ADSORPTION AND MAGNETIC TREATMENT EFFECT ON FLUORIDE-DYE MIXTURE WASTEWATER

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Mechanical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

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ABSTRACT

Semiconductor industry is one of the developing industries in the world, even though it brings high revenue, the semiconductor industry generates fluoride-containing wastewater which could potentially bring severe impacts to the environment and humans. Semiconductor wastewater is usually high in fluoride concentration, dark in colour and slightly acidic (pH 6.3). The source of fluoride content is mainly due to the hydrogen fluoride (HF) used in semiconductor micromachining processes. The wastewater fluoride concentration typically falls in the range of 100-2000 mg/L and one of the substances that contributed to the dark appearance is the dye particles. Therefore, it is necessary to conduct wastewater treatment to remove fluoride and dye particles before releasing to the river. Adsorption treatment is effective in treating wastewater; however, since activated carbon is usually a one-time-usage product, the cost of regularly purchasing activated carbon could cause heavy burden to the semiconductor companies. On top of that, the price range of coconut shell activated carbon (CSAC) has been increasing in the last few years. A method to cut down the cost and wastage of activated carbon is required. Adsorption treatment using coconut shell activated carbon, a low cost biochar adsorbent is chosen to treat the simulated semiconductor wastewater made up of fluoride and methylene blue dye (MB) mixture. The aim is to find the optimum adsorbent dosage to achieve maximum fluoride and MB removal from the mixture, under pH 6.3. By predicting the optimal dosage, the wastage of activated carbon can be avoided. Comprehensive literature review was done to collect reference studies of existing experimental data and mathematical models for fluoride and MB removal. The models are improved and used to predict the adsorption treatment of fluoride-MB mixture based on adsorbent dosage and pH parameters. Mathematical model of the fluoride-MB mixture adsorption was constructed using Response Surface Methodology (RSM). For initial concentration of fluoride (10 mg/L) and MB (100 mg/L), the optimum adsorbent dosage is found to be 9.5 g/L with the fluoride and MB removal to be 81.80 % and 95.43 % respectively. The constructed model is useful in predicting the adsorption treatment of fluoride-MB mixture under different pH condition. Besides, magnetic treatment is also explored as a

potential method to improve the adsorption capacity of activated carbon. By applying magnetic treatment on the activated carbon, the adsorption capacity can be improved and in the long run, it can potentially reduce the amount of adsorbent dosage needed. A mathematical model is constructed based on existing experimental data for the relationship of magnetic field and activation agent, potassium hydroxide (KOH) ratio to the activated carbon adsorption capacity. The constructed model portrays relatively linear relationship between the parameters. All the constructed mathematical models can be further improved in the future by possibly expanding the model parameter range through experimental validation.

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LIST OF SYMBOLS / ABBREVIATIONS

CSAC	coconut shell activated carbon
PAAC	*Populus alba* activated carbon
CLAC	coconut leaf activated carbon
CFD	coconut fibre dust
F	fluoride
MB	methylene blue
KOH	potassium hydroxide
NaOH	sodium hydroxide
HF	hydrogen fluoride
COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
RSM	Response Surface Methodology
OFAT	one-factor-at-a-time
ANOVA	Analysis of Variance
N_2	Nitrogen

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Wastewater is any form of water that has been polluted due to human activities. Wastewater is generated in agricultural activities, industrial areas, domestic or households. Any type of wastewater can be harmful to the environment, humans, animals as well as plants which is why they should be treated. It is compulsory to do wastewater treatment before releasing it to the rivers to avoid any adverse effects.

Semiconductor industry is one of the developing industries in the world which generated at least US$ 40 billion in worldwide marketing sales (Jalil, et al., 2019). Even though it brings high revenue, the semiconductor industry generates fluoride-containing wastewater which could potentially bring severe impacts to the environment and humans. The fluoride concentrations generated in the wastewater usually fall within the range of 100-2000 mg/L and fluoride concentration that exceeds 100 mg/L would be deemed harmful to humans. Semiconductor wastewater is described to be high in fluoride content, dark in colour and slightly acidic (pH 6.3). It has high turbidity, high chemical oxygen demand (COD), low biodegradability, and it is mixed along with several other organic and inorganic substances (Fatehah, Hossain and Teng, 2013) (Lin and Jiang, 2003).

Fluoride is a common substance found in our daily lives such as toothpastes and drinking water but excess fluoride consumption is hazardous to humans. According to the World Health Organization (WHO) guidelines, taking in excess fluoride can cause fluorosis which can affect the teeth and bones. If humans were to consume large amount of fluoride in long term, it can subsequently cause severe skeletal problems. The need to control the fluoride content then emerged where the WHO recommends fluoride concentration of 1.5 mg/L in tap water (Hamamoto and Kishimoto, 2017). As such, the fluoride-containing wastewater generated in the semiconductor industry raises public's concern if they are not handled properly.

On top of that, semiconductor wastewater is described to be dark in colour. The dark appearance of the wastewater is caused by the presence of several different substances such as refractory photoresist, salts and also dye particles (Lin and Jiang, 2003). Even with any treatment process that successfully removes the fluoride content, the treated water may be left with some colour intensity. The higher the intensity of colour in water affects the light penetration and the turbidity will increase despite the low content of suspended particles. High turbidity level is often associated with damaging aquatic life where high turbidity reduces the light penetration required for aquatic plants to carry out photosynthesis. Less photosynthesis, less oxygen is produced, this causes the BOD and COD to increase and can deteriorate the water quality.

1.2 Importance of the Study

Wastewater has been an ongoing issue in Malaysia for years and there is yet to be an optimum solution. The recent case of Sungai Kim Kim toxic pollution incident that happened in 2019 caused thousands to fall ill due to illegal disposal of chemical waste into the river. This case caught many attention since it could have been easily avoided if the waste was treated properly in the first place. Now people are much more aware that illegal waste disposal could be done effortlessly, it is unimaginable how much more industrial wastewater have been discharged irresponsibly in the past without getting caught.

There are several wastewater treatments that are commonly used in treating semiconductor industry wastewater such as electrocoagulation, chemical precipitation, ion exchange and adsorption (Wang, et al., 2017) in removing the fluorides. The adsorption technique appears to be superior among these methods when comparing their flexibility and ease of operation. Coconut shell activated carbon (CSAC) is one of the most common low-cost biochar adsorbent used in Malaysia (Astimar, et al., 2016). However, adsorbents are usually one-time use and no regeneration, the cost of regularly purchasing adsorbents would be a heavy burden to the companies (Crini, et al., 2019). On top of that, due to the global pandemic, several companies have increased the price range from 3-10 % for CSAC (Dr. Gupta Verlags GmbH, 2020) (Goudappel, 2020). This potentially could cause some companies to avoid performing wastewater treatment even if it meant in breaking the law. This would gradually lead to more water pollution problems in Malaysia and disaster may eventually break out.

This dire situation requires a method in minimizing the cost of treating the wastewater. A suitable guideline could be given to predict the optimum adsorbent dosage that is sufficient to achieve maximum adsorption without excess to prevent any wastage of activated carbon.

Other than that, the magnetic field treatment is a method worth exploring for its potential in improving the adsorption treatment. Plenty of research studies were done on the effectiveness of integrating magnetic field into adsorption treatment and majority of the studies gave promising results. Zaidi, et al. (2014) claimed that magnetic field technology is effective in enhancing wastewater treatments and the magnetic field is proven to be beneficial in helping the solid-liquid particles separation. However, it is not implemented commercially worldwide since there are a few studies that have conflicting results even though plenty of them have proven otherwise. The lack of uniform trend in the research studies cause people to lose confidence in the treatment method. If the research on magnetic field treatment were to be found successful, a huge milestone would be built on the wastewater treatment technology.

1.3 Problem Statement

This study mainly focuses on investigating the treatment process on semiconductor industry wastewater using adsorption process and magnetic field treatment. Investigation will be conducted on fluoride mixed with methylene blue (MB) dye wastewater to simulate the treatment process on real semiconductor industry wastewater that has high fluoride content, high turbidity, is dark coloured and also slightly acidic (pH 6.3).

Adsorption technique is already commonly used as the wastewater treatment to remove fluoride ions and it is widely known that adsorption technique is superior in terms of fluoride removal. Not only is that, the adsorption technique is also known to be effective in removing MB dye particles from MB dye wastewater. However, the one-time usage activated carbon and the cost of regularly purchasing activated carbon would be unsustainable for some companies. On top of that, the cost of CSAC has been steadily increasing in the last few years. In order to avoid any wastage of activated carbon and to minimize the adsorbent cost, we are interested to find out the optimum adsorbent dosage to be used to achieve the best adsorption treatment on a fluoride-MB mixture wastewater under different conditions. However, there are limited studies in applying adsorption wastewater treatment on fluoride and MB mixture solution. The adsorption treatment on individual fluoride and MB dye wastewater could be very different from the adsorption treatment done on the mixture of fluoride and MB dye. Hence in this project, the focus is to construct a mathematical model that can be used to predict the adsorption treatment using coconut shell activated carbon (CSAC) on fluoride-MB mixture based on parameters of adsorbent dosage, pH and contact time. The mathematical model can be served as a guideline to find optimum adsorbent dosage.

To improve the adsorption treatment process, magnetic treatment is also investigated to observe the magnetic effect on both the fluoride and MB adsorption. However, there are not sufficient sources that involve magnetic treatment using RSM modelling on both fluoride and MB dye wastewater. Therefore, the focus is tuned to investigate the effect of magnetic field on the preparation process of activated carbon. There were successful studies on applying magnetic treatment during preparation process of activated carbon which can improve the activated carbon adsorption capacity. The study has shown the difference in the adsorption capacity of the prepared activated carbon with or without magnetic field applied; however, there was no clear mathematical model that can portray the relationship between the magnetic field intensity applied with the adsorption capacity of the activated carbon. Hence, we are interested to construct a mathematical model according to the experimental data that can predict the effect of magnetic field intensity on the adsorption capacity of the activated carbon.

1.4 Aim and Objectives

This project aims to investigate the effects of adsorption treatment on a fluoride-MB dye mixture solution through mathematical modelling to simulate the adsorption treatment of actual raw semiconductor wastewater. Besides, this study also aims to construct a mathematical model of magnetic effect on the adsorption capacity of activated carbon. Detailed objectives are listed as follows:

i) To improve current existing individual fluoride and MB adsorption treatment mathematical models based on the parameters of coconut shell activated carbon (CSAC) adsorbent dosage, pH, and contact time.

ii) To construct a mathematical model for the adsorption treatment on fluoride-MB mixture through prediction using the improved individual mathematical models of fluoride and MB adsorption treatment.

iii) To determine the optimal CSAC dosage used for achieving the maximum fluoride and MB removal from the fluoride-MB mixture under pH 6.3, which is the pH condition of an actual raw semiconductor wastewater.

iv) To construct a mathematical model of magnetic effect on the activated carbon adsorption capacity.

1.5 Scope and Limitation of the Study

The mathematical modelling of the adsorption and magnetic treatment are conducted using the University campus laboratory software Design Expert within the time duration of four months from January to April 2021.

The scope covers simulated semiconductor industrial wastewater by using fluoride-MB mixture in the mathematical modelling. Information is obtained from current existing experimental results through comprehensive research to ensure the reliability of the mathematical modelling process.

The independent variables of adsorption treatment involve the CSAC adsorbent dosage, pH and treatment contact time. The initial fluoride and MB concentration of the simulated wastewater is close to the real wastewater content based on the data compiled from the other studies. Whereas for the magnetic treatment, the independent variables are the magnetic field intensity and activation agent, potassium hydroxide (KOH) ratio.

The improvement of the mathematical models are limited since there is no experimental study carried out to verify the mathematical models; hence, the construction of the mathematical models has to be validated in the future.

1.6 Contribution of the Study

This project is able to provide a mathematical model solution as a guideline to find the optimum condition of adsorption treatment on fluoride-MB mixture based on parameters of CSAC adsorbent dosage and pH. The purpose is to minimize any wastage of activated carbon during the adsorption treatment and to avoid the extra cost. The mathematical model is utilised to find the optimum dosage in order to achieve maximum fluoride and MB removal under the real pH condition of semiconductor wastewater which is pH 6.3.

Besides, another mathematical model is constructed to model the magnetic effect on the improvement of the activated carbon adsorption capacity and to predict the relationship between magnetic field strength and the adsorbed amount by the activated carbon.

1.7 Outline of the Report

This report begins with introduction on topics related to semiconductor wastewater, adsorption treatment and magnetic treatment, followed by the problem statement and objectives. Literature review is done to gather studies required as reference for the methodology and results. The studies related to fluoride and MB dye wastewater are gathered for their experimental results and also mathematical models. Then, this is followed by the methodology that explains on how to obtain the final mathematical models and results. Results and discussions further discuss the findings on the constructed mathematical models and also the optimization. Finally, this report ends with conclusion with the objectives achieved along with several recommendations listed for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Semiconductor industry is one of the worldwide leading industries and it is unavoidable that the byproduct of the industry's success may bring hazardous effects to the environment. The wastewater usually contains various types of harmful contaminants. Engineers have come up with different approaches to develop better treatment solutions for the wastewater. Since a ban was launched by the Carbon Disclosure Project on the dangerous substances that are unsustainable, the semiconductor industry has been receiving the public's pressure to take action regarding the wastewater issues (Hsu, et al., 2011).

Semiconductor manufacturing process generates significant amount of wastewater due to the large usage of ultrapure water in the chemical and mechanical polishing process. There are six common toxic emissions from the semiconductor industry including Hydrogen Fluoride (HF), Ammonia (NH_3), Nitric Acid (HNO_3), Hydrochloric Acid (HCl), N-methy-2-pyrrolidone (NMP), Nitrate Compounds (NO_x) and Sulphuric Acid (H_2SO_4). Among these hazardous chemicals generated (Shen, Tran and Minh Ly, 2018), HF accommodates 40 % of the total harmful substances generated from the semiconductor industry (Chuang, Huang and Liu, 2002).

2.2 Fluoride Wastewater

HF is mainly used in the chemical vapour deposition process as a cleaning gas to remove any unused chemical substances that adhere to the inside of the furnace, or as an etchant to strip away the silicon dioxide layer in micromachining process. HF in the form of either gas or liquid, it reacts with water to form hydrofluoric acid and this is where the fluoride ions in the semiconductor wastewater originate from.

A sample of HF semiconductor wastewater was obtained from a fabrication company in Kulim Hi-Tech, Malaysia for the study in characterization and transformation behaviour of HF (Saipudin and Omar, 2017). The parameters of the raw HF wastewater was tested and the initial pH was found to be 6.35 and the fluoride content was 35.58 mg/L.

2.2.1 Health Hazards of Fluoride Ions

Fluoride may not be considered as an essential mineral element since humans do not need it to survive but it is an important element required in maintaining dental health and we can also find fluoride in our daily drinking water. Other than that, consumption of fluoride serves no purpose for human's growth or sustainability.

As opposed to that, fluoride ions can actually cause adverse effects to the human's health. As mentioned previously, when fluoride reacts with water it forms hydrofluoric acid and if ingested excessively this may result in burning of human tissues due to the low pH (Ullah, Zafar and Shahani, 2017). Next, it has the possibility of inhibiting the nerve impulse because of the chemical complexes between calcium and fluoride that will affect the nerve functions. Apart from that, chronic exposure to fluoride may eventually results in skeletal fluorosis. This condition is described as the increment in bone mass and density due to the excess fluoride that deposits within the bone matrix. If not treated in early stage, skeletal fluorosis may lead to arthritis, osteoporosis, spinal cord compression etc.

Hence it is important that the authority needs to strengthen and enforce the law to ensure the complete cooperation of the companies in treating the semiconductor wastewater and to avoid any tragedy falling upon the citizens. Engineers are also expected to contribute in developing more efficient and cost effective treatment methods to encourage companies taking part in the proper wastewater treatment procedure.

2.2.2 Hydrogen Fluoride Waste Management Performance by Companies

A study was done by (Shen, Tran and Minh Ly, 2018) to examine the performance of the existing local companies in their chemical waste management in United States. Table 2.1 below shows their clustering results of the hydrogen fluoride (HF) waste managed by the local companies.

4 types of HF waste management were clustered where companies categorized under Type 1 showed the best performance and Type 4 showed the worst performance. As shown in the tabulated results, there is only 1 company that was categorized in the best performance class. More than 65.4 % of their HF waste was sent to be recycled, around 20 % was treated either on-site or off-site and the remaining 13 % of the waste was released. Majority of the companies participated in the study were classified under Type 2 category, these companies did minimal recycling on the HF waste which was only around 0.3 % and they mostly implement the treatment process on site which was 95.9 %. There is only 1 company categorized in Type 3 as well where the company did 100 % off-site treatment on the HF waste. The 2 worst performing companies classified under Type 4 did not do any recycling or treatment process and did 100 % on-site release of the HF chemical waste.

Based on the results, we can observe that 34 out of 37 companies preferred to conduct treatment processes as opposed to recycling the HF waste. Though not the best performance expected, it was satisfactory that they conduct treatment processes on the waste before releasing it to the river. However regarding the worst performing companies, it was concerning that they did not commit to any procedures required for safe discharge of wastewater. Even though majority of the companies abide by the rules to do the necessary course of actions, these 2 companies are the epitome of the problems. This shows that a few companies are all it takes to possibly cause serious pollution accidents.

This study results validate the purpose of this project which is to study on wastewater treatment method in removing fluoride ions and possibly designing better treatment solutions since majority of the companies go for wastewater treatment rather than recycling. Cost effective treatment solution is required as well to urge all the companies to cooperate for safe wastewater disposal.

Table 2-1 Clustering results of the HF waste. (Shen, Tran and Minh Ly, 2018)

Approach	Type 1	Type 2	Type 3	Type 4
On-site Release	1.6%	2.6%	0%	100%
Off-site Release	11.4%	0.3%	0%	0%
On-site Treated	19.3%	95.9%	0%	0%
Off-site Treated	2.3%	0.9%	100%	0%
Recovery	0%	0%	0%	0%
Recycle	65.4%	0.3%	0%	0%
Number of Companies	1	33	1	2

2.3 Dye Wastewater

Dye wastewater is already a common topic that has been studied by researchers. Dye effluents are high in colour intensity, pH, suspended particles, COD, and BOD (Yaseen and Scholz, 2019). Textile industry is one of the major contributor to the environmental pollution problems due to the dye effluents. Holkar, et al. (2016) stated that textile industry utilizes many types of artificial dyes to produce the vibrant clothings and this leads to great amount of dye wastewater discharge, especially when the dye-uptake by the fabrics is poor. The textile industry in India partakes 80 % of the total dye production because of the huge demand for polyester and cotton globally. The dyeing and finishing operations done in the textile industry contributed about 17-20 percent of industrial wastewater according to the World Bank estimation (Naik, Desai and Desai, 2013).

2.3.1 Health Hazards of Dye Particles

The untreated dye wastewater greatly impacts the aquatic life once they are discharged. The high intensity of colour reduces the light penetration in the water and affect the photosynthetic function of the aquatic plants. Reduced photosynthesis activity causes lower oxygen produced underwater and this directly affects the oxygen consumption by the fish. Not only it affects the oxygen level underwater, dye particles may be lethal to some marine life because of the metal components content.

Different types of dye consist of different components, some of the dye contains sulphur, chromium compounds and heavy metals lead, making the dye effluent highly toxic. Other than that, around 40 percent of the dye used globally contain the carcinogenic chlorine compound (Kant, 2011). By breathing in or absorbing through humans skin, these chemicals could cause allergic reaction in some people and even affect the unborn children.

2.4 Acceptable Conditions for Discharge of Industrial Effluent

Jalil, et al., (2019) mentioned that in general, the semiconductor industry generates about 100-2000 mg/L of fluoride concentration in the discharged wastewater whereas Saipudin and Omar (2017) found that the fluoride content of a sample HF wastewater discharged by one of the companies in Malaysia is to be 35.58 mg/L. Both the stated amount of fluoride concentration far exceeds the permissible amount of 1.5 mg/L which was the guideline provided by World Health Organization (WHO) (World Health Organization, 1993). Malaysian Department of Environment (DOE) also regulated the baseline amount of fluoride content to be not more than 2.0 mg/L for Standard A and 5.0 mg/L for Standard B as shown in Table 2.2.

Table 2-2 Acceptable conditions for discharge of industrial effluent for mixed effluent of Standards A and B in Malaysia (Department of Environment, 2010)

ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT FOR MIXED EFFLUENT OF STANDARDS A AND B

	Parameter	Unit	Standard	
			A	B
	(1)	(2)	(3)	(4)
(i)	Temperature	°C	40	40
(ii)	pH Value	-	6.0-9.0	5.5-9.0
(iii)	BOD_5 at 20°C	mg/L	20	40
(iv)	Suspended Solids	mg/L	50	100
(v)	Mercury	mg/L	0.005	0.05
(vi)	Cadmium	mg/L	0.01	0.02
(vii)	Chromium, Hexavalent	mg/L	0.05	0.05
(viii)	Chromium, Trivalent	mg/L	0.20	1.0
(ix)	Arsenic	mg/L	0.05	0.10
(x)	Cyanide	mg/L	0.05	0.10
(xi)	Lead	mg/L	0.10	0.5
(xii)	Copper	mg/L	0.20	1.0
(xiii)	Manganese	mg/L	0.20	1.0
(xiv)	Nickel	mg/L	0.20	1.0
(xv)	Tin	mg/L	0.20	1.0
(xvi)	Zinc	mg/L	2.0	2.0
(xvii)	Boron	mg/L	1.0	4.0
(xviii)	Iron (Fe)	mg/L	1.0	5.0
(xix)	Silver	mg/L	0.1	1.0
(xx)	Aluminium	mg/L	10	15
(xxi)	Selenium	mg/L	0.02	0.5
(xxii)	Barium	mg/L	1.0	2.0
(xxiii)	Fluoride	mg/L	2.0	5.0
(xxiv)	Formaldehyde	mg/L	1.0	2.0
(xxv)	Phenol	mg/L	0.001	1.0
(xxvi)	Free Chlorine	mg/L	1.0	2.0
(xxvii)	Sulphide	mg/L	0.50	0.50
(xxviii)	Oil and Grease	mg/L	1.0	10
(xxix)	Ammoniacal Nitrogen	mg/L	10	20
(xxx)	Colour	ADMI*	100	200

ADMI- American Dye Manufactures Institute

Table 2-3 Characteristics of textile wastewater according to process (Carmen and Daniela, 2012)

Process	COD	BOD	TS	TDS	pH	Colour	Water usage
	g O_2/L	g O_2/L	g/L	g/L		ADMI	L/kg product
Dyeing	1.1-4.6	0.01-1.8	0.5-14.1	0.05	5-10	1450-4750	8-300

Table 2-4 Acceptable conditions for discharge of industrial effluent and mixed effluent containing COD (Department of Environment, 2010)

Extracted from Environmental Quality (Industrial Effluents) Regulations 2009 (PU(A) 434)

SEVENTH SCHEDULE
(Regulation 12)
ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT CONTAINING CHEMICAL OXYGEN DEMAND (COD) FOR SPECIFIC TRADE OR INDUSTRY SECTOR

(1) Trade/Industry	(2) Unit	(3) Standard	(4) Standard
(a) Pulp and paper industry			
(i) Pulp mill	mg/L	80	350
(ii) Paper mill (recycled)	mg/L	80	250
(iii) Pulp and paper mill	mg/L	80	300
(b) Textile industry	mg/L	80	250
(c) Fermentation and distillery industry	mg/L	400	400
(d) Other industries	mg/L	80	200

EIGTH SCHEDULE
(Regulation 13)

ACCEPTABLE CONDITIONS FOR DISCHARGE OF MIXED EFFLUENT CONTAINING CHEMICAL OXYGEN DEMAND (COD)

(1) Unit	(2) Standard A	(3) Standard B
mg/L	80	200

As for the dye wastewater, the typical characteristics of textile wastewater according to process are shown in Table 2.3. The dyeing process generates the wastewater with the colour intensity of about 1450-1750 ADMI. Based on the DOE guideline in Table 2.2, the maximum allowable colour intensity is only 100 ADMI for Standard A and 200 ADMI for Standard B.

Other than that, the sample textile wastewater has a BOD level of 0.01-1.8 g O_2/L and COD level of 1.1-4.6 g O_2/L. In Table 2.2 Malaysian DOE requires the BOD level to be lesser than 20 mg/L (0.02 g O_2/L) for Standard A and 40 mg/L (0.04 g O_2/L) for Standard B. For the COD level, Table 2.4 shows the maximum COD level allowed to be only 80 mg/L (0.08 g O_2/L) for Standard A and 250 mg/L (0.25 g O_2/L) for Standard B.

2.5 Adsorption Treatment

There are several wastewater treatments that are commonly used in treating semiconductor industry wastewater such as electrocoagulation, chemical precipitation, ion exchange and adsorption in removing the fluorides (Wang, et al., 2017). The adsorption technique appears to be superior among these methods when comparing their flexibility and ease of operation.

In brief explanation, adsorption describes the process of adhesion of gas, liquid or solid molecules onto the adsorbent's surface. Adsorption technique is widely known and used in the wastewater treatment for removing different types of compounds from various industrial discharged wastewater (Crini, et al., 2019). In industrial wastewater treatment, adsorption is a process used in separating solid, liquid or gas substances by binding the substances onto the exterior or interior surfaces of a solid material known as the adsorbents. However there are numerous types of adsorbent material being used in industrial wastewater treatment and they can be mainly categorized into five groups such as natural materials, treated natural materials, manufactured materials, agricultural solid wastes and biosorbents. Among the adsorbents available, activated carbon is the conventional adsorbent used at industrial scale and it is abundantly used not just for treating wastewater but for removing impurities from the drinking water supply as well.

Even though adsorption treatment is very effective, adsorbents are usually one-time use and no regeneration, the cost of regularly purchasing adsorbents would be a heavy burden to the companies (Crini, et al., 2019).

2.5.1 Coconut Shell Activated Carbon

Activated Carbon has a strong affinity for trapping organic substances even with low concentration of contaminants (Cooney, 1998). It is made by using various types of carbonaceous materials such as coals, wood, peat, coconut shells and etc. In order to produce activated carbon, the materials have to go through carbonization and activation processes. Activated carbon is manufactured in such a manner that they have immense network of pores within its structures and the total surface area within the porous structures is usually within 500 to 1500 m^2/g which is relatively huge. The higher the surface area the more adsorption process could take place. This makes activated carbon a huge feat in adsorption treatment process.

The production of highly effective activated carbon is still limited in some developing countries (Aljeboree, Alshirifi and Alkaim, 2017). Nowadays people seek for efficient and cost effective activated carbon that does not bring harm to the environment. This brings attention to the activated carbon synthesised from biomaterials which includes coconut shells. Coconut shell activated carbon (CSAC) is commercially used for adsorption treatment. Coconut shell waste can be found abundantly in Malaysia due to the agricultural industry. Hence, it is a good source to be manufactured into activated carbon where it can supply the demand for activated carbon and also disposal of the coconut shell waste at the same time. CSAC is one of the mostly used activated carbon in Malaysia (Astimar, et al., 2016). CSAC has a high surface area estimated around 1244-1768.8 m^2/g with the pore size of 2.3-2.9 nm (Iqbaldin, et al., 2013). The cost of CSAC highly depends on the final product quality, the price range of CSAC in Malaysia is around RM 600-1000 per metric tonne (Daud, et al., 2017). However, due to the coronavirus outbreak, the production of activated carbon is severely affected globally, the production is decreased which causes the activated carbon availability to decrease as well (Market Research Report, 2020). Several companies have increased the price range for activated carbon due to the global pandemic, Cabot company has announced a 3-8 % of price increment on their general activated carbon product (Dr. Gupta Verlags GmbH, 2020), and Jacobi Carbons announced a price increment of 10 % for all the CSAC (Goudappel, 2020). Besides, Calgon Carbon Corporation actually implemented 8-10 % of price increment on CSAC since July 2017 due to the scarcity of the raw material of coconut shell which led to the spike in the material cost (Calgon Carbon Corporation, n.d.). The price of CSAC is observed to be increasing steadily in the last few years.

2.5.2 Activated Carbon Adsorption Treatment on Fluoride Wastewater

Bonyadi, et al. (2019) conducted studies on fluoride removal using activated carbon synthesised from a tree species named *Populus alba* (PAAC).

Adsorption treatment was done on different samples of synthetic and real wastewaters.

The effect of activated carbon dosage is shown in Figure 2.1 where, by increasing the adsorbent dosage from 1-4 g/L, the fluoride adsorption increases and the adsorption peaks at around 90 % with 4 g/L dosage. The adsorption remains constant at around 92 % for dosage from 4-7 g/L. Hence, the optimum dosage was found to be 4 g/L for this study.

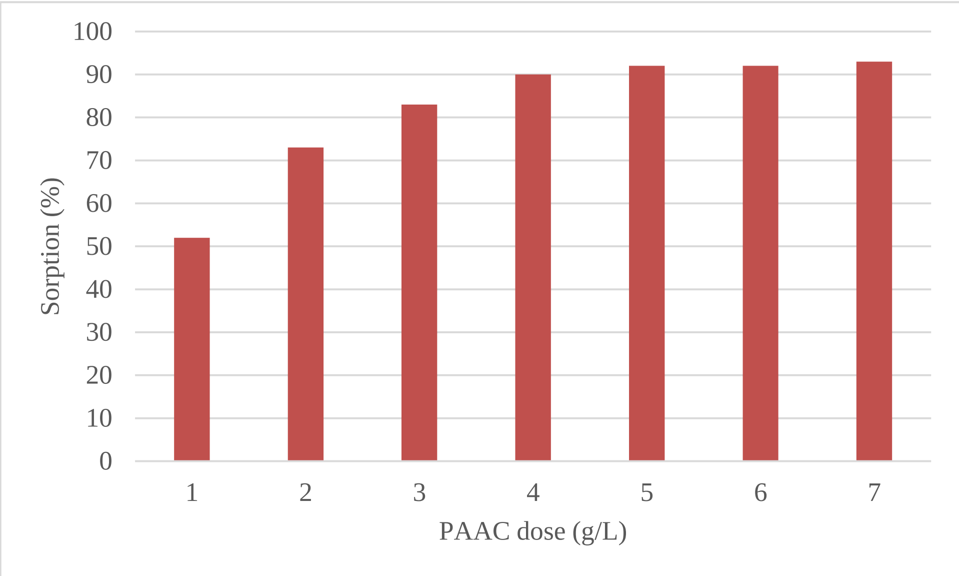

Figure 2-1 Effect of PAAC dose on the fluoride removal (Experimental condition: 10 mg/L initial F concentration, 100 min contact time, pH 6, 25 °C temperature) (Bonyadi, et al., 2019)

In Figure 2.2 shows that the adsorption increases when the pH increases from 2 to 6 and then decreases drastically afterwards from pH of 6 to 10. This indicates that the fluoride removal by adsorption will be at maximum at the pH of 6.

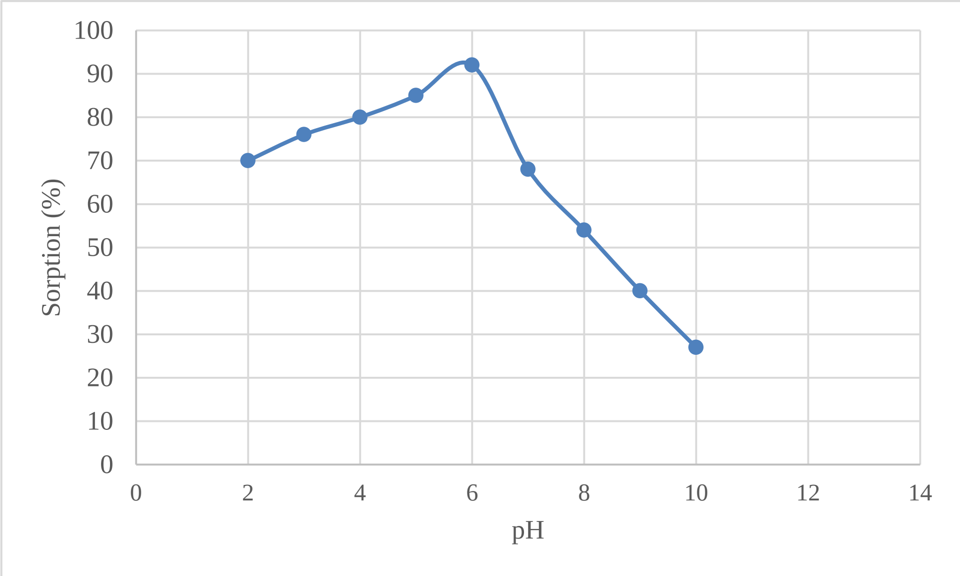

Figure 2-2 Effect of pH on the fluoride removal using PAAC (Experimental conditions: 10 mg/L initial F concentration, 100 min contact time, 4 g/L PAAC dose, 25 °C temperature) (Bonyadi, et al., 2019)

Figure 2.3 shows that the fluoride adsorption percentage increases as well when the contact time is increased. The adsorption gradually increases from 5 to 60 minutes and from 60 minutes onwards, it shows very slow increment until it reaches a maximum of 90 % adsorption at 100 minutes. The adsoprtion then remains constant for 120-180 minutes.

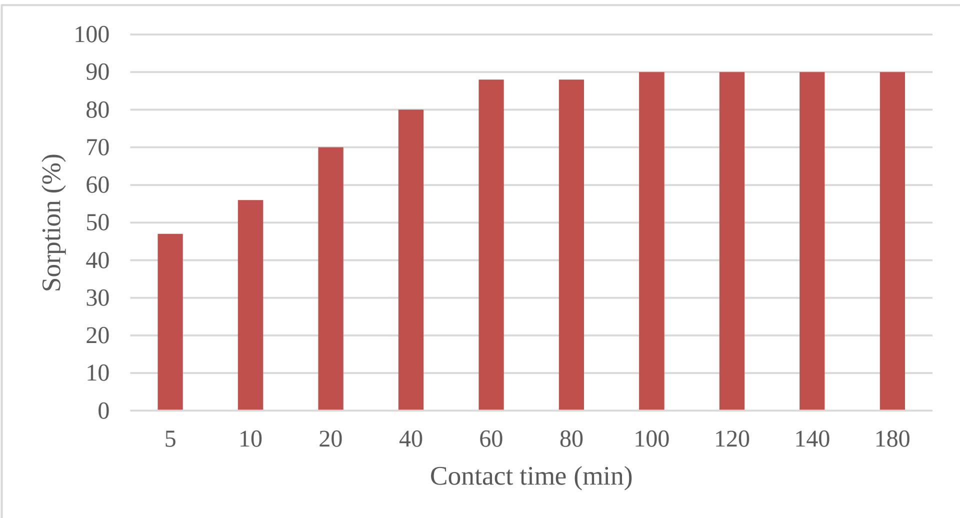

Figure 2-3 Effect of contact time on the fluoride removal using PAAC (Experimental conditions: 10 mg/L initial F concentration, pH 6, 4 g/L PAAC dose, 25 °C temperature) (Bonyadi, et al., 2019)

Whereas for the studies done on real wastewaters, the before and after physicochemical properties of the two treated wastewaters can be referred from Table 2.5. In terms of the fluoride removal, the fluoride content of glass wastewater was reduced from 24.38 to 8.26 mg/L and for the shipyard wastewater, the fluoride content was reduced from 11 to 3.8 mg/L.

Table 2-5 Before and after physicochemical properties of treated real wastewater (Bonyadi, et al., 2019)

WASTEWATER TYPE	FACTOR	UNIT	RAW	TREATED
GLASS WASTEWATER	pH	Unit of pH	6.30±0.27	6.68±0.09
	BOD_5	mg/L	208.19±3.11	185.27±2.1
	COD	mg/L	129±5.91	99.1±3.29
	F	mg/L	24.38±0.15	8.26±0.18
	Ni	mg/L	10.02±0.31	5.56±0.51
	Co	mg/L	4.81±0.13	0.97±0.15
	Pb	mg/L	2.08±0.98	Not detectable
SHIPYARD WASTEWATER	pH	Unit	6.35±0.3	6.89±0.21
	BOD_5	Unit of pH	258.9±1.92	237.9±2.03
	COD	mg/L	173±0.93	128.11±1.87
	F	mg/L	11±0.71	3.8±0.55
	Ni	mg/L	12±0.71	6.18±0.28
	Co	mg/L	13±0.71	6.14±0.27
	Pb	mg/L	14±0.71	3.93±0.67

For coconut shell activated carbon (CSAC) (Halder, Khan and Dhawane, 2016), Figure 2.4 shows similar trend from 2-7 g/L, where fluoride removal increases as the adsorbent dosage increases gradually. The increment then becomes minimal from 7-9 g/L and reaches maximum removal at 9 g/L. Figure 2.5 shows another similar study using coconut shell activated carbon on fluoride removal (Shehu, et al., 2019). The removal reaches 82 % at 1.5 g/L and decreases when the adsorbent is increased to 2.5 g/L. Figure 2.6 shows another study using coconut fibre dust activated carbon (CFD) (Bhaumik and Mondal, 2015). The removal hits around 90 % at 0.5 g/L and then decreases when the adosrbent increases to 2 g/L.

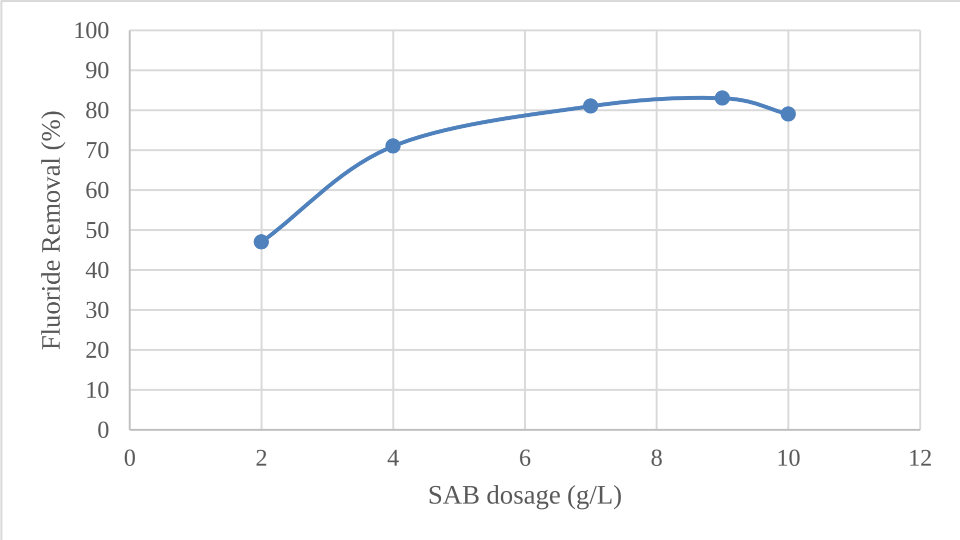

Figure 2-4 Effect of CSAC dose on the fluoride removal (Experimental condition: 10 mg/L initial F concentration, 30 °C temperature) (Halder, Khan and Dhawane, 2016)

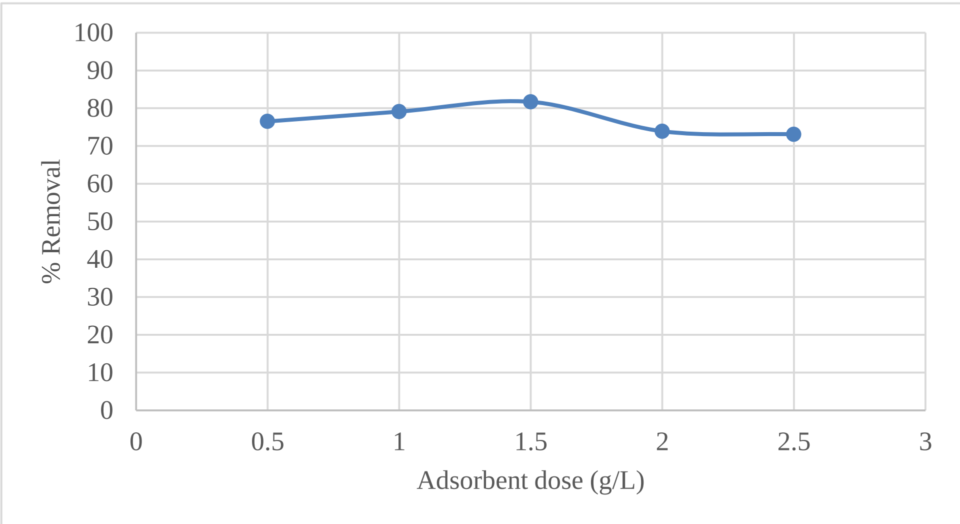

Figure 2-5 Effect of CSAC dose on the fluoride removal (Experimental condition: 5 mg/L initial F concentration, 50 min contact time, pH 7, 25 °C temperature) (Shehu, et al., 2019)

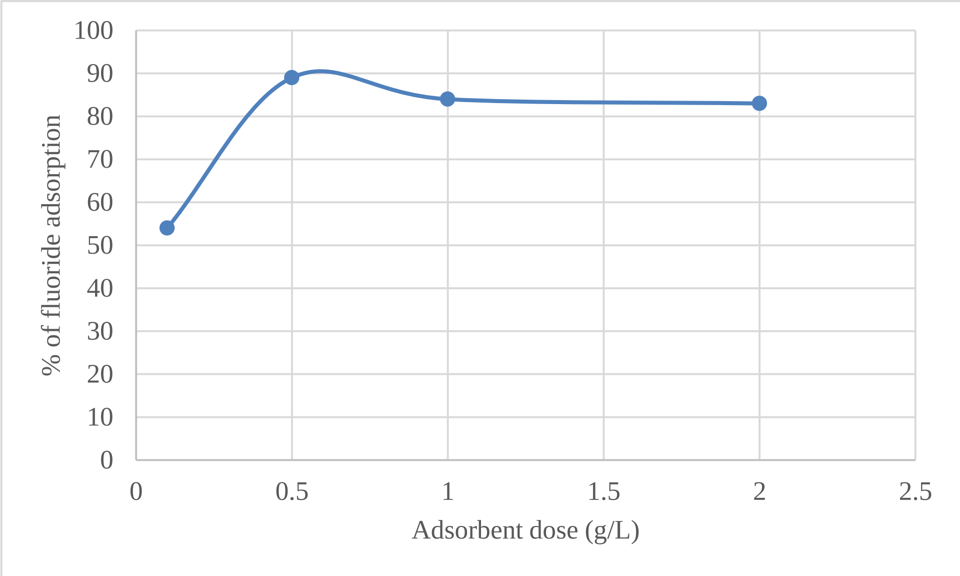

Figure 2-6 Effect of CFD dose on the fluoride removal (Experimental condition: 10 mg/L initial F concentration, 60 min contact time, pH 6, 30 °C temperature) (Bhaumik and Mondal, 2015)

Figure 2.7 (Halder, Khan and Dhawane, 2016) and 2.9 (Bhaumik and Mondal, 2015) show similar trend for the effect of pH on fluoride adsorption. The adsorption increases when the pH is increased from 4 to 6 and reaches maximum adsorption at pH 6. When pH is increased further from 6 to 9, the fluoride adsorption decreases gradually. Whereas for Figure 2.8, the fluoride removal reaches maximum at aroung pH 6.5-7.

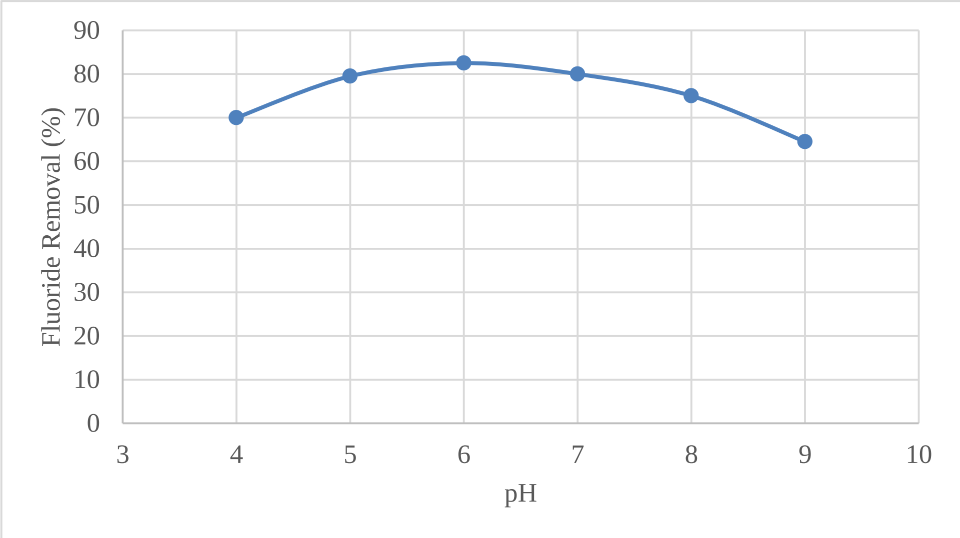

Figure 2-7 Effect of pH on the fluoride removal using CSAC (Experimental conditions: 10 mg/L initial F concentration, 30 °C temperature) (Halder, Khan and Dhawane, 2016)

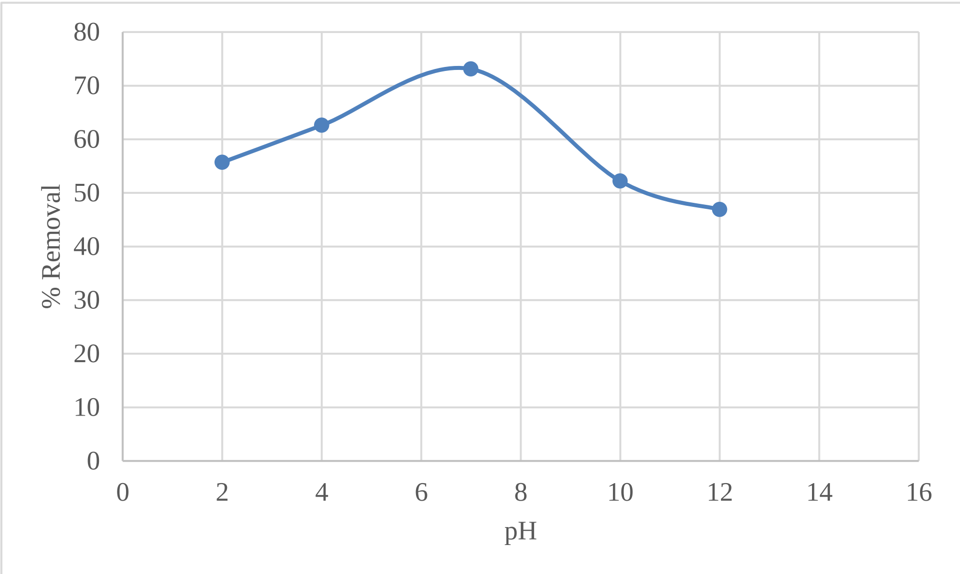

Figure 2-8 Effect of pH on the fluoride removal using CSAC (Experimental conditions: 5 mg/L initial F concentration, 50 min contact time, 1.5 g/L dose, 25 °C temperature) (Shehu, et al., 2019)

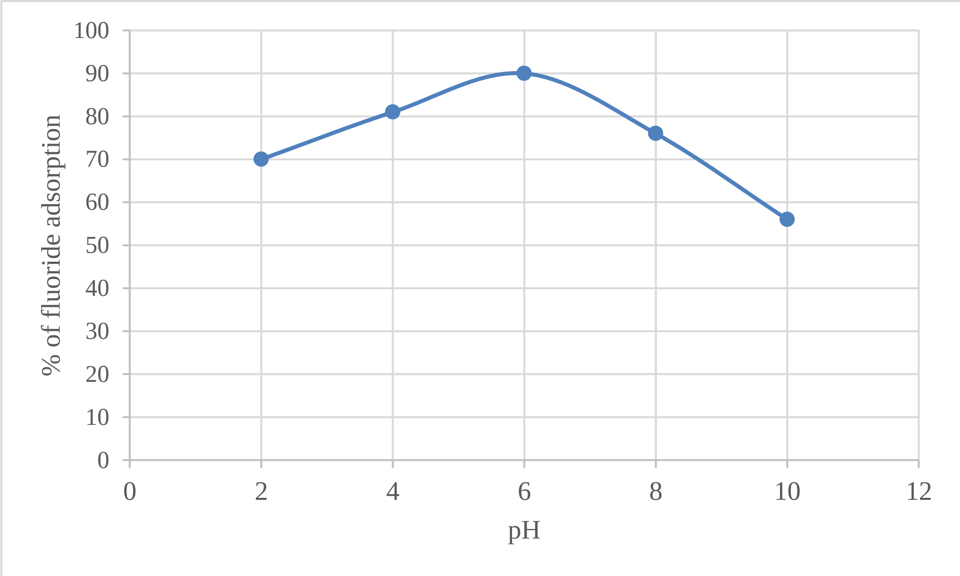

Figure 2-9 Effect of pH on the fluoride removal using CFD (Experimental conditions: 10 mg/L initial F concentration, 60 min contact time, 0.5 g/L dose, 30 °C temperature) (Bhaumik and Mondal, 2015)

Figure 2.10 (Halder, Khan and Dhawane, 2016) shows the increment of contact time increases the fluoride removal from 30-80 minutes. However, the fluoride removal decreases as the adsorption process is prolonged from 90-130 minutes and remains constant until 150 minute-mark. Figure 2.11 and Table 2-6 show another similar study using coconut shell activated carbon on fluoride removal (Shehu, et al., 2019). This study uses lower initial Fluoride concentration which allows shorter contact time to reach higher removal. At the 50-minute mark, 84.3 % of fluoride removal can be achieved while at 60 minute, it reduced slightly to 84 %. Figure 2.12 shows another study using coconut fibre dust activated carbon (Bhaumik and Mondal, 2015). It shows similar trend where the increment goes up to around 93 % after 75 minutes and when the contact time is prolonged further until 120 minutes, it slightly decreases to around 90 %. The removal then remains constant from 120-240 minutes.

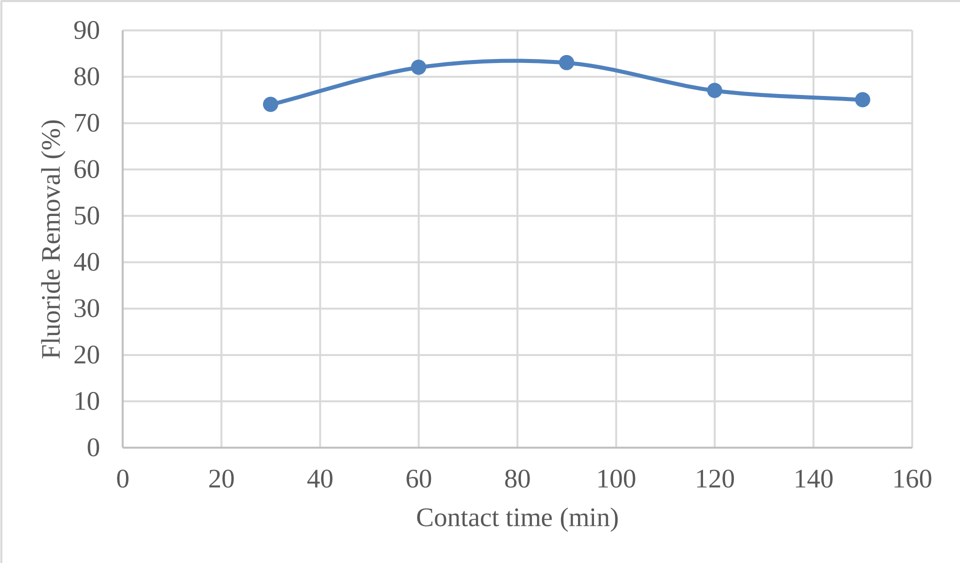

Figure 2-10 Effect of contact time on the fluoride removal using CSAC (Experimental conditions: 10 mg/L initial F concentration, 30 °C temperature) (Halder, Khan and Dhawane, 2016)

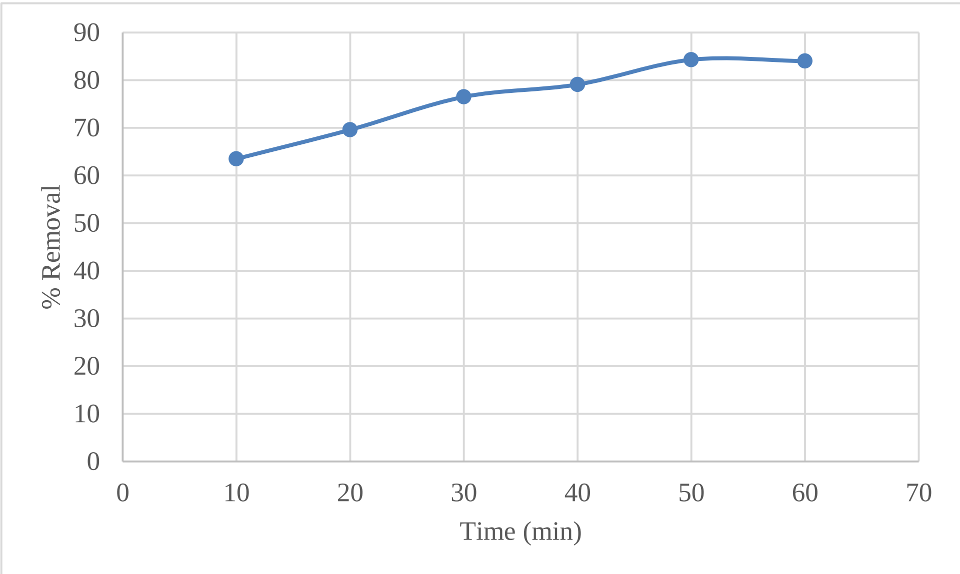

Figure 2-11 Effect of contact time on the fluoride removal using CSAC (Experimental conditions: 5 mg/L initial F concentration, pH 7, 1.5 g/L dose, 25 °C temperature) (Shehu, et al., 2019)

Table 2-6 Effect of contact time on the fluoride removal using CFD (Bhaumik and Mondal, 2015)

Time (min)	% Fluoride Removal
10	63.5
20	69.6
30	76.5
40	79.1
50	84.3
60	84.0

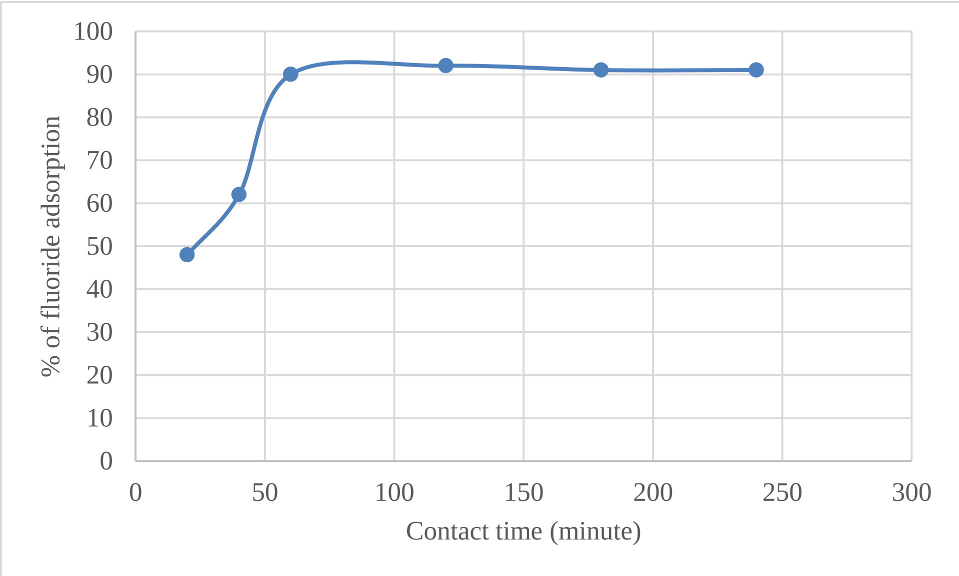

Figure 2-12 Effect of contact time on the fluoride removal using CFD (Experimental conditions: 10 mg/L initial F concentration, pH 6, 0.5 g/L dose, 30 °C temperature) (Bhaumik and Mondal, 2015)

2.5.3 Activated Carbon Adsorption Treatment on Dye Wastewater

Jawad, et al. (2016) conducted a study on adsorption of methylene blue (MB) dye using activated carbon developed from biomass waste of coconut leaf (CLAC). Figure 2.13 shows the effect of adsorbent dosage on the MB removal. The removal increases consistently as the adsorbent increases from 0.2 to 1.5 g/L. With the amount of 1.5 g/L adsorbent, the MB removal is able to achieve around 99 %.

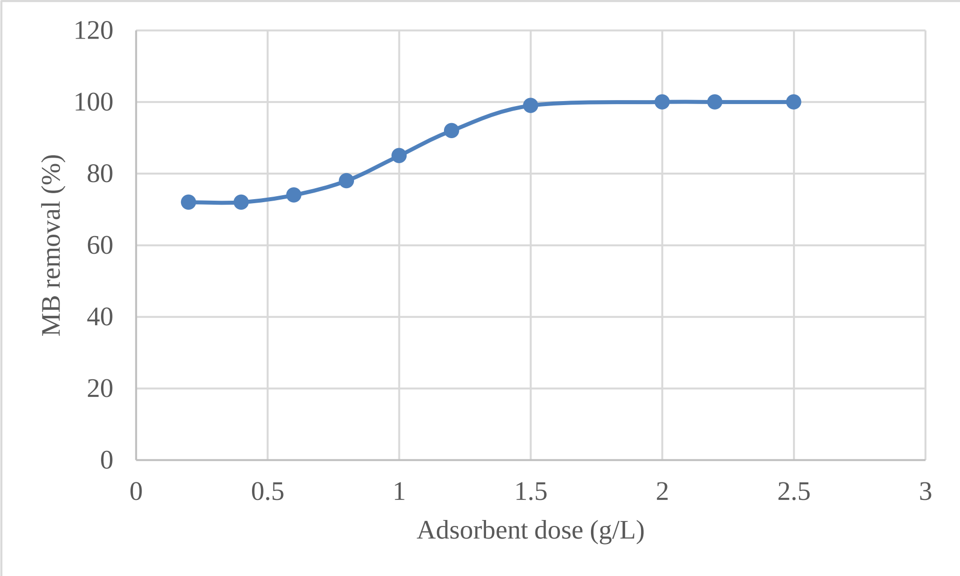

Figure 2-13 Effect of CLAC dose on the MB removal (Experimental condition: 100 mg/L initial MB concentration, 60 min contact time, pH 5.6, 30 °C temperature) (Jawad, et al., 2016)

The effect of pH factor is shown in Figure 2.14, the removal percentage increases from pH 3 to pH 6 and no obvious change is observed from pH 6 to pH 9 even when the condition turns even more alkaline. After that, as the pH increases further to 10, the removal slightly decreases.

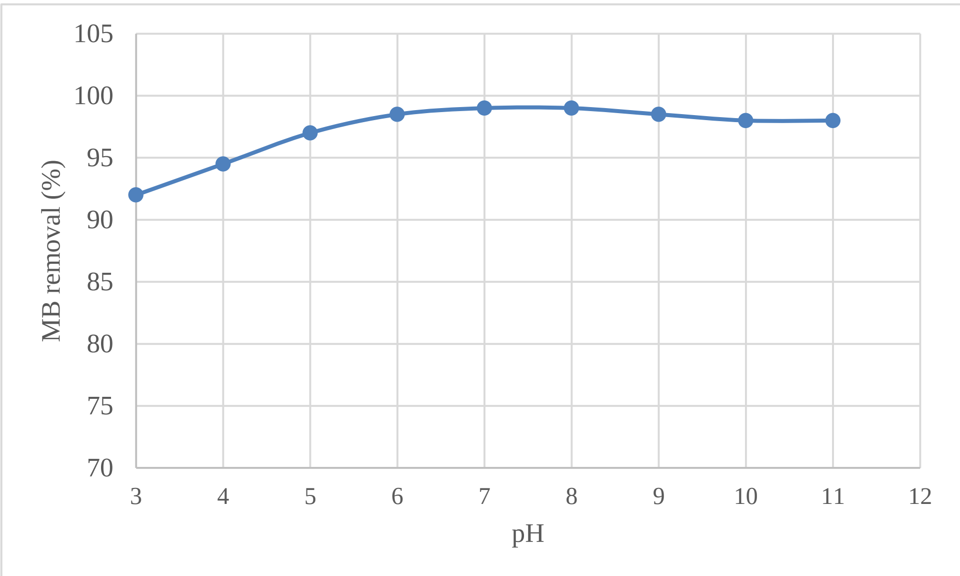

Figure 2-14 Effect of pH on the MB removal using CLAC (Experimental conditions: 100 mg/L initial MB concentration, 60 min contact time, 1.5 g/L CLAC dose, 30 °C temperature) (Jawad, et al., 2016)

As for the contact time, Figure 2.15 shows the MB removal increases rapidly from 0-60 minutes. The increment in removal percentage then slows down as the contact time prolonged. The maximum MB removal is achieved at around 120 minutes.

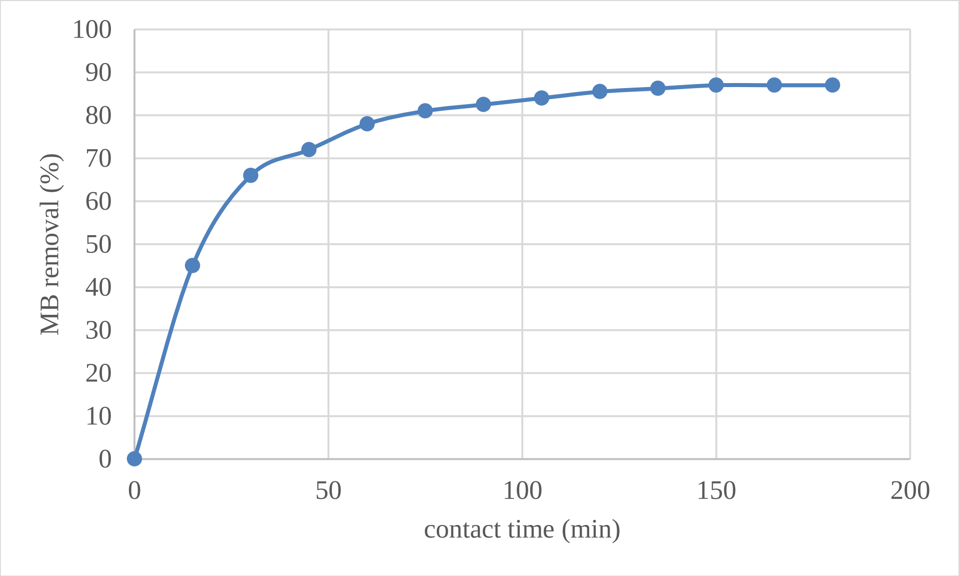

Figure 2-15 Effect of contact time on the MB removal using CLAC (Experimental conditions: 100 mg/L initial MB concentration, pH 6, 1.5 g/L CLAC dose, 30 °C temperature) (Jawad, et al., 2016)

Figure 2.16 shows MB removal using coconut shell activated carbon (CSAC) (Abd Rashid, Ishak and Hello, 2018). The removal percentage increases rapidly from 0.2-1 g/L and the increment slows down from 1-2 g/L. The maximum is achieved at 2.5 g/L with 95 % removal.

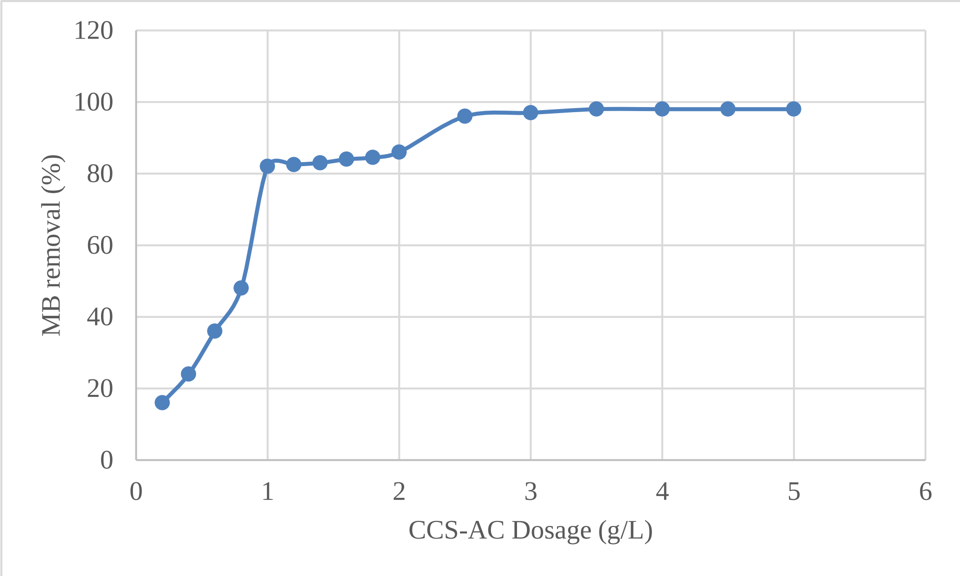

Figure 2-16 Effect of CSAC dose on the MB removal (Experimental condition: 100 mg/L initial MB concentration, 120 min contact time, pH 5.8, 30 °C temperature) (Abd Rashid, Ishak and Hello, 2018)

Figure 2.17 shows that pH does not have major effect on the MB removal (Abd Rashid, Ishak and Hello, 2018). The removal does increase slowly when the pH is increased from 3 to 8 and remains constant from 8 to 12. However, all the removal maintains in the range from 91 to 93 %. On the other hand, based on another study using coconut shell activated carbon, Figure 2.18 shows drastic change in MB adsorption with changing pH values (Mondal, Ahmad and Kumar, 2014). Both studies do have similarity where pH 8 is the optimum pH value to achieve maximum removal.

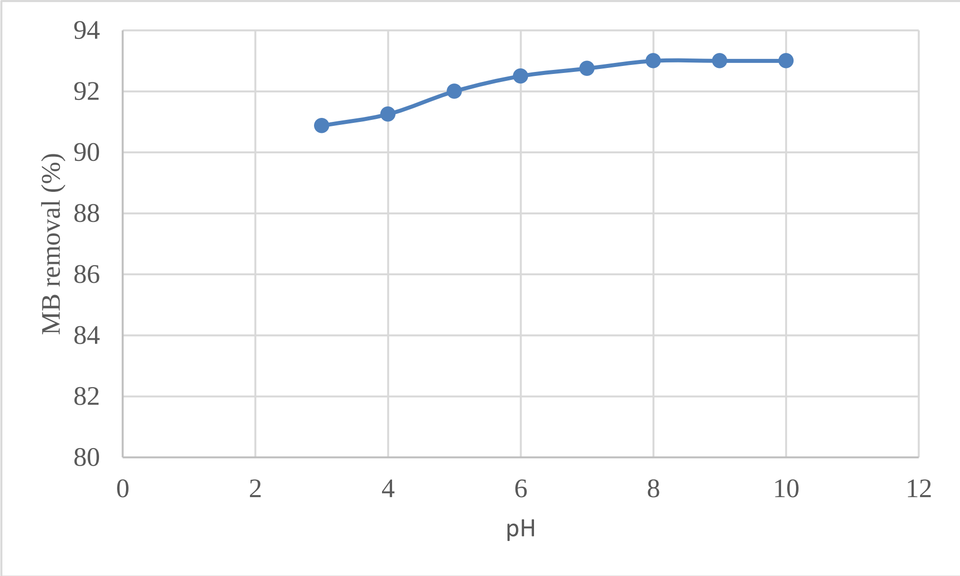

Figure 2-17 Effect of pH on the MB removal using CSAC (Experimental conditions: 100 mg/L initial MB concentration, 60 min contact time, 2.5 g/L CSAC dose, 30 °C temperature) (Abd Rashid, Ishak and Hello, 2018)

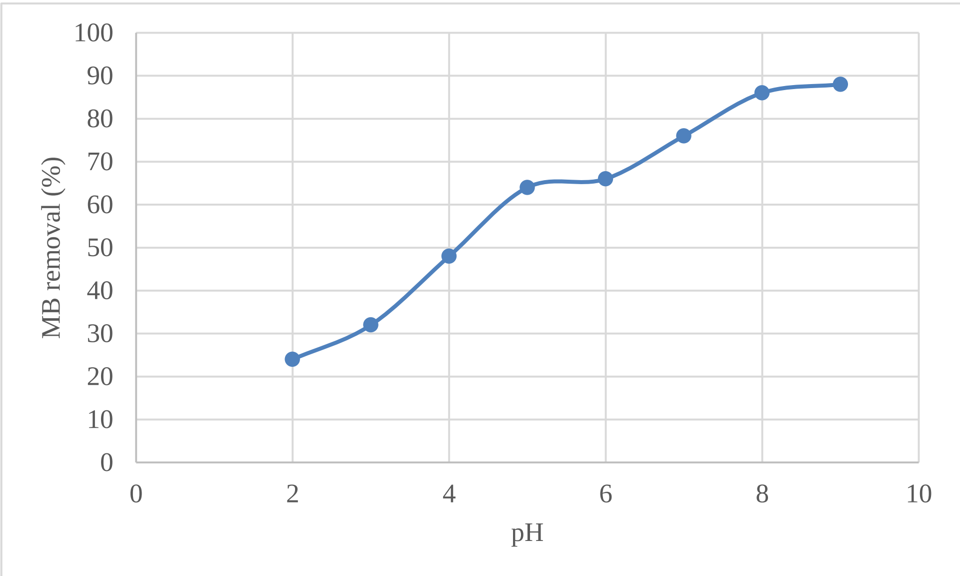

Figure 2-18 Effect of pH on the MB removal using CSAC (Experimental conditions: 10 mg/L initial MB concentration, 180 min contact time, 1 g/L CSAC dose, 30 °C temperature) (Mondal, Ahmad and Kumar, 2014)

Figure 2.19 shows the effect of contact time on MB removal (Abd Rashid, Ishak and Hello, 2018). The removal increases rapidly until the 120-minute mark and slowly reaches maximum of 90 % removal after 240 minutes.

Whereas for Figure 2-20 (Mondal, Ahmad and Kumar, 2014), the removal reaches maximum of 96 % after 150 minutes.

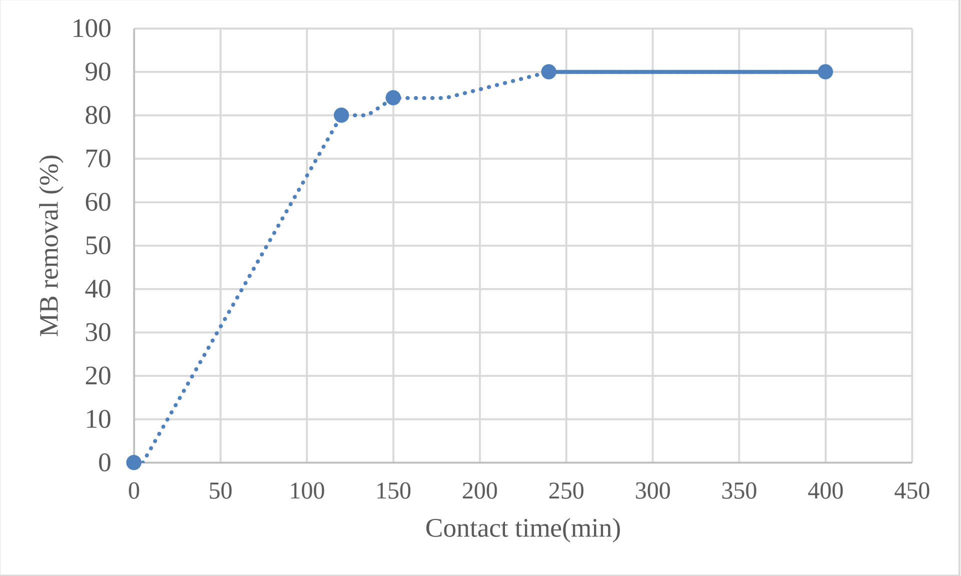

Figure 2-19 Effect of contact time on the MB removal using CSAC (Experimental conditions: 100 mg/L initial MB concentration, pH 5.8, 2.5 g/L CSAC dose, 30 °C temperature) (Abd Rashid, Ishak and Hello, 2018)

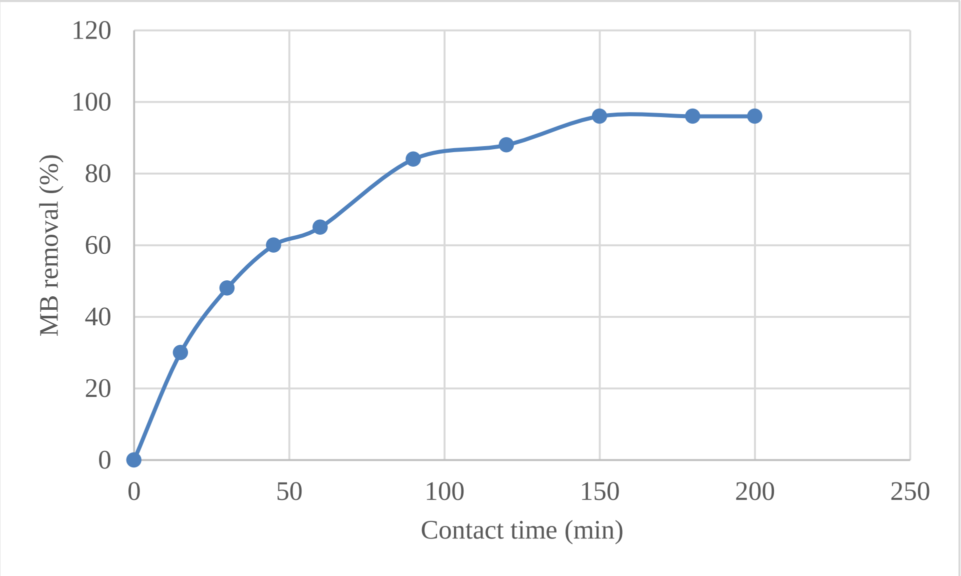

Figure 2-20 Effect of contact time on the MB removal using CSAC (Experimental conditions: 10 mg/L initial MB concentration, 1 g/L CSAC dose, 30 °C temperature) (Mondal, Ahmad and Kumar, 2014)

2.5.4 Summary on Effect of Adsorbent Dosage

For fluoride removal, all the studies show similar trend where the fluoride increases as adsorbent dosage increases. The studies have different optimum amount of dosage used for achieving maximum removal due to different adsorbent material, different initial conditions and also different activation process used for preparing activated carbon.

For PAAC (Bonyadi, et al., 2019), the removal reaches maximum at about 4 g/L and further increment of dosage does not have much impact as the removal percentage remains constant afterwards. This trend can be explained that the equilibrium between adsorbate and adsorbent is achieved at 4 g/L of dosage and any further adsorption is prevented (Kardam et al. 2014).

However for CSAC (Halder, Khan and Dhawane, 2016) (Shehu, et al., 2019) and CFD (Bhaumik and Mondal, 2015) studies, the three papers show slightly different trend where, after the optimal fluoride removal is achieved, any further increase in adsorbent dosage causes the removal to decrease. Assuming there was no human errors affecting the results, this could be caused by the overlapping of active sites with the overcrowding of adsorbents (Garg, et al., 2003). The increment of dosage beyond the optimum amount could give higher surface area and pore volume for adsorption (Bhaumik and Mondal 2014; Yadav et al. 2013; Anwar et al. 2010; Satish et al. 2007). However, at high adsorbent dosage, large portion of lower energy sites are occupied, causing the higher energy sites to decrease, resulting in low adsorption capacity, q_e (Bhaumik and Mondal, 2015).

For MB removal, despite having different adsorbent material and different activation process, Figure 2.13 and 2.16 show consistent results where maximum removal can be achieved with very little adsorbent dosage. Besides, MB removal increases with adsorbent dosage and upon reaching maximum removal, the adsorption rate decreases and further increment of adsorbent dosage does not have impact on MB removal.

In summary, fluoride ions require 7-9 g/L while MB require around 2.5 g/L of CSAC dosage for maximum removal. MB removal requires lesser adsorbent dosage than fluoride ions. Besides, MB percentage removal is even higher than fluoride removal even with lesser dosage.

2.5.5 Summary on Effect of pH

For fluoride removal, the studies generally have optimum range of pH 6-7 to achieve maximum adsorption. PAAC (Bonyadi, et al., 2019), CSAC (Halder, Khan and Dhawane, 2016) and CFD (Bhaumik and Mondal, 2015) reported to perform best under the condition of pH 6 whereas CSAC (Shehu, et al., 2019) achieved maximum fluoride removal under the pH of 7. It can be deduced that the fluoride adsorption is most efficient at the pH of 6-7, which aligns with the pH of the raw semiconductor wastewater of 6.35 (Saipudin and Omar, 2017).

As observed from Figure 2.2, 2.7, 2.8 and 2.9, the fluoride removal drastically decreases as the condition becomes more alkaline. This might be due to the competition between hydroxyl ions and fluoride ions for the adsorption (Dehghani, et al., 2018.).

For MB removal, CLAC (Jawad, et al., 2016) achieves optimum removal in the range of pH 6-9 while CSAC has the optimum removal under condition of pH 8 or more. This could be due to different adsorbent material or different activation process. However it can be deduced that higher MB removal can be achieved under high pH condition. It was suggested that the lower adsorption at the lower pH was caused by the competition between MB cations and the hydrogen ions for the adsorption. As opposed to the fluoride ions, higher initial pH does not have significant effect on the MB removal rate by adsorption.

In summary, fluoride adsorption process performs best under condition of pH 6-7 while MB adsorption should be carried out under alkaline condition.

2.5.6 Summary Effect of Contact Time

For fluoride removal, the studies show similar trend where the higher the contact time, the higher the fluoride adsorption. The studies have different peak removal contact time due to different adsorbent material, different initial conditions, and also different activation process used.

The fluoride removal increases rapidly with the increasing contact time from 5-60 minutes and after 60 minutes the increment rate slows down. The maximum removal is achieved at 100-minute for PAAC (Bonyadi, et al., 2019) and on 100 minutes onwards the removal remains constant. The removal rate slows down upon reaching maximum adsorption can be explained due to the active sites of the adsorbent decreases as contact time increases. As the active sites become limited, the remaining vacant sites become difficult to be occupied by the fluoride ions because of the repulsive forces forming between the fluoride ions on the adsorbent surface and the liquid phase (Bhaumik and Mondal 2014; Bhaumik et al. 2012).

However for the CSAC (Halder, Khan and Dhawane, 2016) and CFD (Bhaumik and Mondal, 2015), after reaching maximum removal at optimum contact times, it can be observed that further prolonged contact times decrease the fluoride removal. Assuming no human errors were made, it was deduced that the adsorbate adsorbed onto the adsorbent's surface by weak Van der Waals forces of attraction as contact time increases; hence, longer contact time with a high stirring rate during the process may cause the desorption of adsorbed fluoride ions and led to a lower fluoride removal. As seen in Figure 2.12, when contact time is prolonged even further, the removal then remains constant afterwards.

For MB removal, all studies show the same trend with increasing removal as contact time increases and upon reaching maximum removal, the removal rate decreases. However as opposed to the fluoride removal trend, the removal remains constant even when contact time is further prolonged. CLAC (Jawad, et al., 2016) and CSAC (Abd Rashid, Ishak and Hello, 2018) (Mondal, Ahmad and Kumar, 2014) have different optimum contact time due to different material adsorbent and different initial conditions used.

In summary, the contact time varies and is heavily dependent on the adsorbent material, initial conditions and also the activation process of activated carbon. It can be deduced that fluoride removal may be affected if the contact time is prolonged but prolonged contact time does not affect MB removal.

2.5.7 Response Surface Methodology on Adsorption Treatment

Response Surface Methodology (RSM) is a method to analyse the relationships between multiple parameters in an experiment. The interaction between parameters can be determined using the RSM statistical technique and generate mathematical models accordingly to the output. It is also one of the statistical approaches to maximize the experimental output through optimization.

Design Expert is a software that integrates RSM to allow users create designs and input experimental data to generate results automatically. The software provides analysis results of the input experimental data like ANOVA, fit summary, model graphs, etc.

One RSM study is chosen from each individual fluoride and MB adsorption study to be the main RSM reference in predicting the final outcome of the adsorption treatment.

2.5.7.1 RSM on Fluoride Removal

In (Halder, Khan and Dhawane, 2016), experimental data of fluoride removal using CSAC adsorbent was provided in one-factor-at-a-time (OFAT) method as well as response surface method (RSM). The mathematical model obtained using RSM is used as the main RSM reference to predict the final outcome of fluoride removal in the wastewater treatment.

Figure 2.21 to 2.23 show 3D surface plots of the RSM mathematical model obtained using CSAC adsorbents on fluoride removal. The parameters are adsorbent dosage, pH and contact time. The maximum removal achieved was 83.04 % at 8.7 g/L of CSAC dosage, pH 6.5 and 90 minutes contact time, whereas the optimized removal was found to be 82.45 % at CSAC dosage of 7 g/L, pH 6.27 and 60 minutes contact time. The existing mathematical model for fluoride removal is as follows (Halder, Khan and Dhawane, 2016):

$$\begin{aligned} Fluoride\ removal\ \% &= -31.08 + 28.92 \times Dosage + 10.98 \times pH - 0.8629 \\ &\times Time - 0.01667 \times Dosage \times pH + 0.003444 \times Dosage \\ &\times Time - 0.03887 \times pH \times Time - 2.315 \times Dosage^2 \\ &- 0.155 \times pH^2 + 0.005785 \times Time^2 \text{------------------------} \textcircled{1} \end{aligned}$$

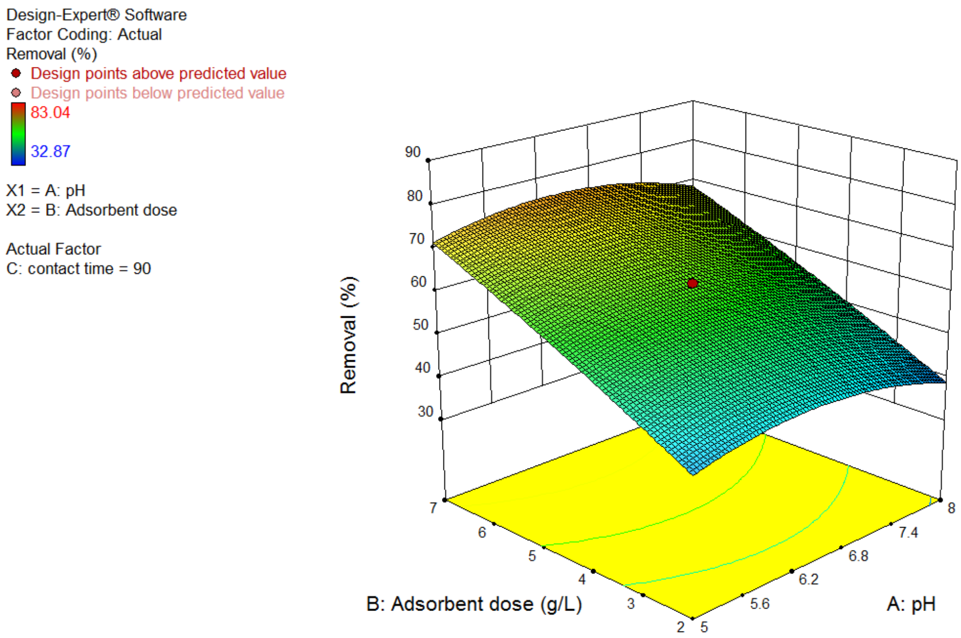

Figure 2-21 3D surface plots of individual fluoride removal against adsorbent dosage and pH (Halder, Khan and Dhawane, 2016)

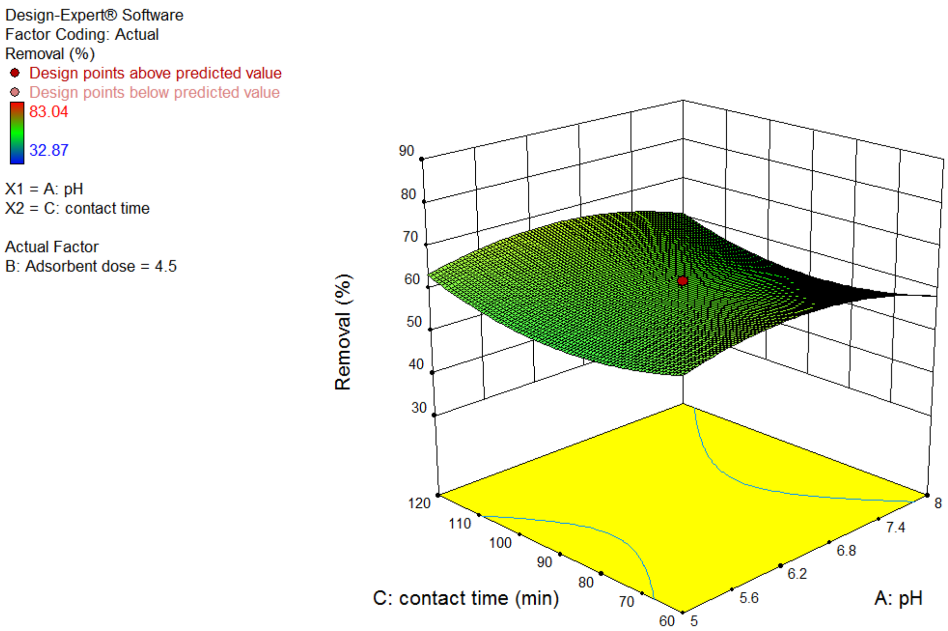

Figure 2-22 3D surface plots of individual fluoride removal against pH and contact time (Halder, Khan and Dhawane, 2016)

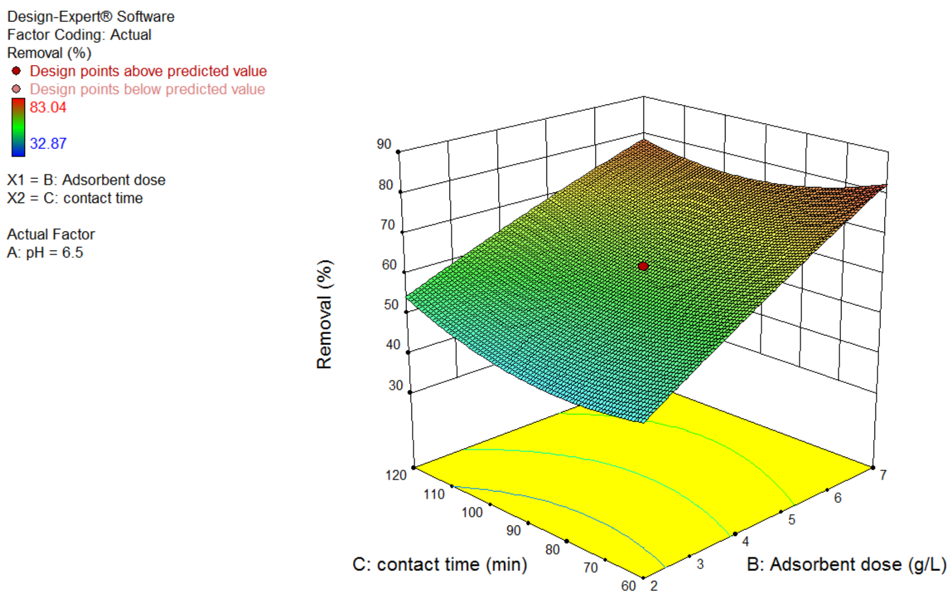

Figure 2-23 3D surface plots of individual fluoride removal against adsorbent dosage and contact time (Halder, Khan and Dhawane, 2016)

2.5.7.2 RSM on MB Removal

In (Jawad, et al., 2016), the RSM mathematical model obtained using coconut leaf activated carbon (CLAC) is used as the RSM reference to predict the final MB removal in wastewater treatment. Two other studies on MB removal using CSAC (OFAT) will be used as the main references (Abd Rashid, Ishak and Hello, 2018) (Mondal, Ahmad and Kumar, 2014).

Figure 2.27 to 2.29 show 3D surface plots of the RSM mathematical model obtained using CLAC adsorbents on MB removal. The parameters are adsorbent dosage, initial MB concentration, pH, and contact time. The maximum removal achieved was 90.97 % at 1.5 g/L CLAC dose, 10 mg/L initial MB concentration, pH 10 and 45 minutes contact time; whereas the optimized removal was found to be 86.38 % at 1.26 g/L CLAC dose, 19.01 mg/L initial MB concentration, pH 8.65 and 5 minutes contact time. The existing mathematical model for MB removal is as follows (Jawad, et al., 2016):

$$MB\ removal\ \% = 5.186 + 63.41 \times Dosage + 0.7624 \times MB\ conc + 7.556 \times pH - 0.6353 \times Time - 0.05713 \times Dosage \times MB\ conc + 1.371 \times Dosage \times pH - 0.1674 \times Dosage \times Time - 0.004479 \times MB\ conc \times pH + 0.0001 \times MB\ conc \times Time + 0.04427 \times pH \times Time - 28.36 \times Dosage^2 - 0.01866 \times MB\ conc^2 - 0.4934 \times pH^2 + 0.0127 \times Time^2 \quad (2)$$

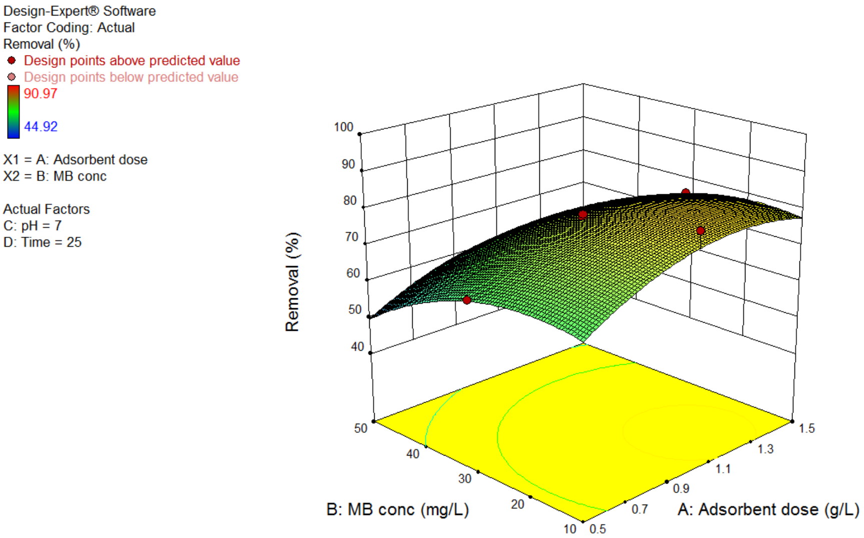

Figure 2-24 3D surface plots of individual MB removal against adsorbent dosage and MB initial concentration (Jawad, et al., 2016)

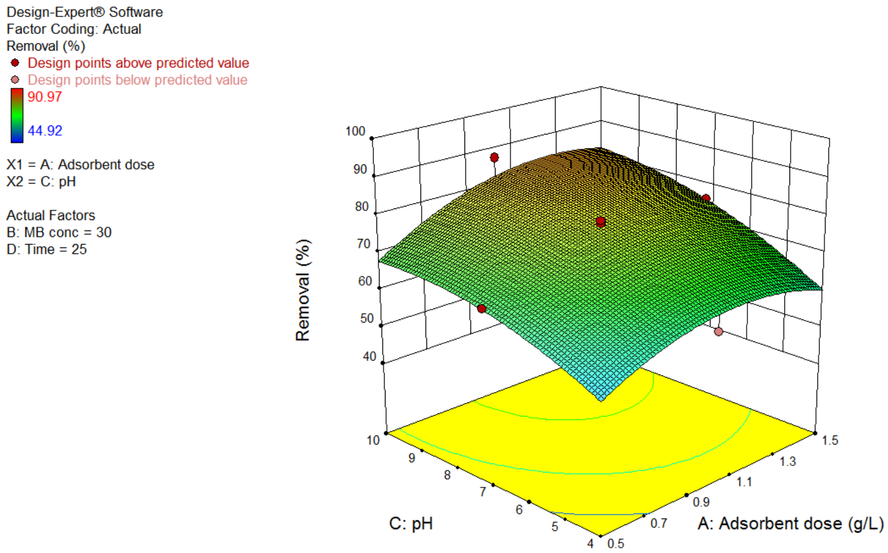

Figure 2-25 3D surface plots of individual MB removal against adsorbent dosage and pH (Jawad, et al., 2016)

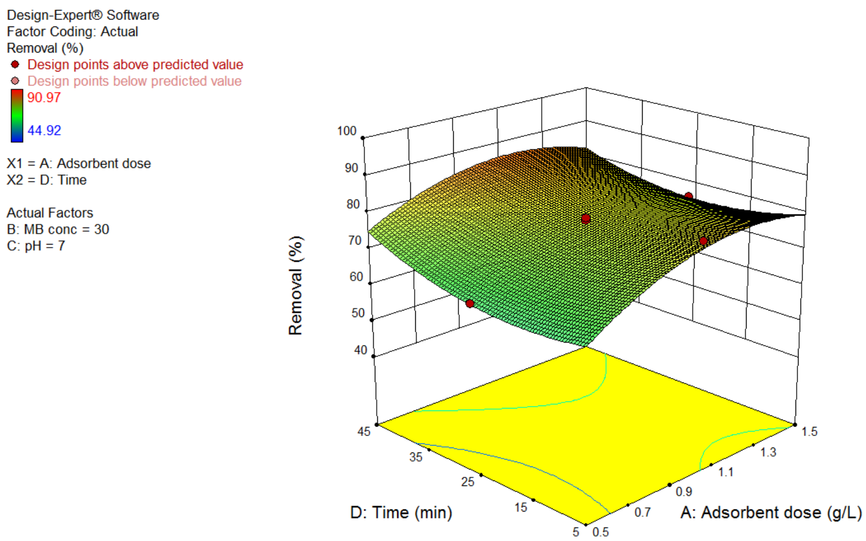

Figure 2-26 3D surface plots of individual MB removal against adsorbent dosage and contact time (Jawad, et al., 2016)

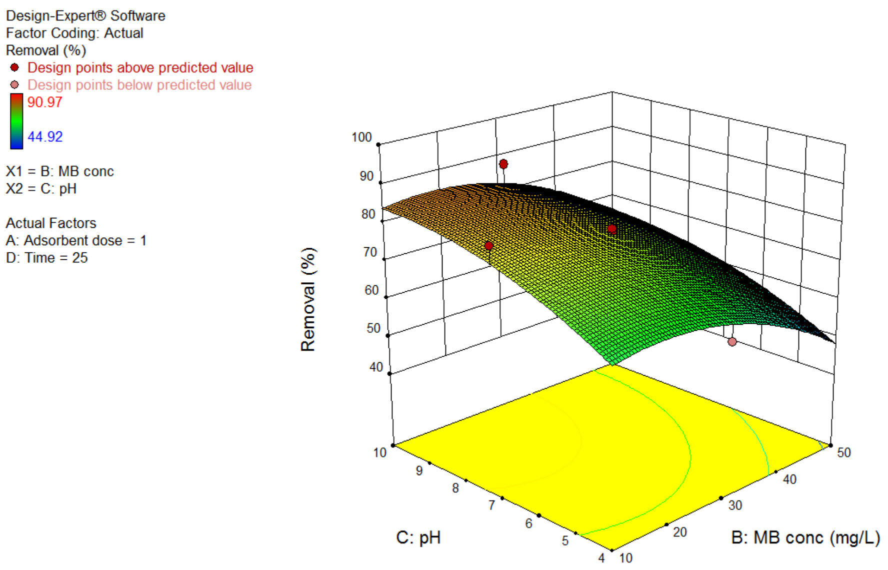

Figure 2-27 3D surface plots of individual MB removal against MB initial concentration and pH (Jawad, et al., 2016)

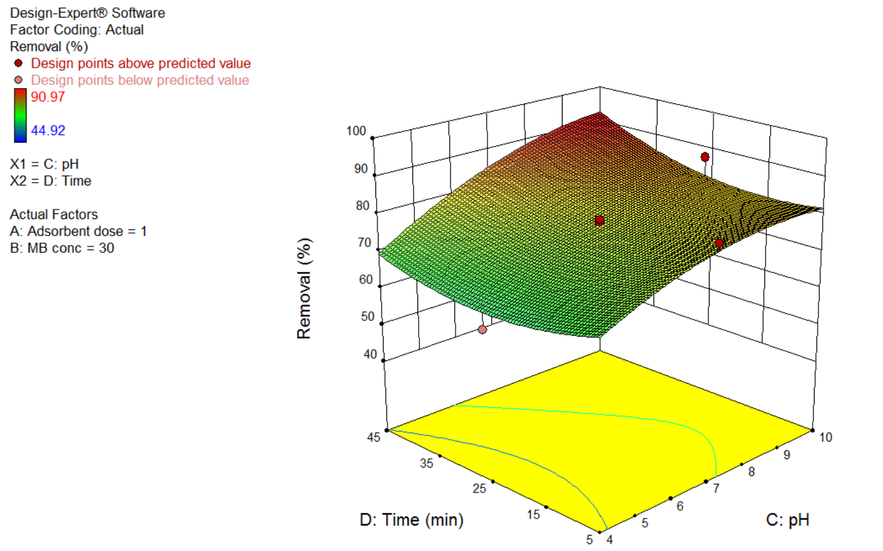

Figure 2-28 3D surface plots of individual MB removal against pH and contact time (Jawad, et al., 2016)

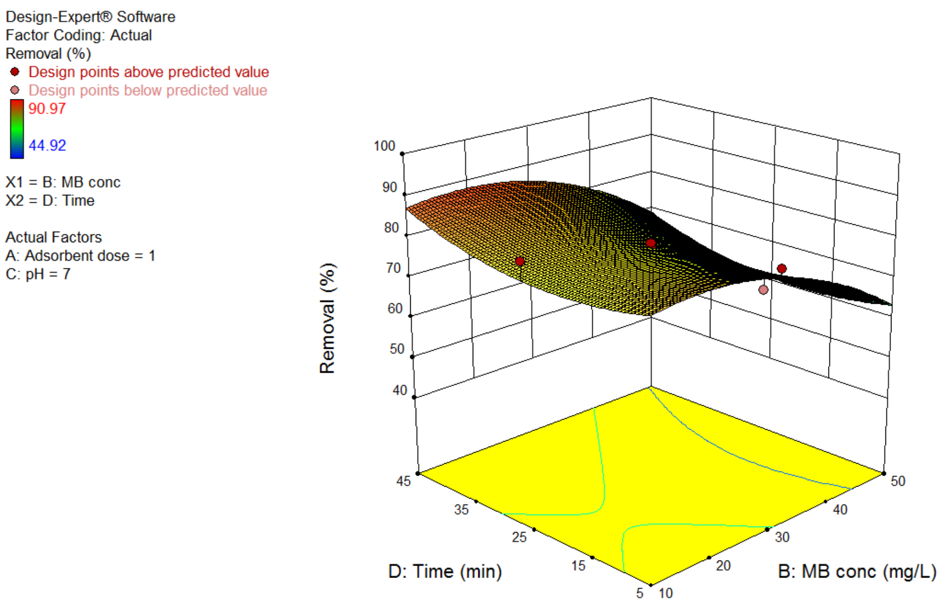

Figure 2-29 3D surface plots of individual MB removal against MB initial concentration and contact time (Jawad, et al., 2016)

2.5.8 Recycling of Coconut Shell Activated Carbon (CSAC)

As mentioned previously, activated carbon is usually a one-time usage product for adsorption treatment and this could cause a heavy burden on companies economically wise in the long run. Hence, people have looked into methods to reuse the exhausted activated carbon. There are chemical regeneration method done on used activated carbon using different types of solvents, acids, bases and redox agents (Lu, et al., 2011). The exhausted activated carbon will go through the desorption process to remove the adsorbed particles on the activate carbon surface and regeneration treatment will follow.

Table 2.7 shows a chemical regeneration study using NaOH treatment on used CSAC for Malachite Green dye readsorption (Bello and Ahmad, 2012). The exhausted CSAC is subjected to adsorption-desorption process and then regeneration treatment in between each cycle. The first exhausted CSAC is used for readsorption without any treatment and it only shows 53.76 % of readsorption. Whereas for the exhausted CSAC that has gone through NaOH treatment, the first cycle is able to achieve 90.75 % of readsorption and further increases until a maximum of 95.98 % of readsorption at the fourth cycle. By doing the chemical regeneration treatment using NaOH base, not only the readsorption performance of a used CSAC does not drop, it is possible to further improve the readsorption performance.

Figure 2.30 shows another study using only 40 % ethanol solution for desorption process (DasSharma, Samanta and Halder, 2020). As opposed to the previous study in Table 2.7, this study does not do any regeneration treatment after the desorption step. It can be observed in the graph that after each cycle of adsorption-desorption process, the removal efficiency of the CSAC drops significantly. The study deduced that with desorption process using 40 % ethanol, the exhausted CSAC is able to be reused for five cycles at maximum before being disposed of. This shows that with proper regeneration treatment, the reusability of the exhausted CSAC can be improved rather than just the desorption process.

At the end of the activated carbon life, they have to be handled with precaution as well, to avoid becoming another source of pollution. Currently there are a few ways to dispose of the exhausted activated carbon which are mainly incineration. One of the methods involve carbon micronization process where the exhausted activated carbon is ground into powder and then blown into the deactivation furnace system to proceed with the incineration process. Besides, there is also another method that double bags the exhausted activated carbon into polyethylene before sending it for incineration (National Research Council, 2009).

Table 2-7 Percentage of dye readsorption after NaOH treatment (Bello and Ahmad, 2012)

Dye	**Adsorbent**	**Percentage of dye readsorption**				
		without NaOH treatment	with 0.2M NaOH treatment			
			First Cycle	Second Cycle	Third Cycle	Fourth Cycle
Malachite Green	Coconut Shell Activated Carbon (CSAC)	53.76	90.75	93.87	94.23	95.98

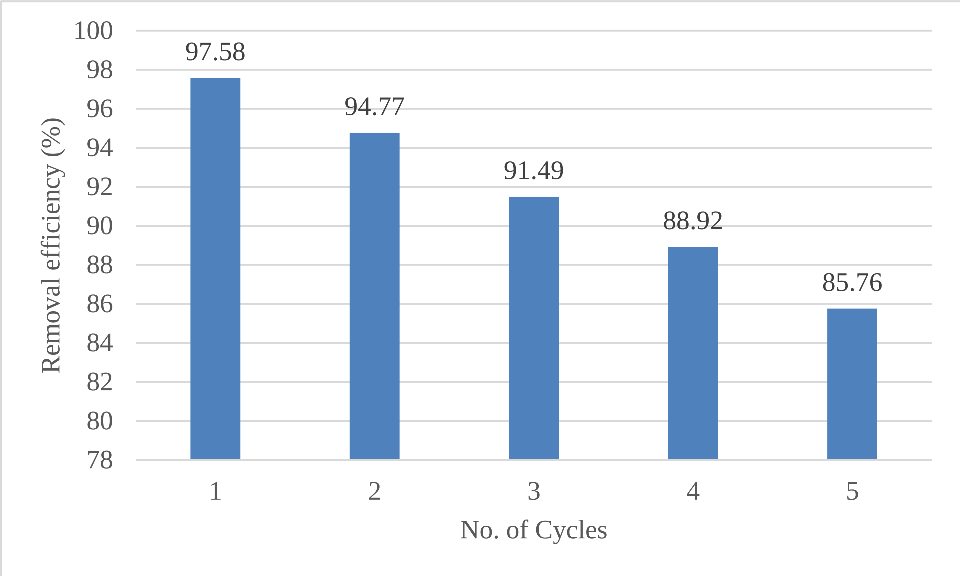

Figure 2-30 Removal efficiency of regenerated CSAC against number of cycles (DasSharma, Samanta and Halder, 2020)

2.5.9 Summary on Adsorption Treatment

This project focuses on using coconut shell activated carbon (CSAC) for the adsorption treatment on fluoride-MB dye mixture wastewater. Coconut shell waste is relatively abundant in Malaysia which is a good source for activated carbon production and it also has high surface area of around 1244-1768.8 m^2/g. However, it can be observed that the price range of CSAC has been increasing steadily the last few years. It is important for companies to minimize any wastage of CSAC to avoid extra cost.

Literature review is done on both individual fluoride and MB removal using CSAC and other activated carbon to find the consistent trend of each parameter of adsorbent dosage, pH and contact time. The trends are compiled into respective parameter summary to ensure the reliability of the reference studies. The inconsistent trend found in each parameter is taken into consideration during methodology to avoid causing more uncertainties in the mathematical modelling.

For fluoride and MB adsorption treatment, one study using Response Surface Methodology (RSM) is chosen to be the RSM model reference for each individual fluoride and MB adsorption treatment, where the individual models will be improved with the modification of the experimental data due to the inconsistencies found.

The improved mathematical models are then used to construct a mathematical model for fluoride-MB mixture removal. The model can be then optimized to find the optimal adsorbent dosage to achieve the highest removal which can minimize any CSAC wastage.

Activated carbon is usually a one-time-usage product but there are a few ways to regenerate the exhausted CSAC with chemical regeneration. The exhausted CSAC can be recycled multiple times after desorption and also chemical regeneration process. This can be another method to minimize the regular purchase of activated carbon.

2.6 Magnetic Treatment

Magnetic treatment method is currently used in preventing scale buildup of deposits on the inner walls of industrial systems like heat exchangers. The magnetic treatment has been applied for several decades (Salman, Safar and Al-Nuwaibit, 2015) and numerous magnetic devices have been developed to achieve a good scale prevention efficiency (Mahmoud, Yosra and Nadia, 2016).

Other than that, a number of studies were done on the effect of magnetic field towards wastewater and majority showed positive outcomes. However, despite the long history of successful magnetic treatment in enhancing the wastewater treatment process such as adsorption treatment (Yusuf, Obalowu and Abubakar, 2020), there is still no hard evidence of the direct magnetic treatment effect on water due to the inconsistent or non-significant published data.

2.6.1 Concepts of Magnetic Application

Many studies describe different magnetic mechanisms and as mentioned previously, some of them are even contradictory, it was claimed that this is because the entire effect of the magnetic field was not considered yet (Zaidi, et al., 2014). Kronenberg (1985) explained that the basic concept of magnetic application is associated with the molecular nucleation but this does not clarify how it was achieved or why the magnetic field has different effect depending on the variables.

One of the factor considered is the magnetization and magnetic field exhibition. Particles can have positive or negative charges which contributes to their magnetic susceptibility if exposed to magnetic field. Molecules can also be polar or non-polar, without magnetic field, polar molecules are randomly positioned with low possibility that opposite charges attracted to each other, whereas non-polar molecules move randomly with no fixed alignment of positive and negative charges. Without any external forces, the molecules tend to move randomly with very low chances of collision between molecules and this affects the coagulation process. Under the influence of magnetic field, both polar and non-polar molecules are able to align in orderly arrangement and help improve the attraction between opposite charges. Hence this effect explains the enhancement in the coagulation and aggregation process.

Next, Lorentz force is also one of the factor that affects the magnetic mechanism. With the visual aid of Figure 2.31, Lorentz force is induced when charged particles are allowed to flow in perpendicular direction of the magnetic field produced with the Lorentz force in z-direction. This induced force disturbs the position of the particles and causes the molecules to become unstable. The increase in random movement of the particles increases the frequency of collision between each particles which helps the aggregation.

Moreover, magnetic memory of the particles could be one of the factor contributing to the magnetic mechanism. Magnetic memory describes the period where the particles hold their magnetization properties after the exposure to magnetic field. It was explained that magnetic field changes the water molecules kinetic energy. The formed aggregates after the magnetic treatment are stable and large in size which are difficult for them to restore their original state even after the magnetic field is removed.

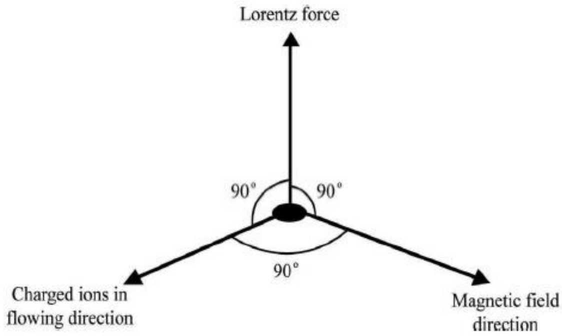

Figure 2-31 Lorentz force induced from flowing charged particles and magnetic field (Zaidi, et al., 2014)

2.6.2 Magnetic Treatment on Fluoride Wastewater

González Vázquez, et al. (2020) analysed the effect of magnetic field applied to the adsorption treatment of water contaminants that contained lead ions (cation) and fluoride ions (anion). The results showed that the adsorption of the lead ions and fluoride ions are both higher in the presence of the magnetic field where the adsorption of lead ions is 6 % higher than of without magnetic field. However for the fluoride ions, the increase in adsorption has no significant difference since the adsorption capacity of fluoride using bituminous coal was low in the first place. In this study, the magnetic treatment has no effect on the fluoride adsorption.

Another study was done on the effect of magnetic field towards adsorption treatment of dyes and heavy metal by (López, et al., 2018). Experiments were tested on single solutions and binary solutions by mixing different solutions (dye-dye or dye-metal). The study was concluded where the magnetic field applied showed more significant effect on binary solutions rather than single solutions. Besides, it was claimed that magnetic field imposes greater effect on cationic species.

On the contrary, (Aigbe, et al., 2019) presented the results where rotating magnetic field positively impacted the adsorption of fluoride ions at the magnetic field intensity of 0.019 T and it was stated that magnetic field is considered to be a potential solution in dealing with the fluoride ions in wastewater. As shown in Figure 2.32 below, the adsorption of fluoride ions increases when the magnetic field intensity and exposure time are increased. At the magnetic field of 0.0266 T, it can be seen that the magnetic treatment duration of 60 minutes have 78 % of removal and 20 minutes of treatment duration have 74 % of removal. Similarly, (Jiang, et al., 2017) noticed that with the help of magnetic intensity applied, there is significant enhancement in adsorption process on fluoride ions using a paramagnetic adsorbent of $FeAlO_xH_y$. However, both the adsorption process were done using adsorbents that possess magnetic characteristics which will certainly be influenced by magnetic field. The review does not provide a clear justification on the magnetic effect towards fluoride ions removal using non-magnetic biochar.

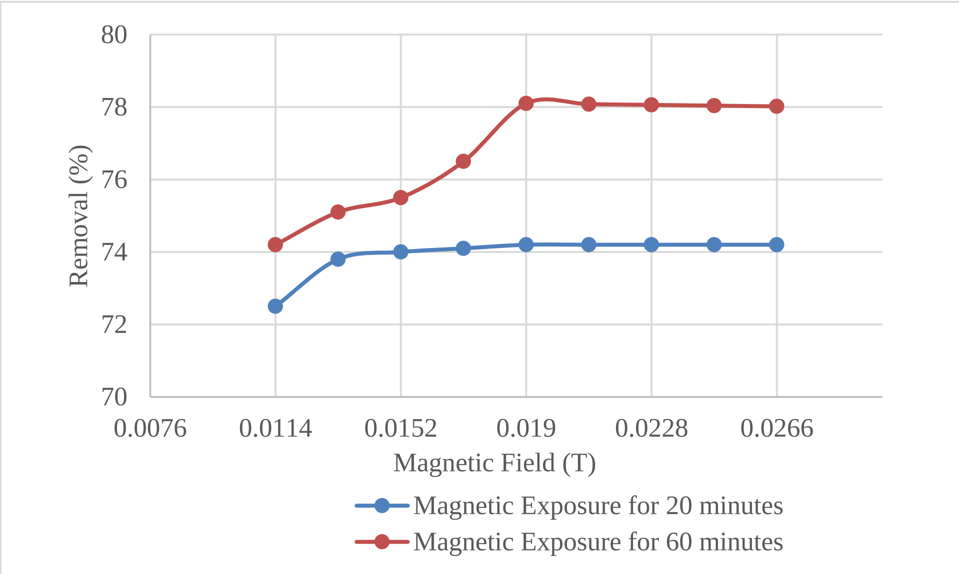

Figure 2-32 Effect of Magnetic Field intensity and exposure time on adsorption of fluoride onto PPy@Fe_3O_4 (Aigbe, et al., 2019)

2.6.3 Magnetic Treatment on Dye Wastewater

Li, et al. (2016) studied the effect of magnetic field on the adsorption of MB onto wheat straw biochar adsorbent and demonstrated that the adsorptive removal of MB was enhanced by the external magnetic field applied. In Figure 2.33, all three sets of experiment using different adsorbent dosages showed improvement in removal percentage with the assistance of external magnetic field applied. Other than that, the increase of adsorbent dosage have significant influence on the removal percentage as well. As stated in the report, the adsorption using wheat straw biochar alone was sufficient in removing a portion of MB efficiently.

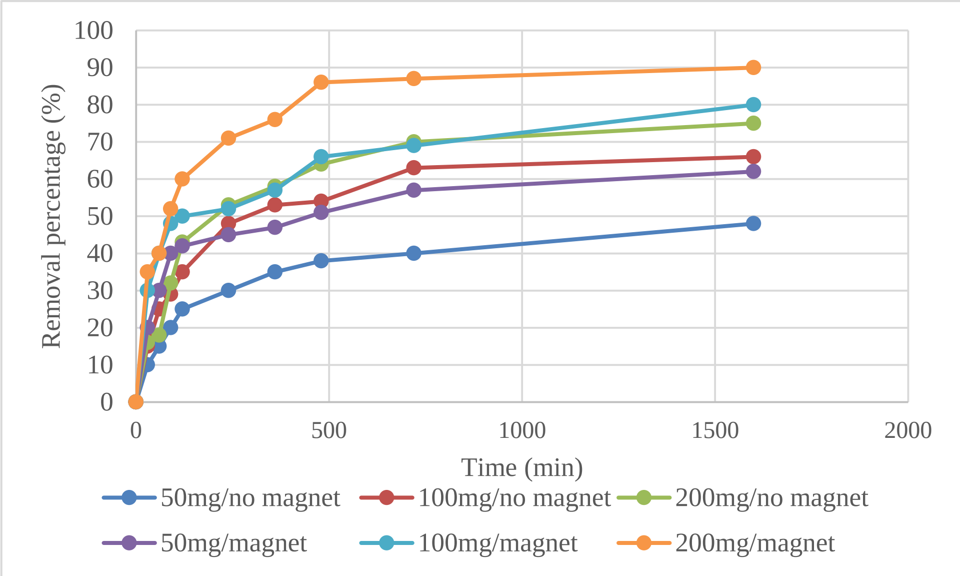

Figure 2-33 Effect of external magnetic field on the adsorption of MB with varying adsorbent dosages (Li, et al., 2016)

Li, et al. (2016) explained that the magnetization of water alters the water molecules bond angle which their dipole moment will be increased and subsequently reduce the cluster structure of water molecules (Zhang, et al., 2014). This increases the mobility of MB dye and allow more dye molecules to be adsorbed onto the biochar. It was deduced that magnetic treatment is able to replace the magnetic sorbents as an improvement in dye removal.

Clay modified with irons were used as adsorbents in removing MB (Tireli, et al., 2014). It was found that magnetic field greatly influenced the adsorption of MB. It was explained that the magnetic field increased the mobility of MB molecules in the solution, and this allows easier penetration of the MB molecules into the adsorption sites of the clays. Similarly in the case of applying magnetic field to the adsorption of MB onto organo-bentonite (Hao, et al., 2012), Figure 2.34 shows that with magnetic exposure, the removal of MB concentration is higher as compared to without magnetic exposure.

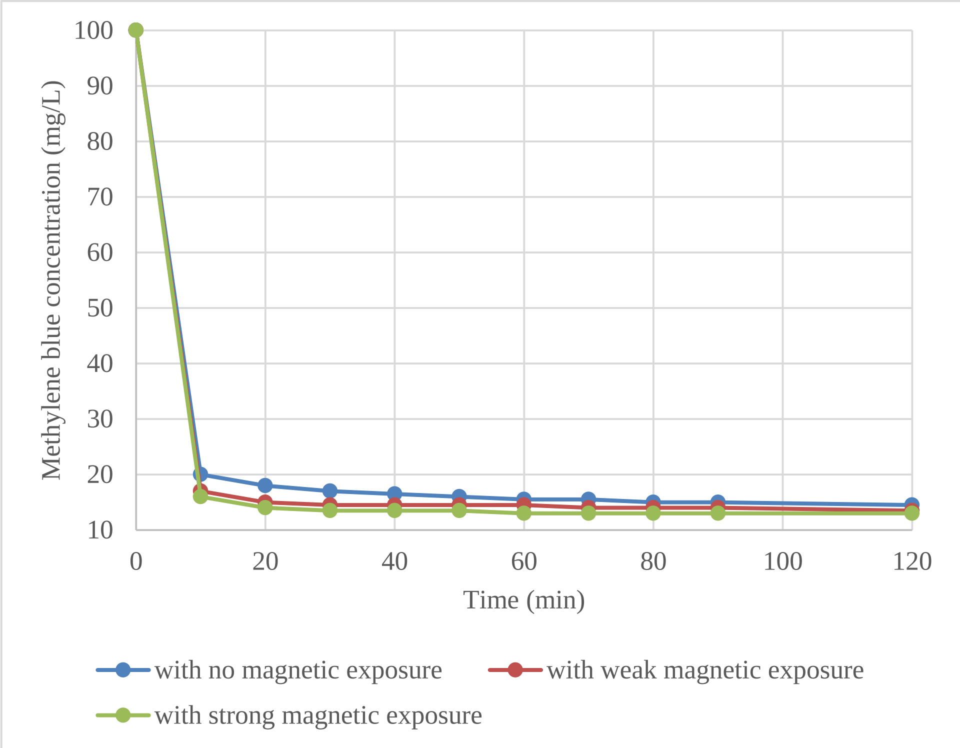

Figure 2-34 Effect of magnetic field intensity on the MB adsorption (Hao, et al., 2012)

2.6.4 Magnetic Effect on Preparation of Activated Carbon

A few studies have shown promising results where magnetic treatment does improve MB adsorption using biochar activated carbon. However, due to insufficient studies done on magnetic effect on fluoride adsorption using biochar, no concrete evidence is shown that magnetic effect is able to improve fluoride adsorption using biochar like CSAC.

A study was made on the magnetic treatment effect during preparation of the activated carbon (Hamasaki, et al., 2019). The prepared activated carbon was used to adsorb N_2. By preparing activated carbon made of coal tar pitch, under the influence of high magnetic field (10 T), it was found that the magnetic field is able to influence the orientation structure of the carbon crystallites which in turn led to forming large number of micropores. Other than the magnetic field factor, the activation process of the activated carbon was taken into consideration as well. The volume ratio of the activation agent, potassium hydroxide (KOH) to the activated carbon affects the adsorption capacity of the activated carbon.

In Table 2.8, the results have shown that in general, except the case for KOH ratio of 10, by applying magnetic field of 10 T to the preparation process, the total pore volume of activated carbon is more than those without the magnetic effect. As a result of increment of total pore volume, the total adsorbed amount of N_2 also increases. This shows an alternative method of applying magnetic field to improve the activated carbon adsorption capacity.

Table 2-8 Results of preparing activated carbon using different activation agent KOH ratio with and without magnetic field (Hamasaki, et al., 2019)

KOH ratio	Magnetic Field (B/T)	Adsorbed amount of N_2 (w/mg g^{-1})	BET surface Area (A_S/m^2 g^{-1})	Total pore Volume (V_{total}/cm^3 g^{-1})	Micropore volume (V_{micro}/cm^3 g^{-1})
1	0 T	20	61	0.026	0.025
1	10 T	25	76	0.032	0.031
3	0 T	436	1275	0.55	0.51
3	10 T	591	1697	0.74	0.71
5	0 T	592	1619	0.74	0.67
5	10 T	798	2063	1	0.76
8	0 T	1065	2503	1.33	0.88
8	10 T	1105	2623	1.38	0.96
10	0 T	1196	2443	1.49	0.98
10	10 T	1003	2156	1.25	0.89

2.6.5 Summary on Magnetic Treatment

Another method of minimizing the cost of adsorption treatment is to improve the adsorption treatment process. The concept of magnetic treatment is widely discussed and numerous studies have shown promising results in enhancing the wastewater treatment performance. However, only sufficient studies were made on MB removal while very little studies were made on fluoride removal with non-magnetic biochar adsorbent.

The focus is then moved to investigating the effect of magnetic treatment on the adsorption capacity of the activated carbon. By applying magnetic field during the preparation process, the micropore structure of the activated carbon is increased which led to increment of adsorption amount of the activated carbon. The experimental data is used to construct a mathematical model for the magnetic field effect on the activated carbon adsorption amount. The mathematical model can be used to investigate the relationship between the magnetic field, KOH to activated carbon ratio, and the improvement in activated carbon adsorption capacity.

2.7 Summary

Semiconductor wastewater containing more than 100 mg/L of fluoride ions is lethal to humans, the dark coloured wastewater is also concerning where it can affect the turbidity of the river water. Hence, appropriate wastewater treatment must be done on the wastewater before releasing it to the river.

Adsorption treatment is one of the most common method to do the treatment since it is more superior to the other methods in terms of flexibility and ease of operation. However, the cost of regularly purchasing the activated carbon can be burdensome to some companies. On top of that, it can be observed that the price range of CSAC has been increasing steadily the last few years. It is important for companies to minimize any wastage of CSAC to avoid extra cost. Literature review is done to collect reference studies regarding fluoride and MB adsorption treatment. Based on the literature review, adsorption technique showed positive evidences in removing both fluoride ions and MB dye components, where the removal rate was relatively high for both cases. The reviewed reference studies can be used to construct a suitable mathematical model that can predict the optimum adsorbent dosage to be used on a simulated semiconductor wastewater under different condition to avoid any wastage of activated carbon.

Besides, to improve the adsorption treatment process, magnetic treatment is also investigated to observe the magnetic effect on both the fluoride and MB adsorption. For magnetic treatment, the stand alone effect on treating fluoride ions was not able to be justified, whereas the magnetic treatment studies on dye wastewater has shown significant effects on MB removal and it was even claimed that magnetic adsorbents were not required for the magnetic treatment to enhance the adsorption treatment. However, there are limited sources that involve magnetic treatment using RSM modelling on both fluoride and MB dye wastewater. The focus is then paid on investigating the effect of magnetic field on the activated carbon by applying high magnetic field during the preparation process of activated carbon. By applying the high magnetic field and suitable activation agent to the activated carbon ratio during the preparation process of activated carbon, the micropore capacity is improved which led to improvement in the activated carbon adsorption capacity as well. The studied experimental data can be used to construct a mathematical model for magnetic field effect on the activated carbon adsorption capacity. The mathematical model can be used to investigate the relationship between the magnetic field and the improvement in activated carbon adsorption capacity.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Introduction

For the adsorption treatment, the project focuses on coconut shell activated carbon (CSAC), a low cost biochar adsorbent. To construct a mathematical model for the fluoride-MB mixture adsorption, comprehensive literature review is done to collect reference studies using existing experimental data and mathematical models for individual fluoride and MB adsorption treatment based on the parameters of adsorbent dosage, pH and treatment contact time. The reference studies are then being compared with each other to find the common trend in the graphs to ensure the reliability of experimental data. Then, the individual models are improved by modifying the graph trend through trial and error method. The trial and error stops when the model graph aligns with the most reliable reference studies. The improved models are used to construct a mathematical model by predicting the adsorption treatment on fluoride-MB mixture with suitable assumptions. The constructed model will be optimized to find the optimum condition to achieve maximum fluoride and MB removal from the mixture.

For the magnetic treatment, a reference study is used to construct a mathematical model for the magnetic effect on improving the micropore capacity of activated carbon using high magnetic field of 10T. A mathematical model will be constructed using the experimental data provided in the paper to find the relationship between magnetic field and activation agent ratio parameters with the activated carbon adsorption capacity.

All the construction of mathematical models are done using Design Expert software.

3.2 Reference studies

In order to modify or construct mathematical models for adsorption treatment, existing experimental data from previous studies are required as reference. Existing papers related to CSAC, fluoride removal, MB removal, adsorption and magnetic treatment are all relevant. To obtain as many useful data as possible, papers that use either Response Surface Methodology (RSM) mathematical modelling or one-factor-at-a-time (OFAT) methods are all taken into consideration. In case of no related RSM papers at all, the closest related RSM model will be used instead.

For adsorption studies, the related OFAT papers are mostly individual fluoride removal and individual MB removal studies with CSAC adsorbent. The parameters used are focused on adsorbent dosage, pH and treatment contact time. For each parameter, one RSM model will be compared with at least one OFAT study to find the common trend between the graphs. OFAT studies are required to ensure the reliability of the RSM study since the mathematical model may deviate from the actual experimental results. Besides, the reliable range of the parameter also depends on the range where the reference studies align better. When the papers may have different constant parameters or initial experimental conditions which causes comparison between graphs to be difficult, choice will be made to choose the most suitable graph to represent the parameter trend. Suitable assumptions are also made when predicting the fluoride-MB mixture adsorption.

For magnetic treatment, only one reference study is used due to lack of RSM study on magnetic treatment with fluoride and MB removal. The mathematical model constructed will be fully based on the experimental data in the paper. Suitable assumptions are necessary to find the relationship between magnetic field and activation agent ratio on the micropore capacity.

3.2.1 Fluoride Adsorption Reference Studies

Figure 3.1 to 3.3 compares the RSM model below (Halder, Khan and Dhawane, 2016) with other OFAT studies regarding the fluoride removal against the parameter trend of CSAC dosage, pH and contact time.

$$
\begin{aligned}
Fluoride\ removal\ \% &= -31.08 + 28.92 \times Dosage + 10.98 \times pH - 0.8629 \\
&\times Time - 0.01667 \times Dosage \times pH + 0.003444 \times Dosage \\
&\times Time - 0.03887 \times pH \times Time - 2.315 \times Dosage^2 \\
&- 0.155 \times pH^2 + 0.005785 \times Time^2 \text{-------------------------} \textcircled{1}
\end{aligned}
$$

Figure 3.1 compares the RSM study (Halder, Khan and Dhawane, 2016) and OFAT study from the same paper against the adsorbent dosage parameter. The RSM model is applied with varying adsorbent dosage, constant pH 6 and 60 minutes contact time. It can be observed that the RSM study deviates from OFAT study at the mark of 7 g/L CSAC dosage. The OFAT study clearly reaches a saturation point at 8 g/L and the fluoride removal even decreases beyond 8 g/L while RSM model does not reach a stopping point. Thus, the optimum adsorbent dosage is decided to be around 7 g/L.

Figure 3.2 compares several studies on the pH parameter. The RSM model is applied with varying pH values, constant 7 g/L CSAC dosage and 60 minutes contact time. It can be observed that all the graphs trend have the maximum fluoride removal at the mark of pH 6. Even though the graphs may not align perfectly with each other due to different experimental initial conditions, it can be deduced that the condition pH 6 is the most favourable for fluoride removal.

Figure 3.3 compares the studies on the contact time parameter. The RSM model is applied with varying contact time, constant 7 g/L CSAC dosage and pH 6. There is an obvious difference between the RSM model with the rest of the OFAT studies. It also differs from the common understanding where increment in contact time should not decrease the adsorption which can be seen from the 30-90 minutes range in the graph. Hence, the contact time parameter of the RSM model should be improved to modify the model to align with the OFAT studies. Based on the OFAT studies, the fluoride removal should reach its saturation point at around 60-90 minutes range.

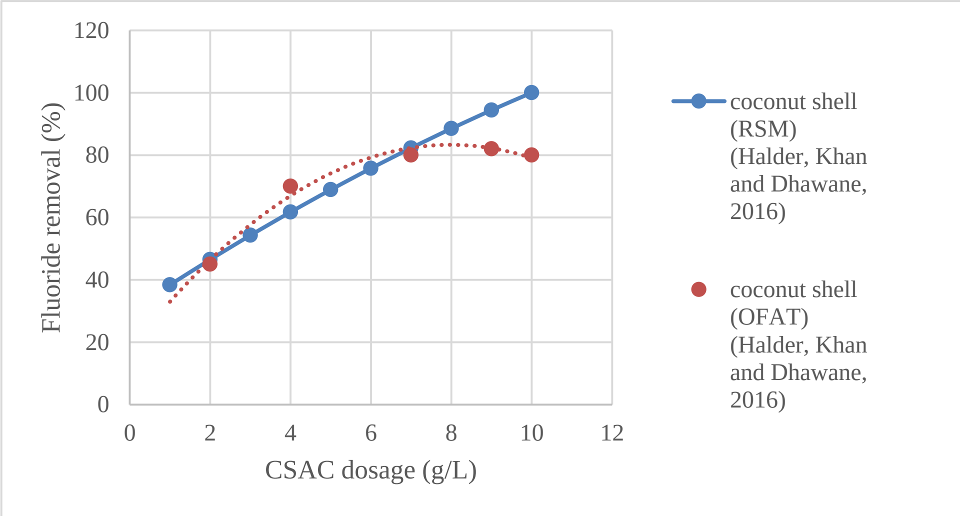

Figure 3-1 Comparison between reference studies of the effect of CSAC dosage on fluoride removal

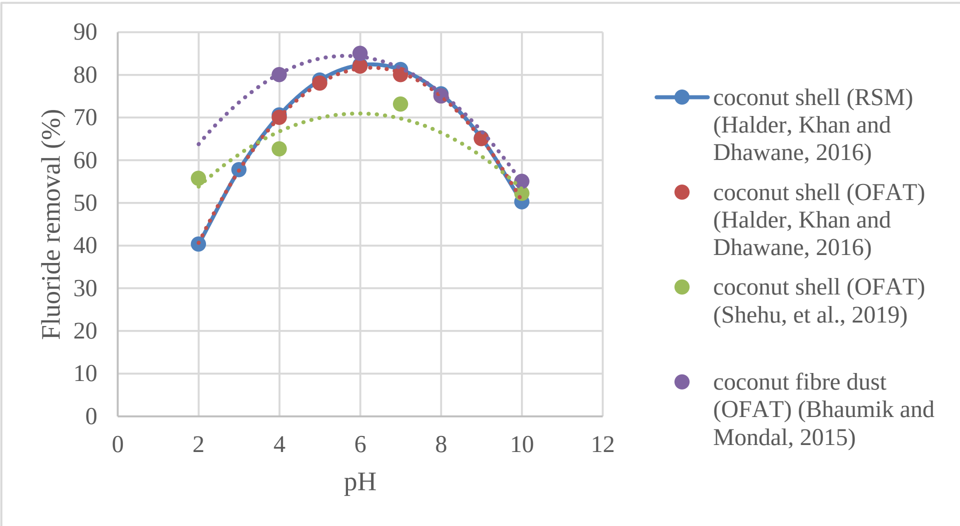

Figure 3-2 Comparison between reference studies of the effect of pH on fluoride removal

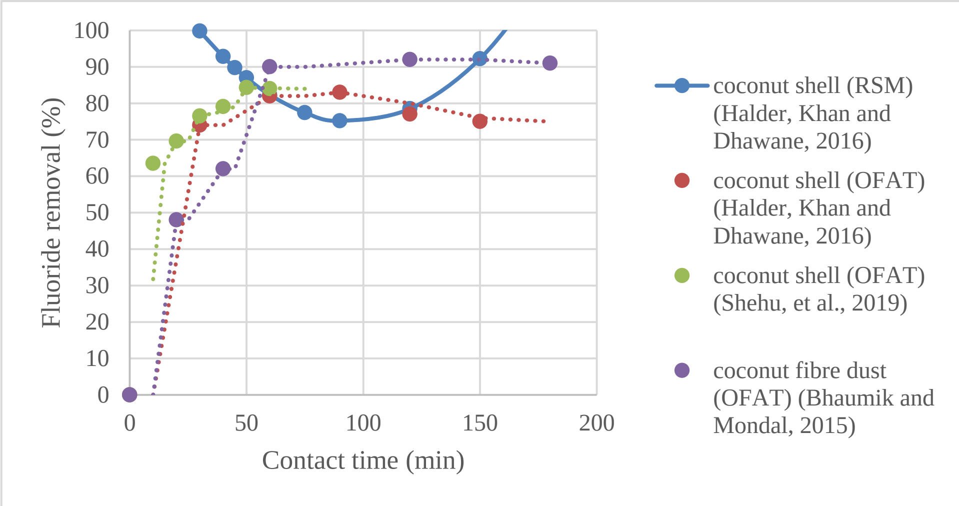

Figure 3-3 Comparison between reference studies of the effect of contact time on fluoride removal

3.2.2 MB Adsorption Reference Studies

Figure 3.4 to 3.6 compares the RSM model below (Jawad, et al., 2016) with other OFAT studies regarding the MB removal against the parameter trend of adsorbent dosage, pH and contact time.

$$MB\ removal\ \% = 5.186 + 63.41 \times Dosage + 0.7624 \times MB\ conc + 7.556 \times pH - 0.6353 \times Time - 0.05713 \times Dosage \times MB\ conc + 1.371 \times Dosage \times pH - 0.1674 \times Dosage \times Time - 0.004479 \times MB\ conc \times pH + 0.0001 \times MB\ conc \times Time + 0.04427 \times pH \times Time - 28.36 \times Dosage^2 - 0.01866 \times MB\ conc^2 - 0.4934 \times pH^2 + 0.0127 \times Time^2 \text{------------} \textcircled{2}$$

Figure 3.4 shows the comparison between coconut leaf (CLAC) RSM model (Jawad, et al., 2016) with CSAC OFAT paper against adsorbent dosage parameter. Due to insufficient RSM papers using CSAC adsorbent, the CLAC paper is used as reference RSM instead since it is a close material to CSAC. The RSM model is applied with varying adsorbent dosage, constant pH 8, 5 minutes contact time and initial MB concentration of 30 mg/L. The RSM model does not align well with the OFAT paper, mainly due to different adsorbent material used and also different experimental initial conditions. The CLAC RSM paper reaches saturation at around 1 g/L with only 83 % MB removal while CSAC OFAT paper requires 2.5 g/L to reach 93 % MB removal. Since this project focuses on CSAC adsorbent, the CSAC OFAT paper (Abd Rashid, Ishak and Hello, 2018) will be the main reference to modify the mathematical model. The optimum dosage is deduced to be 2.5-3 g/L of CSAC dosage.

Figure 3.5 compares several studies on the parameter pH. RSM model is applied with varying pH values, constant 1.2 g/L adsorbent dosage, 5-minute contact time and 30 mg/L initial MB concentration. The RSM model does not align well with the OFAT studies as well. The CSAC OFAT paper (Abd Rashid, Ishak and Hello, 2018) does not show distinct difference in the MB removal results despite drastic change in pH values. Another CSAC OFAT paper (Mondal, Ahmad and Kumar, 2014) fits better with the RSM model but slight modification is still required. Despite using the same coconut shell based activated carbon, the difference in the two studies could be due to different activation agent used which possibly affect the pH parameter. However, overall the graphs do show common trait where MB removal is higher within the range of pH 8 to pH 12.

Figure 3.6 compares the studies on treatment contact time parameter. The RSM model is applied with varying contact time, constant 1.5 g/L adsorbent dosage, pH 8 and 30 mg/L initial MB concentration. There is also a distinct difference in contact time trend in MB removal. RSM only shows very little range of contact time and the graph trend also goes against the common knowledge of adsorption treatment contact time where the increment of contact time should not decrease the adsorption which can be seen from 0-20 minutes range in the graph. Meanwhile the other two CSAC OFAT papers have similar graph trend; hence the OFAT papers will be used as main reference for the contact time parameter. The optimum treatment contact time is deduced to be in the range of 150-240 minutes.

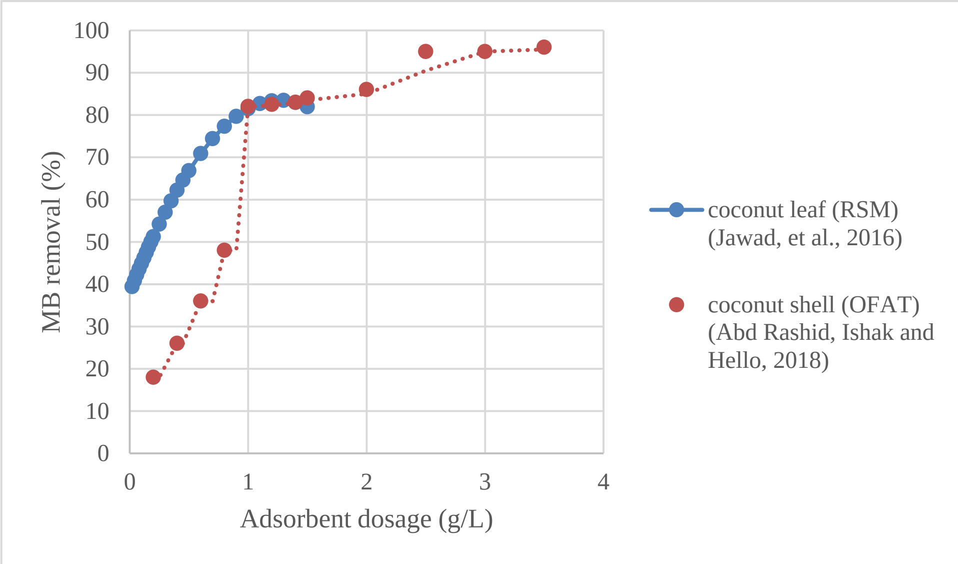

Figure 3-4 Comparison between reference studies of the effect of CSAC dosage on MB removal

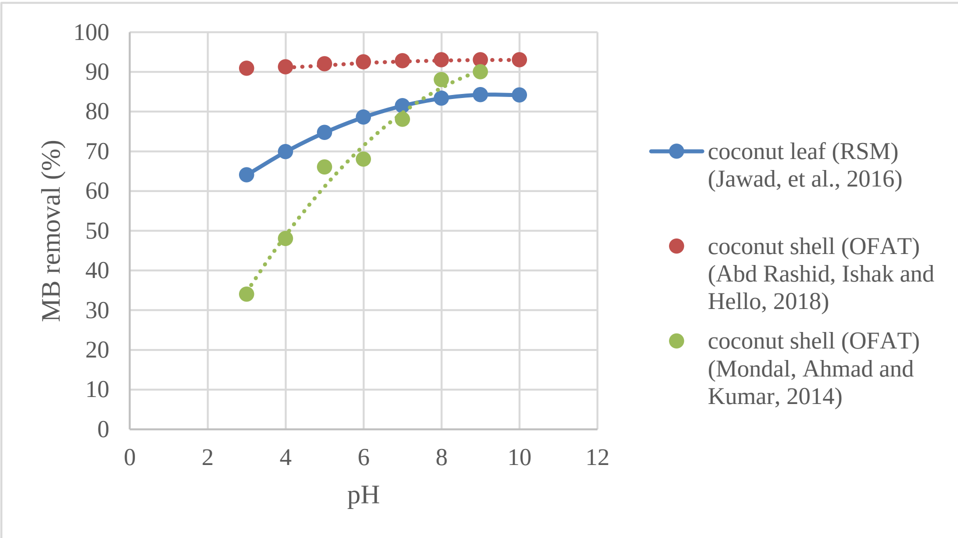

Figure 3-5 Comparison between reference studies of the effect of pH on MB removal

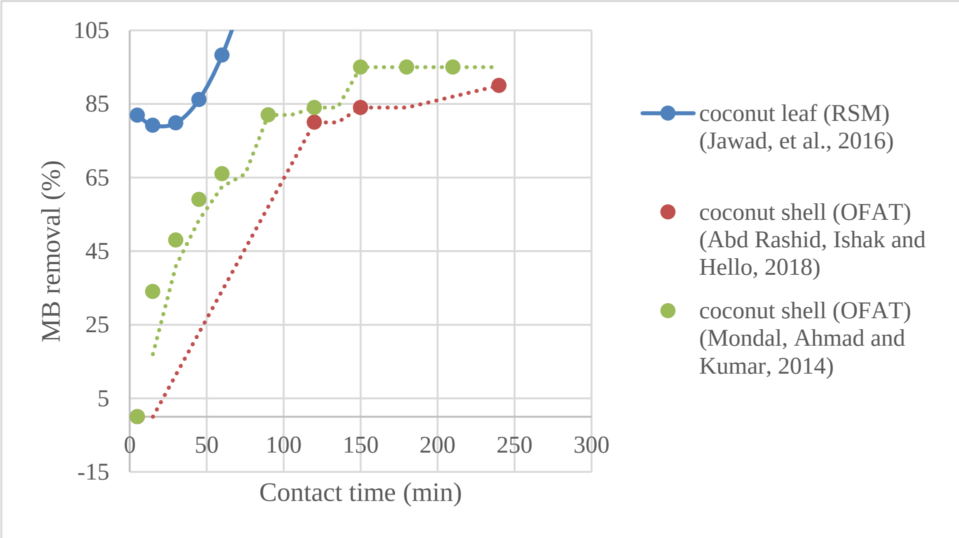

Figure 3-6 Comparison between reference studies of the effect of contact time on MB removal

3.2.3 Magnetic Effect Reference Studies

The paper of magnetic effect on improving micropore capacity using high magnetic field is used as the main reference for magnetic treatment study (Hamasaki, et al., 2019). Since there is a lack of magnetic treatment RSM study on either fluoride or MB removal, this project focuses on the effect of magnetic field on the preparation of activated carbon.

Table 2.7 shows that the study mainly compares the prepared activated carbon of either with 10 T high magnetic effect or without magnetic effect. The study actually compared the influence of all 0 T, 2 T and 10 T magnetic effect in terms of the structure orientation through microscopy imaging of the prepared activated carbon. The 10 T magnetic field gives the best effect but to produce a magnetic field as high as 10 T cannot be generated by normal strong electromagnet. The 2 T magnetic field is easier to be produced but according to the study, the 2 T magnetic field is able to influence the structure orientation but it is not complete in comparison with the effect of 10 T magnetic field.

Figure 3.7 shows the comparison of the adsorption amount of the activate carbon between the activated carbon prepared with or without high magnetic field (10 T). A mathematical model is constructed using the experimental results in Table 2.7 which can be used to predict the actual relationship between magnetic field and activation agent to activated carbon ratio with the micropore capacity.

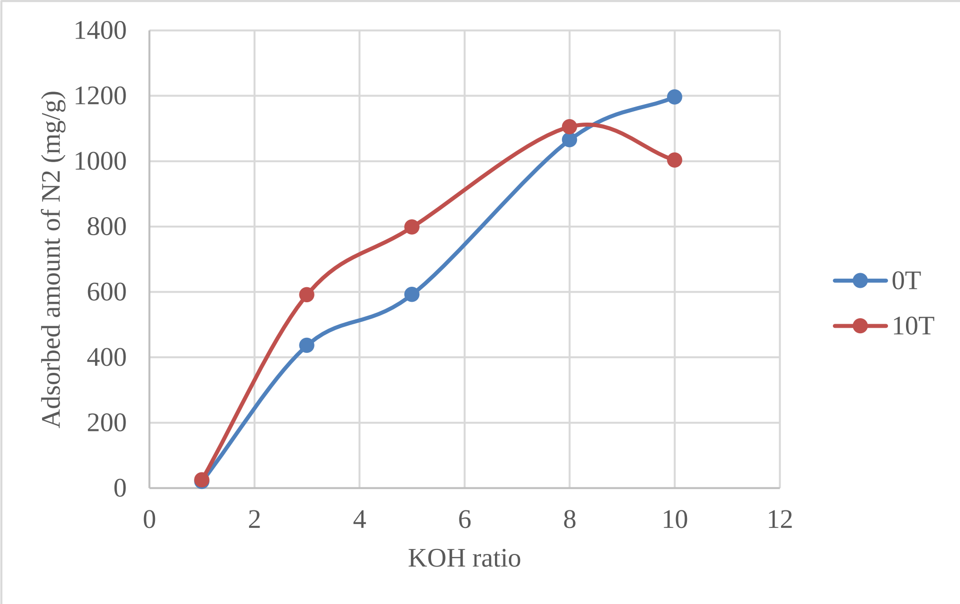

Figure 3-7 Adsorbed amount of N_2 against activated carbon prepared using different activation agent (KOH) ratio with or without high magnetic field (Hamasaki, et al., 2019)

3.2.4 Reference Studies Summary

Reference studies are collected for both adsorption treatment and magnetic treatment. For the individual fluoride and MB adsorption treatment, the parameters of adsorbent dosage, pH and contact time are being carefully compared with each other using the Response Surface Methodology (RSM) graph and the rest of one-factor-at-a-time (OFAT) graphs. For each parameter, a RSM study is compared with at least one OFAT study to ensure the reliability of the RSM model. If the graph is found inconsistent, selection is made to choose one main reference study to follow in the modification of the individual fluoride and MB removal RSM mathematical model.

For individual fluoride adsorption treatment, the adsorbent dosage graphs are able to align well within the range of 1-7 g/L, the pH graphs align perfectly where pH 6 is the optimum condition for fluoride removal, while for the treatment contact time graphs, the RSM model greatly differs with the rest of the OFAT studies. The OFAT studies are made the main reference for contact time parameter where the optimum contact time is in the range of 60-90 minutes range.

For individual MB adsorption treatment, the adsorbent dosage graphs are not able to be aligned and one of the OFAT study is chosen as the main reference for the parameter where the optimum dosage is around 2.5-3 g/L. The pH graphs show common trend where the optimum removal is in alkaline condition of pH more than 8. For the treatment contact time, the RSM graph again differs greatly from the other OFAT studies, hence the OFAT studies are made the main reference where the optimum contact time in the range of 150-240 minutes.

In the study, it could be observed that RSM might have limitation in predicting certain parameters trend such as the treatment contact time. Hence, modification is required to fix the mathematical model in terms of contact time parameter.

For magnetic treatment study on improving the activated carbon adsorption amount, the treatment of 10 T magnetic field shows higher adsorbed amount of N_2. The existing experimental data is used as the direct input for the construction of mathematical model to predict the relationship between the magnetic field intensity and the adsorption capacity by the activated carbon.

3.3 Design of experimental matrix

After reviewing the reference studies, the design of experimental matrix has to be defined before constructing the mathematical model. The range of the parameters are decided based on the reliable range of the chosen reference studies. For adsorption treatment, there are a total of five levels for each parameter and each level is assigned with a code value and its parameter actual value. The other parameters that are kept constant which are 10 mg/L initial concentration of fluoride and 100 mg/L initial concentration of MB.

Table 3.1 and 3.2 shows the design for improving the individual fluoride and MB removal RSM model. Table 3.3 on the other hand shows the design for predicting the fluoride-MB mixture adsorption model after the individual models are improved.

Table 3-1 Chosen parameters range and coded values for fluoride removal

Variable	-α	-1	0	+1	+α
CSAC dosage (g/L)	4	5	7	9	10
pH	3	4	6	8	9
Contact time (min)	0	20	60	100	120

Table 3-2 Chosen parameters range and coded values for MB removal

Variable	-α	-1	0	+1	+α
CSAC dosage (g/L)	1	1.75	2.5	3.25	4
pH	6	7	8	9	10
Contact time (min)	5	65	125	185	245

Table 3-3 Chosen parameters range and coded values for fluoride-MB mixture removal

Variable	-α	-1	0	+1	+α
CSAC dosage (g/L)	1	3.25	5.5	7.75	10
pH	5	6	7	8	9

Whereas for magnetic treatment, by following the experimental data, the chosen parameter range is shown in Table 3.4. There are only three levels for magnetic treatment mathematical model since there is insufficient data available.

Table 3-4 Chosen parameter range and coded values for KOH ratio and magnetic field effect on activated carbon adsorption

Variable	-1	0	+1
KOH ratio	3	5	8
Magnetic field (T)	0	5	10

3.4 Improving Individual Fluoride and MB Removal Mathematical Model

In order to improve the individual models, the main reference studies decided for each parameter are needed to estimate the experimental data. The RSM mathematical model is applied with each parameter according to the parameter value generated by Design Expert. To adjust the experimental value, the RSM model value will be increased or decreased accordingly with other OFAT studies. The increase or decrease of the value remains linear most of the time unless the experimental conditions are believed to reach the adsorption saturation point. This process requires multiple trial and error since there is no specific method to adjust the results. Each trial involves adjusting the values and generating the model to test if the model aligns with the reference studies. The trial and error process is done once the model fits the reference studies. Table 3.5 and 3.6 show the final adjusted results for individual fluoride and MB adsorption treatment.

Table 3-5 Adjusted experimental data to improve individual fluoride removal model

Run no.	Adsorbent Dosage (g/L)	pH	Contact Time (min)	Fluoride Removal (%)
1	5	4	20	49
2	10	6	60	83
3	7	6	30	74
4	7	6	60	82
5	7	6	60	83
6	9	4	20	74
7	7	6	60	82
8	7	6	60	83
9	7	6	60	82
10	7	9	60	65
11	4	6	60	66
12	9	8	20	79
13	5	8	100	63
14	7	6	120	82
15	9	8	100	80
16	7	3	60	57.74
17	7	6	60	83
18	9	4	100	82
19	5	4	100	58
20	5	8	20	54

Table 3-6 Adjusted experimental data to improve individual MB removal model

Run no.	Adsorbent dosage (g/L)	pH	Contact time (min)	MB removal (%)
1	1	8	125	82
2	2.5	8	245	98
3	2.5	8	125	95
4	4	8	125	97
5	2.5	8	125	95
6	3.25	7	65	48
7	1.75	9	65	43
8	1.75	7	65	41
9	2.5	6	125	92
10	1.75	9	185	85
11	1.75	7	185	83
12	2.5	8	125	94
13	3.25	7	185	95
14	2.5	8	125	93
15	2.5	8	125	93
16	2.5	10	125	95
17	2.5	8	125	95
18	3.25	9	185	97
19	3.25	9	65	50
20	2.5	8	5	18

3.5 Constructing Fluoride-MB Mixture Removal Mathematical Model

After the improvement of the individual fluoride and MB removal mathematical models, the models are used to predict the adsorption treatment on the fluoride-MB mixture. One of the literature review major findings is that MB is able to achieve higher percentage removal with lesser adsorbent dosage even with higher initial concentration. Hence, one of the assumptions made in predicting the mixture adsorption treatment is that MB has higher affinity with the CSAC adsorbent than fluoride.

While comparing the RSM with OFAT reference studies, it is found that fluoride requires around 7 g/L of CSAC while MB requires around 3 g/L to achieve optimum removal. It is deduced that a total of 10 g/L is able to achieve the optimum results for both fluoride and MB removal from the mixture. The reliable range stays within 1 to 10 g/L since it is observed from reference studies that excess adsorbent dosage may cause decrease in fluoride removal. The decrease in fluoride removal may be hard to predict and may affect inaccuracy of the mathematical model; thus, the adsorbent dosage range is chosen to be within 1 to 10 g/L. Another assumption is made that by increasing the adsorbent dosage from 1 to 10 g/L, the adsorbent tends to adsorb fluoride and MB with the amount ratio of 3:7. When the amount of adsorbent dosage acquired for MB reaches 3 g/L, MB removal reaches a saturation point under its optimal pH condition and the remaining adsorbent starts to pick up fluoride.

Besides, the parameter of treatment contact time is made constant at 120 minutes. It is decided at 120 minutes since fluoride reaches maximum removal after 90-minutes whereas MB reaches maximum removal after 180 minutes. The midpoint between two maximum removals is at around 120 minutes. It is made constant for the model since there is a possibility that fluoride removal may decrease when the contact time is prolonged too much, as observed from the reference studies; while too short of a contact time is insufficient for the MB adsorption to take place.

Besides, after the improvement of individual fluoride and MB removal models. Fluoride removal model has a reliable range of pH 2 to 10 while MB removal model has a reliable range of pH 3 to 8. In order to predict the fluoride-MB mixture removal using the two individual models, the reliable range for the model should be pH 3 to 8 which is overlapped by both individual fluoride and MB removal models.

Table 3.7 shows the prediction of the adsorption treatment of fluoride-MB mixture using CSAC adsorbent.

Table 3-7 Prediction of fluoride-MB mixture removal experimental data

Run no.	Adsorbent dosage (g/L)	pH	Fluoride removal (%)	MB removal (%)
1	3.25	8	23.05	80
2	5.5	7	46.97	90
3	5.5	9	31.28	93
4	1	7	18.79	61.8
5	5.5	7	46.97	90
6	10	7	81.8	100
7	5.5	7	46.97	90
8	5.5	7	46.97	90
9	7.75	8	61.5	100
10	3.25	6	28.94	80
11	7.75	6	69.5	92
12	5.5	5	44.4	88
13	5.5	7	46.97	91

3.6 Optimizing Fluoride-MB Mixture Removal Mathematical Model

After constructing the mathematical model for fluoride-MB mixture removal, the optimum adsorbent dosage to achieve maximum fluoride and MB removal is obtained using Design Expert. The range of adsorbent dosage is set to be within 1 to 10 g/L shown in Figure 3.8. Then Figure 3.9 shows that the pH condition is targeted at pH 6.3 in order to fit the actual condition of the sample semiconductor wastewater. Lastly, Figure 3.10 and 3.11 show that the fluoride removal and MB removal are maximized and the results will be generated to show the optimum CSAC adsorbent dosage.

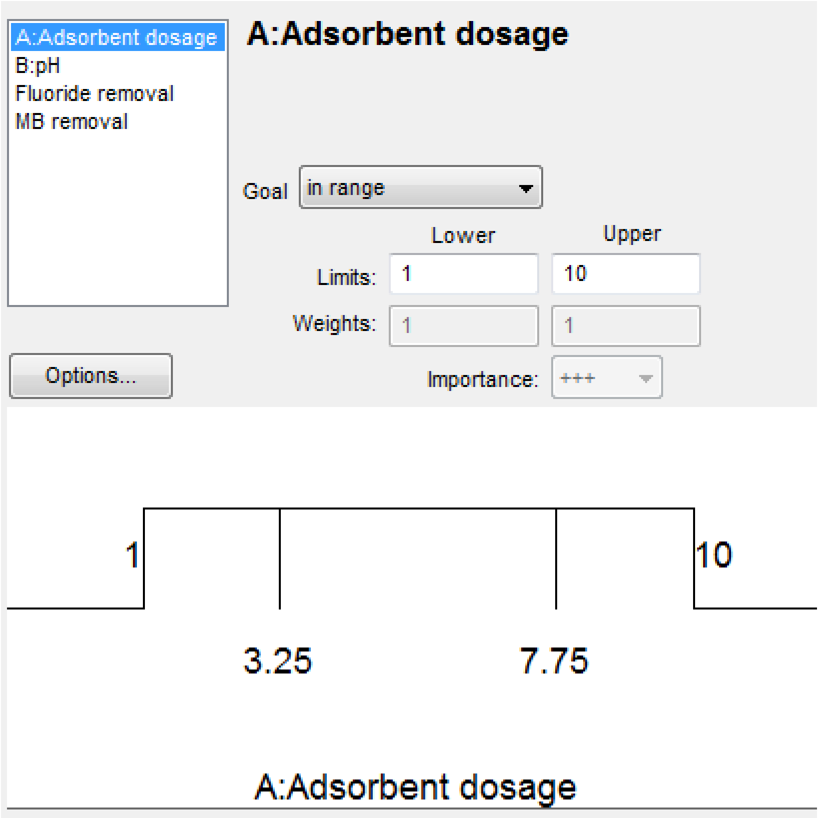

Figure 3-8 Input range of adsorbent dosage for optimization

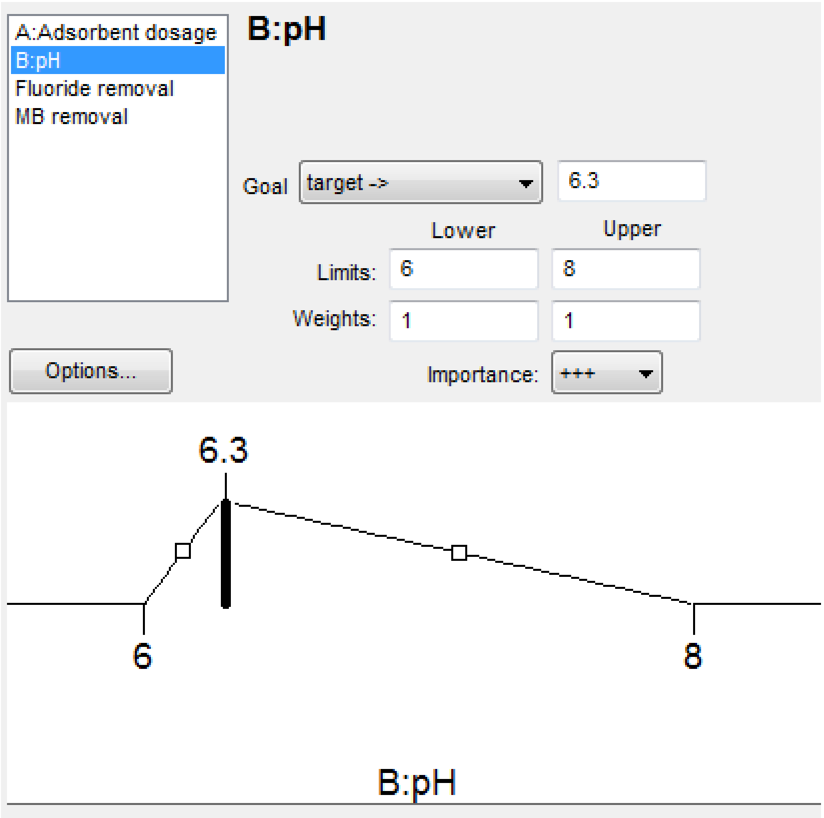

Figure 3-9 Targetted input of pH for optimization

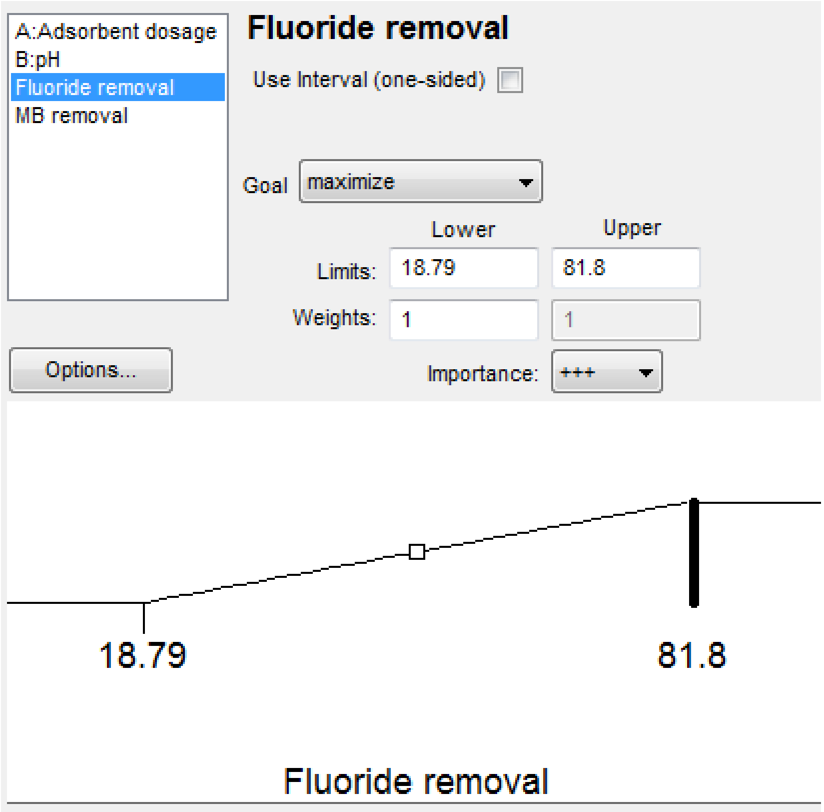

Figure 3-10 Input of maximizing fluoride removal for optimization

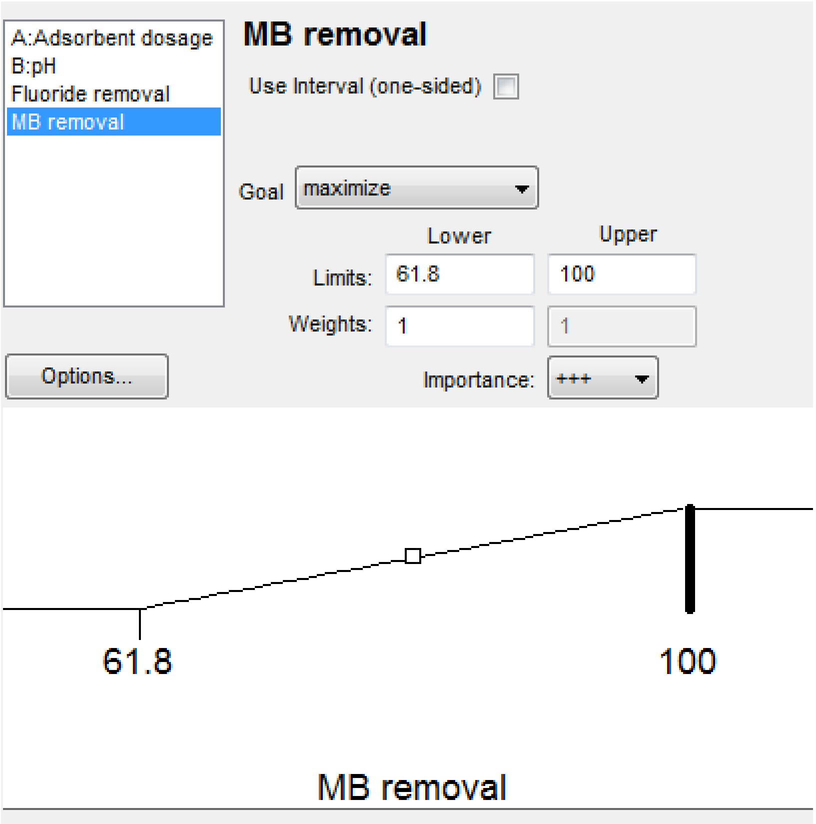

Figure 3-11 Input of maximizing MB removal for optimization

3.7 Constructing Mathematical Model for Magnetic Field and Activation Ratio Effect on Improving Micropore Capacity

The experimental data from the reference study (Hamasaki, et al., 2019) is directly inserted as input to construct the mathematical model. According to the design of matrix for this mathematical model, the parameter of magnetic field 5 T is required for the model construction but there is insufficient data on this parameter value. Hence, the design of experiment is adjusted manually to reduce the frequency of 5 T magnetic field value needed to avoid more empty space of "adsorbed amount" experimental value. The remaining experiment runs with the parameter of 5 T magnetic field are left with empty spaces in the results of "adsorbed amount". Table 3.8 shows the input of experimental data from the reference study before generating the mathematical model.

Table 3-8 Direct input of experimental data from reference study of magnetic field on improving micropore capacity

Run no.	KOH ratio	Magnetic field (T)	Adsorbed amount (mg/g)
1	5	0	592
2	5	0	592
3	3	5	
4	5	10	798
5	8	0	1065
6	3	0	436
7	8	10	1105
8	5	10	798
9	5	10	798
10	8	5	
11	3	10	591
12	5	0	592
13	5	10	798

3.8 Project Planning

Figure 3.12 and 3.13 show the complete flowchart for this project for adsorption and magnetic studies.

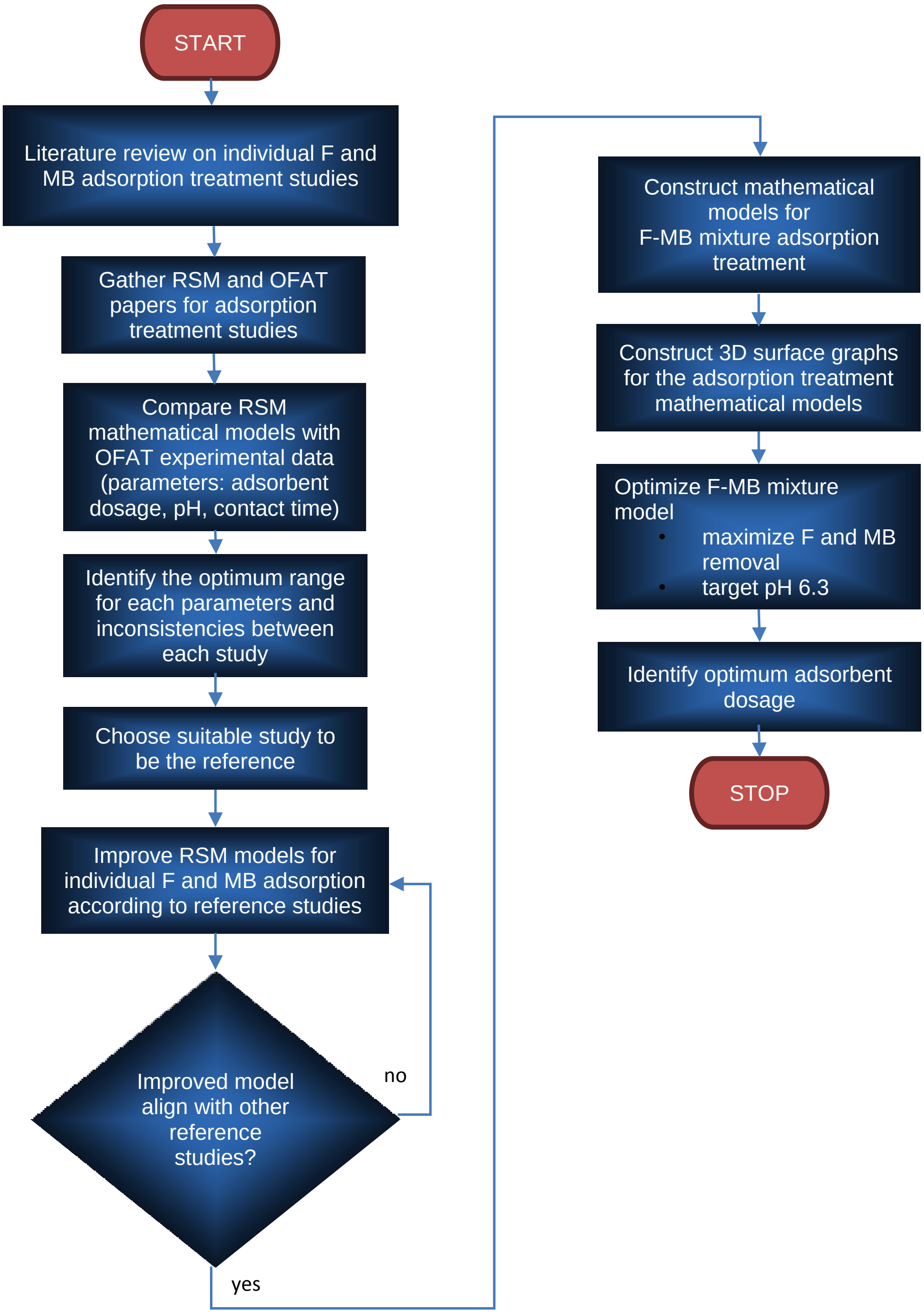

Figure 3-12 Flow chart of the adsorption studies

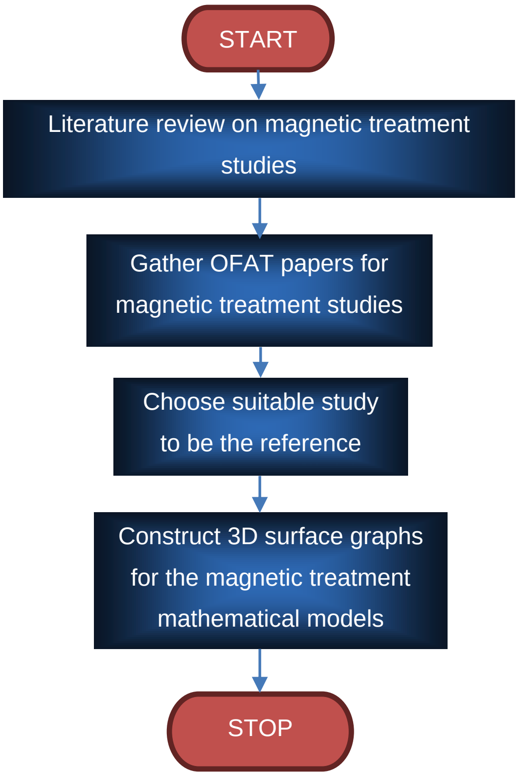

Figure 3-13 Flow chart of the magnetic studies

3.9 Summary

To construct a mathematical model for a fluoride-MB mixture adsorption treatment, literature review is needed to collect as many data as possible to find the accurate trend of each parameter in the adsorption treatment. The parameters involved are coconut shell activated carbon (CSAC) adsorbent dosage, pH and treatment contact time. The optimum range of each parameters are identified in order to improve the individual fluoride and MB mathematical models.

After identifying the trend, the individual models are designed accordingly with 5 levels of parameter range. The experimental data is then adjusted accordingly to the literature findings to fix the mathematical model inaccuracies. After the data input, the mathematical models and graphs are generated. The improved individual models are then applied to predict the final outcome of fluoride-MB mixture adsorption and the step is repeated by designing the 5 levels of parameter range again, and the mathematical model is generated. Then optimization is done to find the optimum adsorbent dosage used under the condition of pH 6.3, to predict the optimum amount of coconut shell activated carbon used on actual semiconductor wastewater.

For magnetic treatment on preparation of activated carbon, the same process is used but only 3 levels of parameter range is available due to lack of information. The existing experimental data from the study is directly input and the mathematical model is generated.

CHAPTER 4

RESULTS & DISCUSSION

4.1 Introduction

The construction of mathematical models are all done using Design Expert. The individual fluoride and MB removal adsorption treatment are improved and generated, the fluoride-MB mixture adsorption treatment mathematical model as well as the mathematical model for magnetic effect are constructed. Each developed mathematical model has its own specific reliable parameter range which is applicable in this project, any value outside the parameter range may generate inaccurate results with the reference studies.

4.2 Improved Individual Fluoride Removal Mathematical Model

The improved individual mathematical model for fluoride removal is

$$Fluoride\ removal\ \% = -109 + 18.33 \times Dosage + 30.52 \times pH + 0.4529 \times Time - 0.2188 \times Dosage \times pH - 0.01406 \times Dosage \times Time - 0.01094 \times pH \times Time - 0.8227 \times Dosage^2 - 2.282 \times pH^2 - 0.00164 \times Time^2 \text{---------------------------------------} ③$$

Figure 4.1 to 4.3 show the comparison between the improved RSM model generated and the previous RSM model and OFAT reference studies for fluoride removal. Based on Figure 4.1, the improved RSM model fits perfectly with the previous RSM study from the range of 4 to 7 g/L regarding adsorbent dosage. After 7 g/L, the improved RSM model reaches saturation point which is more similar to the OFAT study and much closer to realistic adsorption treatment. Since the optimum adsorbent dosage found in the OFAT study to be 7 g/L, the reliable range of 1 to 7 g/L of the individual fluoride removal model is used for constructing fluoride-MB mixture model.

Figure 4.2 compares the improved model with previous studies on pH parameter. The improved model fits perfectly with the old RSM model and also one of the OFAT study. The improved model also shows maximum fluoride removal at pH 6 which is similar to the other OFAT studies as well. The reliable range to be used remains from pH 2 to 10 as the old RSM study.

Figure 4.3 compares the improved model with the studies on treatment contact time. The old RSM model shows very distinct graph trend from all the other studies, hence the contact time parameter is highly modified in particular as compared to adsorbent dosage and pH parameters. The improved model shows that it aligns with the CSAC OFAT study (Halder, Khan and Dhawane, 2016) from the range of 30-150 minutes. The improved model fits well with other studies as well apart from the coconut fibre dust (CFD) study (Bhaumik and Mondal, 2015). It could be mainly due to the difference of adsorbent material used for the adsorption treatment.

The ANOVA test of the improved fluoride adsorption model can be found in Appendix A-1. The ANOVA test shows R-squared value of 0.9564 but there is a significant lack of fit and the difference between adjusted R-squared and predicted R-squared values is found to be more than 0.2. It is advised by the software to do confirmation runs to verify the improved fluoride adsorption model.

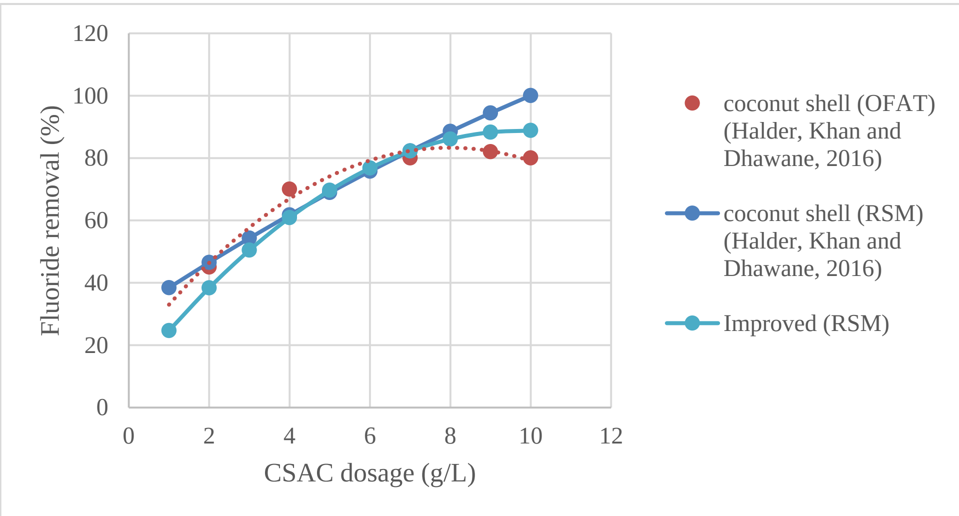

Figure 4-1 Comparison between improved RSM model and previous reference studies of the effect of CSAC dosage on fluoride removal

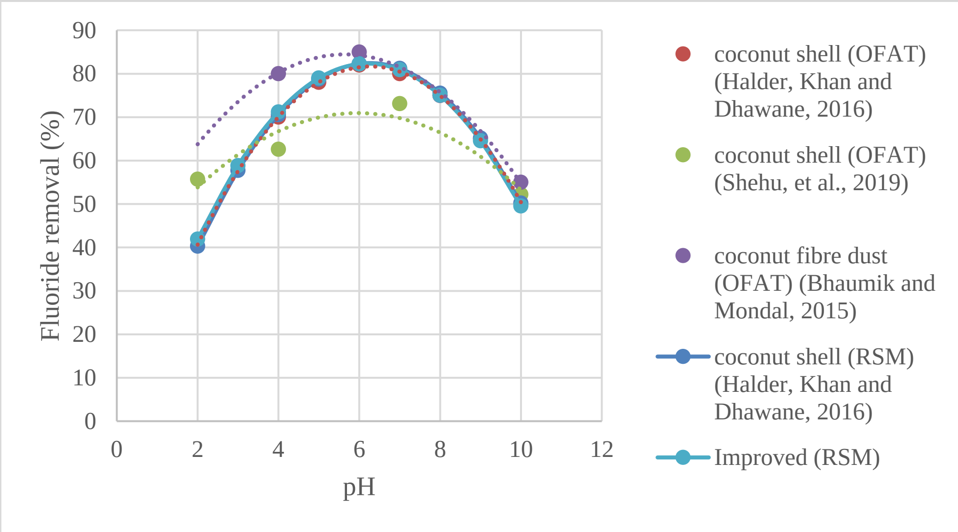

Figure 4-2 Comparison between improved RSM model and previous reference studies of the effect of pH on fluoride removal

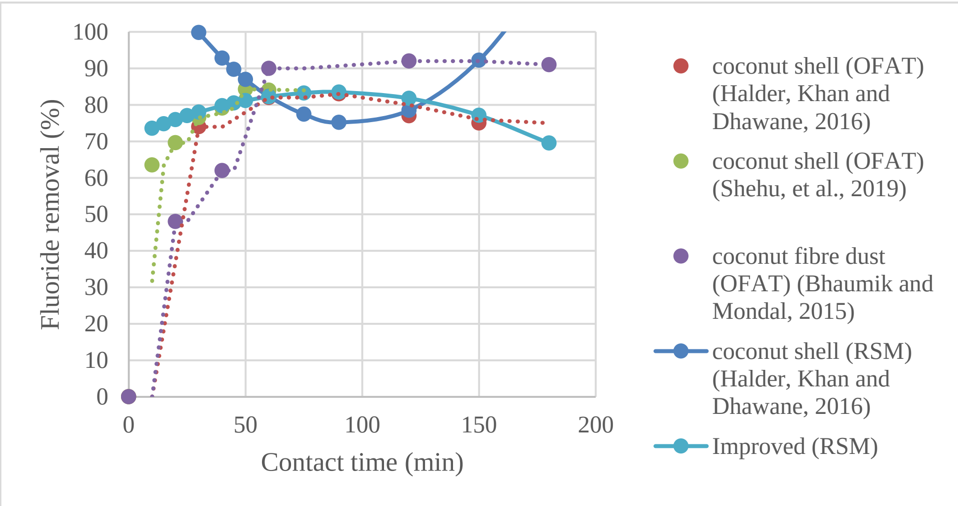

Figure 4-3 Comparison between improved RSM model and previous reference studies of the effect of contact time on fluoride removal

4.3 Improved Individual MB Removal Mathematical Model

The improved individual mathematical model for MB removal is

$$MB\ removal\ \% = -144 + 25.53 \times Dosage + 26.88 \times pH + 1.012 \times Time + 0.02778 \times Dosage \times Time - 4.667 \times Dosage^2 - 1.625 \times pH^2 - 0.00292 \times Time^2 \text{------} (4)$$

Figure 4.4 to 4.6 show the comparison between the improved RSM model generated and the reference study RSM model and OFAT reference studies for MB removal. Based on Figure 4.4, the improved RSM model aligns with the CSAC OFAT (Abd Rashid, Ishak and Hello, 2018) study from the range of 1.5-3 g/L regarding adsorbent dosage. After 3 g/L, the improved RSM model starts decreasing which does not fit with the reference study; hence, the reliable range of adsorbent dosage for MB removal stays within 1.5-3 g/L.

Figure 4.5 compares the improved model with previous studies on pH parameter. The improved model stays between the reference study RSM model and one of the OFAT (Mondal, Ahmad and Kumar, 2014) study. The improved model shows maximum MB removal at pH 8, which fits the trend of the RSM model and reference studies. However after pH 8, the MB removal is observed to be decreasing which is inconsistent with the reference studies. Hence, the reliable range to be used will be from pH 3 to 8.

Figure 4.6 compares the improved model with the studies on treatment contact time. Similar to the fluoride removal contact time parameter, the reference study RSM model shows very distinct graph trend from all the other studies, hence the contact time parameter is highly modified in particular as compared to adsorbent dosage and pH parameters. The improved model aligns with the CSAC OFAT (Mondal, Ahmad and Kumar, 2014) study from the range of 15-150 minutes. The improved model is slightly higher than the other CSAC OFAT (Abd Rashid, Ishak and Hello, 2018) study. It could be mainly due to the lack of experimental data from the paper for the treatment contact time of 0 to 120 minutes. However, the improved model and the reference studies still exhibit similar trend.

The ANOVA test of the improved MB adsorption model can be found in Appendix A-2. The ANOVA test shows R-squared value of 0.8989 but there is also a significant lack of fit and the difference between adjusted R-squared and predicted R-squared values is found to be more than 0.2. It is advised by the software to do confirmation runs to verify the improved fluoride adsorption model.

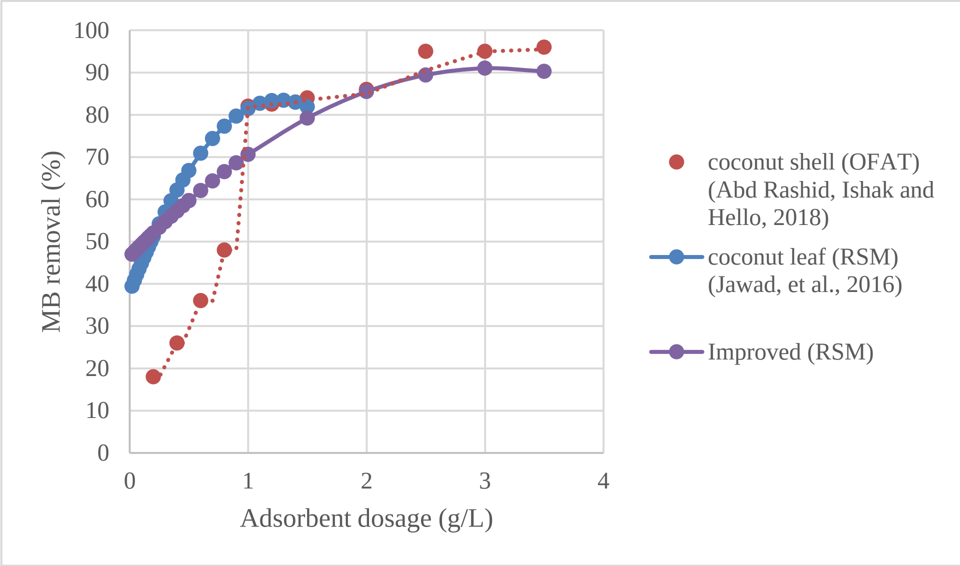

Figure 4-4 Comparison between improved RSM model and previous reference studies of the effect of CSAC dosage on MB removal

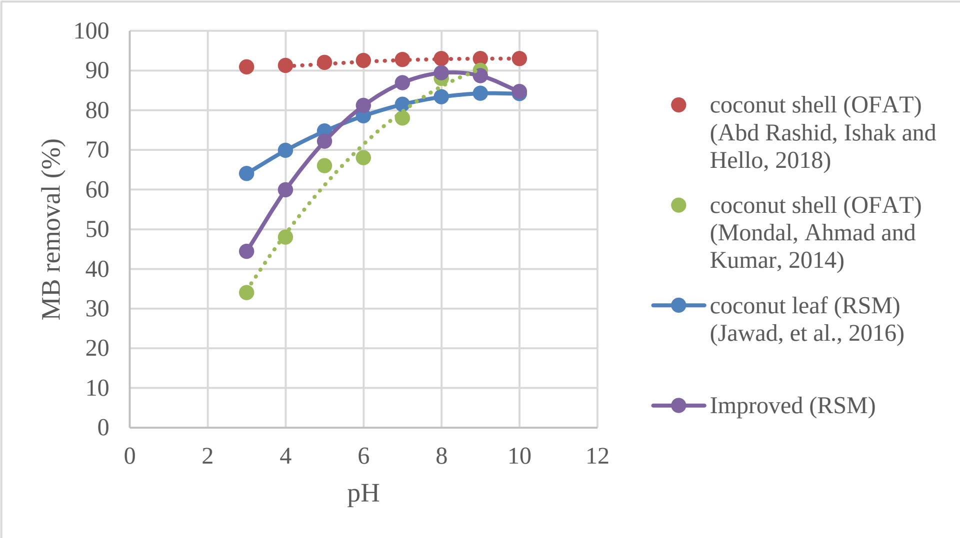

Figure 4-5 Comparison between improved RSM model and previous reference studies of the effect of pH on MB removal

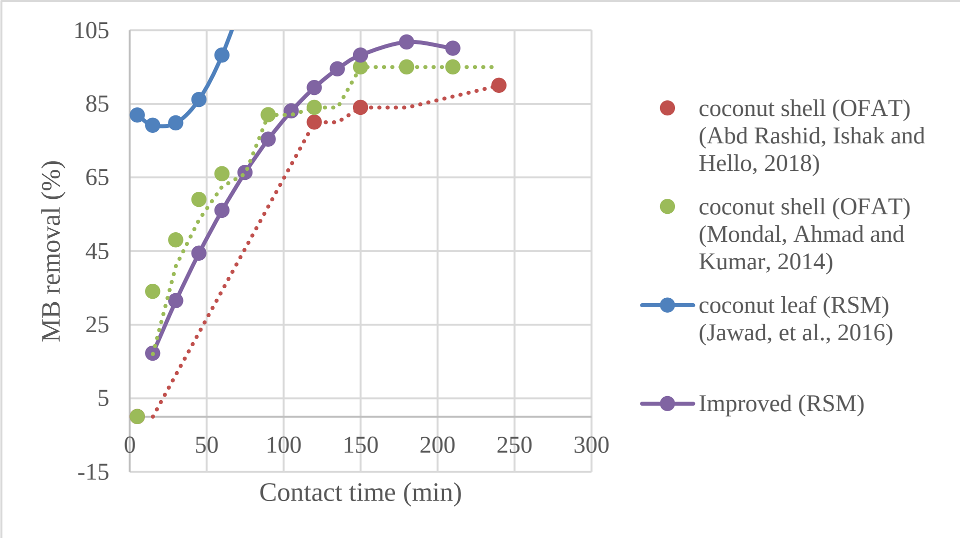

Figure 4-6 Comparison between improved RSM model and previous reference studies of the effect of contact time on MB removal

4.4 Constructed Fluoride-MB Mixture Mathematical Model

After improving the individual mathematical models for fluoride and MB removal, the individual models are used to construct the mathematical model for fluoride-MB mixture adsorption treatment. The individual models are used to predict the possible outcomes of fluoride and MB removal from a fluoride-MB mixture with suitable assumptions made from comprehensive literature review. The assumption is made that fluoride-MB adsorption take place with the amount ratio of 3:7. The treatment contact time is also made constant at 120 minutes in the individual models. The reliable parameter range for the mathematical model for adsorbent dosage is within 1 to 10 g/L whereas the range for pH is 5 to 9. Due to the significant lack of fit for the improved models, outliers are identified during the trial and error process and removed to increase the reliability of the fluoride-MB mixture model.

The fluoride-MB mixture removal mathematical model constructed is as follows:

$$Fluoride\ removal\ \% = -87.01 + 7.42 \times Dosage + 29.85 \times pH - 0.2344 \times Dosage \times pH + 0.165 \times Dosage^2 - 2.279 \times pH^2 \text{------} ⑤$$

$$MB\ removal\ \% = 81.68 + 2.843 \times Dosage - 4.451 \times pH + 0.8889 \times Dosage \times pH - 0.4591 \times Dosage^2 + 0.07586 \times pH^2 \text{-----} (6)$$

Figure 4.7 and 4.8 show the 3D surface plots of the mathematical model constructed.

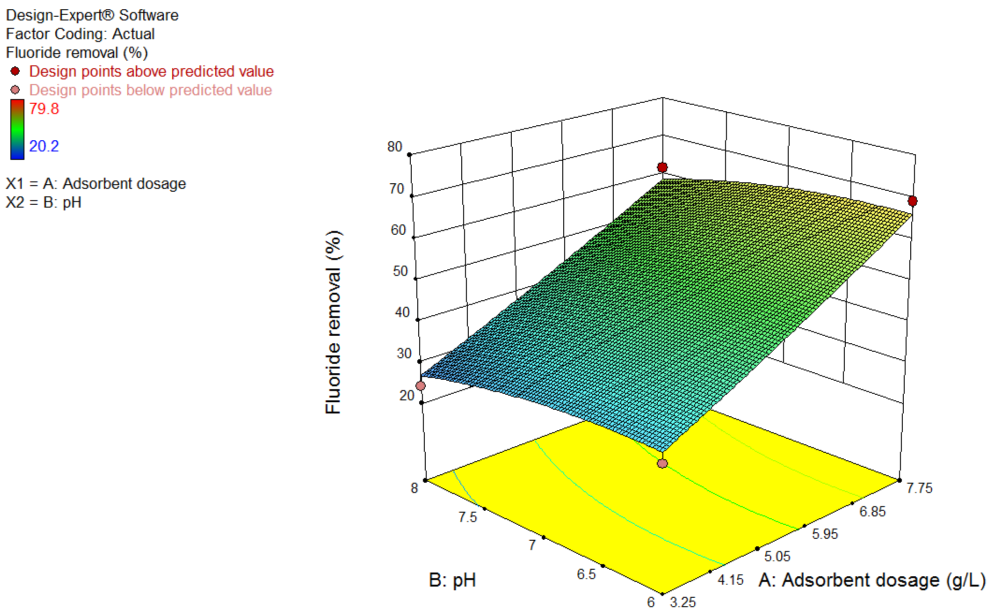

Figure 4-7 3D surface plots of fluoride removal from mixture against adsorbent dosage and pH (Constant parameter: 10 mg/L initial F concentration, 120 min contact time)

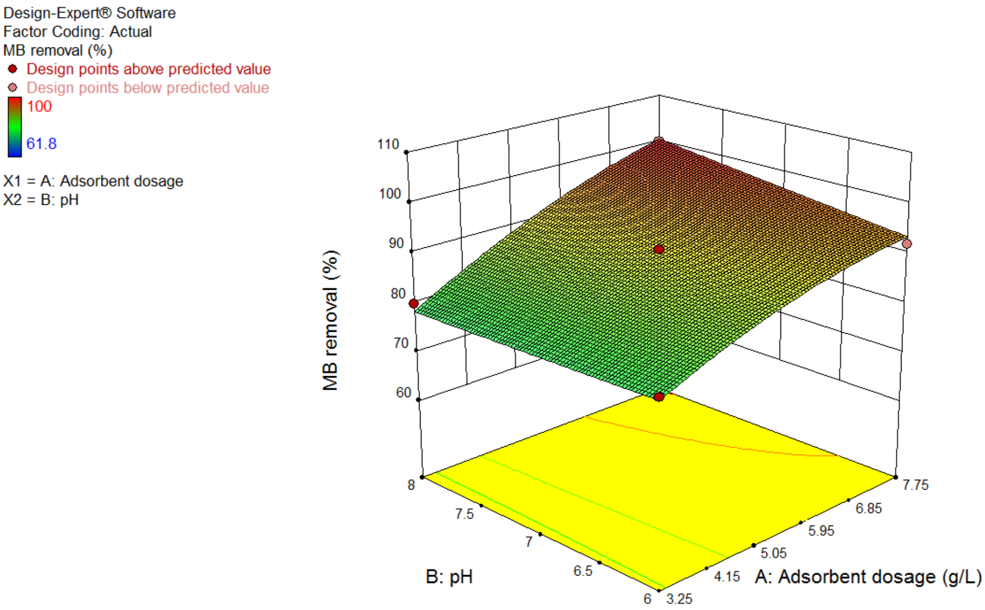

Figure 4-8 3D surface plots of MB removal from mixture against adsorbent dosage and pH (Constant parameter: 100 mg/L initial MB concentration, 120 min contact time)

The ANOVA test of the constructed fluoride-MB adsorption model can be found in Appendix A-3 and A-4. The ANOVA tests show R-squared values of 0.9889 for fluoride removal and 0.9225 for MB removal. As opposed to the improved individual models, the difference between adjusted R-squared and predicted R-squared values for both fluoride and MB removal are less than 0.2, which is an improvement from the individual models. The R-squared values are also higher than the individual models; however for MB removal, there is still significant lack of fit.

4.4.1 Effect of Adsorbent Dosage

From literature review, it is deduced that a total of 10 g/L of adsorbent dosage is able to achieve optimum removal for both fluoride and MB removal. The reliable range of the adsorbent dosage parameter of the mathematical model is within 1 to 10 g/L.

By applying the pH 6.3 to the mathematical model, which is the pH condition of a real semiconductor wastewater, Table 4.1 shows that the general trend where higher CSAC adsorbent dosage guarantees higher fluoride and

MB removal from the fluoride-MB mixture. The assumption was made where MB has higher affinity with adsorbents, MB removal increases drastically as the adsorbent dosage increases from 1 to 5 g/L. This can deduce that 3 g/L is able to achieve optimum MB removal but since pH 6.3 is not the most favourable condition for MB adsorption, hence more adsorbents are required. Around 6 g/L is required to achieve over 90 % MB removal which is optimum MB removal in reference studies.

As opposed to the drastic MB removal, fluoride removal only increases steadily and almost linearly to the adsorbent increment. This can deduce that fluoride requires around 7 g/L to achieve optimum removal whereas in fluoride-MB mixture study while around 10 g/L is required to achieve over 80 % removal which is the optimal fluoride removal in reference studies.

For the adsorbent dosage above 10 g/L is hard to be predicted since it is shown in reference studies where there is a possibility of over saturation of adsorbent causing the fluoride adsorption to reduce.

Table 4-1 Effect of pH 6.3 on fluoride and MB removal under different adsorbent dosage

CSAC dosage (g/L)	pH	Fluoride removal %	MB removal %
1	6.3	16.69	64.64
2	6.3	23.13	71.70
3	6.3	29.89	77.85
4	6.3	36.99	83.08
5	6.3	44.42	87.39
6	6.3	52.18	90.78
7	6.3	60.27	93.26
8	6.3	68.68	94.81
9	6.3	77.43	95.45
10	6.3	86.51	95.17

4.4.2 Effect of pH

As observed from the mathematical model and also from literature review, it is more favourable for fluoride removal under slight acidic condition, specifically pH 6, whereas alkaline condition is more favourable for MB removal, at the range of pH more than 8.

Based on the mathematical model constructed, by applying the deduced optimum adsorbent dosage of 10 g/L, Table 4.2 shows that 10 g/L of CSAC dosage could achieve 65 to 86 % of fluoride removal and 78 % to almost complete MB removal under pH condition range of pH 3 to 8. This shows that regardless of the pH condition, 10 g/L of CSAC adsorbent dosage could still achieve over 70 % MB removal whereas fluoride removal is more affected by the pH condition.

As observed from Table 4.2, MB removal may go over 100 % which is not applicable in real life situations. As mentioned previously, RSM has the limitation in predicting certain parameter trend. It is difficult to construct the parameter trend that achieves saturation point which explains why RSM models obtained from reference papers may be inaccurate as well. It is important that the models are only applied within its own reliable parameter range.

Table 4-2 Effect of 10 g/L CSAC dosage on fluoride and MB removal under different pH conditions

CSAC dosage (g/L)	pH	Fluoride removal %	MB removal %
10	3	65.69	78.20
10	4	77.24	83.17
10	5	84.23	88.29
10	6	86.67	93.56
10	7	84.55	98.98
10	8	77.87	104.56

4.5 Optimization of Fluoride-MB Mixture Removal Mathematical Model

Figure 4.9 shows the results of optimization using Design Expert. It shows that the optimum adsorbent dosage of 9.49 g/L under pH condition 6.3 is able to achieve 81.80 % of fluoride removal and 95.43 % MB removal.

Figure 4.10 shows the mathematical model graph of the fluoride and MB removal under the condition of pH 6.3. At the dosage of 9 g/L, it can be observed that the MB removal has reached the peak while the fluoride removal is still increasing steadily. At 9.5 g/L, MB removal does not increase further while fluoride removal achieves more than 80 % fluoride removal.

Even though acidic condition is not as favourable for MB removal, it can still reach saturation point above 90 % as long as the adsorbent dosage is sufficient. In fluoride-MB mixture adsorption with pH 6.3, it requires 6 g/L to achieve more than 90 % MB removal as opposed to the optimal adsorbent dosage of 3 g/L in reference studies. As for fluoride removal, even though pH 6.3 is the most favourable condition, the competition from MB that has higher affinity with adsorbents causes the slow fluoride uptake when the adsorbent dosage is low. Hence, in fluoride-MB mixture adsorption, fluoride removal requires 9.5 g/L to achieve more than 80 % as opposed to 7 g/L in reference studies.

Both fluoride and MB removal decrease when the adsorption treatment is done on the mixture as compared to the individual adsorption treatment.

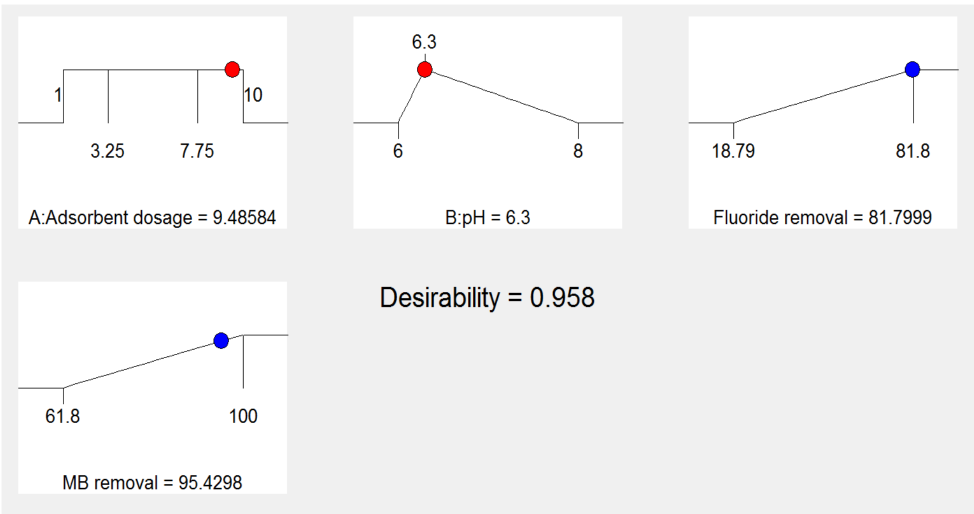

Figure 4-9 Optimization results of the fluoride-MB mixture removal mathematical model

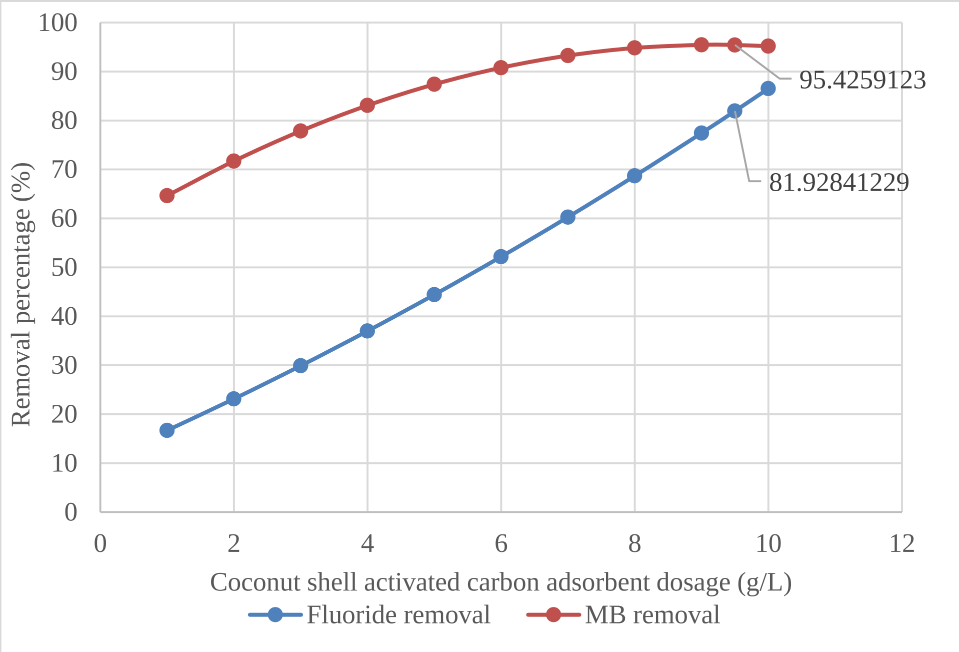

Figure 4-10 Graph of fluoride and MB removal against CSAC adsorbent dosage at pH 6.3

4.6 Constructed Mathematical Model for Magnetic Field and Activation Ratio Effect on Improving Micropore Capacity

The RSM mathematical model constructed for magnetic field and activation ratio effect on the activated carbon adsorption capacity is as follows:

$$Adsorbed\ N_2 amount\ (mg/g)$$
$$= 49.67 + 116.5 \times KOH\ ratio + 16.31$$
$$\times Magnetic\ field \text{---} ⑦$$

Figure 4.11 shows the 3D surface plots of the mathematical model. Figure 4.12 and 4.13 show the comparison of the RSM mathematical model with the reference study experimental data. As observed from the graph, the mathematical model is linear to both KOH ratio and magnetic field parameter.

Due to the lack of results data, the mathematical model constructed do not align well with the experimental data when the KOH ratio is 10. To achieve the quadratic shape shown in the range of KOH ratio of 8-10, the experimental data for using KOH ratio of more than 10 is required, for example, KOH ratio of 12 and 14. This is because more data is able to construct models with higher accuracy.

When all the experimental data is applied to construct the model, the model do not align with the experimental data at all since the KOH ratio range of 3-8 is linear while KOH ratio of 10 has a drastic drop. On top of that, there is a lack of data available. The constructed model will neither have the linear trend nor the quadratic shape in the KOH ratio range of 8-10. Hence, only the experimental data that is within the linear range is taken into consideration, which is the KOH ratio range of 3-8. Hence, in Figure 4.13, the mathematical model graph for 10 T only align with the experimental graph within the range of KOH ratio 3-8, which will be the reliable range of the mathematical model.

The ANOVA test of the constructed magnetic model can be found in Appendix A-5. The ANOVA tests show R-squared values of 0.964. There is no significant lack of fit.

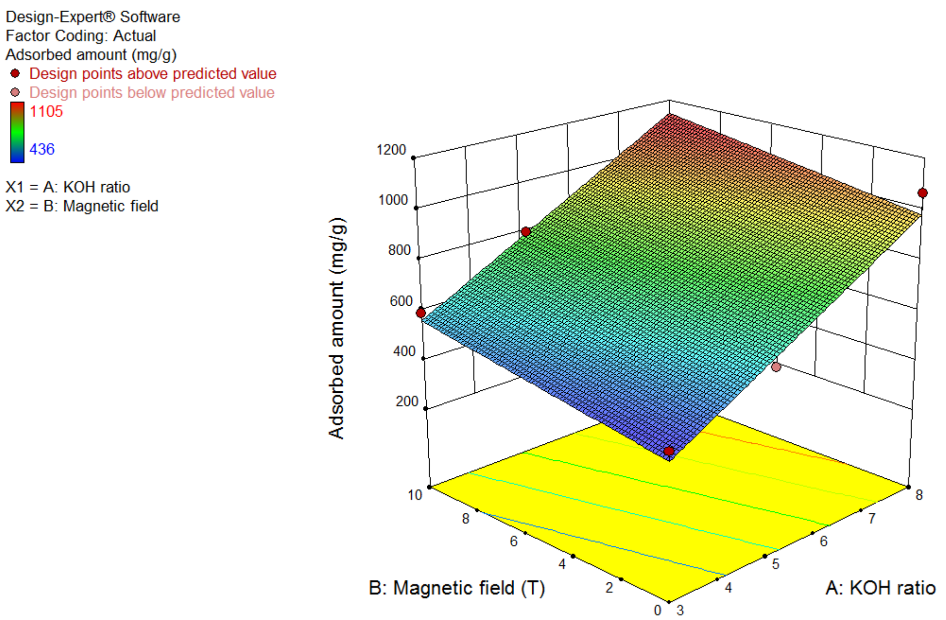

Figure 4-11 3D surface plots of adsorbed N_2 amount against KOH ratio and magnetic field

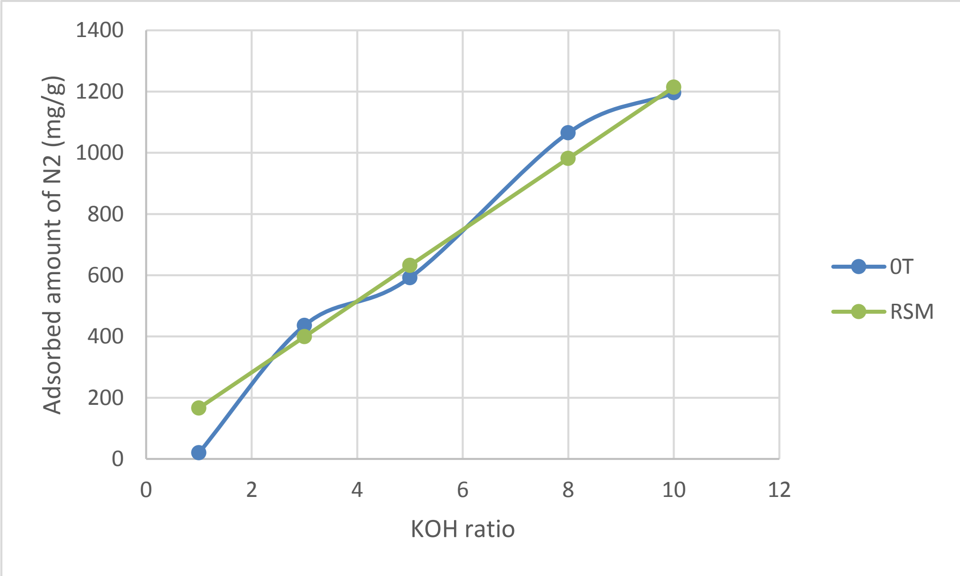

Figure 4-12 Comparison of reference study with mathematical model for 0T magnetic field

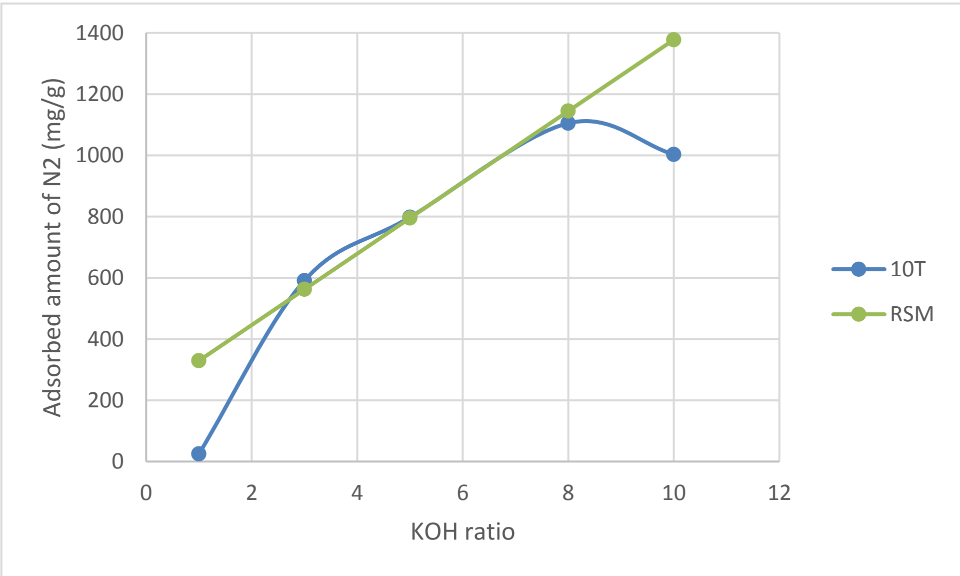

Figure 4-13 Comparison of reference study with mathematical model for 10T magnetic field

4.7 Summary

The individual models of fluoride and MB removal are improved accordingly with comprehensive literature review. The improved models have R-squared values of around 0.9; however, the ANOVA tests also show significant lack of fit and significant difference between adjusted R-squared values and predicted

R-squared values. This could be due to experimental errors in the reference studies which may cause outliers and anomalies in the experimental data.

Next, mathematical model is constructed for the fluoride-MB mixture wastewater. In order to increase the reliability of the model, outliers are identified and removed accordingly. The ANOVA tests show the difference between adjusted and predicted R-squared values are reduced which increases the reliability. The lack of fit for both fluoride and MB removal are reduced significantly compared to the individual models; however for MB removal, the lack of fit is still significant. The models can be further improved in the future and experimental studies are required to verify the models.

The mathematical model is then optimized to find the optimal adsorbent dosage used for achieving the highest fluoride and MB removal from the mixture under pH 6.3, as an effort to predict the optimal dosage for treating an actual semiconductor wastewater. The mathematical model is also potentially useful in the future for predicting the optimal adsorbent dosage for treating a semiconductor wastewater with other different pH condition.

A mathematical model is constructed based on the study regarding magnetic effect on adsorb ability of activated carbon. The constructed model is an attempt to find the relationship between magnetic field intensity and the activated carbon adsorption capacity. The model is constructed aligning with the linear range of the actual experimental data. The model has more than 0.9 R-squared value and does not have significant lack of fit.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

For adsorption treatment study, the objectives are achieved where the individual mathematical models of fluoride and MB removal are obtained through literature findings and they are improved with the modification of experimental data based on other reference studies. Besides, a mathematical model is constructed using the help of the improved individual models to predict the adsorption treatment on fluoride-MB mixture. The initial fluoride and MB concentrations are 10 mg/L and 100 mg/L respectively. To achieve the aim of finding the optimum adsorbent dosage used in order to reduce the wastage of activated carbon, the mathematical model is optimized to find the optimal adsorbent dosage to be used to achieve the highest fluoride and MB removal from the mixture under condition of pH 6.3 which is the actual pH of a raw semiconductor wastewater. The optimization results show the optimal CSAC adsorbent dosage of 9.5 g/L is able to achieve 81.80 % of fluoride removal and 95.43 % MB removal. Furthermore, the constructed model has the potential to be used to predict the adsorption treatment on fluoride-MB mixture removal under different pH condition.

For magnetic treatment study, the objective of constructing a mathematical model to represent the magnetic effect on activated carbon adsorption capacity by applying magnetic field during the preparation of activated carbon is achieved. The mathematical model is able to show a relatively linear relationship between the magnetic field intensity and activation agent KOH to activated carbon ratio with the adsorption capacity of activated carbon.

In conclusion, the objectives to construct the mathematical models for adsorption and magnetic treatment are achieved respectively. Hence, the aim to investigate the adsorption and magnetic treatment effect through mathematical modelling is achieved through the objectives. The constructed adsorption model is able to predict the adsorption treatment on fluoride-MB mixture and predict the optimal adsorbent dosage to be used. By using optimal amount of adsorbent, the amount of wastage can be minimized and reduce the cost of purchasing adsorbent. Besides, the constructed magnetic model is able to predict the magnetic effect on improving activated carbon adsorption capacity. By improving the adsorption capacity, the amount of adsorbent dosage can be further reduced and it is another method to reduce the cost of purchasing adsorbent.

5.2 Recommendations for Future Work

For the future studies, the method of constructing mathematical models that serves as guidelines for adsorption treatment may be useful to the industries in predicting the adsorption process, where it can potentially reduce any activated carbon wastage.

All the improved and constructed mathematical models have their own specific reliable parameter range. Further improvement can be made on the mathematical models to expand the parameter range that could be applicable for other adsorption studies. The parameters can be expanded itself to include the initial concentration of the substances, agitation speed, or any other relevant parameters as well. By expanding and improving the mathematical models, it can be adopted by various industries and can be helpful for the wastewater treatment processes.

Other than that, without physical experimental data, the reliability of the mathematical models can be limited. The ANOVA tests show that a few of the constructed models have significant lack of fit even though the R-squared values are more than 0.9. This could be due to the outliers that occurred in the reference studies. The mathematical models constructed can be verified through experimental studies in the future and further improvement can be made with more experimental data. It was also advised to do more confirmation runs to avoid outliers.

Last but not the least, the method of recycling activated carbon can be explored using the similar mathematical modelling method. This is another way to minimize the expenses for regularly purchasing activated carbon. By constructing mathematical models based on activated carbon regeneration, we can also find the optimum conditions for recycling the exhausted activated carbon which can be helpful to the companies as well.

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APPENDICES

APPENDIX A-1: ANOVA table for improved fluoride removal model

Response 1 Fluoride removal

ANOVA for Response Surface Quadratic model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2390.82	9	265.65	24.39	< 0.0001	significant
A-Adsorbent	*213.10*	*1*	*213.10*	*19.57*	*0.0013*	
B-pH	*685.51*	*1*	*685.51*	*62.95*	*< 0.0001*	
C-Contact tin	*78.66*	*1*	*78.66*	*7.22*	*0.0228*	
AB	*6.12*	*1*	*6.12*	*0.56*	*0.4706*	
AC	*10.12*	*1*	*10.12*	*0.93*	*0.3577*	
BC	*6.12*	*1*	*6.12*	*0.56*	*0.4706*	
A^2	*110.01*	*1*	*110.01*	*10.10*	*0.0098*	
B^2	*846.20*	*1*	*846.20*	*77.70*	*< 0.0001*	
C^2	*49.47*	*1*	*49.47*	*4.54*	*0.0589*	
Residual	108.90	10	10.89			
Lack of Fit	*107.40*	*5*	*21.48*	*71.60*	*0.0001*	*significant*
Pure Error	*1.50*	*5*	*0.30*			
Cor Total	2499.72	19				

Std. Dev.	3.30	R-Squared	0.9564
Mean	73.09	Adj R-Squared	0.9172
C.V. %	4.52	Pred R-Square	0.6266
PRESS	933.40	Adeq Precisior	16.879
-2 Log Likeliho	90.65	BIC	120.61
		AICc	135.10

The "Pred R-Squared" of 0.6266 is not as close to the "Adj R-Squared" of 0.9172 as one might normally expect; i.e. the difference is more than 0.2. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response transformation, outliers, etc. All empirical models should be tested by doing confirmation runs.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 16.879 indicates an adequate signal. This model can be used to navigate the design space.

APPENDIX A-2: ANOVA table for improved MB removal model

Response 1 MB removal

ANOVA for Response Surface Quadratic model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	10242.70	9	1138.08	9.88	0.0007	significant
A-Adsorbent	*35.34*	*1*	*35.34*	*0.31*	*0.5919*	
B-pH	*59.32*	*1*	*59.32*	*0.51*	*0.4895*	
C-Contact tir	*363.39*	*1*	*363.39*	*3.15*	*0.1061*	
AB	*0.000*	*1*	*0.000*	*0.000*	*1.0000*	
AC	*12.50*	*1*	*12.50*	*0.11*	*0.7487*	
BC	*1.819E-012*	*1*	*1.819E-012*	*1.579E-014*	*1.0000*	
A^2	*173.25*	*1*	*173.25*	*1.50*	*0.2482*	
B^2	*66.39*	*1*	*66.39*	*0.58*	*0.4653*	
C^2	*2772.00*	*1*	*2772.00*	*24.06*	*0.0006*	
Residual	1152.25	10	115.23			
Lack of Fit	*1147.42*	*5*	*229.48*	*237.40*	*< 0.0001*	*significant*
Pure Error	*4.83*	*5*	*0.97*			
Cor Total	11394.95	19				

Std. Dev.	10.73	R-Squared	0.8989
Mean	79.45	Adj R-Squared	0.8079
C.V. %	13.51	Pred R-Square	0.2059
PRESS	9048.56	Adeq Precisior	12.779
-2 Log Likeliho	137.83	BIC	167.79
		AICc	182.28

The "Pred R-Squared" of 0.2059 is not as close to the "Adj R-Squared" of 0.8079 as one might normally expect; i.e. the difference is more than 0.2. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response transformation, outliers, etc. All empirical models should be tested by doing confirmation runs.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 12.779 indicates an adequate signal. This model can be used to navigate the design space.

APPENDIX A-3: ANOVA table for fluoride removal from fluoride-MB mixture model

Response 1 Fluoride removal

ANOVA for Response Surface Quadratic model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	3812.14	5	762.43	124.38	< 0.0001	significant
A-Adsorbent	*20.84*	*1*	*20.84*	*3.40*	*0.1078*	
B-pH	*87.92*	*1*	*87.92*	*14.34*	*0.0068*	
AB	*1.11*	*1*	*1.11*	*0.18*	*0.6828*	
A^2	*15.98*	*1*	*15.98*	*2.61*	*0.1504*	
B^2	*118.96*	*1*	*118.96*	*19.41*	*0.0031*	
Residual	42.91	7	6.13			
Lack of Fit	*42.91*	*3*	*14.30*			
Pure Error	*0.000*	*4*	*0.000*			
Cor Total	3855.05	12				

Std. Dev.	2.48	R-Squared	0.9889
Mean	45.70	Adj R-Squared	0.9809
C.V. %	5.42	Pred R-Square	0.8868
PRESS	436.40	Adeq Precisior	40.631
-2 Log Likeliho	52.42	BIC	67.81
		AICc	78.42

The "Pred R-Squared" of 0.8868 is in reasonable agreement with the "Adj R-Squared" of 0.9809; i.e. the difference is less than 0.2.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 40.631 indicates an adequate signal. This model can be used to navigate the design space.

APPENDIX A-4: ANOVA table for MB removal from fluoride-MB mixture model

Response 2 MB removal

ANOVA for Response Surface Quadratic model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1159.48	5	231.90	186.29	< 0.0001	significant
A-Adsorbent	*3.06*	*1*	*3.06*	*2.46*	*0.1610*	
B-pH	*1.96*	*1*	*1.96*	*1.57*	*0.2503*	
AB	*16.00*	*1*	*16.00*	*12.85*	*0.0089*	
A^2	*123.77*	*1*	*123.77*	*99.43*	*< 0.0001*	
B^2	*0.13*	*1*	*0.13*	*0.11*	*0.7543*	
Residual	8.71	7	1.24			
Lack of Fit	*7.91*	*3*	*2.64*	*13.19*	*0.0153*	*significant*
Pure Error	*0.80*	*4*	*0.20*			
Cor Total	1168.19	12				

Std. Dev.	1.12	R-Squared	0.9925
Mean	88.14	Adj R-Squared	0.9872
C.V. %	1.27	Pred R-Square	0.9300
PRESS	81.72	Adeq Precisior	49.670
-2 Log Likeliho	31.69	BIC	47.08
		AICc	57.69

The "Pred R-Squared" of 0.9300 is in reasonable agreement with the "Adj R-Squared" of 0.9872; i.e. the difference is less than 0.2.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 49.670 indicates an adequate signal. This model can be used to navigate the design space.

APPENDIX A-5: ANOVA table for magnetic effect model

Response 1 Adsorbed amount

These rows were ignored for this analysis.

3, 10

ANOVA for Response Surface Linear model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	4.170E+005	2	2.085E+005	107.07	< 0.0001	significant
A-KOH ratio	*3.478E+005*	*1*	*3.478E+005*	*178.62*	*< 0.0001*	
B-magnetic fi	*72585.35*	*1*	*72585.35*	*37.28*	*0.0003*	
Residual	15578.07	8	1947.26			
Lack of Fit	*15578.07*	*3*	*5192.69*			
Pure Error	*0.000*	*5*	*0.000*			
Cor Total	4.326E+005	10				

Std. Dev.	44.13	R-Squared	0.9640
Mean	742.27	Adj R-Squared	0.9550
C.V. %	5.94	Pred R-Square	0.8901
PRESS	47541.78	Adeq Precisior	32.353
-2 Log Likeliho	111.03	BIC	118.22
		AICc	120.46

The "Pred R-Squared" of 0.8901 is in reasonable agreement with the "Adj R-Squared" of 0.9550; i.e. the difference is less than 0.2.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 32.353 indicates an adequate signal. This model can be used to navigate the design space.

APPENDIX A-6: Gantt chart for FYP 1

No.	Project Activities	W 1	W 2	W 3	W 4	W 5	W 6	W 7	W 8	W 9	W 10	W 11	W 12	W 13	W 14
M1	Project Planning & Formulation: Determine project's problem statement, objectives, experimental setup and materials to be used														
M2	Literature review of scholarly articles related, determine experimental parameters and variables														
M3	Research methodology, determine experimental procedures and testing variables														
M4	Report writing: Introduction, Problem Statement & Objectives, Literature Review, Methodology														

APPENDIX A-7: Gantt chart for FYP 2

No.	Project Activities	W 1	W 2	W 3	W 4	W 5	W 6	W 7	W 8	W 9	W 10	W 11	W 12	W 13	W 14
M1	Data collection from published articles and journals														
M2	Simulation using Design Expert to predict trend and construct mathematical models														
M3	Update on FYP part 1 report: Literature review														
M4	Report writing: Results & Discussion, Conclusion Presentation														