbent

To The selection criteria of the adsorbents depend on their free availability, inexpensiveness, efficiencies and regeneration. Adsorbents used in water treatment can be obtained from natural origin and industrial production or activation process.

Adsorbents must have high surface area since adsorption is a surface process and large surface area can be obtained by using materials with high number of pores in the interior material. While a high degree of porosity within the adsorbent granules also contributes to an effective adsorbent which adsorbs into a vast amount of interior surface area onto which adsorption process takes place (Howe et al., 2012; Worch, 2012).

(Odoemelam et al., 2015) conducted a research by comparing three adsorbents which are chitosan, activated charcoal and a combination of both (composite) adsorbents in removing Ni^{2+} and Pb^{2+} from aqueous solutions in a batch adsorption study. The affinity of adsorbents for the metal ions also follows the trend composite adsorbent > charcoal > chitosan. Therefore, composite adsorbent provided some synergistic effect leading to improved removal of the metal ions from aqueous solutions. Carmen Apostol et al. (2016) reported that the adsorbent produced from agriculture waste such as pumpkin seed hulls were applied as potential adsorbent for the removal of Erythrosine B from aqueous solutions. The results showed that the adsorbent is effective for Erythrosine B removal for a large concentration range in aqueous solutions (5400 mg/L) in batch systems.

There are many types of low-cost adsorbent can be used in adsorption such as coconut shell activated carbon and limestone. In addition, composite adsorbent also shows good performance in adsorption process. The uses of these adsorbents have been widely used to evaluate the efficiency to remove organic and inorganic pollutants (Benhouria et al., 2015; Halim et al., 2012; Sabir Hussain et al., 2011; Kamaruddin, 2015). However, the uses of these adsorbents were more widely applied in treating industrial wastewater, leachate and synthetic solution. So, further studies are needed in evaluating the potential of these adsorbents to treat river water.

2.6.1 Activated carbon

Activated carbon (AC) is the most common used adsorbent because of its larger surface area, microporous structure, high adsorption capacity and high degree of reactivity. However, commercially available activated carbons are so expensive. There is a growing interest in using low cost commercially available materials for colour adsorption. A wide variety of low cost materials such as agricultural by product, waste coir pith, Indian rosewood sawdust, pine sawdust, banana pith, rice husk, orange peel, industrial solid waste such as Fe(III)/Cr(III) hydroxide and silica are the low cost alternatives to activated carbon. The advantage of activated carbon is its large surface area that makes it an effective adsorbent, but the main problem is its high cost. However, mixing of activated carbon with a lower-cost material has been shown to be effective in the removal of heavy metals, ammoniacal nitrogen and colour (Aziz et al., 2001; S Hussain et al., 2007). This would also render the treatment economical.

2.6.2 Limestone

The use of natural sorbent for removing various metals from wastewater has been found to be an effective alternative. Especially, the use of natural limestones (LS) as cheap medium for toxic metals removal has been investigated by multiple researchers (Aziz et al. 2001; Sanchez and Ayuso 2002; Godelitsas et al. 2003; Prieto et al. 2003; Komnitsas et al. 2004; Cave and Talens-Alesson 2005; Rouff et al. 2006; Aziz et al. 2008; Sdiri et al. 2012b), pointing out that limestones could be an efficient natural geological materials for the treatment of heavy metals in contaminated water. In addition, the limestone from northern Tunisia, containing higher impurities such as silica and iron and aluminium oxides, showed better removal efficiency than the limestones of southern area. Akbar et al. (2015) also concluded that the limestone could be used as an alternative for the removal of Fe and Mn from groundwater.

Limestone is an alkaline media and a low-priced material compared to the cost of activated carbon because of an abundant in nature. However, the adsorption capacity of limestone is lower than the activated carbon. In previous studies, Aziz et al. (2001) found that limestone, as a low-cost adsorbent, was very effective in leachate treatment for metal and ammonia removal. Based on the previous work, LS composition contained 97.93% $CaCO_3$, 0.8682% MgO and 1.2% others (Akbar et al., 2015). Meanwhile, the results of chemical analysis reported by Hamidi Abdul Aziz et al. (2008) on limestone indicated that limestone had high amount of $CaCO_3$ (95.6%) with less amount of impurities (2.39% $MgCO_3$, 0.271% Fe_2O_3, 0.213% Al_2O_3, 1.441% SiO_3, and 0.085% others. Hamidi Abdul Aziz et al. (2011) discovered 96.5% $CaCO_3$, 2.5% of $MgCO_3$ and 1.0% others in LS composition.

Limestones helped more effectively towards removal of heavy metal such as arsenic (III) and iron through filtration process (Devi et al., 2014). According to an investigation by Ahmad et al. (2012), the significant removal of heavy metal ions such as Zn^{2+}, Cr^{3+}, Pb^{2+}, Cd^{2+}, Cu^{2+} and Fe^{3+} indicated an efficiency of calcium carbonate as an adsorbent. The authors reported that the higher adsorption capacity of calcium carbonate is attributed due to the differences between metal sorption capacities and affinity of calcium carbonate adsorption. In a research conducted by Hamidi Abdul Aziz et al. (2008), it was found that the presence of carbonate is useful to eliminate heavy metals from water. Therefore, Hamidi Abdul Aziz et al. (2008) concluded that LS has potential as a low-cost effective adsorbent in water treatment.

2.6.3 Composite adsorbent

By means of the combination of a single adsorbent with other adsorbent such as clay minerals, polymeric adsorbents, oxidic adsorbents, carbonaceous adsorbent, rice husk, and zeolite, improvement of the heat and mass transfer performance of the original adsorbents has been made in a wide range of pollutant removal in water. According to Hadjar et al. (2004), developed composite materials were improved on their adsorptive properties and subsequently resulted in fast adsorption kinetic of metallic ions such as lead. Other than that, recent study about selenium (Se(IV)) detection and removal from water by ligand functionalized organic–inorganic based composite adsorbent was reported by Awual et al. (2015). They found that the presence of diverse competing ions did not affect the Se(IV) sorption capacity and the adsorbent had almost no sorption capacity for these coexisting ions, which implies the high selectivity to Se(IV) ions. Conclusively, the adsorbent is cost-effective and environmentally friendly and also a potential candidate for treatment of water containing Se(IV).

Additionally, Benhouria et al. (2015) observed that activated carbon-bentonite-alginate beads (ABA) produced more than 70% adsorption uptake capacity after six times of regeneration. It showed that ABA can be applied many times before disposal. The findings proposed that the maximum monolayer adsorption capacity of ABA beads for the adsorption of methylene blue (MB) was 756.97 mg/g at 30 °C. Therefore, ABA is a high potential adsorbent for the removal of MB and other cationic dyes and can be recycled a few times before disposal. Conclusively, based on the review studies, alginate is a potential polymer which helps to enhance the performance of composite adsorbent in removing pollutants in water.