PERFORMANCE OF ZWITTERIONIC ADSORBENT COATING FOR REAL INDUSTRIAL EFFLUENTS

KARTIYANI A/P YOGANATHAN

UNIVERSITI SAINS MALAYSIA

2021

PERFORMANCE OF ZWITTERIONIC ADSORBENT COATING FOR REAL INDUSTRIAL EFFLUENTS

by

KARTIYANI A/P YOGANATHAN

Thesis submitted in fulfilment of the requirements for the bachelor degree of Chemical Engineering

August 2021

ACKNOWLEDGEMENT

I would like to express my special appreciation and thanks to my main supervisor Associate Professor Dr Suzylawati Ismail for being a tremendous mentor to me in guiding me through this research. I would like to thank my co-supervisor Dr. Syahida Farhan Azha for the scientific advice and knowledge and many insightful discussions and suggestions.

I would especially like to thank MUDA Paper Mills SDN BHD, Simpang Ampat, Pulau Pinang and Jabi Landfill, Pokok Sena, Kedah for providing me the required effluent sample to run my research project. Also, not forgetting the laboratory members in School of Chemical Engineering, Universiti Sains Malaysia, and all the laboratory members in Chemical Engineering Integrated Space Laboratory for giving me the best cooperation and support during my final year project laboratory work.

A special thanks to my family and friends. Words cannot express how grateful I am especially to my parents who have been supporting me and for all the sacrifices that you have made on my behalf. Thank you for all my friends who supported me through this journey and incented me to strive towards my goal.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF ABBREVIATIONS

ADMI	American Dye Manufacturers Institute
AC	Activated Carbon
COD	Chemical Oxygen Demand
DOE	Department of Environmental Engineering
EDX	Energy Dispersive X-ray
IWRM	Integrated Water Resource Management
OFAT	One Factor at Time
PAC	Poly-aluminium Chloride
RSM	Response Surface Methodology
SDG	Sustainable Development Goal
SEM	Scanning Electron Microscope
TSS	Total Suspended Solid
TDS	Total Dissolved Solid
UN	United Nation

LIST OF APPENDICES

PRESTASI LAPISAN PENJERAP ZWITTERIONIK UNTUK SISA INDUSTRI

ABSTRAK

Dalam laporan ini salutan penjerap zwitterionik digunakan untuk mengurangkan intensiti warna, permintaan oksigen kimia (COD) dan logam zink. Sisa bahan industri dikumpulkan dari Jabi Landfill, Kedah dan Muda Paper Mills SDN. BHD, Pulau Pinang. Prestasi penjerapan dinilai dari segi warna, COD, penyingkiran zink dan pH. Pendekatan 'one-factor-at-a-time' (OFAT) digunakan untuk mengkaji kesan setiap faktor. Bilangan jalur penjerap, suhu dan pH adalah antara pemboleh ubah yang disesuaikan dalam eksperimen ini. Secara perbandingan sampel dari tapak pelupusan menunjukkan penurunan parameter air sisa yang ketara dengan bantuan jalur penjerap zwitterionik. Keadaan optimum untuk penjerapan adalah melalui penggunaan 2 jalur penjerap (warna: 76.01%, COD: 74.73% dan Zn (II): 63.16%),

pada suhu 80 ℃ (warna: 41.61%, COD: 73.91 % dan Zn (II): 47.37%) dan pH 7 (warna: 57.55%, COD: 74.46% dan Zn (II): 57.89%). Morfologi dan kumpulan fungsi penjerap sebelum dan selepas proses dicirikan menggunakan analisis SEM-EDX. Berdasarkan gambar yang diperoleh, molekul-molekul yang melekat pada jaringan gentian kain kapas dapat diperhatikan. Sementara itu, elemen seperti Vanadium (V), Kobalt (Co), Nikel (Ni), Kromium (Cr), Plumbum (Pb), Kalsium (Ca), dan sebagainya dapat yang berasal dari sisa industry dapat dilihat dari puncak graf EDX.

PERFOMANCE OF ZWITTERIONIC ADSORBENT COATING REAL INDUSTRIAL EFFLUENTS

ABSTRACT

In this report zwitterionic adsorbent coatings are used to reduce color intensity, chemical oxygen demand (COD) and zinc metal. Industrial waste is collected from Jabi Landfill, Kedah and Muda Paper Mills SDN. BHD, Penang. Adsorption performance was evaluated in terms of color, COD, zinc removal and pH. The 'one-factor-at-a-time' (OFAT) approach was used to study the effects of each factor. The number of adsorbent bands, temperature and pH were among the adjusted variables in this experiment. Comparatively the samples from the landfill showed a significant decrease in wastewater parameters with the help of zwitterionic adsorbent strips. Optimal conditions for adsorption are through the use of 2 adsorbent strips (color: 76.01%, COD: 74.73%and Zn (II): 63.16%), at a temperature of 80 °C (color: 41.61%, COD: 73.91%and Zn (II): 47.37%) and pH 7 (color: 57.55%, COD: 74.46%and Zn (II): 57.89%). The morphology and functional groups of the adsorbent beforeand after the process were characterized using SEM-EDX analysis. Based on the images obtained, the molecules attached to the cotton fiber network can be observed. Meanwhile, elements such as Vanadium (V), Cobalt (Co), Nickel (Ni), Chromium (Cr), Lead (Pb), Calcium (Ca), etc. can be derived from industry waste can be seen from the top of the EDX graph.

CHAPTER 1

INTRODUCTION

1.1 Background Study

"When the Well's dry, we know the worth of water" by Franklin (1746). Though this may sound as a cliché, there is much wisdom in this simple word of advises. Now that, scenario today portrays a critical stage of clean and freshwater accessibility due to the imprudent act of mankind towards our resources. Water is a precious commodity which is very crucial for the survival of living organisms in the planet. With a rapid development of human population and their activities majority of our water resources has been exposed to water pollution crisis. Water pollution refers to an introduction of substances and which poses harm to living resources, mankind health, disruption of aquatic ecosystem and poor water quality (Fatine Ezbakhe, 2018).

Industrializations and human activities utilize a huge volume of water in their process which end up generating more amount of pollutant in their discharged wastewater. Effluents originated from industries such as textiles, paper, paint, and food processing exhibit a complex chemical molecules and structures and comprise of multiple dyes, heavy metals, organic materials and other toxic particles (Abd Hamid et al., 2020).

Thus, effluents from such industries are believed to cause adverse effects to the environment pollution if they are not treated properly before disposing into the water resource. As per the UNESCO, poor water quality brings major threat to sustainable development for developing countries. Thus, water pollution become no less important in the 2030 international agenda and sustainable development goals (SDGs), in which the water quality issues have been put forward. Goal 6 of SDG 'ensures the availability and sustainable management of water and sanitation for all' as a mean to provide solution for the water quality issues (Fatine Ezbakhe, 2018).

So far, many technologies have been devised by researchers to treat the wastewater in accordance with the government legislation to control pollution. They are classified as physical, chemical, and biological methods. Of all, adsorption is regarded as the efficient and economical process to remove dyes, organic pollutants and derivatives in wastewater treatment in terms of initial costs, ease of operation and insensitivity to toxic substances. Conventionally, adsorption using activated carbon is becoming a common method of treating industrial effluents due their extended surface area, high adsorption capacity, microporous structure, and special surface reactivity. However, treating wastewater by using conventional activated carbon are expensive and its regeneration are even costly to be performed (Shamsudin *et al.*, 2019). Regeneration ensures that the adsorbent can be reused for the next consecutive cycles. However, the interactions between the surface of adsorbents and adsorbates servesas a barrier for the regeneration of spent adsorbents.

This has paved a way towards a search for low-cost material as alternative adsorbent materials. Removal of toxic and organic compounds on low-cost adsorbents such as bentonite clay on wastewater treatment has become a topic of interest. Since adsorbent with a single ionic charge unable to remove different charged compounds and heavy metals, zwitterionic adsorbent coating approach has been adopted. Zwitterionic adsorbent-based composite coating (ZACC) was explored so that the adsorption of both anionic and cationic molecules in wastewater can take place simultaneously (Azha *et al.*, 2018). In another study, binders and polyelectrolyte have been incorporated onto the synthesized adsorbent to enhance the functionality of the surface charges for a great removal of pollutants and heavy metal. The modified adsorbents were coated on the inert solid support such as cotton fibers, glass plate and so on to aid the separation of adsorbent after the process (Azha *et al.*, 2017). Using a powdery form of adsorbent will leads to the formation of secondary pollutant in the wastewater further explains the fundamental theory behind the usage of inert solid support (Azha *et al*., 2020). Overall, via a proper selection and modification on adsorbent we can reduce the amoun ts of contaminants in the wastewater and achieve the requirement towards a sustainable and greener future.

1.2 Problem Statement

Pollutants are present in high concentrations in industrial effluent, which may damage the water after it is dumped into the environment. Heavy metals are elements with a specific gravity greater than five times that of water, such as arsenic, chromium, copper, zinc, aluminium, cadmium, lead, iron, nickel, mercury, and silver. They are one of the most dangerous sorts of pollutants in the water. At least 20 metals are toxic, and around half of these metals are released into the environment in proportions that are detrimental to the environment as well as human (El Nemr et al., 2008).

Many industries in Malaysia, such as textile, paper and pulp, food processing, palm oil mills, and others, discharge enormous amounts of wastewater into the environment. Each of these enterprises discharge large levels of various metals into coastal water bodies, polluting them which eventually increases the chemical oxygen demand (COD) and heavy metal and posing danger to the living organism. Because of these constraints and requirements imposed by government agencies, technologies to remove these metals and contaminants are required. Precipitation with coagulation and flocculation, ion exchange, dry biomass complexation, and adsorption are some of the treatment procedures that have been utilised to remove heavy metals and pollutants from wastewater (Safoniuk, 2004).

There are, however, some limitations: Precipitation produces huge amounts of heavy metals-rich effluent sludge; ion exchange and biomass techniques are both expensive and difficult to apply on a wide scale. Adsorption is a strategy that is used because of its low cost and large-scale applicability. Activated carbon, which adsorbs dissolved organic compounds in water treatment, is a most common adsorbent in this process. Although activated carbon provides benefits such as the capacity to remove colours and the ability to treat a wide range of organic compounds, it also has limits that prevent it from treating highly soluble organics and large concentrations of organic and inorganic compounds. Conventionally adsorption of wastewater involving single ionic charges has been performed extensively which seems less efficient when it comes to the removal of variety of contaminants in industrial wastewater which poses different charges. In such cases, this research paper will adopt the novel approach of adsorption using zwitterionic adsorbent coating which can remove both anionic and cationic components in effluents such as from paper mill industry and landfill, thus reducing the COD and other wastewaterparameters.

1.3 Objectives

This research aims to study water pollution in paper mill effluent and leachate. Physico-chemical parameters, heavy metals contaminant, colour, pH and COD value were measured in this study. To handle such contamination, treatment of such industrial effluents using zwitterion adsorbent coating made up from bentonite powder was investigated.

Following objectives were set to achieve the aim of the research:

- To evaluate the effect of adsorption towards pH, reduction of colour, chemical oxygen demand (COD) and heavy metal.
- To compare and analyse the performances based on the nature of the leachate sample and paper mill effluents.

1.4 Scope of study

The goal of this thesis is to use an inexpensive and easily available zwitterion adsorbent to test wastewaters for COD, colour, and zinc removal. The wastewater was gathered from the nearby wastewater treatment plant. Batch adsorption tests was employed in this study, which were carried out on a laboratory scale. The HACH DR6000 spectrophotometer was used to analyse the water quality for heavy metals, COD, and colour.

There are three manipulating variables that need to be considered during this test. They are number of adsorbent strips, temperature, and pH of the solution. Following the completion of the experiment, the data gathered is utilised to classify the effluent quality from public places using the Environmental Quality Act (Sewage and Industrial Effluent) Regulations 1979, Maximum Effluent Parameter Limit Standard A and B as specified in the appendix.

1.5 Organization of thesis

The research report is divided into following chapters:

Chapter One: Presents the background study of the thesis research. It provides a brief introduction about the current scenario of wastewater related issue and the problem arises in their management. This chapter consist of problem statement, scope of study and objective of the research.

Chapter Two: Presents the literature review of studies conducted by other researchers. It consists of background of the theory and explains various approaches other than adsorption to treat industrial wastewater.

Chapter Three: Presents the methodology employed to achieve the objectives of the thesis. It discusses the procedures, methods, equipment, apparatus, and analysis required to carry batch adsorption study.

Chapter Four: Presents the results and discussion that were obtained during the experimentations. The chapter emphasizes on obtaining optimal conditions that lead to the best removal percentages were studied.

Chapter Five: Presents the conclusion to the research. It summarises overall results and recommendations required for future improvement in the next study.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewaters in Malaysia

Wastewater or known as sewage refers to polluted water which contain organic and inorganic substance, industrial waste, groundwater that infiltrates and mix with contaminated water, storm, runoff, and other similar liquids (Miretzky *et al*, 2004). In other terms, wastewater is defined as water containing dissolved or suspended solids that is discharged from households, businesses, farms, and enterprises. Inappropriate discharge of wastewater into water bodies leads to water pollution which eventually harms the living organism. The problem of water pollution is currently becoming more serious with reports indicating a declining trend year by year. Figure below shows composition of water pollution by industrial sectors.

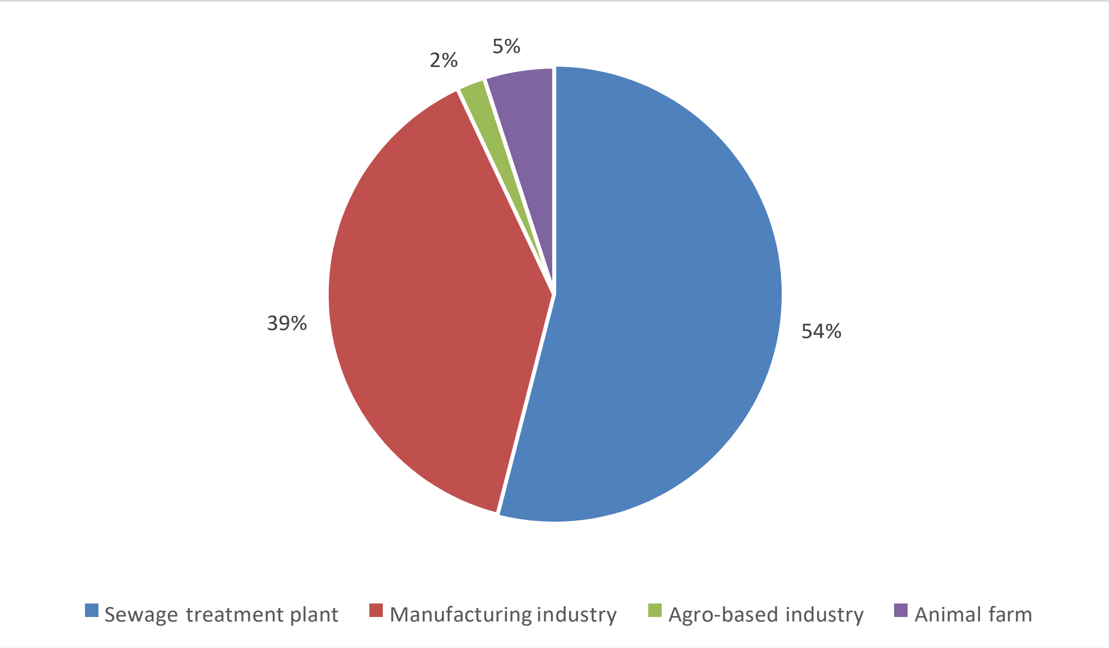


Figure 2.1 Statistic of water pollution by sectors in 2008 (Afroz et al., 2014)

From the figure 2.1 above, sewage treatment plant contributes to more than half (54%) of the water pollution to the environment followed by manufacturing industry (34%), animal farm sector (5%), and agro based industry (2%). In this study, we will be focusing more on wastewater generated from pulp and paper industry and landfill as well. In this chapter, we will learn about the concept of adsorption from selected wastewater research and present bench and field scale research studies for adsorption technology to remove various contaminants from public wastewater treatment, as well as adsorption from other research papers. This chapter summarises all of the literature reviews acquired from a variety of academic sources, such as journals and other publications.

2.2 Landfill

Landfills are a type of solid waste treatment system that has been utilised for a long time to discard municipal solid wastes (MSW). Landfilling, on the other hand, is not a long-term solution because if the landfill fails, it will release methane gas and generate liquid by-products (leachate). Rainfall travelling through the landfill is responsible for the production of leachate. The landfill will continue produce toxic leachate for 30-40 years as the decaying material is decomposedby rains (Bhalla, 2013). High concentrations of biodegradable refractory organic matter, ammonia nitrogen, heavy metals, chlorinated organic salts and inorganic salts, as well as some essential humus components, make up the leachate.

2.2.1 Characteristic of leachate

The basic metrics COD, BOD, the ratio BOD/COD, pH, suspended solids (SS), and heavy metals are commonly used to describe the characteristics of landfill leachate. In the literature, the constituents of leachate from various sanitary landfills are studied, and there are significant discrepancies. Many factors can affect the quality of leachates, including landfill age, precipitation, seasonal weather variance, waste type and composition (Kulikowska & Klimiuk, 2008).Out of all, age plays a major in influencing the characteristic of the leachate. Water quality of young landfill leachate is identified by high organic matter content and strong biodegradability, whereas water quality of old landfill leachate is defined by high ammonia nitrogen content and poor biodegradability, as shown in the table below.

Table 2.1 Characteristic of landfill leachate vs age (Bhalla, 2013).

Parameter	Young	Intermediate	Old
Age (years)	<5	5-10	>10
pH	6.5	6.7 – 7.5	>7.5
COD (mg/L)	>10 000	4 000 – 10 000	<4 000
BOD_5/COD	>0.5	0.1 – 0.3	<0.1
Organic Compounds	80% volatile fatty acids	5 – 30% VFA + humic and fulvic acids	Humic and fulvic acids
Heavy metals	Low-medium	Low	Low
Biodegradability	Important	Medium	Low

2.2.2 Composition of leachate

The composition of leachate can be categorized into four groups as shown in the table 2.1 below. This composition is classified with different test that shows a rough detail on the pollutant content which creates harm to the organism.

Table 2.2 Composition of MSW leachate (Kjeldsen *et al.*, 2002)

Groups	Pollutants
Dissolved organic matter	Volatile fatty acids, refractory compounds such as fulvic-like and humic-like compounds
Inorganic macrocomponents	Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^{+}), iron (Fe^{2+}), manganese (Mn^{2+}), and chloride (Cl^{-})

Heavy metals	Cadmium (Cd^{2+}), Chromium (Cr^{3+}), Copper (Cu^{2+}), Lead (Pb^{2+}), and Zinc (Zn^{2+})
Xenobiotic organic compounds	Aromatic hydrocarbons, phenols, chlorinated aliphatics, pesticides and plastizers

The removal of organic matter is the main goal of leachate treatment, including chemical oxygen demand (COD) removal, colour removal, and heavy metal removal, depending on the content of landfill leachate. As such, a suitable method needs to be devised to eliminate pollutants from the landfill leachate.

2.3 Paper and pulp industry

With the rise in paper demand in educational and information-oriented culture, the pulp and paper industry has become one of the most important sectors in most of the countries in recent years. Statistics showed that in the year 2015, Malaysia has produced nearly 7 737 000 metric tons of paper which is synonymous to 2.19% of the total production of paper and cardboard in Asia. Table 2.2 below shows the major producers of paper in Malaysia.

Table 2.3 List of major paper and pulp industry in Malaysia (Pokhrel & Viraraghavan, 2004)

Companies	Year Founded
Muda Paper Mills Sdn Bhd	1964
Genting Sanyen Paper and Packaging Group (GSPP)	1992
Malaysia Newsprint Industries Sdn. Bhd. (MNI)	1999
Nibong Tebal Paper Mill Sdn. Bhd. (NTPM)	1975
Pascorp Paper Industries Berhad	1954

The pulp and paper industry's expansion has been accompanied by a considerable amount of wastewater as a result of the industry's extensive use of freshwater resources throughout its entire manufacturing process. In the presence of a lot of organic matter, the wastewater has high biological oxygen demand (BOD) and chemical oxygen demand (COD) concentrations, as well as significant toxicity from harmful substances and a strong black-brown colour from lignin (Pokhrel *et al*., 2004). The black-brown effluent may raise the water temperature and reduce dissolved oxygen concentrations. The characteristics and components of paper mill effluent will be discussed in the next section below.

2.3.1 Characteristic of paper and pulp effluent

The characteristics of pulp and paper wastewater vary based on the type of process, the type of wood used, the process technologies used, internal recirculation, and the amount of water used. Chemical pulping produces a considerable volume of effluent, compared to other paper making process. Calculating the Total Suspended Solids is one of the quantitative approaches used to assess the quality of wastewater (TSS). The pulp and paper industry generates a lot of wastewaters with a lot of total suspended particles. According to research, per tonne of paper produces, 90 to 240 kg of suspended particles (Kumar *et al*, 2015). TSS levels in the wastewater from the P&P business ranged from 1175 to 1976 mg/L (Pokhrel *et al.*,2004).

2.3.2 Composition of paper and pulp effluent

There are 4 stages in pulp and paper making process which consist of raw material preparation, pulping, bleaching and paper making. At the end of each this process there will be a certain proportion of effluent released. Figure 2.3 below describes the overall process in paper making industry. In each stage of the process, there are various types of pollutants being discharged. Emitting these effluents prior before treatment will results in pollution which will affect the environment and organisms adversely. Thus, a proper wastewater treatment selection will ensure the elimination of toxic compounds and reduces the occurrences of water pollution.

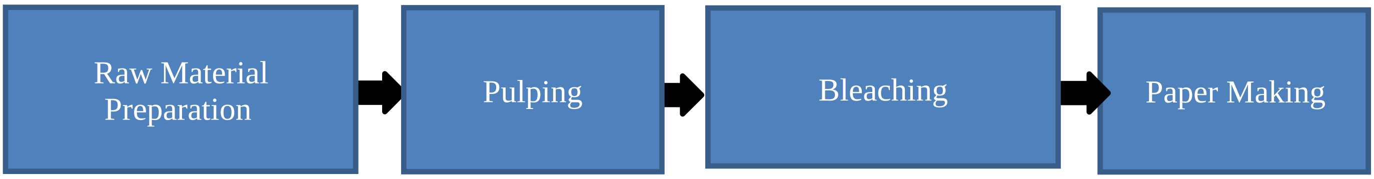


Figure 2.2 Process of pulp and paper making (Pokhrel & Viraraghavan, 2004).

2.4 Common method to treat industrial wastewaters

The discharge of industrial effluents resulted in water contamination, prompting numerous researchers to investigate the removal of pollutants and heavy metal compounds from wastewater to avoid any environmental problems. Conventional, advanced, biological, and enzymatic treatments are the most often used treatment methods.

2.4.1 Conventional treatment

Most of the industries discharge effluents containing toxic contaminants into the water bodies. In light to this, steps must be taken to obviate the water pollution. Currently, wastewater treatment evolves with adsorption, coagulation/flocculation, chemical precipitation and distillation method to separate the contaminants from the wastewater itself. They are used due to their simplicity of, ease of operation and h igh efficiencies towards different industrial wastewaters.

Table 2.4 Conventional treatments for wastewater (Crini & Lichtfouse, 2019)

Methods	Advantages	Disadvantages
Adsorption	1. Simple technology and can be adapted to many treatment formats. 2. Suitable for wide range of commercial products.	1. Relatively high investment. 2. Cost of materials.
Coagulation/flocculation	1. Simple in design 2. Integrated physicochemical process. 3. Inexpensive capital cost.	1. Requires adjunction of non-reusable chemicals such as coagulants, flocculants, and aid chemicals. 2. Physicochemical monitoring of the effluent (pH). 3. Increased sludge volume generation.
Chemical precipitation	1. Simple technology. 2. Adapted for high pollutant loads. 3. Significant reduction in chemical oxygen demand (COD).	1. Chemical consumption 2. Physicochemical monitoring of the effluent (pH) 3. Ineffective in removal of the metal ions at low concentration 4. Requires an oxidation step if the metals are complexed.
Distillation	1. Able to purify water containing. 2. Environmentally friendly process.	1. High energy requirement.
Ion exchange	1. Wide range of commercial products available from several manufacturers. 2. Well-established and tested procedures; easy	1. Not effective for certain target pollutants (disperse dyes, drugs, etc.)

	control and maintenance. 3. Easy to use with other techniques.	
Biological	1. Energy saving and environmentally friendly.	1. Optimum favourable environment is necessary. 2. Unsuitable to treat high concentration pollutants.
Enzymatic	1. Large number of species used in mixed or pure cultures.	1. Slow process. 2. Possible sludge bulking and foaming.

2.4.2 Advanced treatment

Advanced wastewater treatment is any process that able to reduce the impurities with lower usage of chemicals as compared to conventional ones. However, it has high energy costs which needs to be considered.

Table 2.5 Advanced treatment for wastewater (Crini & Lichtfouse, 2019)

Methods	Advantages	Disadvantages
Fenton process	1. Reduce the toxicity of pollutants.	1. Regeneration of iron (III) is required.
Ozonation	1. A great disinfectant.	1. Ozone's reactivity makes it a toxic chemical. 2. Efficiency influenced by ozone's concentration.
Membrane separation	1. Wide range of commercial membrane available from several manufacturers. 2. Reliable and economically feasible.	1. Investments costs are often too high for small and medium industries. 2. Low throughput and limited flow rates.

Wet air oxidation	1. Destruction of complex molecules in water solution. 2. No production of sludge	1. pH dependence. 2. High pressure and energy intensive conditions.

2.5 Adsorption Theory

Of all the method mentioned above, adsorption has been undertaken in this present research work to study the effectiveness of pollutant removal from landfill and paper mill effluent. Adsorption is when the adsorbate molecules or ions (liquid or gas) is adhered to the surface of a solid (adsorbent). It can be categorized as physisorption and chemisorption depending on the modes of adsorbate species attached onto the adsorbent surface (Ahmad et al., 2015). In order to achieve large surface area of adsorption per unit volume, porous solid particles with small diameter with interconnected pores are used. Dye molecules present in the industrial wastewaters may adsorbed on the adsorbent surfaces via hydrogen bonding, Van der Wall forces, electrostatic interaction etc. Thus, adsorption is regarded as simple and economical method to remove dyes and other molecules from wastewater.

The figure below shows the mechanism of adsorption (Scholes, 2012). Here, the solute adsorbate particles diffuse from the bulk fluid to the active surface where the adsorption takes place. This is followed by regeneration via desorbing the sorbed substance from the surface once after the adsorbent becomes saturated with the adsorbate.

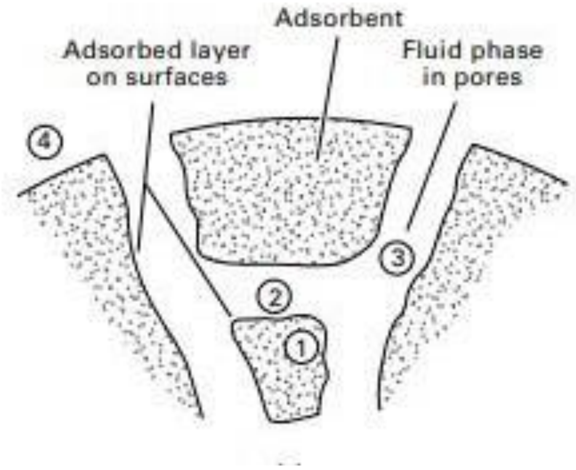


Figure 2.3 Adsorption mechanism (Seader, 2009)

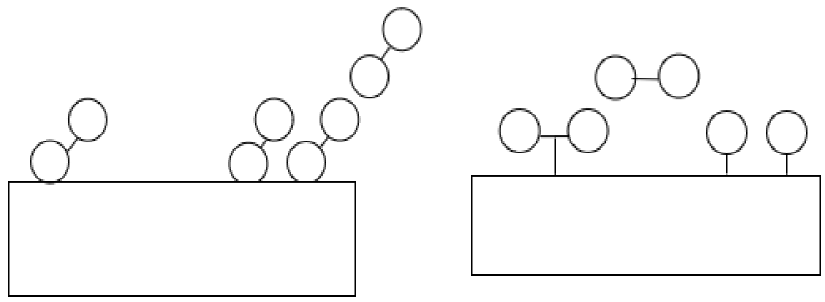
2.6 Types of adsorption

Adsorption can be divided into physical and chemical adsorption, in which the uptake of solutes on adsorbent surface occurs due to Van der Waals forces while for chemical adsorption the bonds are formed due to chemical forces. The differences between a physical and chemical adsorption are depicted as below (*Adsorption*, 2019):

Table 2.6 Comparison between physical adsorption and chemical adsorption

Physical Adsorption	Chemical Adsorption
Not specific as any fluid can be adsorbed.	Specific which means only occur if there is chemical bond formed between adsorbate and adsorbent.
Reversible and fully dependent on temperature and pressure.	Irreversible and often assisted by increase in temperature.
Occurs at low temperature and the adsorption decreases with increase in temperature as stated in Le Chateliar's principle.	Occurs slowly at low temperature and higher with increase in the pressure.
Porous substances allow greater surface area which favours efficient adsorption.	Directly proportional to the surface area, thus the adsorption increases with surface area.
No activation energy required.	Certain amount of activation is required.
Multimolecular layer is formed.	Unimolecular layer is formed.

The figure below illustrates the mechanism and general differences between chemical and physical adsorption.



Physical adsorption   Chemical adsorption

Figure 2.4 Different between chemical and physical adsorption

2.7 Paper Review for the selected wastewater

Many studies have been conducted in the recent years mainly on adsorption to eliminate suspended solids and toxic pollutants from wastewater. These studies revealed that adsorption is an efficient process due to its simplicity and ease operation in the treatment of real industrial effluents. Following section will discuss about the research work done on both leachate and paper mill effluent via adsorption process.

2.7.1 Leachate

Several studies have been reported on the usage of activated carbon (AC) to treat landfill leachate. Synthesis of recent works reveal that activated carbon are more efficient than any other adsorbent, resulting in great removal of COD, colour, and heavy metals. Activated carbon (AC) is known for their greater surface area and high adsorption ability towards various pollutants present in wastewater (Dias et al., 2007). At low concentration, AC possess stronger affinity to bind organic substances making it a promising adsorbent to treat wastewater. Being an oldest adsorbent, AC can be derived from any carbonaceous material such as charcoal, wood and peat *(Katheresan et al.*,2018). In a batch study conducted by (Chávez *et al*., 2019), AC were synthesised from coffee waste using various reagents and chemicals to reduce the COD in leachate sample. Here AC of different pore size diameter was synthesised and highest COD removal (51.3%) was obtained for AC with 65.3230µm. On the other hand, (Li et al., 2010) reported low level of COD removal using AC. However, this could be due to the compositions of the leachate sample which owns different affinities towards the adsorption sites. (Halim et al., 2010) investigated the use of composite adsorbent that is made from combination of activated carbon, zeolite, and low-cost materials such as limestone, rice husk carbon waste and ordinary Portland cement (OPC). Based on the comparison study, activated carbon recorded the highest adsorption capacity of 37.88 mg/g, followed by composite media with 22.99 mg/g, and zeolite with 2.35 mg/g. The usage of activated cow dung ash (ACA) was studied to remove the COD and contaminant from the landfill leachate. A COD removal of 73% was obtained using ACA of 20g/L dose with a contact time of 180 min. Variation of pH was studied in the similar paper where a COD removal of 75.6% and 74% were obtained at pH 6 and pH 8 respectively. Also, at temperature of 30°C and 40°C, ACA gives a COD removal of 79% and 79.9% respectively. Another interesting technology that can be used to treat landfill leachate is by performing magnetic adsorption (Reshadi *et al.*, 2020). This method has drawn the interest of many researchers due to its low toxicity, chemical stability, and simplicity. Though there are limited studies and researchworks been done, this method can be one of the promising approach to treat landfill leachates.

Table 2.7 Comparison of various adsorbent to treat landfill leachate

Adsorbent	Optimal Conditions	COD removal	
		%	mg/g
Activated carbon from coffee waste (Chávez *et al*., 2019)	4g/L of AC, 150rpm and 120min with different pore diameter of:		
	• 3.01 µm	36.1	-
	• 88.48 µm	44.7	-
	• 65.32 µm	51.3	-
	• 77.54 µm	43.0	-
Activated carbon		-	37.88
Zeolite		-	2.35
Composite media (combination of activated carbon, zeolite and low-cost adsorbent) (Halim et al., 2010)	Shaking speed of 200rpm, contact time 105min and pH 7	-	22.99
Activated Cow Dung Ash (ACA) (Kaur *et al*., 2016)	• 20g/L of ACA, contact time 180min, pH 7.8	73	-
	• 20g/L of ACA, contact time 180min, pH 6	75.6	-
	• 20g/L of ACA, contact time 120min, pH 8	74	-
	• 20g/L of ACA, pH 6, contact time 120min, temperature 30°C	79	
	• 20g/L of ACA, pH 6, contact time 120min, temperature 40°C	79.9	

2.7.2 Paper and pulp effluent

Activated carbon adsorption was found to be superior for wastewater treatment compared to other physical and chemical techniques, according to (Gong *et al*., 2008) because they have inherent limitations such as high cost, formation of hazardous by-products, and intensive energy requirements. In another study by (Pongnam *et al*, 2018) the color removal efficiency of pulp and paper effluent were tested using Lignite fly ash, Bagasse fly ash and Rice husk ash. 7 grams of lignite fly ash, bagasse fly ash and rice husk ash resulted in color removal of 46.3%, 85.8% and 17.4% respectively. The results showed that Bagasse fly ash was the most effective at removing colour from effluent, with a 94.2% removal efficiency and a pH of 7.5 - 8, despite the fact that the ash content increased by up to ten times. The influence of several operating variables, including contact time, initial concentration, adsorbent dosage, and particle size, on colour removal has been investigated by (Jain *et al.*, 2009). At a dosage of 2 g/l of baggase fly ash, the contact time for adsorption equilibrium equals 60 minutes for optimal colour removal. The material has a high removal capacity (86%) and is compatible with both the Langmuir and Freundlich models. (Qinglin Zhang, 2001) studied the adsorption of bleach plant effluent from the Kraft paper mills using activated carbon and polymer resin. The amount of colour removed increased when the adsorbent/wastewater ratio was increased. When 6g of resin and 30g of activated carbon were used, 95 percent of the colour was removed. This can be due to the narrow pore structure of activated carbon that creates difficulties for the large molecular pollutants unlike the resin.

Table 2.8 Comparison of adsorbent used to treat paper mill effluent.

Adsorbent	**Optimal condition**	**Removal**	
		Color (%)	Heavy metal (mg/g)
Lignite fly ash Bagasse fly ash Rice husk ash (Pongnam *et al.*,2018)	7g of ash dose, contact time of 60min	46.3 85.8 17.4	- - -
Bagasse fly ash (Jain, Kumar *et al.*, 2009)	2g/L of ash dose, contact time of 60min	86	-
Resin Activated carbon (Qinglin Zhang, 2001)	6g of resin dose, pH of 10 30g of AC dose, pH of 7.09	95	- -
Carrot residues (Nasernejad et al., 2005)	-	- - -	45.09 of Cr(III) 32.74 of Cu(II) 29.61 of Zn(II)

Orange peel (Pehlivan *et al*., 2006)	-	-	0.15 of Cu(II) 0.18 of Zn(II)

2.8 Zwitterionic adsorbent coating

Pollutants can be present in a mixture of ionic charges in a wastewater. There are only limited amount of sorbent that have the capability to remove wide ranges of pollutants. Thus, to eliminate both cationic and anionic compounds a novel approach of using a zwitterionic adsorbent has been adopted in which a single adsorbent able to give affinity towards specific types of ionic molecules. In simple words zwitterionic adsorbent coating will reduce non-specific adsorption and paves a way for an efficient charged pollutant removal. The advantages of implying the zwitterionic coating is that adsorption can be performed throughout the entire coated surface of the substrate which further reduce the amount of solid adsorbent required and cut down the operation process.

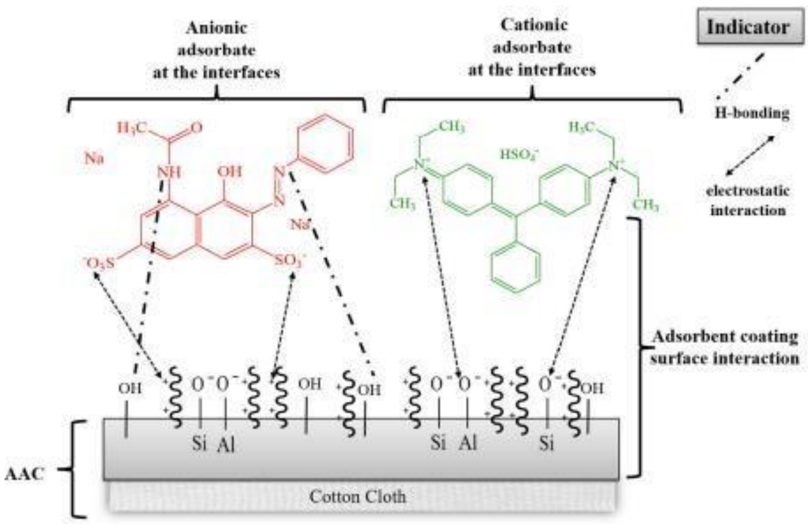


Figure 2.5 Mechanism of zwitterionic adsorbent coating (Azha *et al.,* 2018)

Figure 5 above shows how the compounds of different ionic charges are being removed with the introduction of amphoteric coating layer. The components that are involved in the coating process is binder, additive, suspension agent, liquid carrier and filler that forms a composite adsorbent solution. Figure below illustrates on a formation of coated adsorbent (clay) with zwitterion functionality.

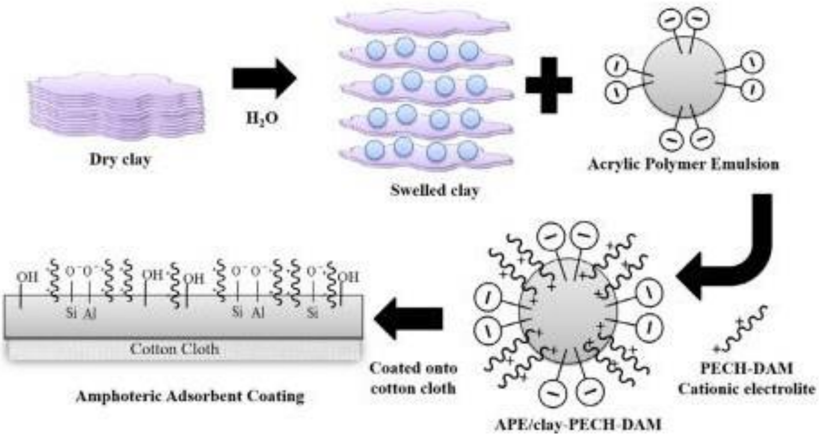


Figure 2.6 Process synthesis of zwitterion coating on clay based adsorbent (Azha *et al.,* 2018).

Current studies on zwitterionic adsorbent coating focuses mainly on the color removal and heavy metal reduction in batik wastewater. Thus, this research paper will be a pioneer for the exploration of zwitterion adsorbent towards other industrial wastewater such as landfill leachate and paper mill effluent. The performance of zwitterion adsorbent coating towards the coloured dye adsorption will be discussed below.

Based on a recent study conducted by (Azha *et al.*, 2018) a low cost zwitterionic adsorbent coating (ZACC) that has a functionality of adsorbing both anionic (Acid Red 1) and cationic (Brilliant Green) dyes have been synthesized by mixing bentonite clay, acrylic polymer (AP) and polyethylene-diamine (EPIDMA). The synthesized adsorbent has been coated on a solid support such as cotton fabric to achieve a good mechanical stability and to ease the separation of adsorbent after the process. The EPIDMA molecules serve as a cationic polymer that produces positive charges on the adsorbent surfaces which makes it capable of removing anionic charges from wastewater. Meanwhile the AP act as binder and provides a net negative charged surface which in turn allows cationic dye removal. The effect of adsorbent coating dosage can be seen when increase in the adsorbent coating mass followed by an improvement in Brilliant Green (BG) removal up to 100%. Increment in the adsorbent dosage is associated with the larger surface area and more available adsorption sites for the process to take place. On the other hand, the percentage of dye removal declines when the initial concentration of the dyes increased. This is due to the saturation of the adsorption sites with more dye molecules being engaged. At a pH range of 2 to 9 a percentage removal of 70±0.3% and at a pH of 11 a percentage removal 56.6% have been recorded respectively. Higher pH synonymous to a greater hydroxyl, OH^- concentration on the ZACC surfaces which favors the attraction of cationic BG dyes via electrostatic bonding. A lower pH is suitable for the greater anionic AR1 dyes removal due to presence of H^+ and H_3O^+ ions.

Another research has been carried out using Iron-Modified Composite Adsorbent Coating (IMCAC) for azo dye removal (Lotfi Sellaoui *et al.*, 2018). In this study, the composite adsorbent coating was further modified with iron salts to perform photo-Fenton process that yields OH^- radicals in the presence of light and hydrogen peroxide to aid the regeneration of spent adsorbents. The adsorbent was synthesized by modifying bentonite clay with Iron (III) nitrate nonahydrate, $Fe(NO^3)^3$. Similarly, EPIDMA acts as a cationic polyelectrolyte and acrylic polymer emulsion (APE) acts as a binder. The adsorbent was later coated on the cotton cloth where a strong adsorbent has been established. No peel off is observed at the end of the process. The IMCAC which was in brownish orange color originally turns to red, proves that the AR1 dye has been adsorbed on IMCAC. Sulphur which was absent in the raw IMCAC is found later after the dye adsorption. The sulphur is believed to be originated from SO_3^- groups of the AR1 molecules. Chlorine which was initially present in the EPIDMA is absent after the dye adsorption. This statement implies that ion exchange has taken place between Cl^- ions from EPIDMA and SO_3^- groups from AR1. At different contact time, IMCAC shows a drastic increase in AR1 removal in 10min which is from 0 to 76.56% and further rise to 100% at 120 min. At a pH range of 3 to 11, the color removal was greater than 97% which portrays that the adsorption using IMCAC is independent with pH. This could be due to the strong attachment of cationic EPIDMA that allows adsorption at any pH condition. The regeneration of spent IMCAC obtained was 10 cycles, in which for the first 4 cycle 80% of dye removal has been recorded and it maintained a constant value followed by a drop in the removal for the consecutive cycles.

In another study, coating paint (CP) adsorbent has been opted to perform the same task (Azha *et al*., 2017). The CP formulation contains bentonite clay, distilled water as a carrier and binder. Different type of binders which were water based, water-glossy based and oil based was incorporated to study the adsorption performance respectively. Of all, water-based binder shows a speedy adsorption with a complete removal of methylene blue (MB) dye within 2hour. Meanwhile, oil-based binder recorded a dye removal of 0% within 3 hours due to its non-polarity and as for the water- glossy a 50% of dye removal was achieved in 3hour. Using a thin coated adsorbent coating (TCAL) enhanced the surface area to weight ratio and reduce the amount of solid adsorbent required. With increase in the initial dye concentration, the amount MB adsorbed per unit mass also increases. However, there is drop in the percentage of dye removal. For the initial MB concentration of 20ppm-100ppm the contact time needed to reach equilibrium was lower than that of 200ppm-500ppm. At a high temperature,