Removal of textile dyes from aqueous solutions using clay minerals and agricultural waste (*carica papaya* seeds)

A thesis submitted for the degree of Doctor of Philosophy

By

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Abstract

In most developing countries, many textile dyes known to be toxic for the environment, are released directly into rivers and other environmental compartments. The effluent streams, containing dyes and other toxic materials, are generally treated with activated carbon to remove these toxic materials from wastewater streams originating from different industries. However, the cost of activated carbon is very high and most small to medium size textile dye houses in developing countries cannot afford to use this adsorbent material for the treatment of effluent streams. Hence, to reduce the impact of dispersed textile dyes into the environment, easily accessible and affordable wastewater treatment materials need to be used. In this research work, the adsorption of Methylene blue and Reactive blue 4 in aqueous solution onto uncalcined and calcined adsorbents prepared using kaolin clay (KC), bentonite clay (BC) and *carica papaya* seeds (CPS) were studied. These adsorbents were prepared using different proportions of clay and CPS mixtures. Five experimental parameters studied to optimise these adsorbents, *viz*:, calcination temperature (100-600^{O}C), contact time (2-30 mins), solution pH (2-10), adsorbent dosage (0.4-1.8 g) and initial concentration (150-300 mg/L) of dye. Experimental data were analysed using Langmuir and Freundlich isotherm models to evaluate the maximum adsorption capacities. The adsorbents were characterised using scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy and energy-dispersive x-ray (EDX) spectroscopic techniques.

Experimental data obtained indicated that uncalcined kaolin (T0), 100% bentonite (T500), CPS/BC for 25/75 and 75/25 proportion (T300) are suitable adsorbents for the adsorption of Methylene Blue in aqueous solution. For Reactive Blue 4, results showed that uncalcined kaolin (T0), CPS/KC at 25/75 (T300) and CPS/KC at 25/75 (T400) are suitable adsorbents. Adsorption kinetics were compared to Lagergren pseudo-first-order and pseudo-second-order curves and results found to agree better with pseudo-second-order. This study showed that adsorbents prepared using clay minerals (kaolin and bentonite) and CPS could be used as alternative adsorbents to remove Methylene blue and Reactive blue 4 present in aqueous solutions.

Keywords: Synthetic textile dyes, *carica* papaya seeds, clay minerals, removal efficiency, adsorption capacity, kinetics, adsorption isotherms.

Supervisor(s)
Dr Abdul Chaudhary
Dr Edwin Routledge

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DECLARATION

The work submitted in this thesis was conducted between 2015 and 2019 at Brunel University, London. This research was conducted independently and has not been submitted for any other degree.

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“Rest, the sun will rise tomorrow”

CHAPTER 1

Introduction

The value of water resources over time has been known to be very important as it is used every aspect of human life such as domestic, industrial and agricultural sectors. However, over the years, the increasing discharge of chemicals in waste streams has resulted in the scarcity of clean water because these sectors are known to pollute water sources with waste products. The industrialisation has intensified over time in line with population rise and increasing demand for products, resulting in even higher consumption of water to meet this production. Textile industries use large quantities of water, and large quantities of wastewater containing dyes are released into the environment (Cheruiyot *et al.,* 2019; Siddqui *et al.,* 2019).

In Nigeria, the pollution of water bodies by the textile industry is a significant concern. Some textile industries that can afford to treat textile wastewater do not do it properly. Odjegba and Bamgbose (2012) carried out a toxicity assessment of treated effluent from textile industries around Ibeshe river in Lagos. Authors exposed *Celossia argentea* to the surface water beside the discharge point and found that the effluent inhibited growth and decreased chlorophyll. Similarly, Iwuala *et al.,* (2017), used *Rhizophora mangle L* to analyse surface water by discharge point of Challawa stream around textile industries and found that growth and chlorophyll to be reduced as well. Furthermore, authors stated that this river serves as a source of water supply to herdsmen and farmland owners which hinders plant growth and causes other harmful effects to the human population (Iwuala *et al.,* 2017).

Although some industries treat its textile wastewater, for most small scale and medium textile industries, wastewater is discharged into drainage systems without treatment and thus affecting surface water quality. This practice is of great concern (Awomeso *et al.,* 2010; Dan'azumi and Bichi, 2010; Awomeso *et al.,* 2019). The standard treatment process generally used by most textile industries is expensive to maintain for most small scale textile industries (Okareh *et al.,* 2017).

1.1. Textile operations

The production of textile is in two categories: the dry process and the wet process. The dry process (without water) often referred to as the spinning process whereby raw materials such as cottonseeds, spun into yarns are weaved into clothes, fibre-forming, fabric forming and are set to undergo wet processing. Wet processing includes sizing and de-sizing, bleaching, mercerisation, dyeing, printing and finishing is the vital part of the textile production and a large quantity of water used in this phase of textile production. This process includes cleaning, bleaching, dyeing and finishing of textile fibres and yarns are categorised into three steps; preparation, dyeing, finishing and rinsing (Figure 1.1). The wet processing system is responsible for the presence of toxic compounds released into the water bodies (Dos Santos *et al.,* 2007; Madhav *et al.,* 2018).

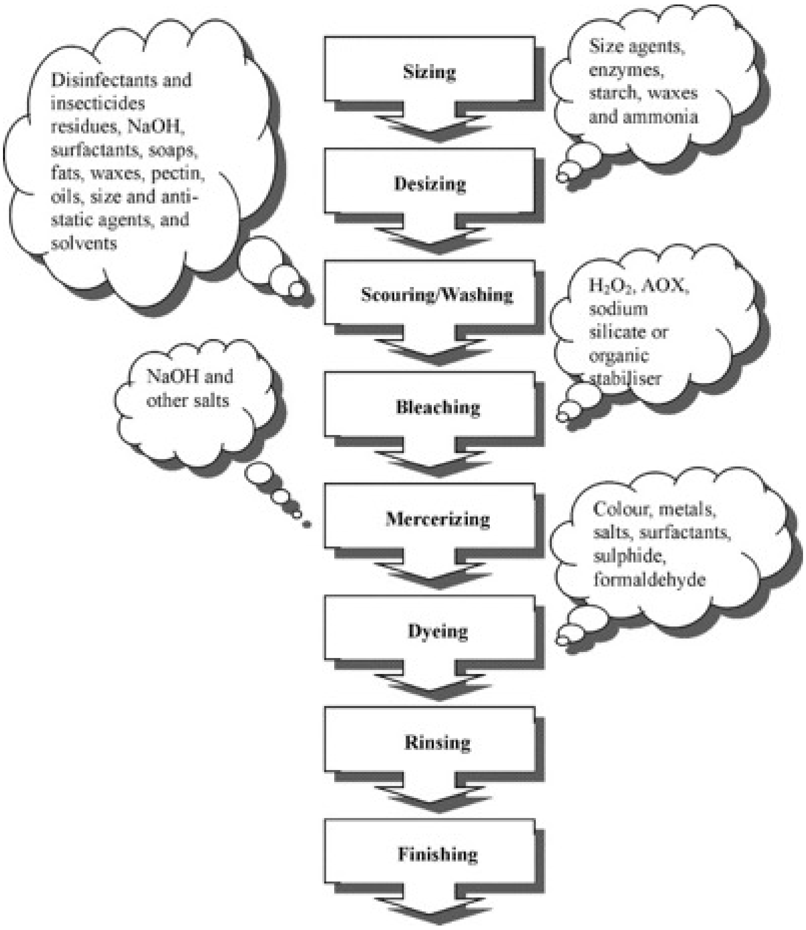

Figure 1. 1: Schematic of operations in a textile industry (Adapted from Dos Santos et al., 2007)

Synthetic dyes commonly used for dyeing textiles are resistant to biological breakdown, stable in water and sunlight; therefore, they do not degrade easily (Saini, 2018; Yaseen and Scholz, 2018). Although these characteristics are suitable for the textile material because it increases its durability, however, these characteristics do not favour removal within the environment. The effect of synthetic dyes in the aquatic environment, even at small concentrations, has had negative impacts on aquatic organisms (Ghaly *et al.,* 2014). Different treatment methods for the removal of synthetic dyes in textile effluent have been studied and researched. These include sedimentation, filtration technology, oxidation, Fenton oxidation, electro-coagulation, advanced activated process, aerobic and anaerobic treatment, adsorption and ion exchange (Wang, 2008; Gupta, 2009; Karthikeyan *et al.,* 2011; Vilar *et al.,* 2011; Bharathi and Ramesh, 2013; AbdurRahman *et al.,* 2013; Unuabonah *et al.,* 2015).

Each textile industry decides the type of treatment they can afford because some of these treatment methods are capital intensive and require technical know-how (Ghaly *et al.,* 2014). Several authors have emphasized that amongst all these treatment methods, however, adsorption method is quite cheap and it has been used extensively for the removal of organic compounds and heavy metals from a variety of industrial effluent streams. This treatment method has also been used successfully for the removal of dyes even though the adsorbent used differs due to the different characteristics of synthetic dyes (Aboua *et al.,* 2015; Zare et al., 2015; Tahir *et al.,* 2016; Ngulugbe *et al.,* 2017; Bellachir and Makhoukhi, 2017; Shaban *et al.,* 2018; Oyekanmi *et al.,* 2019)

1.2. The use of low-cost adsorbents

For the removal of different toxic compounds, commercially available activated carbon is commonly used as an adsorbent and has established as an excellent adsorbent over the years. However, in a developing country like Nigeria, access and use of activated carbon for wastewater treatment in textile industries could be expensive for large and small scale textile production. Consequently, the search for an alternative, sustainable and cost-effective adsorbent for the removal of dye in textile wastewater is relevant (Pavan *et al.,* 2014; Bretanha *et al.,* 2016).

This research aims to study the use of agricultural waste and clay minerals for their ability to remove textile dye from wastewater. Different cheaper and readily available materials such as clay minerals (bentonite, kaolinite, vermiculite, diatomite) (Kausar *et al.,* 2018), agricultural waste (rice husk, orange peels, banana peels, corncob, sawdust, *carica* papaya, coir pith, peanut hull, mango seeds, grapefruit peel) have been used as adsorbent materials for the removal of dyes from aqueous solutions (Mo *et al.,* 2018; Zhou *et al.,* 2019). The preparation of an adsorbent that will be useful to the Nigerian textile-producing community, it was imperative that the choice of materials be easily accessible and available in Nigeria. For this research work, two clay minerals (bentonite and kaolinite) and one agricultural waste (*carica* papaya seeds) were used to prepare a mixed adsorbent with the purpose of removing dyes from textile waste streams.

Carica papaya popularly called pawpaw is part of the caricaceae family, and it grows in tropical and subtropical parts of the world. As reported by Food and Agricultural organisation, Nigeria is the largest producers of pawpaw globally, (Makunjuola and Makunjuola, 2018). Pawpaw is grown in Nigeria and eaten year-round. It is sold in open markets, the seeds are tossed away, and the flesh of the fruit is eaten. Aside from the medicinal properties of the seeds (Vij and Prashar, 2015; Sagadevan *et al.,* 2019), this research will investigate the adsorptive properties of the seeds when used for the removal of dyes in aqueous solutions. For the clay mineral of interest, kaolinite clay and bentonite clay were selected because they are clay minerals deposited in most of the states in Nigeria.

1.3. Aim and objectives

The aim of this research is to prepare, optimise and characterise mixed adsorbents prepared from *carica* papaya seeds and clay minerals (bentonite and kaolinite) for removing synthetic dyes associated with textile wastewater. These mixed adsorbents will be used for the adsorption of Basic Blue 9 (Methylene Blue) and Reactive Blue 4 (Procion blue MX-R) dyes in aqueous solutions. The efficiency of these mixed adsorbents will be investigated through different parameters such as dosage, calcination temperature, contact time, adsorption kinetics and isotherms. Statistical analysis will be used to identify the adsorbents with the highest adsorption efficiency for both dyes and surface characterization will be carried out for the optimized adsorbents.

The objectives of this research are:

- Highlight the problems associated with the treatment and management of wastewater streams originating from textile industries.
- Highlight the use of various treatment technologies that are currently being used for the treatment of textile wastewater streams.
- Prepare, characterise and optimise different mixed adsorbent for the removal of Methylene Blue and Reactive Blue 4.
- Determine the removal efficiency and adsorption properties of the prepared mixed adsorbents for each proportion compared to pure clay minerals and *carica* papaya seeds for the adsorption Methylene Blue and Reactive Blue 4
- Optimise suitable adsorbents within each proportion and determine the effect of initial concentration, the dosage of optimised adsorbents and pH of the selected adsorbent.
- Characterisation of optimised adsorbents using SEM, EDX and FTIR

1.4. Novelty of study

The novelty of this study can be identified in the combination of carica papaya seeds (CPS) and mineral clays (kaolinite and bentonite) in different proportions. Unuabonah *et al.,* (2014) prepared composite adsorbent using carica papaya seeds and kaolinite clay for the adsorption of Methylene Blue dye, however, the adsorbent used was prepared in one proportion (equal weight of materials). Findings, however, revealed that there is a gap in this area. Hence this a key motivation for this study.

CHAPTER 2

Literature review

2.1. Introduction

2.1.1. Dyes

Since the beginning of civilisation, coloured materials have fascinated man for aesthetic and social purposes. In ancient times, dyes were extracted from natural resources such as vegetables, insects, lichens, plants and berries and these natural dyes have been used to colour natural fibres such as wool, cotton, fur, leather and silk (Cristea and Vilarem, 2006). In 1856, the first synthetic dye was invented by Perkins which gradually led to the decline of natural dyes used and over the years, a wide range of research was carried out to create new dyes for different products and materials in order to meet the growing demands of consumers. Dyes are used in different industries such as pulp and paper, plastics, paint, printing, textile, leather, cosmetics, food, drugs and medical science. Currently, the textile industry is one of the largest consumers of dyes produced annually (Eren, 2010; Bharathi and Ramesh, 2013; Ghaly *et al.,* 2014; Anirudhan and Ramachadran, 2015; Oussalah *et al.,* 2019). Total dye production is estimated at $7x10^5$ tonnes per year of which the textile industry consumes 10,000 tonnes per year and discharges 1000 tonnes/year into water bodies (Simion Beldan-Galea *et al.,* 2018; Khalque *et al.,* 2018; Zhou *et al.,* 2019).

2.1.2 Classification of dyes

There are different types of synthetic dyes, and all dyes are comprised of two main components: chromophores and auxochromes. Chromophores are a group of atoms, responsible for dye colour and are electron-withdrawing groups. The common chromophores are –C=C-, -C=N-, -C=O-, -N=N-, $-NO_2-$ and -NO-. The auxochrome is an electron-donating constituent; it intensifies the colour of chromophores, enhances solubility and enables the dye to stick to the fibre with the help of the mordant as well. Common auxochromes are $–NH_2$, $-NR_2$, -COOH, SO_3H_4, -OH, $-OCH_3$. Textile industries differ in the type of textile material produced thus different textile dyes are used. However, dyes with azo and anthraquinone chromophores are commonly used in textile industries to dye textiles (Dutta *et al.,* 2016; Tahir *et al.,* 2016; Liu *et al.,* 2017).

Dyes can be classified by the type of material they can colour effectively (Table 2.1). However, dyes can also be classified according to their solubility, for example, acid, basic, reactive and direct dyes are soluble in water but vat and disperse dyes are not soluble (Gupta, 2009; Gok *et al.,* 2010; dos Santos *et al.,* 2007; Salleh *et al.,* 2011; Rangabhashiyam *et al.,* 2013).

Table 2. 1. Classification of dyes

Class	Substrate	Solubility
Acid	Wool, nylon, silk, inks, leather	Water-soluble
Basic	Inks, paper, polyacrylonitrile, treated nylon and polyester	Water-soluble
Direct	Nylon, rayon, paper, leather and cotton	Water-soluble
Disperse	Polyamide, acrylic polyester, acetate, and plastics	Not water soluble
Reactive	Wool, cotton, silk and nylon.	Water-soluble
Vat.	Wool and cotton	Water-insoluble

Source: Salleh *et al.,* 2011; Yagub *et al.,* 2014.

2.2. Environmental impacts of textile wastewater

Textile industries require the use of chemically intensive processes and most of these chemicals are harmful to the environment. Large quantities of wastewater are generated during the wet process stage of textile production, and this requires proper treatment before it is discharged to the environment. Textile dyes are resistant to degradation, soluble and they are very stable in water with an exemption to VAT dyes. This makes it difficult for conventional treatment process to decolourise and degrade these dyes in textile effluents properly (Robinson *et al.,* 2001; Bali *et al.,* 2004; Ghaly *et al.,* 2014; Yagub *et al.,* 2014; Reddy *et al.,* 2014; Silva *et al.,* 2016).

Table 2. 2. Physio- chemical properties of wastewater discharge limits in different countries

Parameter	CCME	China	BIS	Hong Kong	EPA	FMENV	EA
pH	6.5-8.5	6-9	5.5-9	6-10	6-9	6-9	
Temperature (°C)	30	-	50	43	40	40	
TDS, mg/L	2000	-	2100	-	2000	2000	30
TSS, mg/L	40	150	100	800	30	30	
Sulphide, µg/L	200	1000	2000	1000	200	200	
Free Chlorine, µg/L	1000	-	1000	-	1000	1000	
COD, mg/L	80	200	250	2000	80	80	25
BOD, mg/L	50	60	30	800	50	50	20
Oil & Grease, mg/L	-	-	10	20	10	10	
Dissolved Oxygen, µg/L	6000	-	-	4000	-		
Nitrate, µg/L	13000	-	10000	-	20000	20000	
Ammonia, µg/L	0.1	-	-	500	0.2	200	
Phosphate, µg/L	4000	1000	5000	5000	5000	5000	
Calcium, µg/L	-	-	-	-	200000	200000	
Magnesium, µg/L	200000	-	-	-	200000	200000	
Chromium, µg/L	1	-	100	100	100		
Aluminium, µg/L	5	-	-	-	1000		
Copper, µg/L	<1000	1000	3000	1000	1000		
Manganese, µg/L	5	2000	2000	500	5.0		
Iron, µg/L	300	-	3000	1500	20000		
Zinc, µg/L	30	5000	5000	600	10000		
Mercury, µg/L	0.026	-	0.01	1	0.05		0.005

Table adapted from Yusuff and Sonibare (2004); Ghaly *et al.,* (2014), Environment Agency, The textile sector (EPR6.05).

CCME - Canadian Council of Ministers of the Environment

BIS - Bureau of Indian Standards

EPA - Environmental Protection Agency (United States)

FMENV- Federal Ministry of Environment (Nigeria)

EA- Environment Agency

Also, de Campos and Marin-Morales (2013) stated that despite having similar structures, each dye exhibits different biological activities and the toxicological properties are not generalised. Therefore to control the discharge of textile wastewater into the environment and monitor compliance, environmental agencies are in existence in several countries that have set discharge limits for textile industries in their countries. Table 2.2 shows the different discharge limits set according to the environment protection agencies in different countries. However, global textile manufacturing has largely moved to the developing countries (such as India), most textile production is carried out in small factories with limited resources for a standard wastewater treatment system (Tang *et al.,* 2017; Madhav *et al.,* 2018).

In Nigeria, there are few big textile firms that can afford to have wastewater treatment systems in place but may they not comply to regulatory standards due to weak enforcement by regulatory bodies (Kanu and Achi, 2011). Adeoti (2008) investigated environmental policies and the response of the industries in Nigeria. The study investigated both large and medium scale textile industries.

Table 2. 3. Physico-chemical analysis for large scale textile industry (Adapted from Adeoti,2008)

Parameter	**Raw effluent**	**Treated effluent**	**FEPA standard**
Colour	200	15	7
pH	10.08	6.05	6-9
Total dissolved solids (mg/L)	24.12	214	2000
Total suspended solids (mg/L)	612	*38	30
BOD_5 (mg/L)	112.5	28.2	30
COD (mg/L)	805	99	80
Detergent (mg/L)	4.0	0.55	15
Iron (mg/L)	4.4	2.2	20
Copper (mg/L)	0.2	0.2	1
Calcium (mg/L)	10.5	4.85	200
Magnesium (mg/L)	14.45	9.03	200
Zinc (mg/L)	0.62	0.25	1
Sulphate (mg/L)	180	30	500
Chloride (mg/L)	37.49	2.0	600
Nitrate (mg/L)	22.15	4.43	20

*The only parameter not conforming to FEPA standard

This study showed that the large-scale textile industry chose to comply with standard treatment process because of its international reputation and its wastewater treatment system was imported. However, despite the treatment system in place, the treated effluent does not meet the standard required by the Federal Ministry of Environment for all categories (Table 2.3). However, the medium scale industry had to comply with FEPA standards after residents discovered that their wells were filled with textile wastewater, thereby preventing them from getting clean water. A treatment system was set up, and it reduced toxic compounds that get into the neighbouring water bodies. However, a major complaint was the high cost of wastewater treatment technologies. Similarly, Awomeso *et al.*, (2010) studied the pollution of water bodies around Ibeshe, Ikorodu in Lagos state by the textile industry in Ikorodu. The study found that textile wastewater was being discharged at levels that were negatively impacting water quality. The study recommended that surface and groundwater should not be consumed.

Small-scale textile dyeing occurs in the crudest form in residential areas. The wet process is usually performed in open space in plastic or metal drums and buckets. When the dyeing is complete the wastewater is disposed of directly into gutters without treatment, and some of the finishing for textile production is done in nearby streams. This is a common practice by local dyers (Okareh et al., 2017; Durotoye et al., 2018). Most of these small-scale textile industries have no wastewater treatment system in place. It is important to note that aside from the lack of resources to put a wastewater treatment system in place, the addition of one more step to an established process often comes with resistance to change.

2.3. Textile wastewater

Wastewater is produced at different stages of textile production: scouring, desizing, bleaching, washing, mercerization, dyeing and finishing (Figure 2.1). Although Reddy *et al.*, (2014) stated that sizing and desizing process consumes the most substantial amount of water and are responsible for the highest amount of toxic compounds found in textile effluents, other studies have reported that the dyeing process consumes the largest amount of water (Sarayu and Sandaya, 2012; Ghaly *et al.,* 2014; Desai and Mehta, 2014; Chaari *et al.,* 2019).

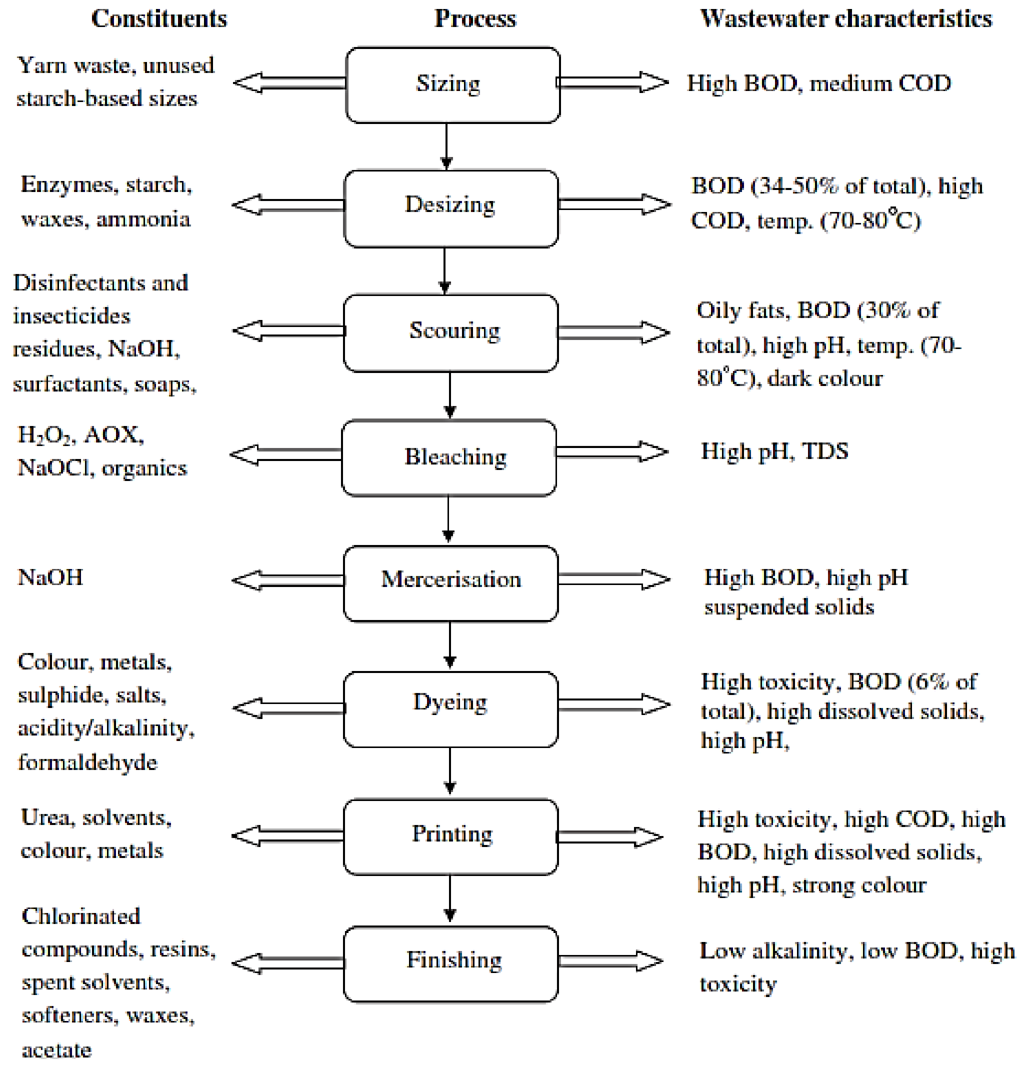

Figure 2. 1: Major pollutants at different stages of textile production.

(Adapted from Arslan et al., 2016)

Textile wastewater and its properties differ from plant to plant, depending on the type of textile produced and the specific chemicals used. Textile wastewater contains high quantities of acids, waxes, fats, salts, binders, thickeners, urea, surfactants, reducing agents, suspended solids and, dissolved solids (Figure 2.1). In addition, they contain trace amounts of metals such as Cr, As, Cu and Zn which can cause considerable harm to the environment as well (Sarayu and Sandaya, 2012; Ghaly *et al.,* 2014; Yaseen and Scholz, 2018).

Human exposure to textile wastewater present in water-bodies is associated with damaging effects such as skin irritation and dermatitis, lung irritations, ulceration of the skin, nausea, headaches and genetic damage (Yagub *et al.,* 2014; Yaseen and Scholz, 2018). Furthermore, chemicals in textile wastewater can cause damage to the reproductive system, liver, brain and central nervous system (Zhou *et al.,* 2019; Okareh *et al.,* 2017; Tang *et al.,* 2017).

Aside from its aesthetic disadvantages of dyes in water bodies, there is a huge concern about the ability of dyes to remain in waster bodies for a long period of time owing to high thermal and photo stability. Hence, resisting degradation, absorbing and reflecting sunlight. Photosynthesis is crucial to all living organisms, and textile dyes in water bodies absorbs the sunlight and thereby reduces the photo activity of algae. Thus, influencing the food chain in the aquatic ecosystem (Gita *et al.,* 2017). The presence of these dyes (soluble and insoluble) in water bodies is harmful and toxic to aquatic species even at very low concentrations (Salleh *et al.,* 2011). In addition, the suspended solids combine with oily scum to hinder oxygen transfer at the air and water interface. Likewise, inorganic chemicals such as hydrochloric acid, sodium hypochlorite, sodium hydroxide found in textile effluents may be toxic to aquatic life (Gupta, 2009; Sallah *et al.,* 2011; Yagub *et al.,* 2014).

2.4. The treatment process in the textile industry

Various treatment methods have been used for the dye removal and degradation in textile effluents prior to release, such as sedimentation, filtration technology, oxidation, Fenton oxidation, electro-coagulation, advanced activated process, aerobic and anaerobic treatment, adsorption and ion exchange (Wang *et al.,* 2008; Gupta, 2009; Karthikeyan *et al.,* 2011; Vilar *et al.,* 2011; AbdurRahman *et al.,* 2013; Bharathi and Ramesh 2013; Unuabonah *et al.,* 2015). Some of these treatment methods have been proven to be highly effective in achieving environmental standards. However, complete degradation and colour removal are not achieved when treatments are used individually. Hai *et al*., (2007) and Nawaz and Ashan, (2014) stressed that the use of one method for dye removal is not effective; rather the synergistic combination of different treatment methods would yield better results.

2.4.1. Chlorination

Chlorine treatment has been used for a long time to decolourize textile water, mostly by applying calcium hypochlorite or sodium hypochlorite (Hao *et al.,* 2000). This treatment method is widely used for water-soluble dyes such as reactive, acid and metal complex dyes. In contrast, disperse, and vat dyes are unaffected by chlorine treatment due to the resistant nature of these dyes based on their non-ionic characteristics. Chlorination is also a strong disinfectant method for water treatment that is widely used in pulp and textile bleaching for reduction of colour. However, the use of chlorine for treatment of textile dye wastewater generates toxic chlorinated organic compounds (i.e halogenated hydrocarbons such as trihalomethane) and when they are found in high concentrations in water poses a serious heatlh problem such as cancer in humans (Chowdhury and Champagne, 2009; Zhang *et al.,*2018) and the environment (Hao *et al.,* 2000; Anjaneyulu *et al.,* 2005; Zaharia *et al.,* 2009; Singh and Arora, 2011).

2.4.2 Oxidation

This widely used method of chemical treatment for the decolourisation of textile wastewater is popular due to the easy mode of application, the small quantities needed and minimal reaction time. Oxidation occurs by chemical oxidation, and UV assisted oxidation using chlorine, hydrogen peroxide, Fenton's reagent, UV/ozone or potassium permanganate as oxidising agents for the decolourisation of wastewater. This process degrades the dyes to lower molecular weight compounds such as aldehydes, sulphates, carboxylates and nitrogen. (Robinson *et al.,* 2001; Zille *et al.,* 2005; Hai *et al.,* 2007; Gupta, 2009; Zaharia *et al.,* 2009).

Hydrogen peroxide (H_2O_2) is a strong and stable oxidising agent and has been applied in treatment plants for the removal of organic and inorganic pollutants. It is also a strong bleaching agent, and it is used for paper and pulp bleaching. The application of hydrogen peroxide in wastewater treatment plants removes pollutants such as sulphides, hypochlorite, nitrites, cyanides and chlorine. In addition, it is used to control the growth of biofilm during the treatment process (Hao *et al.,* 2000; Zaharia *et al.,* 2009). Hydrogen peroxide has been used for the decolourisation of water-insoluble dyes such as chrome dyes, vat dyes, sulphur or sulphur containing dyes and the oxidation process increases the amount of oxygen in the wastewater thus also reducing its COD present in the wastewater.

According to Zahara et al., (2009), the use of hydrogen peroxide for treatment of textile dye effluents is not effective enough, and authors reported that the colour removal was dependent on the pH of the wastewater (Zaharia *et al.,* 2009). Although, Kalra *et al*. (2011) report also showed that H_2O_2 was ineffective for the removal of textile dye effluents in wastewater, however, this report stated that irrespective of the pH of the wastewater the use of H_2O_2 for treatment not good enough. Due to this inefficiency, H_2O_2 needs to be activated when applied as a treatment method. Studies have reported that its efficiency is highly dependent on its activation, although the decolourisation process differs from how the hydrogen peroxide is activated. Hydrogen peroxide can be activated with metal salts (Fe (II)) and UV, yielding hydroxyl radicals (Forgacs *et al*., 2004; Anjaneyulu *et al.,* 2005; Zaharia *et al.,* 2009; AbdurRahman *et al.,* 2013; Unuabonah *et al.,* 2015).

The advanced oxidation process is the application of more than one oxidation process simultaneously because the use of one oxidation process is not suitable for the decolourisation or degradation of dyes. The advanced oxidation process increases the generation of hydroxyl radicals when combined with ozone, hydrogen peroxide, titanium dioxide, heterogeneous photocatalysis, UV radiation or high electron beam radiation. The hydroxyl radical is one of the strongest oxidising species with the potential to oxidize a wide range of organic compounds (Vilar *et al.,* 2011; Bali *et al.,* 2004) and these hydroxyl radicals have the capacity to degrade recalcitrant dye compounds at ambient temperature and pressure. With the use of hydroxyl radical, organic molecules are transformed to oxidized intermediates, carbon dioxide, water, inorganic salts and this process is known as mineralization. Complete mineralization can be gotten when acids on further oxidation produces CO_2 and H_2O (Kumar, 2011). There are different types of advanced oxidation process that have been proposed or used for the treatment of textile wastewater and degradation of dyes such as UV/H_2O_2,TiO_2/UV,H_2O_2/Fe, $H_2O_2/UV/Fe$ (Aleboyah *et al.,* 2003; Vilar *et al.,* 2011; Kalra *et al.,* 2011).

Hydrogen peroxide/UV oxidative process for dye removal and degradation relies on the hydroxyl radicals ($^{\bullet}OH$) reacting with organic contaminants with an oxidation potential of 2.8V. UV/H_2O_2 process destroys the structure of the dyes, although the reaction rates differ for different dyes (Aleboyah *et al.,* 2003). One advantage of applying this process is that sludge is not produced during the treatment; it can be done under ambient conditions and during the treatment process oxygen formed can be used for aerobic biological treatment. (Aleboyah *et al.,* 2003; Hai *et al.,* 2007; Kalra *et al.,* 2011; Singh and Arora, 2011).

The dose of H_2O_2 that is applied during the oxidation process is an important determinant. Studies have shown/reported that an increased dose of H_2O_2 increases discolouration efficiency. Bali *et al.,* (2004) studied the degradation of three dyes: Reactive Black 5, Direct Yellow 12, Direct Red 28 using UV, UV/H_2O_2 process in a photoreactor. H_2O_2/UV was applied to each dye solution at the same concentration at a different dosage from 1 mM to 100 mM. They found that dye removal for Reactive black 5, Direct yellow 12 and Direct red 28 were 99% (25 Mm), 98% (10 Mm) and 7% (50 Mm), respectively after 60 mins of irradiation. Similarly, Aleboyeh *et al*. (2003) studied the decolourisation of Acid 74 using H_2O_2/UV and reported that at initial concentrations of 2, 5 and 9×10^{-5} mol l^{-1}, the decolourisation rate was less than 1% after 3 hours. An additional dose of H_2O_2 into the dye solution increased the amount of light absorbed by photo-decomposition resulting in a further reduction of colour in the aqueous solution. However, they also found that further increases in the concentration of H_2O_2 beyond an optimum decreases the colour removal efficiency. This because hydrogen perioxide scavenges for hydroxyl radicals. Therefore when enough hydrogen perioxide is in the solution, its begins to compete with the dye to react with the hydroxyl radicals. (Amin *et al.,* 2008; Karla *et al.,* 2011).

The oxidation process is highly dependent on the pH, and it has been stated that the decolourisation of dyes is more effective in acidic mediums. During H_2O_2/UV and H_2O_2/UV/O_3 experiments, colour removal and COD show higher values when conducted in an acidic medium at pH 3 (Azbar *et al.,* 2004; Vilar *et al.,* 2011). In an alkaline medium, however, H_2O_2 will be converted into water and oxygen instead of hydroxyl radicals under UV radiation. The increase in the pH, therefore, leads to a decrease in the removal efficiency of H_2O_2/UV , therefore, reducing the production of hydroxyl radicals (Amin *et al.,* 2008; Karla *et al.,* 2011). The difference observed in the decolourisation between both processes highlights the importance of combining UV and H_2O_2 for effective removal of colour in dye solutions and increased decolourisation due to the presence of $^{\bullet}OH$ radicals formed during the photochemical process. The initial dye concentration and the percentage removal have an inverse relationship. This is because the increase in initial dye concentration results in the increase of dye molecules and the hydroxyl radical remains constant at all concentrations. which reduces the amount of UV light that passes through the solution. Therefore, the increase in dye concentration reduces the formation of hydroxyl radicals (Karla *et al.,* 2011). The contact time determines the decolourisation process, and the reaction for dye removal using H_2O_2 differs among dyes. Reactive and azo dyes, degradation occurred after 30-90 minutes (Bali *et al.,* 2004; Karla *et al.,* 2011; Ghaly *et al.,* 2014). However, despite its potential to remove strong toxic compounds, H_2O_2 does not degrade or decolourise all textile dyes.

Fenton oxidation process is one of the oldest chemical treatment methods, and it is the combination of hydrogen peroxide and soluble iron(II) salt for the degradation of organic compounds, the solution is referred to as Fenton reagent. Fenton's oxidation process produces a large amount of $^{\bullet}OH$ radicals ([1]2.8 V) with a short life span, but it is highly reactive and targets dyes by taking hydrogen atoms or attaching itself to double bonds (Papadopoulos *et al.,* 2007; Rodrigues *et al.,* 2009). Due to its short life span, the generation of hydroxyl radicals in the acidic medium must be continuous and can be done via chemical or photochemical reactions (Azbar *et al.,* 2004; Papadopoulos *et al.,* 2007; Zaharia *et al*; 2009; Oturan and Aaron, 2014; Ghaly *et al.,* 2014).

Factors that influence the rate of decolourisation include; pH of the solution, the number of ferrous ions, the concentration of H_2O_2, the initial concentration of the pollutants and other ions present which might affect the process from occurring effectively. Fenton oxidation process has a high decolourisation rate which is mainly dependent on the concentration of the ferrous ion present in the solution. The decomposition of hydrogen peroxide by ferrous ions via catalysis in an acidic medium produces a hydroxyl radical, hydroxyl ion and ferrous ion. Studies have indicated that at pH 3.0 - 3.5, hydrogen peroxide and ferrous ion are very stable which helps the redox and decolourisation processes that occur. However, at a pH higher than 3.5 ferrous ions gradually become ferric ions and these are known to have the potential to form ferric hydroxo complexes. In addition, hydrogen peroxide is not a stable

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[1] The oxidation potential for hydroxyl radicals is approximately 2.8 V

compound, and it will decompose very fast in alkaline solution (Meric *et al.,* 2004; Papadopoulos *et al.,* 2007; Rodrigues *et al.,* 2009; Oturan and Aaron, 2014). Reactive black five was removed from synthetic wastewater and colour removal obtained was 99% (Meric *et al.,* 2004; Nidheesh *et al.,* 2013).

The removal efficiency of Fenton's reagent is limited, as not all dyes are easily decolourised and degraded. Consequently, extensive studies spanning a number of years have attempted to improve the efficiency of this oxidation process by combining it with UV light (photo- Fenton), sunlight (solar photon- Fenton), combinations with electro-chemicals (electro- Fenton, electrochemical advanced oxidation process). Nevertheless, the use of Fenton reagent has certain limitations including (i) the cost of storing and transporting hydrogen peroxide and a number of reagents required for the acidification of the effluent, and (ii) the need to deal with the large quantity of iron sludge that is generated. (Azbar *et al.,* 2004; Rodrigues *et al.,* 2009; Singh and Arora, 2011; Vilar *et al.,* 2011; Oturan and Aaron, 2014; Gupta *et al.,* 2015; Labiadh *et al.,* 2015).

2.4.3. Biological treatment

Biological treatment is regarded as an effective method for removing pollutants from wastewater containing organic compounds. The presence of microorganisms in this treatment process plays a crucial role in the mineralisation of xenobiotic compounds and organic molecules. Microorganisms decolourise dye by cleaving to chromophore and auxochrome of dyes (Lotito *et al.,* 2014; Pokharia and Ahluwalia, 2017; Paździor *et al.,* 2019). Biological treatment of dye effluent can be aerobic (with oxygen), anaerobic (without oxygen) or a combination of anaerobic-aerobic treatment (Hao *et al.,* 2000; Yang *et al.,* 2009; Gupta, 2009; Singh and Arora, 2011; Gupta *et al.,* 2015; Ghaly *et al.,* 2014; Lotito *et al.,* 2014).

2.4.3.1 Aerobic

Aerobic treatment occurs when free oxygen dissolved in wastewater degrades organic compounds. The treatment systems used are stabilisation ponds, aerated lagoons, trickling filters and activated sludge. Amongst these systems, activated sludge is commonly used for the treatment of dye effluent with microorganisms suspended in the aerated wastewater. The use of activated sludge for the removal of dyes is largely dependent on dye properties such as molecular structure, number and position of the substituent in the dye molecule (Holkar *et al.,* 2016; Xu *et al.,* 2018). Bacteria and fungi are the most studied microorganisms for the treatment of dye effluents. Studies have been carried out extensively on the decolourisation of dyes by different fungal strains (Przystaś *et al.,* 2018; Darvishi *et al.,* 2018)

A lignin-degrading white-rot fungus, *Phanerochaete chrysosporium* has been reported to degrade and decolourise a wide range of recalcitrant pollutants. The decolourisation of Acid green 20 at 30^{0}C using *Phanerochaete chrysosporium* in a low-cost medium converted the dye into an unknown colourless compound, thus establishing the potential of the fungus to decolourise dyes under aerobic conditions. Although other strains of fungi such as *Kurthia* sp., *Cyathus bulleri, Coriolus versicolour, Funalia trigoii* and *Laetiporous sulphurous* were used to decolourise some triphenylmethane and azo dyes, *Phanerochaete chrysosporium* (due to the non-specific nature of lignin peroxidase present within it), decolourises a wide variety of dyes compared to other fungi (Rai *et al.,* 2005; Gupta, 2009; Sarayu and Sandhya, 2012; Chengalroyen and Dabbs, 2013; Pang and Abdullah, 2013, Vilar Junior *et al.,* 2015) . *Phanerochaete chrysosporium* contains an enzyme called lignin peroxidase and because of this, *Phanerochaete chrysosporium* can decolorise a wide range of dyes. However, the release of lignin peroxidase by fungal cells for the dye degradation *is released after* strict secondary metabolism depending on the limitation of carbon or nitrogen, hence, the release of this enzyme would be prohibited by the presence of carbon or nitrogen nutrient in the textile effluent (Rai *et al.,* 2005). Therefore, the presence of carbon or nitrogen in dye effluent may prevent the degradation or detoxification of dyes.

However, the use of *Trametes versicolour* covers this deficiency of *Phanerochaete chrysosporium* because it produces an oxidative enzyme (laccase) in the presence of nitrogen and carbon nutrients. Pure fungal laccase alone was not able to decolourise Remazol brilliant blue R, and a low molecular weight redox mediator was also needed for decolourisation to occur (Rai *et al.,* 2005). On the other hand, the identification of bacterial cultures that can degrade different dyes has been ongoing research for over two decades (Rai *et al.,* 2005; Gupta, 2009; Singh and Arora, 2011; Khan *et al.,* 2013; Ghaly *et al.,* 2014).

However, the isolation of these microbes takes a long period because they have to adapt to chemostatic conditions (Kolekar *et al.,* 2008). Authors have reported on the aerobic reduction of simple azo dyes by *Aeromonas hydrophila*, degradation of sulphonated azo dyes by *Pseudomonas strains,* the reductive cleavage of azo dyes by *Pseudomonas cepacia* and the degradation of triphenylmethane dyes by *Bacillus subtilis* (Khan *et al.,*2013; Telke *et al.,* 2015).

In comparison to fungi, bacterial decolourisation is usually faster, and it can mineralise different dyes under aerobic conditions (Rai *et al.,* 2005; Kalyani *et al.,* 2008; Sarayu and Sandhya, 2012; Khan *et al.,* 2013; Pang and Abdullah, 2015). Also, dye removal increases when the chromophores bear hydroxyl and nitro groups but decrease if the chromophore bears sulfonate groups. Some dyes do not undergo biological breakdown, which could be as a result of the recalcitrant characteristics of dyes. In addition, the limitations of aerobic treatment include high capital and running cost and production of sludge which occurs due to the sensitivity of microorganisms to toxic compounds (Singh and Arora, 2011; Lotito *et al.,* 2014; Telke *et al.,* 2015; Punzi *et al.,* 2015).

2.4.3.2 Anaerobic

Anaerobic treatment is usually carried out in sealed tanks and waste is mineralised, producing methane and CO_2. Dyes undergo a biological reduction in anaerobic reactors, and this has been investigated to determine colour removal and chemical degradation of the dyes. The degradation of a wide variety of dyes (mostly azo dyes) have been studied, and decolourisation and degradation of azo chromophores result in the reduction of the azo bond (Gupta *et al.,* 2009, Singh and Arora, 2011). Azo dyes are non-growth substrates which are decolourised by anaerobic consortia by the cleaving of the azo bonds, thus reducing the carbon sources moved to the dye. Acidogenic bacteria turn soluble substrates like carbohydrates into volatile fatty acids or alcohol. Methanol is commonly used as an electron donor for biological wastewater treatment, although other substrates such as glucose, hydrolysed starch and yeast extract can be used as electron donors as well. For reduction cleavage to occur in azo compounds, electrons from the substrates are needed, but the rate of decolourisation is dependent on the type of substrate used (Santos *et al.,* 2005; Kim *et al.,* 2008; Verma, 2008).

Studies have shown that the microbial decolourisation of azo dye occurs as a result of the reduction of azo bonds which forms toxic aromatic amines. However, not all azo dyes form toxic amines (Khan *et al.,* 2013; Pang and Abdullah, 2013; Kim *et al.,* 2008). Gnanapragasam *et al*. (2010) investigated the removal efficiency of COD and colour in dye textile wastewater using upflow anaerobic sludge blanket reactor and reported that COD and colour removal was 96% and 93% respectively. Furthermore, Reactive black 5 and real textile wastewater were treated in an anaerobic sludge system, and investigations were carried out to determine the effect of sulphide and carbon source on the decolourisation process. Colour removal observed in the Reactive black solution for 72 hours at 35^0C in the absence of sulphide was 94% and the addition of sulphide at intervals (10mg/L) led to an increase of microbial decolourisation by 9% within 48 hours, contradicting the reports stating that the presence of sulphide inhibits the decolourisation of dyes (Sarayu and Sandhya, 2012; Amaral *et al.,* 2014). In comparison with the real textile water, the removal of COD was 57.8% which was lower due to the absence of degradable COD for decolourisation and the presence of a toxic compound in the wastewater (Sarayu and Sandhya, 2012).

However, the decolourisation of textile wastewater using anaerobic treatment is very sensitive to toxicity. Therefore heavy metals, sulphide and salts present in real textile effluents inhibit or slow down the rate of colour removal. This is a limitation because it prevents the possibility of applying this method on an industrial scale. It has been reported that the rate of decolourisation depends on the dye structure and the carbon source; however, the type of organism used and dye selected does not influence the reductive cleavage that occurs during the process.

The microbial decolourisation of dyes involves degradation via azo-bond reduction during anaerobic treatment. Toxic aromatic amines formed are then recalcitrant to anaerobic treatment but can be degraded easily by aerobic treatment. Using anaerobic-aerobic treatment methods together, complete mineralisation occurs due to the combined effort of different organisms present in the system. The azo-bond reduction is made in the anaerobic bioreactors, and the colourless aromatic amines are mineralised by aerobic conditions. Indeed, in laboratory reactors Remazol Red RR decolourised by 96% within two days, Remazol Blue RR decolourised by 95% within three days and Remazol Yellow RR decolourised by 86% using the anaerobic-aerobic treatment method (Koupaie *et al.,* 2013). Therefore, the treatment of dyes using the sequential anaerobic-aerobic treatment is a very fascinating and plausible means of achieving optimum degradation and decolourisation of textile wastewater (Gupta, 2009; Singh and Arora, 2011; Jonstrup *et al.,* 2011; Koupaie *et al.,* 2013). However, not all toxic amines produced from the decolourisation process via anaerobic treatment mineralised by the aerobic process (Koupaie *et al.,* 2013).

Dyes are produced to resist degradation; hence, their recalcitrant characteristics are quite high in some dyes over the others (Mohanty *et al.,* 2006; Jonstrup *et al.,* 2011).

The aromatic amine generated during the anaerobic reduction undergoes auto-oxidation and cannot be degraded any further by aerobic treatment due to instability. Thus the azo- dye reduction will not always guarantee permanent decolourisation of dye effluent. Consequently, studies have shown that upflow anaerobic sludge blanket reactor is highly efficient for the treatment of wastewater containing recalcitrant compounds (Gupta *et al.,* 2009; Pang and Abdullah, 2013; Amaral *et al.,* 2014). The decolourisation and detoxification of water-soluble and insoluble dyes such as reactive dyes, disperse dyes, vat, anthraquinones dyes and indigoids was studied using full-scale anaerobic-aerobic treatment. It was reported that colour removal was 80-95% thus indicating that the anaerobic system is efficient for the colour removal of different types of commercially used dyes irrespective of the presence of heavy metals and acids are known to prevent the decolourisation of dyes (Frijters *et al.,* 2006; Gupta, 2009; Singh and Arora, 2011). Limitations of biological treatment include low biodegradability of dyes, lack of flexibility of design and operations and time required for the decolourisation-fermentation process. It should be noted that this method is not cheap, although its application for a wide variety of dyes makes it appealing. Furthermore, some studies have investigated the treatment of textile effluent using aerobic treatment alone. In such systems, the removal of dye will be reduced, and there will be an increase in toxicity. Thus, it implies that that anaerobic treatment is possibly responsible for the colour removal and detoxification of textile wastewater in the sequential anaerobic-aerobic system/treatment.

2.5. Adsorption

Adsorption or carbon adsorption has been used since ancient times for the purification of water and also for medicinal purposes. The use of carbon adsorption for the removal of gases was observed by C.W. Scheele in 1773 and Lowitz in 1785 also observed the reversible removal of colour and odour of compounds in water using wood charcoal. The term adsorption was introduced to differentiate surface accumulation from intermolecular penetration (Gupta, 2009).

Adsorption is the collection of substances at an interface between two phases. The substance that gathers on the interface referred to as the adsorbate and the solid material used is called the adsorbent. There are two types of adsorption: chemical sorption and physical sorption. Chemical sorption is described by chemical associations that occur between molecules or ions of adsorbate to the adsorbent surface as a result of the exchange of electrons. Physical adsorption is illustrated by weak van der Waals bonds between the adsorbate and adsorbent. Adsorption occurs via ion exchange which is a reversible process of an ion in a solution is exchanged for a similarly charged ion attached to an immobile solid particle. However, when an adsorbent is used, the adsorption process depends on the physical forces such as van der Waal forces, hydrogen bonds, polarity and dipole interaction. Adsorption techniques are commonly used for the removal of contaminants especially the ones resistant to conventional treatment methods. The application of adsorption technique for the treatment of textile effluents is not far-fetched based on reported efficiencies to remove soluble contaminants while simultaneously reducing the toxicity of the parent organic compounds in industrial effluents (Rangabhashiyam *et al.,* 2013; Yagub *et al.,* 2014). The decolourisation of dyes in textile wastewater and adsorption efficiency using different adsorbents such as clay minerals (Memhet *et al.,*2009; Nandi *et al.,* 2009; Tehrani-Bagha *et al.,* 2011; Cottet *et al.,* 2014), silica (de Carvalho *et al.,* 2014; Liu *et al.,* 2015; Shasha *et al.,* 2015; Nadaroglu *et al.,* 2015; Volikov *et al.,* 2016), zeolites (Hernández-Montoya *et al.,* 2013; Jin *et al.,* 2014; Hor *et al.,* 2106; Kim *et al.,* 2016), fly ash (Sun *et al.,* 2013; Sulak and Yamtaz, 2012; Noroozi and Sorial, 2013; Zaharia and Suteu, 2013), activated carbon and low cost waste: saw dust, orange peel, coir pith, rice husk, straws, banana peel, pomelo, broad bean peel, peanut hull (Gupta, 2009; Rodriguez *et al.,* 2009; Unuabonah *et al.,* 2013; Bharathi and Ramesh, 2013; Mafra *et al.,* 2013; Yagub *et al.,* 2014) have been used and studied extensively.

2.5.1. Use of activated carbon for adsorption of dyes

Activated carbon is the most commonly used adsorbent in wastewater treatment process. It has a porous structure, large surface area, high adsorption capacity and high degree of surface reactivity, which explains the non-selective nature of activated carbon when used for adsorption (Bharathi and Ramesh, 2013; Yagub *et al.,* 2014; Saleh *et al.,* 2014). Commercially produced activated carbon is of two types; powdered activated carbon (PAC) and granular activated carbon (GAC) and both are well established to be good adsorbents for the removal of contaminants in water bodies. The granular form of GAC increases the ability of the adsorbate (i.e. wastewater) to flow through and make contact with the adsorbent. It is therefore used more often than PAC for the removal of pollutants in water. The use of activated carbon for the removal of colour and organic pollutants in textile wastewater has been said to be effective (Kaykhaii *et al.,* 2018; Katheresan *et al.,* 2018). Colour removal capacity for powdered activated carbon is high when used for the removal of cationic mordant dye and acid dyes although it is minimal for sulphur, disperse, direct and reactive dyes (Khan *et al.,* 2004; Anjaneyulu *et al.,* 2005; Katheresan *et al.,* 2018). The adsorption capacity of activated carbon relies on the functional groups present on its surface, thus resulting in the adsorption efficiency observed when used for acid and basic dyes (Anjaneyulu *et al.,* 2005; Djilani *et al.,* 2015).

Rodríguez *et al.,* (2009) studied the adsorption of Methylene Blue (anionic dye) and Orange II (cationic dye) on activated carbon. At a pH range of 3.0 – 9.0 and temperature at 30-65^{0}C, the maximum adsorption of both dyes was at the temperature of 65^{0}C and pH 7.0 and 3.0, respectively. This indicated that the adsorption capacity increases with increasing temperature thus highlighting endothermic characteristics (Al-Degs *et al.,* 2008). However, it was concluded that activated carbon is effective for the removal of these dyes. Al-Degs *et al.,* (2008) also studied the adsorption of Reactive Blue 2, Reactive Red 4 and Reactive Yellow 2 onto activated carbon and found that at pH 7.0 and temperature of 24.9^{0}C the adsorption capacity was 0.27, 0.24 and 0.11 mmol/g for each dye respectively. Activated carbon was also used for the removal of acid, disperse, basic and direct dyes and successively removed all dyes except direct dyes (Gupta, 2009). The adsorption of Methylene Blue and Methyl Orange was carried out using GAC. In this study, 87-98% and 98% colour removal were observed at a temperature of 40^{O}C for Methylene Blue and methyl orange. The experimental data obtained fitted the Langmuir isotherm model (Djilani *et al.,* 2015). The adsorption capacity of commercial activated carbon is favourable for dye adsorption. However, a major limitation is the cost of the commercially available adsorbent. Hence, research for cheaper and easily accessible alternative adsorbent is necessary.

2.5.2. Use of clay minerals for adsorption of dyes

Due to the relative abundance and availability of clay minerals, they could serve as an alternative to activated carbon as these minerals have been known for decades to have good absorption characteristics. Aside from their adsorptive capacity, another advantage of clay minerals is the fact that they are relatively cheap compared to adsorbents used for treatment processes. Clay minerals have alumina-silicate structures possessing an array of chemical composition, different structure and surface characteristics (Adeyemo *et al.,* 2017; Kausar *et al.,* 2018). Clay minerals have a wide surface area and the capacity to adsorb a wide range of chemical compounds. They are utilized efficiently in a variety of chemical, physical, processes, including industrial purposes which capitalize on the ability of clay minerals to retain organic and inorganic pollutants, thereby reducing the flow and transport of polluted fluids in aquatic and soil into the environment (Caglar *et al.,* 2009; Vinuth *et al.,* 2017). Clay minerals have been used as an adsorbent for the removal of dyes in wastewater, have high adsorption capacity, non-toxic, possess strong ion exchange due to the presence of negative charge on the structure of the minerals (Vimonses *et al.,* 2009). Different types of clay minerals such as kaolinite (Memhet *et al.,*2009; Nandi *et al.,*2009; Tehrani-Bagha *et al.,*2011), bentonite (Gok *et al.,* 2010), sepiolite (Ozcan *et al.,* 2006; Ozcan *et al.,*2007), fuller earth, diatomite, zeolite, montmorillonite, smectite have been used (Aguiar *et al.,*2017; Ngulube *et al.,* 2017). Over the years, there has been an increase in the use of kaolinite, diatomite, bentonite and fuller earth for the removal of dyes in wastewater (Gupta, 2009; Adeyemo *et al.,* 2017; Kausar *et al.,* 2018). However, despite the efficiency report on the use of clay minerals alone studies have also indicated that with different methods of modification, the adsorptive efficiency of clay minerals will increase (Moreira *et al.*, 2017; Vinuth *et al.,* 2017; Belbel *et al.,* 2018). Studies have highlighted the importance of modifying clay minerals to increase their efficiency as adsorbents. Different methods of modifications have been used such as acid activation (Bhattacharyya *et al.,* 2015; Sarma et al., 2016; Stawiński *et al.,* 2017), thermal alteration (Vimonses *et al.,* 2010; Chen et al., 2011; España *et al.,* 2016) and surfactant treatment (Anirudhan and Ramachandran, 2015; Wang *et al.,* 2017). In this research, the use and study of kaolinite, bentonite and vermiculite clay minerals as an adsorbent for the removal of textile dyes will be studied.

Kaolinite is a soft, off white and well-known clay mineral due to its availability in different countries (Karaoğlu *et al.,* 2009; Karaoğlu *et al.,* 2010). It has a chemical structure of $Al_2Si_2O_5(OH)_4$ or $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ and a chemical composition of SiO_2: 40 mol%, Al_2O_3: 20 mol% and H_2O:40 mol%. The adsorption capacity of kaolinite is highly dependent on the surface and edge charges, however, the presence of H^+ and OH^- at the edges are regarded as a major reactive site. Thus, the change in pH of the solution will affect the charge on the edges instead of the basal surface charges (Wang and Su, 2006; Vimonses *et al.* 2009). Vimonses *et al*. (2009) studied the use of kaolinite as an adsorbent for the removal of Congo Red from wastewater and found that at acidic pH and high dye concentration, the adsorption capacity was optimised. A thermodynamics study showed the adsorption process to be exothermic and spontaneous.

Similarly, Karaoğlu *et al.,* (2010) studied the adsorption of Reactive Blue 221 on kaolinite, and the experimental result showed that the adsorption rate increased with increase in initial dye concentration, ionic strength and temperature. Contrary to this, an increase in pH showed a decrease in the adsorption rate. It was also observed that the reaction of Reactive Blue 221 on kaolinite was endothermic and it was not spontaneous. Congo Red and Reactive Blue 221 are both anionic dyes that are quite difficult to decolourise due to their bright colours, water solubility and acidic characteristics. Moreover, the thermodynamics of each of the dyes differs too. An investigation into the decolouration of cationic dyes (Maxilon Yellow 4GL and Maxilon Red GRL) using kaolinite via adsorption indicated that the quantity of cationic dyes adsorbed increased with increasing pH of the aqueous medium but decreased with increasing temperature and the adsorption process was exothermic as well (Karaoğlu *et al.,*2009). Similarly, Tehrani-Bagha *et al*. (2011) studied the decolourisation of Basic Yellow 28, Methylene Blue and Malachite Green from aqueous solution using kaolin. The results showed that the amount of dye adsorbed by kaolin was dependent on the quantity of kaolin used and pH had little effect on dye removal. It was found that the adsorptive process for the three cationic dyes was endothermic and spontaneous. In comparison, anionic dyes and cationic dyes react with kaolinite clay mineral differently due to the charges they carry which have a direct impact on the surface charge and adsorption capacity of the kaolin clay as well. However, cationic dyes have a higher affinity for mineral clays than anionic dyes due to kaolin's assumed negative charge, even though that charge is determined by the pH of the solution. Bhattacharyya *et al.,*(2015) modified kaolinite using 0.25M and 0.50M H_2SO_4 for the removal of Congo Red via adsorption in batch processes. The researchers observed that equilibrium was attained by 120 mins, and the process followed the second-order kinetics. In comparison with natural kaolinite (17.34%- 56.41%), acid-treated kaolinite (18.55%-58.32%) had better adsorption efficiency. Similarly, Ali and Rida (2017) studied the removal of Methylene Blue by adsorption using modified kaolin clay. Kaolin clay was modified using thermal treatment, acid treatment with thermal treatment and alkaline treatment with an acid treatment and thermal treatment. The results obtained showed that the modification of the clay using all three methods enhanced its adsorption capacity. Kaolin clay has the lowest adsorption capacity compared to other clays, hence modification is required to increase its efficiency for dye removal from textile effluent.

Bentonite is natural and hydrated aluminosilicate clay containing mainly smectite mineral- montmorillonite. In comparisons with other types of clay, it has good sorption potential and sorption sites in the interlayer spaces, surface and edges of the crystalline structure (Shahwan *et al.,* 2006; Eren *et al.,* 2009). Bentonite is a 2:1 aluminosilicate, and its small crystalline size has two tetrahedral silica sheets and one alumina octahedral sheet in the middle of the silica sheets. Negative charges present is due to the isomorphous substitutions of Al^{3+} for Si^{4+} in the tetrahedral layers and Mg^{2+} for Al^{3+} in the octahedral layer and it is balanced by designated exchange cations (Na^+, Ca^{2+}) in the lattice structure (Tahir and Rauf, 2006; Adeyemo *et al.,* 2017; Kausar *et al.,* 2018). These factors/characteristics of bentonite are responsible for its active surface area, high cation exchange potential and inter –lamellar surface thus making bentonite a good adsorbent for the removal of dyes (Ayari *et al.,* 2005; Bilgic, 2005; Ozcan *et al.,* 2005; Ozcan *et al.,* 2007; Shahwan *et al.,* 2006, Baik and Lee, 2010). Bentonite has been used for the successful removal of different heavy metal contaminants present in wastewater from industrial or agricultural activities.

Vieria *et al.* (2010) investigated the removal of nickel ion in aqueous solution using calcined bentonite and reported that the adsorption process was exothermic and spontaneous, further stating that pH, the amount of adsorbent and concentration of adsorbate also influence the adsorption process. Similarly, Thakre *et al*., (2010) studied the use of magnesium incorporated bentonite clay for the removal of fluoride in drinking water and reported that the chemical modification of bentonite clay enhanced the removal fluoride from the wastewater (Kamble *et al.,* 2009). Zn^{2+} and Cu^{2+} ions were removed from aqueous solution using sulphate and phosphate modified clay (Olu-owolabi and Unuabonah, 2010). The modification process increases the cation exchange capacity and also the adsorption capacity of clay. In comparison, results showed that the phosphate modified bentonite clay had a higher adsorption capacity for Cu^{2+} and Zn^{2+} and the adsorption process was spontaneous (due to the presence of phosphate ions) and endothermic. Eren *et al.,* (2009) further stated that the adsorption of metal ions on bentonite (montmorillonite) occurs by two mechanisms

1. An ion exchange reaction occurs at the permanent charge sites
2. Complexes are formed with the hydroxyl group present on the surface

The adsorption of anionic dye on untreated bentonite clay was carried out by Errias *et al.,* (2011) and the adsorption kinetics such as contact time, initial dye concentration, pH and concentration of the solution were investigated. The adsorption rate of Reactive Red 120 on untreated bentonite decreases as the temperature was increased, resulting in an exothermic reaction, whereas an acidic pH increases the adsorption of dye. The physiosorption (physical adsorption) that occurred at the broken edges of the crystalline structure was responsible for the high adsorption process observed (Wang and Siu, 2006). Although the adsorption capacity of bentonite clay is quite efficient, it does not remove all textile dyes due to the assumed negative charge in its structure. Studies have shown that the surface and structure of clays materials can be modified to improve the adsorption capacity of the clay mineral by altering the ions present on the surface or edges or the crystalline structure with heat treatment or acid treatment (Gupta, 2009).

Eren and Afsin, (2009) compared the removal of raw bentonite clay and acid-activated bentonite clay for the removal of Crystal Violet (basic dye). The initial concentration of dye, contact time and temperature were studied. It was observed that after activation, there was a reduction in the cations present in the octahedral layer (Al, Mg, and Fe) and an increase in the SiO_2 present on the tetrahedral sheet. This change in the chemical composition is as a result of the acid activation, which was confirmed using XRD. However, despite the changes in the chemical compositions, the adsorption capacity of raw clay is higher than the acid-activated clay. This is probably due to the decrease of cations present on the octahedral layer and an increase in the SiO_2 present on the tetrahedral sheet as a result of acid activation.

Ozcan *et al*. (2007) modified bentonite using a cationic surfactant (dodecyltrimethylammonium (DTMA) bromide) to produce an adsorbent for the removal of Reactive Blue 19 from aqueous solution. Batch adsorption studies showed that the maximum adsorption capacity is 206.58mg/g in an acidic medium. This indicates that there is a strong electrostatic interaction between the adsorption sites and the dye ions. Similarly Gok *et al*. (2010), also modified bentonite clay using 1, 6-diamino hexane (DAH) for the removal of Reactive Blue 19 from aqueous solution. At an optimum pH and temperature (1.5 and 20 respectively), the optimum adsorbent dosage was found to be 0.5g/L. However, the rate of adsorption increased at a higher concentration of dye, and the quantity adsorbed decreases with an increase in temperature; thus, the adsorption process is exothermic. Another cationic surfactant (Hexadecyltrimenthylammonium chloride) was used to activate bentonite clay. The adsorption capacity of the modified bentonite adsorbent was studied for the removal of Methylene Blue, Crystal Violet and Rhodamine B. The authors reported that at pH 9, a dye sorption of 99.99% was achieved for Methylene Blue, 95.0% for Crystal Violet and 83.0% for Rhodamine B and the adsorption capacity was 399.74, 365.11 and 324.36 mg/g for Methylene Blue, Crystal Violet and Rhodamine B, respectively at 30 °C (Anirudhan and Ramachandran, 2015).

2.5.3. Use of agricultural waste for adsorption of dyes

Aside from clay minerals, low cost waste materials such as agricultural waste have been used in their natural forms (untreated) and activated for the removal of synthetic dyes in textile effluent (Hameed *et al.,* 2007; Rafatullah *et al*. 2010; Rangabhashiyam *et al.,* 2013; Aljeboree *et al.,* 2014). Agricultural wastes are very cheap and readily available in large quantities though they are disposed of in landfill sites because their potential to be used as an adsorbent has not been fully explored or embraced in the industrial sector. Agricultural wastes are made up of mostly cellulose, hemicelluloses and lignin with good physical and chemical properties such as porosity, surface area and strength. Agricultural waste has potential as a readily available adsorbent, requiring little processing before it can be used (Hameed, 2009; Rangabhashiyam *et al.,* 2013). Although agricultural waste can be used in its natural form for adsorption studies, increasing studies into the use of agricultural waste and the demand for an alternative to commercial activated carbon due to its cost, a lot of agricultural waste are modified chemically or thermally to increase adsorption capacity (Ahmed, 2016; Zhao *et al.,* 2017).

Rangabhashiyam *et al.,* 2013, studied the use of garlic peel for the removal of Methylene Blue in an aqueous solution. At temperatures of 303, 313, and 323 K the adsorption capacities were 82.64, 123.45, and 142.86 mg/g respectively, and the data obtained fitted the Freudinch isotherm model. Similarly, untreated palm ash was used for the removal of Disperse Blue and Disperse Red from aqueous solutions. The authors reported that under optimum conditions, colour removal was observed at two mins for both dyes with 99% of the colour removed due to the acidic medium (Isa *et al.,* 2007). The Brazilian pine fruit shell and activated carbon made from the Brazillian pine fruit shell were used for the removal of Remozol black B in aqueous solution, and the effects of pH, adsorbent dosage on adsorption efficiency were investigated. The adsorption capacity of untreated pine fruit shell and activated pine fruit shell were 74.6 mg/g and 446 mg/g, respectively. The equilibrium fitted the Sips isotherm model, and the Avrami-order kinetic model gave the best fit for the experimental data (Cardoso *et al.,* 2011). The significant difference observed in adsorption capacity of both adsorbents is due to the improvement of the surface area and pore size due to activation of the shell material (Gupta *et al.,* 2011; Sandeman *et al.,* 2011). Similarly, bamboo-based activated carbon was used for the removal of Methylene Blue in aqueous solution, and maximum adsorption was stated to be 454.2mg/g (Hameed *et al*., 2007); an improvement compared to 143mg/g for untreated bamboo as reported by Kannan and Sundaram (2001). However, cocoa-based activated carbon and commercially available activated carbon were used for the removal of reactive black in aqueous solution, and the adsorption capacities were 603.3 mg/g and 517.1 mg/g respectively, indicating that cocoa shell-based activated charcoal is a better adsorbent (Ribas *et al.,*2014). Although the results obtained fits into the concept of a cheaper and efficient adsorbent, most studies indicate that the removal capacity of commercially activated carbon is above 800mg/g. However, this difference in adsorption capacity obtained could be due to the different type of materials used for the production of commercially available activated carbon materials (Rafatullah *et al.,* 2010; Rangabhashiyam *et al.,* 2013).

Similarly, Bijari *et al.,* (2019) prepared activated carbon from grape wood to study their ability to adsorb Reactive Blue 19 and 21 in aqueous solution. Results obtained showed an adsorption capacity of 1932 and 908 mg/g for RB19 and RB21 dyes, respectively, indicating that the grape wood activated carbon for the adsorption of selected dyes. Kumar *et al.,* (2013) compared the adsorption of Methylene Blue from aqueous solution onto raw (RTS) and surface-modified tamarind seeds (SMTS) and parameters such as pH, temperature, initial concentration and adsorbent dose were studied. The equilibrium data obtained for RTS and SMTS fit the Langmuir and Freundlich isotherms, respectively, with a maximum adsorption capacity of 16.6 and 34.5 mg/g. These results demonstrate the need for surface modification to improve the adsorption capacity of tamarind. Similarly, sugar beet pulp was used for the production of activated carbon, and phosphoric acid was used as an activating agent. The prepared activated carbon was used for the adsorption of Methylene Blue from aqueous solution. However, the adsorption capacity was 244.8 mg/g which is lower than the compared to cocoa activated carbon (603.3 mg/g) and bamboo activated carbon (454.2 mg/g) (Li *et al.,* 2016; Ribas *et al.,* 2014; Kannan and Sundaram, 2001). Subbaih and Kim (2016), studied that adsorption of Methylene Orange from aqueous solution onto pumpkin seed powder. The maximum adsorption was found to be 200.3 mg/g based on Langmuir isotherm. Although most adsorption studies on dye show that equilibrium data fits Langmuir, for this study, the equilibrium data also fit the Sips isotherm. Also, it was discovered via SEM image that the adsorbent surface was porous and irregular, a suitable surface for adsorption. Instead of preparing one low cost activated carbon from waste materials, Hameed *et al.,* (2017) prepared activated carbon using amla seed carbon (ASC), jambul seed carbon (JSC), tamarind seed carbon (TSC) and soapnut carbon (SNC) for the removal of chromotrope dye. They compared their results to that of commercial activated carbon. These authors found that in all cases, increased adsorbent dosage resulted in a decreased amount of dye adsorbed, and optimum pH was found to be 2 (indicating that an acidic pH is favourable). Also, it was stated that the equilibrium data fit Langmuir and Redlich–Peterson equations better than Temkin, Freundlich and Dubinin–Radushkevich (D–R) isotherms. The low-cost adsorbents were arranged in the following order for their adsorption capacities - ASC > JSC > TSC > SNC, with amla seeds being the best and soap nut carbon having the lowest adsorption capacity amongst the low-cost materials used. However, despite the possibility that each low-cost material can be used as a substitute, the adsorption capacity recorded remains low compared to commercial activated carbon. Although, the authors suggested that the increase in dosage might increase the amount of dye adsorbed. From all indication of results obtained regarding adsorption using agricultural waste, it is quite clear that chemical or thermal treatment is necessary before use in order to increase their adsorption capacity.

2.5.4. Use of *carica papaya* seeds for adsorption of dyes

Carica papaya fruit is a fruit crop common in tropical and sub-tropical zones (Acham *et al.,* 2018; Makanjuola and Makanjuola, 2018; Egbuonu, 2018). Papaya is a medicinal fruit, and its parts are used by traditional healers to treat diabetes, inflammation, regulate blood pressure and cholesterol level (Vij and Prashar, 2015; Ghaffarilaleh *et al.,* 2019). Among the parts, the seeds have the most important medicinal value. Also, *carica papaya* seeds (CPS) are used as contraceptives for men (He *et al.,* 2017; Ghaffarilaleh *et al.,* 2019).

Aside from its medicinal purposes, papaya seeds have been used for adsorption studies. Gilbert *et al.,* (2011) assessed and optimised the adsorption of $Pb^{2+}$and Cd^{2+} using defatted CPS. The maximum adsorption capacities were found to be 1666.67 mg/g and 1000.00 mg/g for Pb^{2+} and $Cd^{2+,}$ respectively. The authors stated that the adsorption equilibrium was obtained with 20 mins, thus suggesting that defatted CPS as an efficient adsorbent for the removal of metal ions. Ong *et al.,* (2012) tested the adsorption efficiency of CPS for the removal of zinc in aqueous solution. Looking at experimental parameters such as contact time, adsorbent dose and pH. At pH 5.0, the maximum adsorption of 19.9 mg/g was recorded with equilibrium contact time at 60 mins. Similarly, Yadav et al., (2014) used CPS for the adsorption of Pb^{2+} from aqueous solution, however, CPS was chemically carbonised using sulphuric acid. In comparison to the defatted CPS, the adsorption capacity of chemically carbonised CPS used for the adsorption of Pb^{2+} was 238.09 mg/g. Furthermore, Yadav *et al.,* (2016) compared chemically modified CPS and neutral CPS for the adsorption of

Hg(II) and found that the adsorption capacity was 18.34 mg/g and 10.75 mg/g, respectively.

Aside from the use of CPS for the adsorption of metal ions, the same has been used to investigate the removal of dyes in aqueous solutions. Untreated milled papaya seeds were used for the removal of Methylene Blue in aqueous solution, and the data fitted the Langmuir model with an adsorption capacity of 555.5mg/g, indicating efficient removal (Hameed, 2009). Defatted CPS and undefatted CPS were used for the adsorption of Methylene Blue dye in aqueous solution. It was found that defatting CPS increased its adsorption capacity for the removal of Methylene Blue from 796.23 to 1250 mg/g (Unuabonah *et al.,* 2009).

Weber *et al.,* (2013) described the importance of the microporous and mesoporous texture of CPS for the removal of Direct Black 38 from aqueous solution. The effect of initial dye concentration, contact time and pH were also studied and discovered to have a tremendous impact on the adsorption capacity of CPS. Increasing pH effectively reduced the adsorption capacity of CPS for the removal of Direct black 38 to levels as low as 10-30%, indicating that an acidic pH is favourable. In addition, the data fit the Langmuir isotherm with a maximum adsorption capacity of 440mg/g, which was stated to be higher than most studies on anionic dyes. Similarly, Pavan *et al.,* (2014) used powdered *carica papaya seeds* for the adsorption of crystal violet from aqueous solution. The equilibrium adsorption was studied and results obtained showed that it fit the Langmuir isotherm with a maximum adsorption capacity of 86 mg/g. The effect of initial pH (2.0–8.0) was associated with an increase in percentage removal (from 41–97%The study concluded that for the adsorption of crystal violet (cationic dye) onto powdered CPS, an alkaline pH is better and the point zero charge of powdered CPS (6.85) was used to highlight this point. It was further stated that the use of powered *carica papaya* seeds is promising for the removal of crystal violet.

2.5.5. Use of composite adsorbents made from CPS and clay minerals for adsorption of dyes

The constant search for ways to increase the adsorption capacity of adsorbent material used for removal of dyes has been studied extensively. An adsorbent made by combining adsorbents with other materials for better adsorption properties is generally described as a composite adsorbent (Auta and Hameed, 2014; Haldorai and Shim, 2014; Oladipo and Gazi, 2014; Kumari *et al.,* 2017). Unuabonah *et al.,* (2015) prepared composite adsorbent using carica papaya seeds and kaolinite clay for the adsorption of Methylene Blue dye. The result showed that the maximum adsorption capacity of the composite adsorbent was 35 mg/g.

In this study, further investigations were conducted to identify the extent of research into composite adsorbents made with clay minerals and carica papaya seeds in a bid to understand the effect of different proportions of individual adsorbents on adsorption capacity. Findings, however, revealed that there is a gap in this area. Hence this a key motivation for this study.

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CHAPTER 3

Materials and Methods

3.1. Adsorbent preparation

Carica papaya seeds (CPS) was collected from different local fruit stores in Lagos state, Nigeria as agricultural waste. The seeds were washed, dried, milled and stored in a tight containers. Kaolinite and bentonite clay minerals were purchased from Sigma Aldrich, UK and stored at room temperature. Clay minerals were used without prior treatment.

3.2. Washing and Drying

The *carica papaya* seeds were thoroughly rinsed thrice with distilled water to remove the slimy gel from the seeds. The seeds were dried using sunlight for 3 days

3.3. Milling

Dried papaya seeds were milled using a James Martin mini grinder (Figure 3.1). Each batch (50g) was milled for 15 seconds.

Figure 3. 1: Blender used for milling carica papaya seeds

3.4. Calcination of adsorbent

Using the percentage ratio in Table 3.1, each proportion was weighed into a 250 ml beaker. The materials were stirred together using a glass rod to ensure even distribution of materials. The mixture was transferred into silicon crucibles and calcined at 100-600°C for 6 hours in a CARBOLITE 1100°C & 1200°C Rapid Heating Laboratory Chamber Furnace (Figure 3.2). After calcination, the silicon crucibles were removed from the furnace using long tongs and placed on a red brick surface to cool down. Adsorbent samples were washed with Mill-Q water (Laboratory standard) to remove soot and dried in the oven at 100°C for 24 hours. The adsorbent was stored in an airtight bag. This procedure was done for all proportions seen in Table 3.1.

Figure 3. 2: CARBOLITE 1100°C & 1200°C Rapid Heating Laboratory Chamber Furnace used for the calcination of adsorbents

Table 3. 1. Percentage ratio for preparation of adsorbents with different proportions

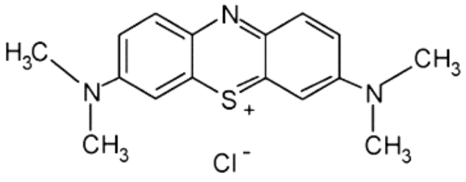
Milled *Carica* papaya seeds (w/w)	**Clay mineral (w/w)**	**Proportion**
0	100	100%CM
25	75	25 CPS /75 CM
50	50	50% CPS/50% CM
75	25	75% CPS/25% CM
100	0	100%CPS

CM= Clay mineral, CPS= *carica* papaya seeds

3.5. Preparation of adsorbate

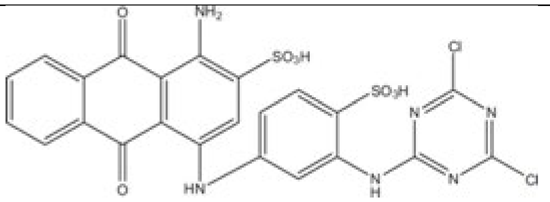
Two dyes *vis*:1) Methylene Blue, 2) Reactive Blue 4 (analytical grade) were purchased from Sigma Aldrich and used without any treatment for this research work. The properties of these dyes are shown in Table 3.2 and Table 3.3.

Table 3. 2. Physical properties of Methylene Blue

Chemical name	**Methylene Blue (C.I. 52015)**
IUPAC name	3,7-bis(Dimethylamino)phenazathionium chloride
Molecular formula	$C_{16}H1_{8}ClN_{3}S$
Molar mass	319.85 g/mol
Wavelength λmax	664nm
Chemical structure	
Dye content	70%

These dyes were selected because they are commonly used in the textile industries. In addition, they were selected because of the different ionic charges they have and one of the focus of this study to observe the efficiency of optimised adsorbents and dye with different charges. Methylene Blue is a cationic dye, whereas reactive blue is an anionic dye. Stock solutions of Methylene Blue and Reactive Blue 4 were prepared in a 1000 ml volumetric flask by dissolving 1.005 g of each dye in Milli-Q water for preparing 1000 mg/L.

Table 3. 3. Physical properties of Reactive Blue 4

Chemical name	**Reactive Blue 4 (CI 61205)**
IUPAC name	1-Amino-4-[3-(4,6-dichlorotriazin-2-ylamino)-4-sulfophenylamino]anthraquinone-2-sulfonic acid
Molecular formula	$C_{23}H_{14}Cl_2N_6O_8S_2$
Molar mass	637.419 g/mol
Wavelength λmax	595 nm
Chemical structure	
Dye content	35%

Subsequently, experimental solutions needed for this study were prepared by dilution of required volume with Milli-Q water. Subsequently, from these stock solutions, standards solutions were prepared at concentrations ranging from 5 mg/L-150 mg/L, the calculated volume was placed in 50ml volumetric flasks and made up to mark with deionised water.

3.6. Batch adsorption study

In this adsorption study, the adsorption of Methylene Blue and Reactive Blue 4 were done using the 44 adsorbents samples. Given the number of adsorbents prepared, for the purpose of optimising the suitable adsorbent for each dye, a non-parametric test called Kruskal-Wallis test was done. The adsorbents that showed rapid adsorption were used for determining the effect of dosage, pH and initial concentration on adsorption of Methylene Blue and Reactive Blue 4.

The parameters considered were percentage dye removal, calcination temperature, adsorbent dose and contact time. Results obtained were used to optimise the proportion and calcination temperature that was most efficient.

The batch adsorption experiments were carried out in 250ml of Erlenmeyer flask containing the prepared adsorbent and 100 ml of dye solution. The flasks were agitated using a shaker set at 8 for all experiments (Figure 3.3). Experiments were repeated 3-5 times. For the adsorption experiment, samples taken at different time intervals and placed in a 50ml centrifuge tube. Samples were centrifuged at 3000 xG for 20 mins and analysed. The final concentrations were calculated using absorbance readings at respective wavelengths of Methylene Blue and Reactive blue 4(665 nm and 595 nm) using a UV- visible spectrophotometer. The effect of different parameters was studied while determining the batch adsorption capacity of adsorbents. The percentage removal (1) and the amount of dye adsorbed (2) and were calculated using the equations below:

$$\text{\% Dye removal} = \left(\frac{C_O - C_f}{C_O}\right) * 100 \qquad (1)$$

$$q_e = \frac{(C_o - C_f)}{W} * V \qquad (2)$$

C_o= Initial concentration

C_f= Final concentration

W= Weight of adsorbent

V= Volume of adsorbate

qe = Amount of dye adsorbed (mg/g)

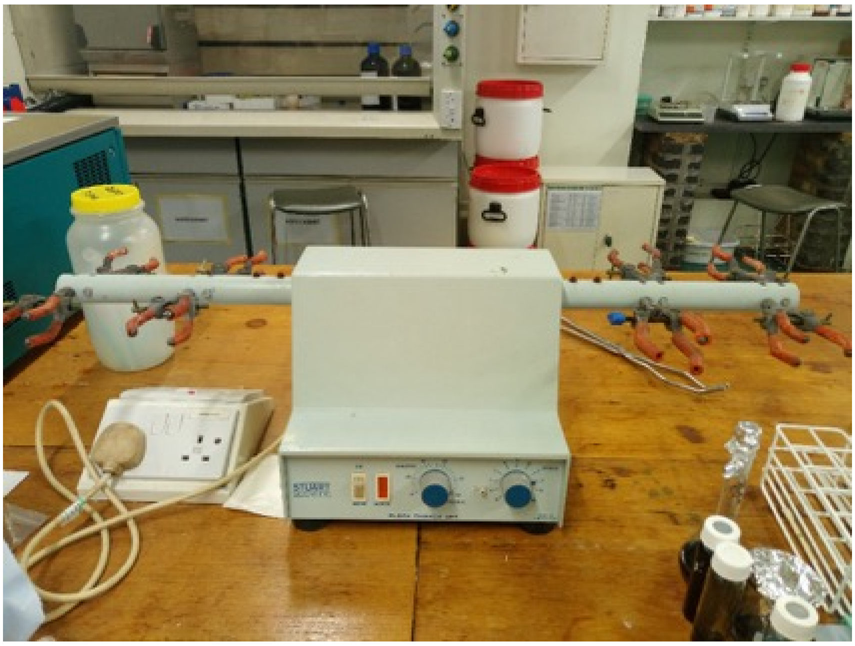


Figure 3. 3: Shaker used for the adsorption process

3.6.1. Effects of calcination temperature and contact time

To determine the effect of calcination temperature on removal efficiency of calcined adsorbents, 2g of adsorbent, 100 ml of 50mg/L dye concentration, put in a 250ml flask and agitated using a thermal shaker at the speed of 8. Samples were taken at time intervals for analysis. The varying factor was the calcination temperature (100-600^{O}C) and different percentage ratio adsorbent used.

3.6.2. Effect of adsorbent dose

The effect of adsorbent dose was studied using 0.4-1.8 g. For this study, not all adsorbents or calcined adsorbents were studied, only the selected or optimized adsorbents.

3.6.3. Effect of initial concentration

Studying the effect of initial dye concentrations ranging from 150-300 mg/L were used to study the removal efficiency and capacity of selected adsorbents at constant dose and pH.

3.6.4. Effect of pH

Effect of pH is an important aspect because it influences the adsorption process. The increase or decrease of the pH value can affect the adsorbent surface by altering the positive or negative charges on it. In addition, the variation pH value can improve or reduce adsorption of dye molecules to the surface of the adsorbent. Effect of pH was investigated at 2.0 – 10.0.

3.7. Adsorption isotherms

Equilibrium data for Methylene Blue and Reactive Blue 4 was obtained using different initial concentrations from 100mg/L to 300mg/L for different adsorbents. The linear forms of Langmuir and Freundlich isotherms were used.

3.7.1 Langmuir isotherm

Langmuir isotherm assumes that monolayer adsorption onto a surface contains a limited no of adsorption sites with uniform strategies of adsorption. Langmuir equation can be written as seen in Table 3.4.

Table 3. 4. Linear forms of Langmuir isotherms

Isotherm	Non-linear form	Linear form	Plot
Langmuir	$q_e = (\frac{q_m\, bC_e}{1 + bC_e})$	$\frac{Ce}{q_e} = \frac{1}{q_m} Ce + \frac{1}{bq_m}$	$\frac{C_e}{q_e}\ vs\ C_e$
		$\frac{1}{q_e} = \left(\frac{1}{bq_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$
		$q_e = q_m - (\frac{1}{K_L})\frac{q_e}{C_e}$	$q_e\ vs\ q_e/C_e$
		$\frac{q_e}{C_e} = K_L q_m - K_L q_e$	$q_e/C_e\ vs\ q_e$

Langmuir isotherm is expressed, as seen in Table 3.4. qe is the amount of adsorbate adsorbed per unit weight of the adsorbent at equilibrium (mg/g), Ce is the equilibrium concentration (mg/L), qm is the maximum monolayer adsorption capacity, and b is the Langmuir constant (L/mg). qm and b values are calculated from the plot of Ce/qe vs Ce and 1/qe vs 1/Ce (Hamdaoui, 2017). In addition, Langmuir isotherm is also expressed by a dimensionless constant called equilibrium character or separation factor (Namasivayam and Kavitha, 2002; Khan *et al.,* 2017) which is expressed as seen in the equation below.

$$R_L = (\frac{1}{1+K_L C_O}) \qquad (3)$$

Co = initial concentration (mg/l)

K_L= Langmuir constant (mg/g)

The value of R_L shows the favorability of the adsorption reaction as well as of the Langmuir isotherm model, i.e., it is irreversible if R_L=0, favourable if 0<R_L<1, linear if R_L=1 or unfavourable if R_L>1. Using dimensionless factor from the Langmuir isotherm, the reversibility of the process of adsorption can be predicted

3.7.2. Freundlich isotherm

Freundlich isotherm assumes that the adsorbate has a heterogeneous surface with different absorbing capacity. Freundlich isotherm is expressed, as seen in Table 3.5. Similarly, its constants K and 1/n are calculated from the slope and intercept.

Table 3. 5. Freundlich isotherm in different forms

Isotherm	Non-linear form	Linear form	Plot
Freundlich	$q_e = K_f C_e^{1/n}$	$log q_e = \log K_f + \frac{1}{n} \log C_e$	$\log q_e$ vs $\log C_e$

3.8. Adsorption kinetic studies

Adsorption kinetics relies on the interaction between adsorbate and adsorbent and the condition of the system. Kinetic experiments were performed at a different contact time, dose and constant proportion temperature. Using Lagergren pseudo-first-order and pseudo-second-order (equation 4 and 5), dye removal for each proportion was examined.

For Pseudo-first-order, the adsorption rate is required to be proportional to the first power of the concentration. The adsorption is characterised by diffusion through a boundary. To determine K_1 and q_e (slope and intercept respectively) for the Pseudo-first-order, log (q_e-q_t) was plotted against time. In some instances, when the pseudo-first-order model did not fit and failed theoretically to prove the amount of dye adsorbed, pseudo-second-order is used.

$$\text{Log } (q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad (5)$$

t = Time
q_t=Amount of dye adsorbed per unit of adsorbent (mg/g)
K_1 = Pseudo-first order rate constant of adsorption
K_2 = Pseudo-second-order rate constant of adsorption
q_e = Amount of dye adsorbed at equilibrium (mg/g)

Pseudo-second-order considers chemisorption, which controls the rate of adsorption and is expressed as seen in equation 6. To determine K_2 and q_e (intercept and slope respectively), t/q_t was plotted against time. Although most studies have indicated that the adsorption kinetics of dye adsorption fits beset with the pseudo-second-order model, both models: pseudo-first-order and pseudo-second-order were used for the experimental data (Salleh *et al.,* 2011; Bharathi and Ramesh 2013; Pavan *et al.,* 2014; Elmoubarki *et al.,* 2015).

3.9. Surface characterisation of adsorbent materials

For FTIR anaylsis, Perkin Elmer Spectrum One Fourier Transform Infrared (FTIR) spectrometer was used. FTIR anaylsis is an analytical technique used to identify organic and polymeric materials. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties. The adsorbents were anaylsed before and after dye adsorption process at absorption bands of 4000 - 400 cm-1. (Malik *et al.,* 2006; Mahmoodi *et al.,* 2011; Hassani *et al.,* 2014).

SEM (scanning electron microscope) is a powerful tool used for the characterization of different materials. Zeiss Supra 35 VP FEG-SEM capable of high resolution imaging was used for analyzing the micromorphology of adsorbents. The double-stick tape was placed on the specimen holder, and the samples were placed on the tape at different sections. Following this, samples were coated with a conductive material and gold was used for this. Samples had to be coated because the adsorbent is non-conductive materials. By doing this, images were viewed at high voltages (Malik *et al.,* 2006; Mahmoodi *et al.,* 2011; Nadaroglu *et al.,* 2014). The EDX (Energy- dispersive x-ray spectroscopy) analysis was done alongside scanning electron microscope. The EDX was used to determine the elemental composition of the adsorbents.

CHAPTER 4

Results

4.1. Prepared adsorbents

For the preparation of adsorbents, colour changes of adsorbents were observed. Kaolin clay is off white; however, after calcination, the colour of the clay mineral changed to off peach for all calcination temperature used in this study. Bentonite clay is greyish, and after calcination, different colour changes were observed at different calcination temperature (Figure 4.1 – 4.3). With the addition of milled *carica papaya* to the clay minerals, similar colour changes were observed with increasing calcination (Figure 4.1 – 4.3).

Figure 4. 1: Morphology of the Carica papaya seeds at various stages of treatment (milling and calcination at 100-300°C)

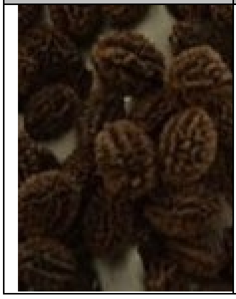
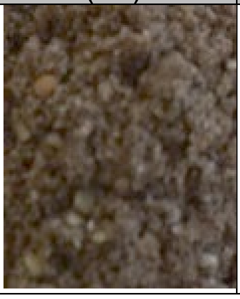
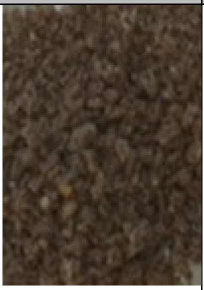
		Calcination time (CT) 6hrs		
Carica papaya seeds	**Milled carica papaya seeds** (T0)	**T100**	**T200**	**T300**
				

Figure 4. 2: Appearance of kaolin clay alone and in combination with CPS in various ratios, before at after calcination at 300-600°C

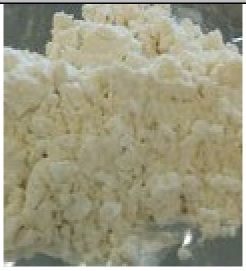
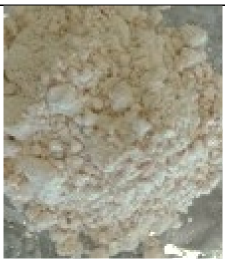
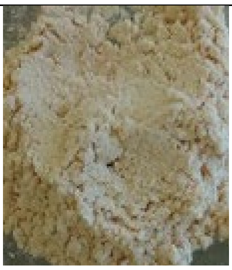
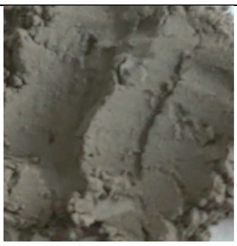
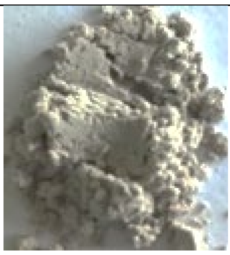
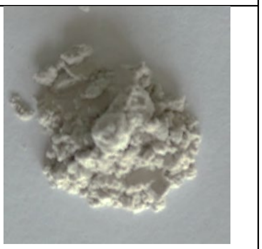
		Mixing ratio (CPS and Kaolin clay) (CT) 6hrs		
Temperature (°C)	**Kaolin**	**25% CPS /75% KC**	**50% CPS/50% KC**	**75% CPS/25% KC**
Before calcination (T0)				
T300				
T400				
T500				
T600				

Figure 4. 3: Appearance of bentonite clay alone and in combination with CPS in various ratios, before at after calcination at 300-600°C

		Mixing ratio (CPS and Bentonite clay) (CT) 6hrs		
Temperature (ºC)	**Bentonite**	**25% CPS/75% BC**	**50% CPS/50% BC**	**75% CPS/25% BC**
Before calcination (T0)				
T300				
T400				
T500				
T600				

4.2. Criteria for selection of adsorbent

The criteria for selecting an adsorbent is crucial for this study due to a large choice of different adsorbents prepared. It is essential that the optimised adsorbent is identified early on, so it can be used for the remaining part of the study (i.e. characterisation of its efficacy to remove selected dyes under various conditions). The selection was made by analysing the preliminary data by using a programming language R. As most of the data do not follow a normal distribution, so a nonparametric test, Kruskal-Wallis, was selected for multiple comparisons.

4.3. Batch process for adsorption of Methylene Blue and Reactive Blue 4

The prepared adsorbents were optimised for dye solution adsorption by carrying out experiments in batches. The parameters considered were calcination temperature, contact time, percentage dye removal, adsorbent dose, initial dye concentration and pH.

For the preliminary experimental design of adsorption experiments, the mixed samples (containing suspended adsorbents in a solution of dye) were passed through a filter paper, and the filtrate was then analysed. However, the Methylene Blue dye was observed to stain the filter paper, hence reducing the colour intensity of the sample by trapping some of the dye colour. Results obtained from the initial adsorption experiments using filter papers were therefore discarded. To resolve this problem, the shaking was stopped, and samples were allowed to settle for 2 mins before taking the sample. Once the adsorbent had settled to the bottom of the flask, the sample was taken carefully from mid-section of the flask using a calibrated pipette and transferred into a plastic tube for centrifugation.

4.4. Adsorption studies using Methylene Blue

4.2.1. Detection limit

Using the USEPA MDL (USEPA, 2016) method, the detection limit (D_L) was calculated for both dyes used as part of this study. For Methylene Blue, the detection limit was 0.0065 mg/L (Figure 4.4).

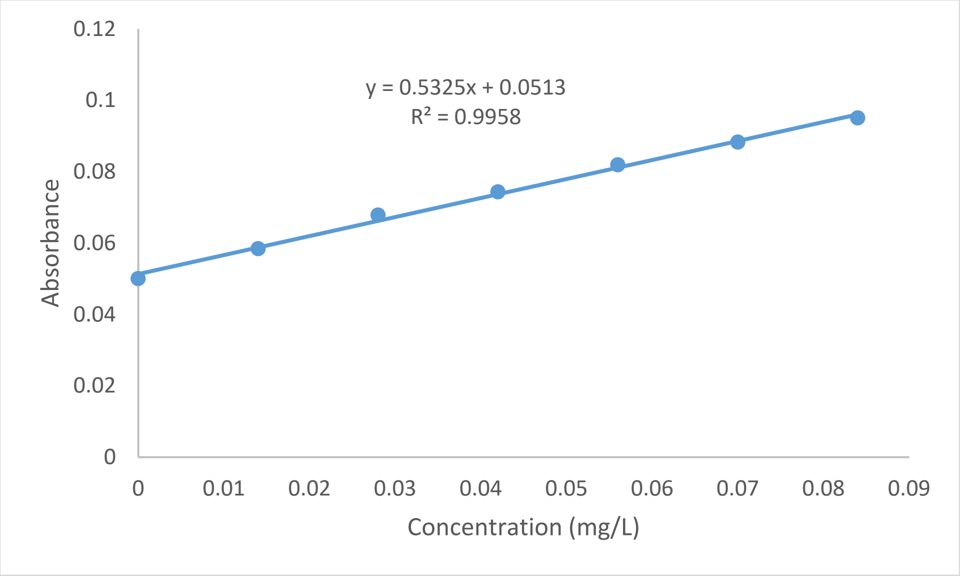


Figure 4. 4: Detection limit (DL) for Methylene Blue

Calculation of detection limit

x	y	$\hat{y}$	y-$\hat{y}$	(y-$\hat{y}$)^2
0	0.05	0.0513	-0.0013	1.69×10^{-6}
0.014	0.0584	0.0587	-0.0003	1.2×10^{-7}
0.028	0.0678	0.0662	0.0016	2.62×10^{-6}
0.042	0.0743	0.0736	0.0006	4.4×10^{-7}
0.056	0.0819	0.0811	0.0007	5.5×10^{-7}
0.07	0.0883	0.0885	-0.0003	9×10^{-8}
0.084	0.0950	0.0960	-0.0010	1.06×10^{-6}
				6.58×10^{-6}

Where,
y= absorbance
a= intercept (Y $_{\text{blank}}$)
x= concentration
n= number of standard solutions

$\hat{y} = bx + a$
$\hat{y} = 0.5325x + 0.0513$
$\hat{y} = 0.5325 \text{ X } 0 + 0.0513$
$\hat{y} = 0.0513$

To calculate the standard deviation of the regression line

$$S_{y/x} = \sqrt{\frac{\sum(y-\hat{y})^2}{n-2}}$$

$$Sy_{/x} = \sqrt{\frac{6.58 \times 10^{-6}}{5}}$$

$$Sy_{/x} = 0.001146$$

Calculation for detection limit

$a = Y_{blank}$

$Sy_{/x} = S_{blank}$

$Y_{LD} = Y_{blank} + 3S_{blank}$

$Y_{LD} = a + 3Sy_{/x}$

To calculate Y_{LD}

Y_{LD} = 0.0513+ (3 X 0.001146)

= 0.05474

Calculating L_D using the regression equation

Y= 0.5325x + 0.0513

0.05474 = 0.5325x + 0.0513

x= (0.05474 – 0.0513)/ 0.5325

x= 0.0065 mg/L

L_D = 0.0065 mg/L

4.2.2. Standard curves for Methylene Blue

A standard curve for Methylene Blue between 0.2 mg/L to 0.8 mg/L was plotted (Figure 4.5). The unknown concentrations of final absorbance readings were calculated using y=mx.

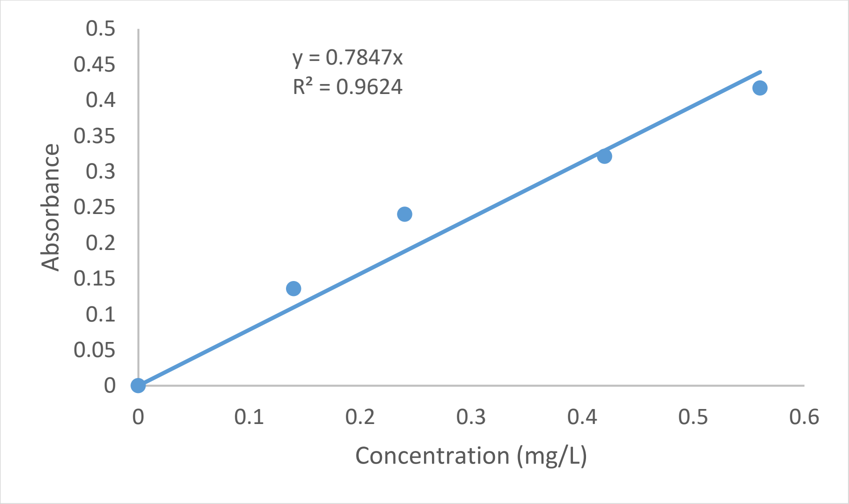


Figure 4. 5: Methylene Blue standard curve

A summary of the batch experiments conducted for selecting the best adsorbents can be seen in Table 4.1.

Table 4. 1. Summary table of the batch experiments carried out to select the best adsorbent for Methylene Blue (MB)

Subsection	**Adsorbent**	**Calcined temperature (ºC)**	**Conditions**
4.2.3	100% Kaolinite (KC)	T0, T300, T400, T500 and T600	*Dose - 2.0 g;* *pH - neutral* *Initial conc., - 50 mg/L*
4.2.4	25% CPS/75% KC (CPS/KC)		
4.2.5	50% CPS/50% KC (CPS/KC)		
4.2.6	75% CPS/25% KC (CPS/KC)		
4.2.7	100% Bentonite (BC)		
4.2.8	25% CPS/75% BC (CPS/BC)		
4.2.9	50% CPS/50% BC (CPS/BC)		
4.2.10	75% CPS/25% BC (CPS/BC)		
4.2.11	100% CPS	CPS0, CPS100, CPS200, CPS300	

4.2.3. Adsorption process optimisation using 100% kaolinite

The adsorption of Methylene Blue onto pure calcined kaolin (300-600°C) and uncalcined kaolin was carried out. The percentage removal of dye at all calcination temperatures is shown in Figure 4.6. Calcined kaolin clay was a good adsorbent with ≥90% removal in less than 10 minutes. In addition, equilibrium adsorption was achieved within 2 mins (Figure 4.6). Figure 4.7 shows an expanded view of the data, which was the percentage removal range for the adsorption of Methylene Blue using calcined kaolin at selected temperatures and uncalcined kaolin.

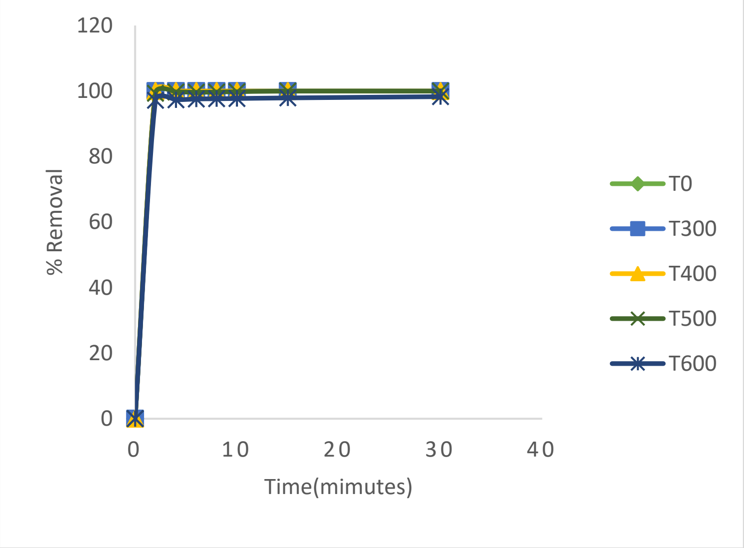


Figure 4. 6: Percentage adsorption of Methylene Blue onto natural and kaolin calcined at different temperatures (300-600°C).

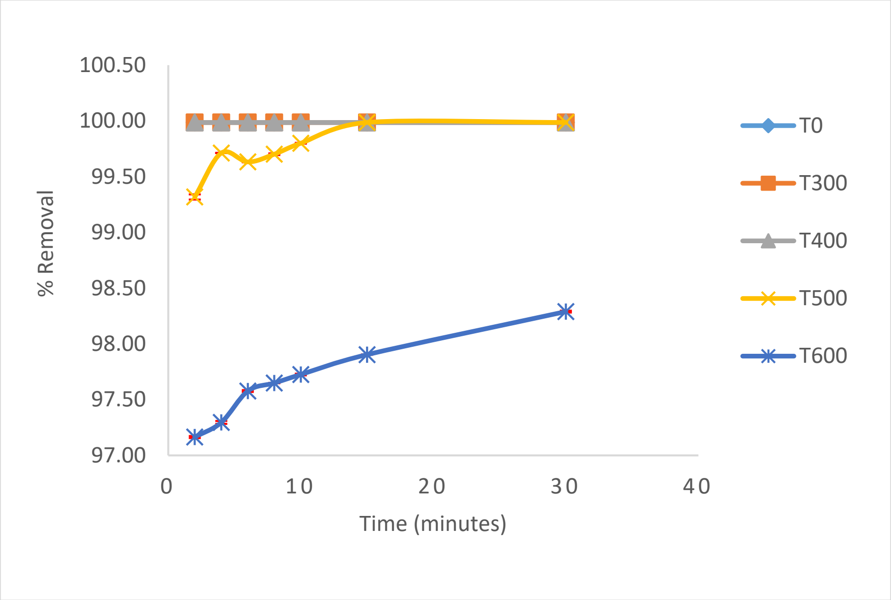


Figure 4. 7: An expanded version for percentage removal of Methylene Blue onto natural and kaolin calcined at different temperatures (300-600ºC).

The comparison of average percentage removal was done to understand and determine if there were similarities or differences in adsorption capacities of the adsorbent used. The goodness-of-fit (GOF) (Table 4.2) and homogeneity of variance (HOV) tests (Table 4.3) were done using the average percentage removal of dye from data shown in Figure 4.2. For normality, the goodness-of-fit done using 3 different types all gave the same result, indicating that it is not normal distribution.

Table 4. 2. Results of various goodness of fit (GOF) tests for adsorption of Methylene Blue onto kaolin using data from Figure 4.6.

Goodness of Fit test	**H_0**	**H_1**	**P-value**
Shapiro-Wilk (SW)	Normal distribution	Not a normal distribution	2.1×10^{-11}
Shapiro-Francia (SF)	Normal distribution	Not a normal distribution	1.0×10^{-9}
Probability plot correl ation coefficient (PPCC)	Normal distribution	Not a normal distribution	1.0×10^{-9}

For homogeneity of variances, two HOV tests were used (Bartlett's test and Levene's test). The results showed that the variances of different groups are not equal.

Each percentage removal is not equal to 1, hence indicating that the data are no equal (Table 4.3).

Table 4. 3. Homogeneity of variance for kaolin using data from Figure 4.6.

HoV test	**P-value**
Bartlett's	2.2×10^{-16}
Levene's	1.9×10^{-17}

The goodness of fit (GOF) and homogeneity of variances (HoV) tests were used to verify the assumptions of the statistical test for more than two groups. The results (Tables 4.2 and 4.3) showed that the data failed to comply with the two assumptions for normality. A nonparametric test (Kruskal-Wallis) was therefore used to investigate whether a significant difference occurred between the efficiency of the adsorbents to remove dyes used as part of this study. The test showed ($p = <0.05$) that there is a significant difference between the absorbent materials. A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.8).

Furthermore, it was observed that results for subsequent adsorption experiments were not normally distributed; hence, the need for non-parametric approaches. For this reason, repeated goodness of fit and homogeneity of variance calculations are not shown.

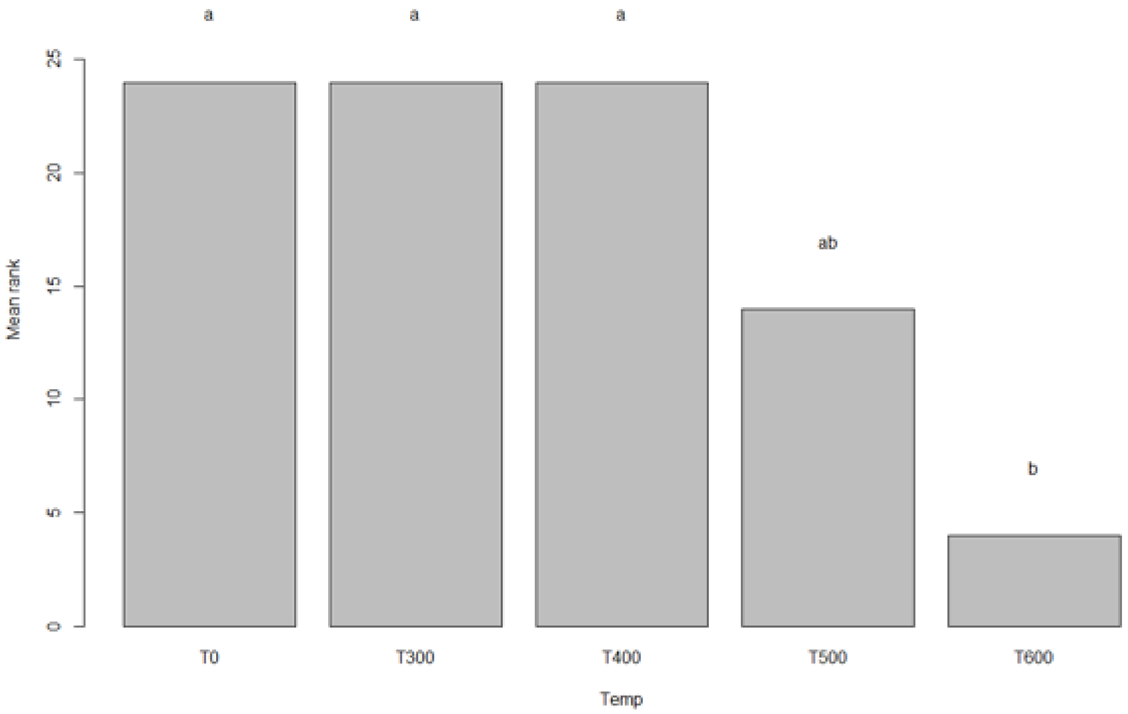


Figure 4. 8: Post hoc test for pairwise comparison (100% kaolinite)

(Same letters on bars indicate no significant difference)

Figure 4.8 helped to show the difference and similarities between the adsorption efficiencies of adsorbents used better. For the KW test, the mean rank was used for comparison; therefore, adsorbents with higher mean ranks were an indication of how fast the reaction occurred.

T0, T300, T400 and T500 share similar adsorption capacities and also showed that rapid adsorption of Methylene Blue occurred. Thus, pointing out that any of these adsorbents can be used for adsorption of Methylene Blue. Besides, T500 share similar adsorption capacity with T600, also indicating that any of both can be used. It was clear that T500 could be a suitable adsorbent for this proportion as it shares similarities with other prepared adsorbents. However, for this proportion, T0 was the suitable adsorbent because it rapidly removes Methylene Blue and requires no calcination to achieve the same adsorption efficiency as the calcined adsorbents (T300, T400 and T500).

4.2.4. Adsorption process optimisation using 25% CPS/75% KC

25/75 homogenous mixture of milled *carica papaya* seeds (CPS) and kaolin clay (KC) calcined at 300-600^{O}C was used for adsorption of Methylene Blue in aqueous solution. The result was compared with the adsorption results obtained for T0 for the adsorption of Methylene Blue in aqueous solution.

The percentage removal of Methylene Blue against time using this proportion at all calcination temperature, as seen in Figure 4.9 showed that calcined kaolin clay was an excellent adsorbent with ≥90% removal. However, in comparison with T0, it was clear that there was no difference in the percentage of removal obtained. As observed, equilibrium was attained within 2 minutes for T0, mixed adsorbents calcined at 300^{O}C and 400^{O}C. For adsorbents calcined at 500^{O}C and 600^{O}C, equilibrium occurred at 4 mins. Figure 4.9 was expanded to give 4.10, and this enabled the focus at 99-100% which was the percentage removal range for the adsorption of Methylene Blue using 25/75 mixed adsorbent and calcined kaolin at selected temperatures and T0.

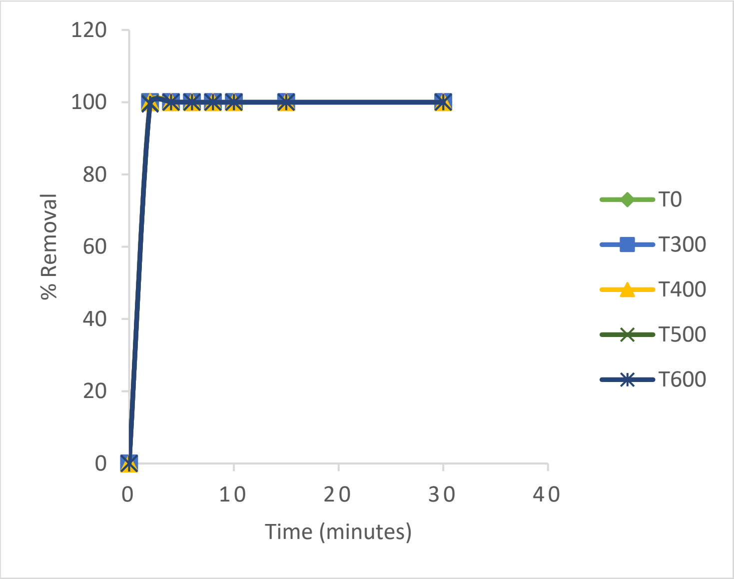


Figure 4. 9: Percentage removal for adsorption of Methylene Blue onto 25% CPS/75% KC.

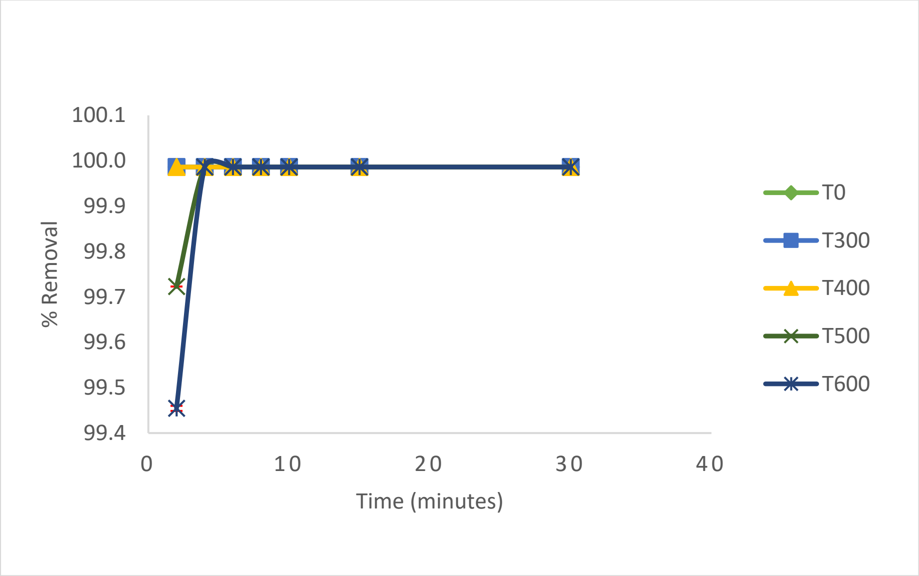


Figure 4. 10: An expanded version for percentage removal for adsorption of Methylene Blue onto 25% CPS/75% KC.

Kruskal-Wallis test was used for the comparison test, and the results obtained showed that there is no difference in the removal efficiency of each adsorbent used (p= 0.54). A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.11). The results seen in figure 4.11 highlights the similarities of adsorption capacity between all prepared adsorbents. T0, T300, T400, T500 and T600 share similar adsorption capacities. Thus pointing out that any of these adsorbents can be used for adsorption of Methylene Blue when using 25/75 mixed adsorbent(CPS/KC) as an adsorbent for adsorption of Methylene Blue in aqueous solution. Considering that any of the adsorbents can be used, adsorbent T0 was selected as the suitable adsorbent as it requires no calcination to achieve the same removal efficiency as the calcined 25/75 mixed adsorbents(CPS/KC). Furthermore, it was seen that the addition of CPS improved the adsorption efficiency of kaolin clay. For the adsorption of Methylene Blue done using 25/75 mixed adsorbent at any calcination temperature (300 – 600^{O}C) due to their similarities whereas for 100% kaolin, not all adsorbent shared the same adsorption efficiency.

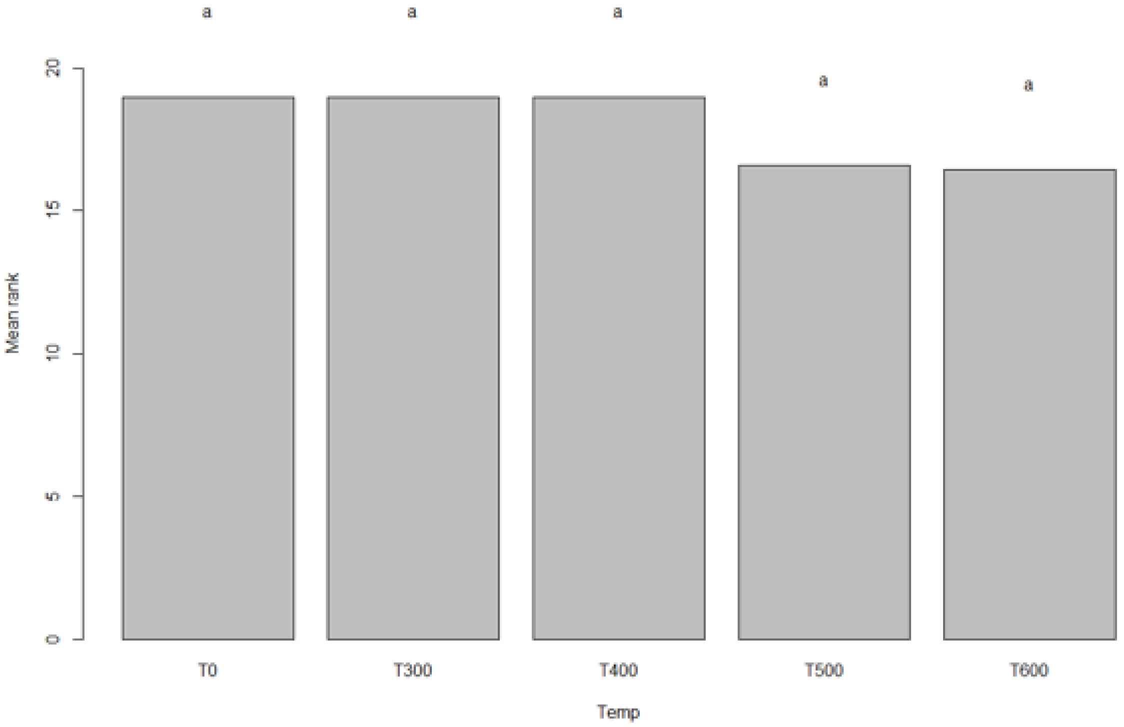


Figure 4. 11: Post hoc test for pairwise comparison for 25% CPS/75% KC.

(Same letters on bars indicate no significant difference)

4.2.5. Adsorption process optimisation using 50% CPS/50% KC

For the 50% CPS/50% KC mixed adsorbent (CPS/KC) the results showed that equilibrium adsorption was observed within 2 minutes, and no absorbance reading was obtained for T300-T500. Thus, the concentration calculated for the detection limit was used as final concentration for adsorbents T300-T500 (Figure 4.12). For adsorption of Methylene Blue using adsorbent calcined at 600°C, the UV-spectrophotometer could not provide an absorbance reading as the absorbance value was above the instrumental range. Ideally, the filtrate should have been diluted; however, an adsorbent that will require the dilution of its filtrate after it has been used for adsorption will probably not make a good adsorbent. Thus, no value for adsorbent calcined at 600°C for 50% CPS/50% KC mixed adsorbent (CPS/KC) was given.

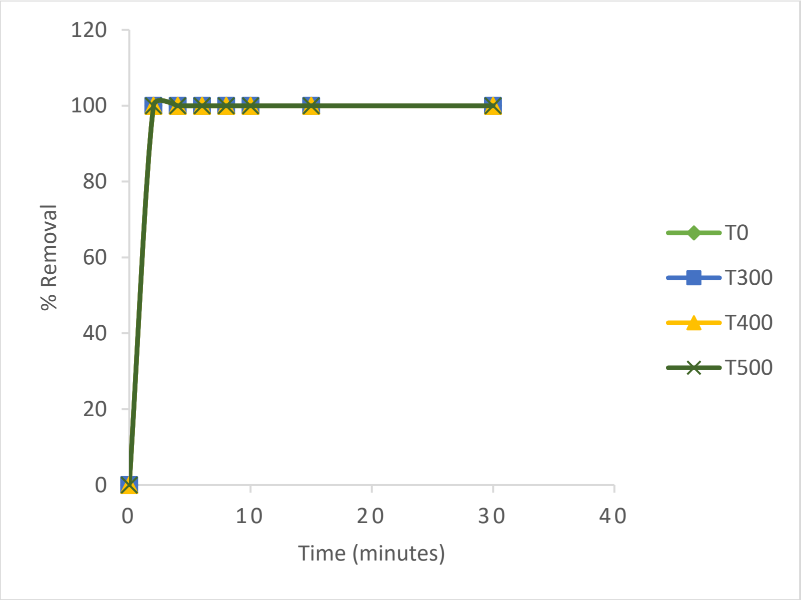


Figure 4. 12: Percentage removal for the adsorption of Methylene Blue onto 50% CPS/50% KC

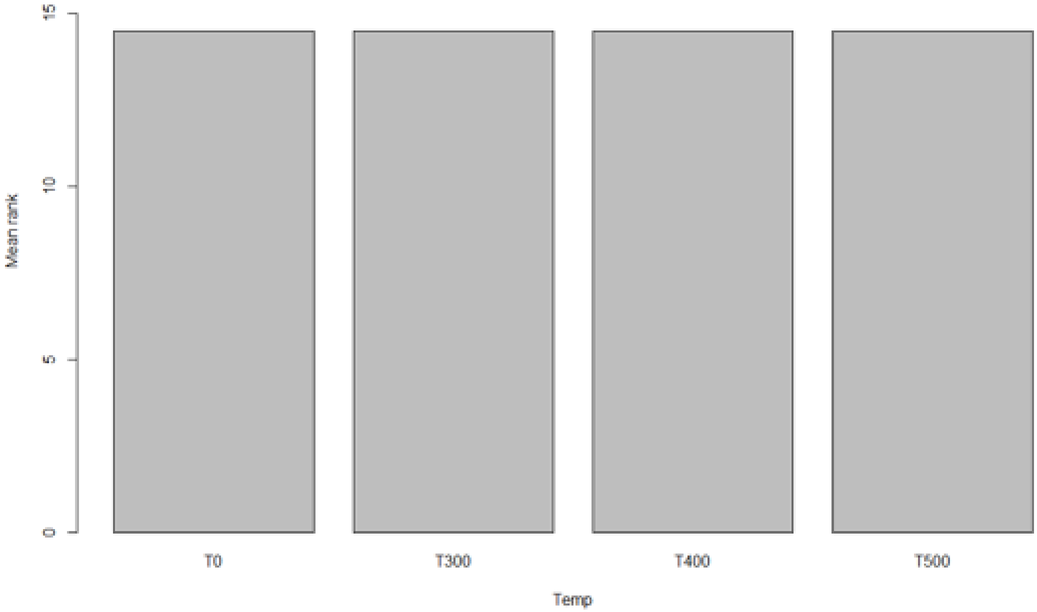


Figure 4. 13: Post hoc test for pairwise comparison (50% CPS/50% KC)

(Same letters on bars indicate no significant difference)

KW test was used for the comparison test, and the results obtained showed that there is no difference in the removal efficiency of each adsorbent used (p= NA). A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.13). Comparing the post-hoc test for 50% CPS/50% KC to 25% CPS/75% KC, results were seen to be similar. Results seen in figure 4.13 shows the similarities of adsorption capacity between all prepared adsorbent. T0, T300, T400 and T500 share similar adsorption capacities. Thus pointing out that any of these adsorbents can be used for adsorption of Methylene Blue when using 50% CPS/50% KC mixed adsorbent(CPS/KC) as an adsorbent. Considering that any of the adsorbents can be used, adsorbent T0 was selected as the suitable adsorbent.

4.2.6. Adsorption process optimisation using 75% CPS/25% KC

For 75% CPS/25% KC, the results showed that >90% removal occurred within 2 mins (Figure 4.14). This rapid adsorption happened for all calcined adsorbents. Similar to 50% CPS/50% KC, the UV- spectrophotometer did not give an absorbance reading at T600 due to the high concentration of Methylene Blue in the filtrate. Although the filtrate should have been diluted, however, the use of an adsorbent that will require the dilution of the filtrate will probably not be a good adsorbent. Thus no report of adsorbent calcined at 600°C for 75% CPS/25% KC mixed adsorbent was included. An expanded version of figure 4.14 provided more information on the percentage removal of Methylene Blue against time using this proportion of this mixed adsorbent (Figure 4.15).

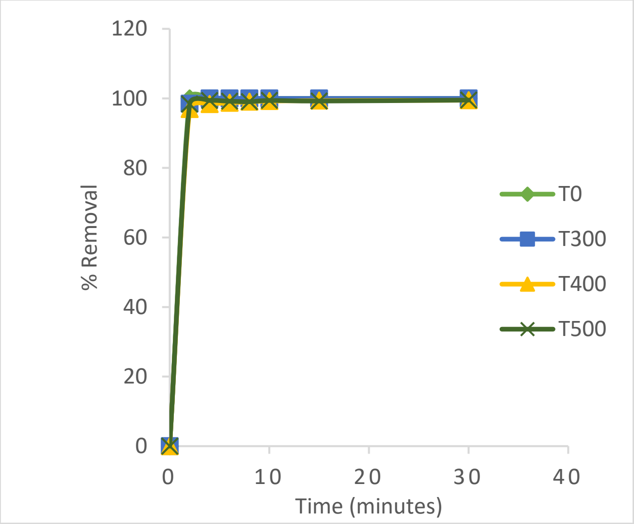


Figure 4. 14: Percentage removal for adsorption of Methylene Blue onto 75% CPS/25% KC.

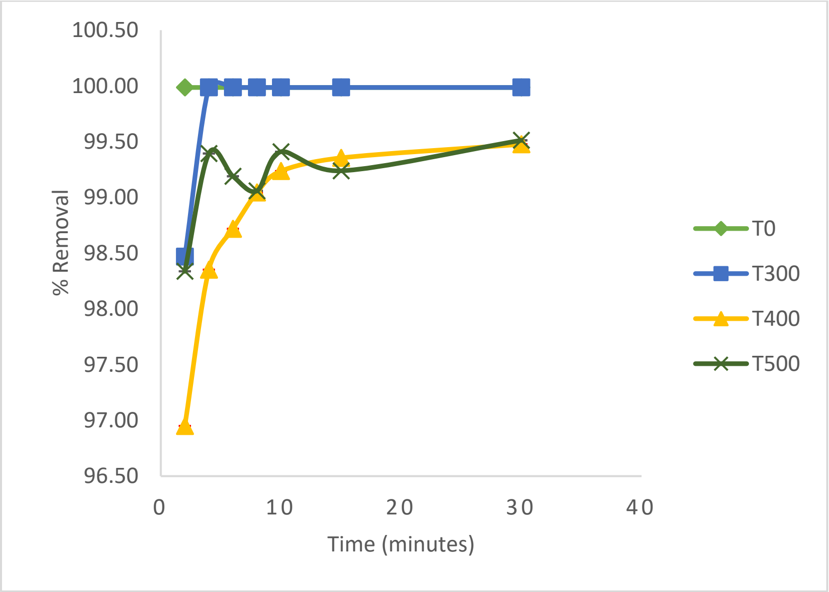


Figure 4. 15:An expanded version for percentage removal for adsorption of Methylene Blue onto 75% CPS/25% KC.

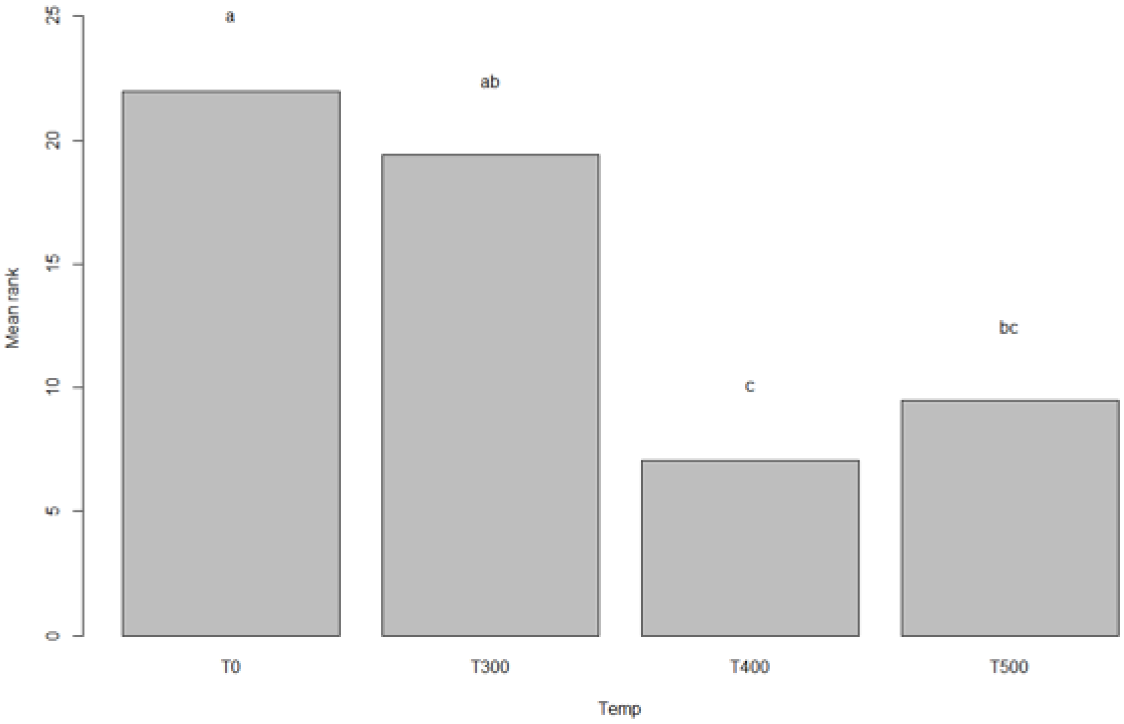


Figure 4. 16: Post hoc test for pairwise comparison (75% CPS/25% KC)

(Same letters on bars indicate no significant difference)

KW test was used to investigate if there is a difference in the efficiency of the adsorbents used. The test showed ($p=<0.05$) that there was a significant difference between the absorbent materials. A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.16), and it indicated that some of the adsorbents share similar adsorption efficiencies and others do not. Looking at figure 4.16 it shows that there is a difference in the efficiency of the adsorbents for this proportion. T0 and T300; T300 and T500; T400 and T500 have the same adsorption capacity. The increase in mean rank indicates the rapidness of the adsorption process for each adsorbent. Hence, T400 and T500 were not selected as suitable adsorbents for this proportion. For T0 and T300, both adsorbents share similar adsorption efficiencies despite the uncalcined state of T0. Hence, T0 was selected as the suitable adsorbent for the 75% CPS/25% KC mixed adsorbent since it had the fastest adsorption process when compared to other adsorbents used.

4.2.7. Adsorption process optimisation using 100% bentonite

At selected temperatures (300–600°C) calcined bentonite and uncalcined bentonite (T0) were used for the adsorption of Methylene Blue, and the percentage removal observed was >90% for adsorbents that were calcined. However, for T0, the percentage of removal was observed to be < 90%. The difference observed in percentage removal for calcined and uncalcined bentonite for the adsorption studies of Methylene Blue indicates that the thermal modification of bentonite clay improves its adsorption properties (Figure 4.17). Figure 4.18 is an expanded version of figure 4.18, which gave an in-depth view of the difference in percentage removal amongst the adsorbents used.

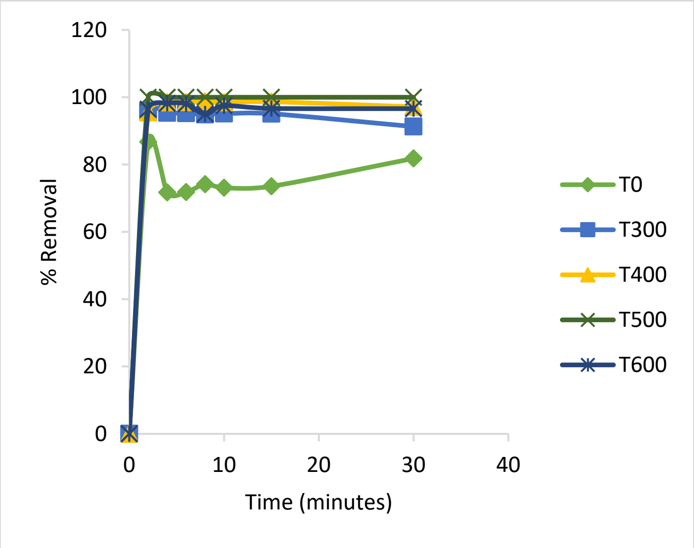


Figure 4. 17: Percentage removal for adsorption of Methylene Blue onto 100% bentonite.

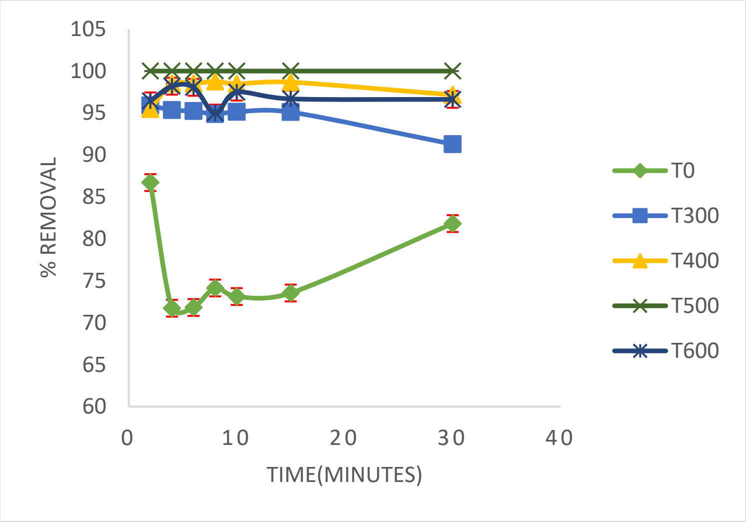


Figure 4. 18: An expanded version for percentage removal for adsorption of Methylene Blue using 100% bentonite.

For statistical analysis, the first step was to analyse the data to determine if it follows the assumptions of the parametric test. The variance and normality of the data were analysed using the percentage removal. For normality, three goodness-of-fit tests were used (Table 4.4)

Table 4. 4. Results of various goodness of fit test for adsorption of Methylene Blue onto bentonite using data from Figure 4.17

Goodness of Fit test	H_O	H_1	P-value
SW	Normal distribution	Not a normal distribution	1.4×10^{-10}
SF	Normal distribution	Not a normal distribution	5.5×10^{-9}
PPCC	Normal distribution	Not a normal distribution	5.5×10^{-9}

For variances, Bartlett's test and Levene's Test for Homogeneity of Variances were used. The results obtained showed that the variance ratio of each percentage removal is not equal to 1, hence indicating that the variances are no equal (Table 4.5).

Table 4. 5. Homogeneity of variance (HOV) for bentonite using data from Figure 4.17

HoV test	P-value
Bartlett's	2.2×10^{-16}
Levene's	1.3×10^{-5}

Doing both tests showed that the result obtained for the adsorption of Methylene Blue with bentonite did not have a normal distribution; hence, it was non-parametric. Furthermore, the results for subsequent adsorption experiments were not normally distributed, hence, non-parametric. Thus, repeated writing of goodness-of-fit and homogeneity of variance tests was not done.

Consequently, a non-parametric test called Kruskal-Wallis (KW) test was done to determine the difference in the efficiency of adsorbents used. Results indicated that some adsorbents shared similar removal efficiencies. However, there was a significant difference (p= <0.05) between the adsorbents. A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.19). Figure 4.19 shows that the following adsorbents have similar adsorption capacities when used for adsorption of Methylene Blue; 1) T0, T300 and T600, 2) mixed adsorbent calcined at T300 and T400, 3) mixed adsorbent calcined at T400, T500 and T600. The increase in mean rank indicates how fast the colour removal occurred for each adsorbent. T500 gave the fastest reaction and was selected as a suitable adsorbent for this proportion.

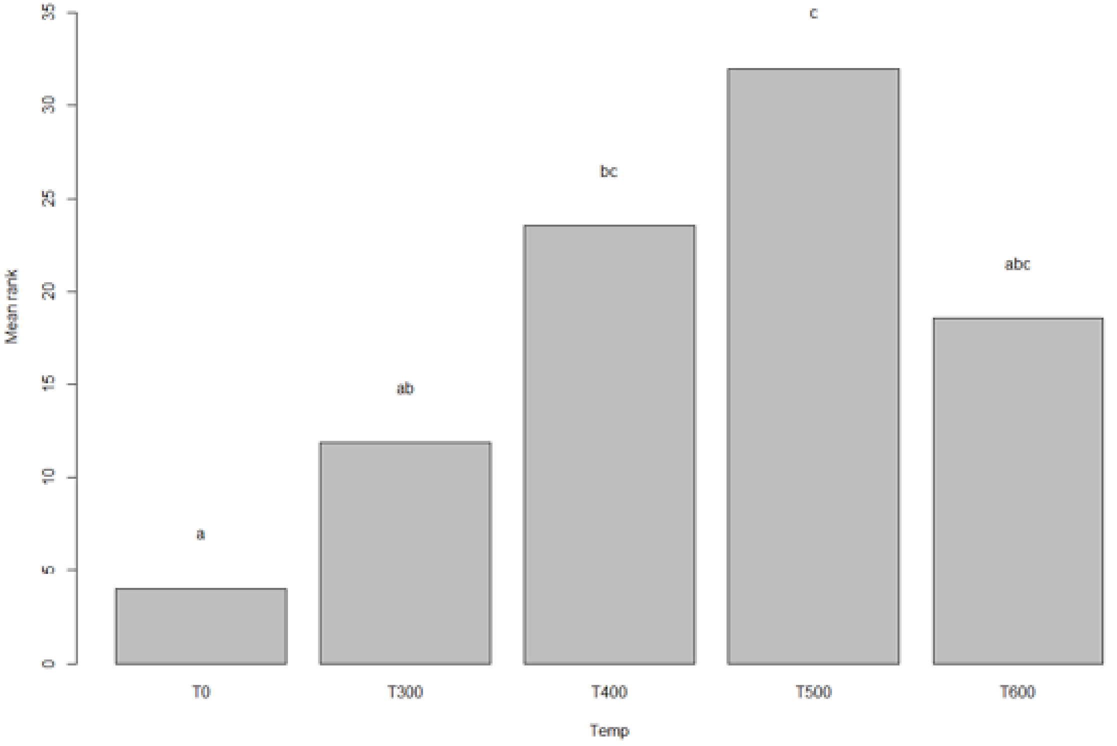


Figure 4. 19: Post hoc test for pairwise comparison (100% bentonite)

(Same letters on bars indicate no significant difference)

4.2.8. Adsorption process optimisation using 25% CPS/75% BC

For 25/75 mixed adsorbents (CPS/BC) calcined at selected temperatures (300–600^{o}C), the adsorption of Methylene Blue was rapid. Within 2 mins of agitation time, no absorbance reading was recorded, and none was recorded for other time intervals (Figure 4.20). The expanded version of figure 4.20 can be seen in figure 4.21. The absence of absorbance reading indicated that the final absorbance was below the detection limit. The concentration calculated for below detection limit was used for calculating the percentage removal.

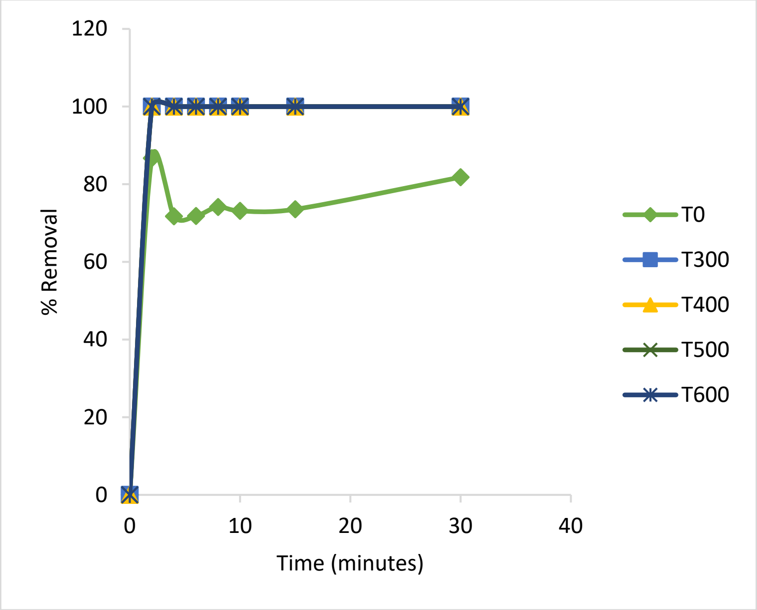


Figure 4. 20: Percentage removal for adsorption of Methylene Blue onto 25% CPS/75% BC.

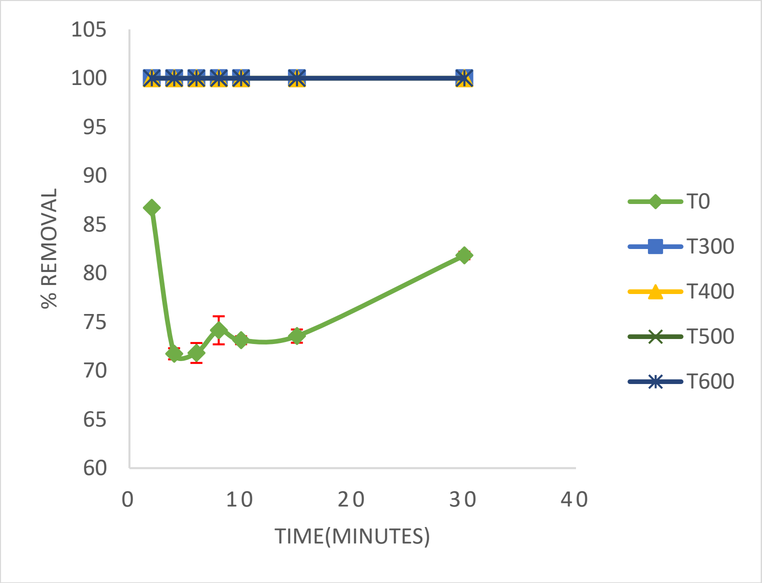


Figure 4. 21: An expanded percentage removal for adsorption of Methylene Blue using 25% CPS/75% BC.

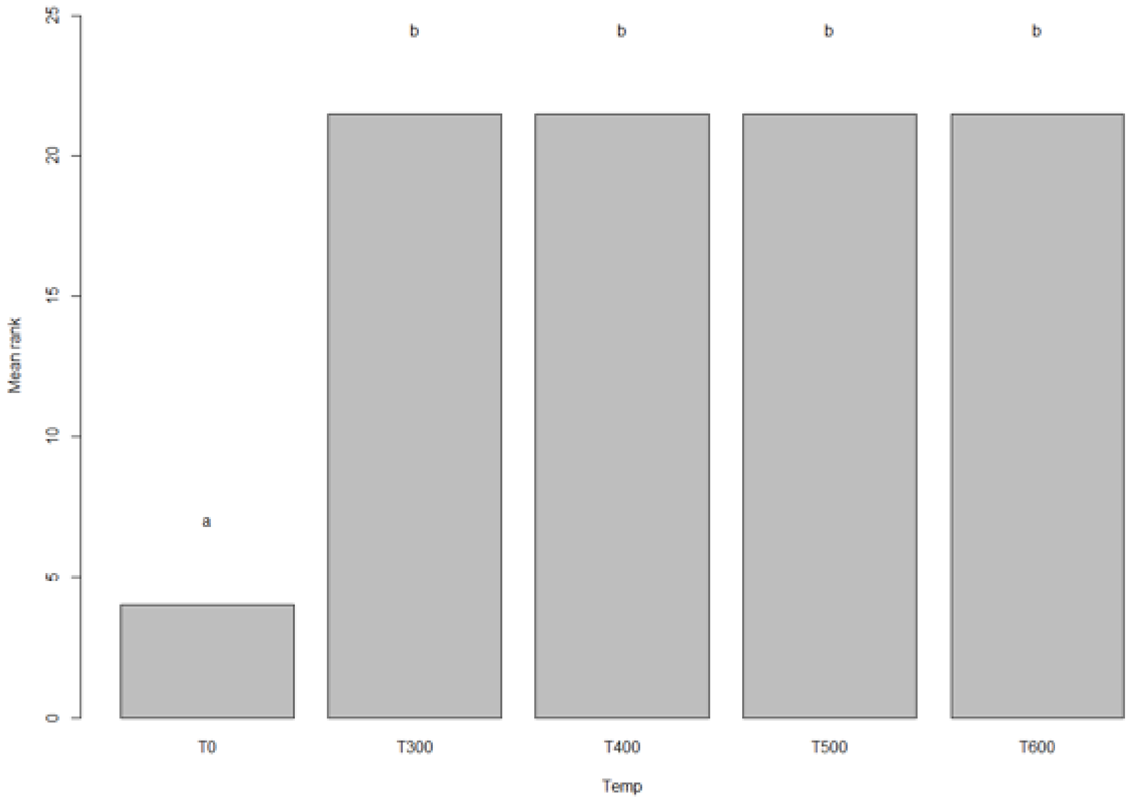


Figure 4. 22: Post hoc test for pairwise comparison (25% CPS/75% BC).

(Same letters on bars indicate no significant difference)

A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.22). Figure 4.22 shows that all calcined 25/75 mixed adsorbent (CPS/BC) have similar adsorption capacities when used for adsorption of Methylene Blue. Also, for all calcined 25/75 adsorbents (CPS/BC), the colour removal was rapid; hence, the same mean rank observed. Therefore, adsorbent T300 was selected as a suitable adsorbent for this proportion.

4.2.9. Adsorption process optimisation using 50% CPS/50% BC

Similar to adsorption of Methylene Blue using 25% CPS/75% BC mixed adsorbents, adsorption of Methylene Blue using 50% CPS/50% BC mixed adsorbents (CPS/BC) was also rapid, and after 2 mins there was no change in absorbance reading recorded as well. No absorbance reading was recorded at other time intervals as well. The absence of absorbance reading indicated that the final absorbance was below the detection limit. The concentration calculated for below detection limit was used for calculating the percentage removal (Figure 4.23). By observing Figure 4.23, there is an indication that the adsorption efficiency for calcined 25/75 mixed adsorbents is the same at 300-600^{O}C

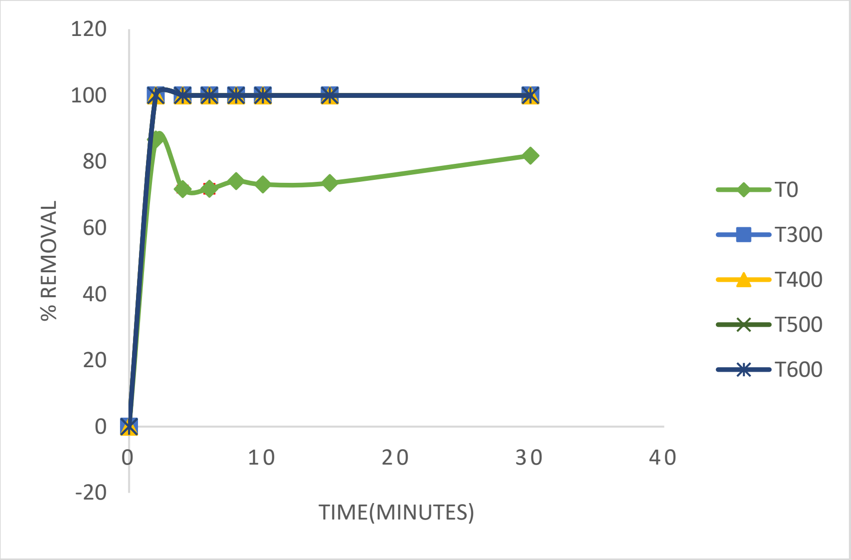


Figure 4. 23: Percentage removal for adsorption of Methylene Blue onto 50% CPS/50% BC.

KW test was done and results (p=<0.05) showed that there was a significant difference in efficiency in adsorbents used. Therefore, a post-hoc test was used for pairwise comparison in order to select the best adsorbent material (Figure 4.24). Figure 4.24 shows that all calcined 50% CPS/50% BC mixed adsorbent have similar adsorption capacities when used for adsorption of Methylene Blue. T0 shares no similarity with calcined adsorbents for this proportion. Since all calcined adsorbent has the same removal efficiency which has a high mean rank indicating good adsorption quality, the selection of a suitable adsorbent for this proportion was done by selecting the adsorbent that requires lowest of calcination temperature but shows excellent removal efficiency. Hence, T300 was selected.

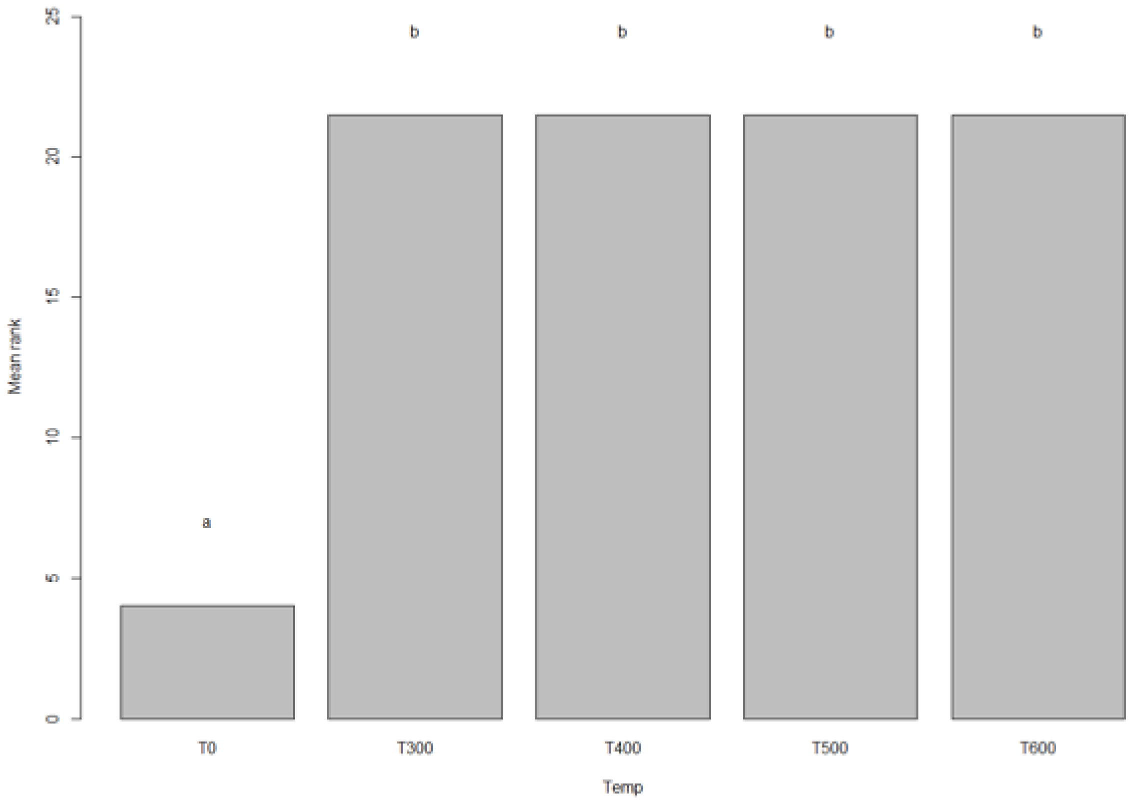


Figure 4. 24: Post hoc test for pairwise comparison (50% CPS/50% BC CPS/Bentonite)

(Same letters on bars indicate no significant difference)

4.2.10. Adsorption process optimisation using 75% CPS/25% BC

Using 75% CPS/25% BC mixed adsorbents, absorbance results were similar to that obtained for 25% CPS/75% BC and 50% CPS/50% BC mixed adsorbents. Rapid colour removal was observed, and the results were below the detection limit. Hence the value for BDL was used for the calculation of percentage removal. Unlike T0, calcined adsorbents showed better removal efficiency (Figure 4.25 and 4.26).

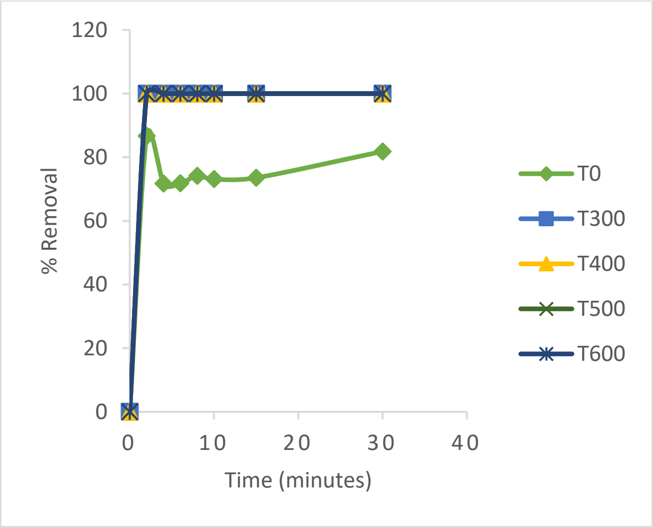


Figure 4. 25: Percentage removal for adsorption of Methylene Blue onto 75% CPS/25% BC.

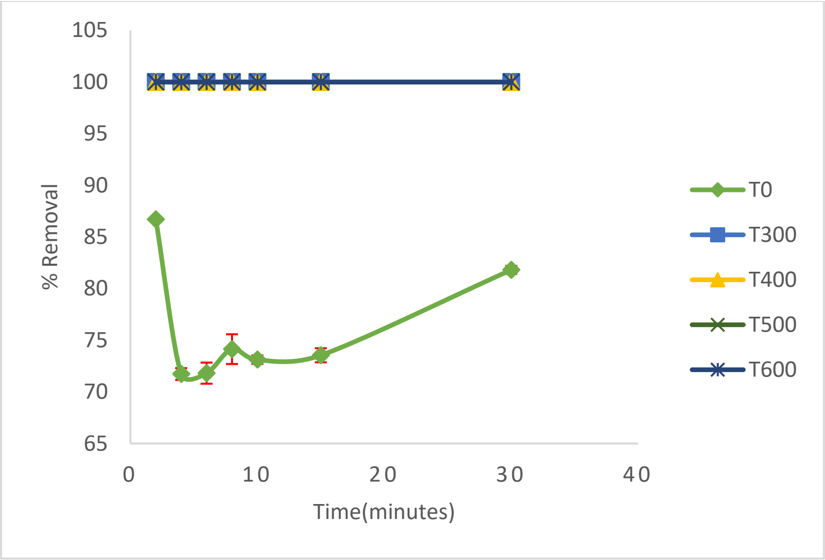


Figure 4. 26: An expanded version of percentage removal for adsorption of Methylene Blue onto 75% CPS/25% BC.

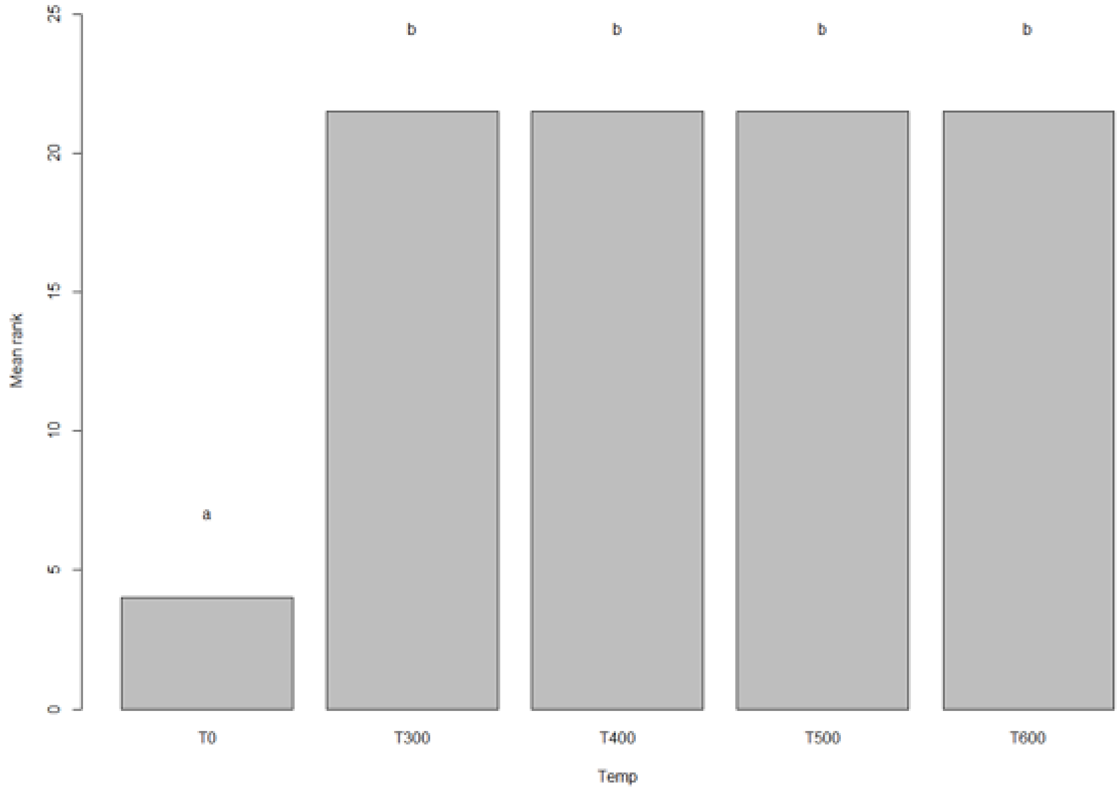


Figure 4. 27: Post hoc test for pairwise comparison (75% CPS/25% BC)

(Same letters on bars indicate no significant difference)

KW test was used to check for similarities efficiency and the result (p=<0.05) showed that there was a significant difference. Therefore, a post-hoc test was used for pairwise comparison in order to select the best adsorbent material (Figure 4.27). Figure 4.27 showed that all calcined 75% CPS/25% KC mixed adsorbent have the same adsorption capacities when used for adsorption of Methylene Blue. T0 shares no similarity. Since all calcined adsorbents for this proportion have similar removal efficiency and the adsorption was rapid; hence, any of the adsorbents can be selected as the suitable adsorbents. The selection of adsorbent was done by selecting the adsorbent that requires the least amount of calcination temperature, and T300 was selected as the suitable adsorbent.

4.2.11. Adsorption process optimisation using milled *carica papaya* seeds

For adsorption of Methylene Blue using calcined milled *carica papaya* seeds the adsorption results on close observation of Figure 4.28, all adsorbent share similar adsorption efficiency due to rapid dye removal with 30mins. Upon expansion (Figure 4.29), the removal efficiency of uncalcined CPS can be seen to increase with increased agitation time. Thus indication the possibility that calcination of CPS improves its removal efficiency when used for adsorption of Methylene Blue.

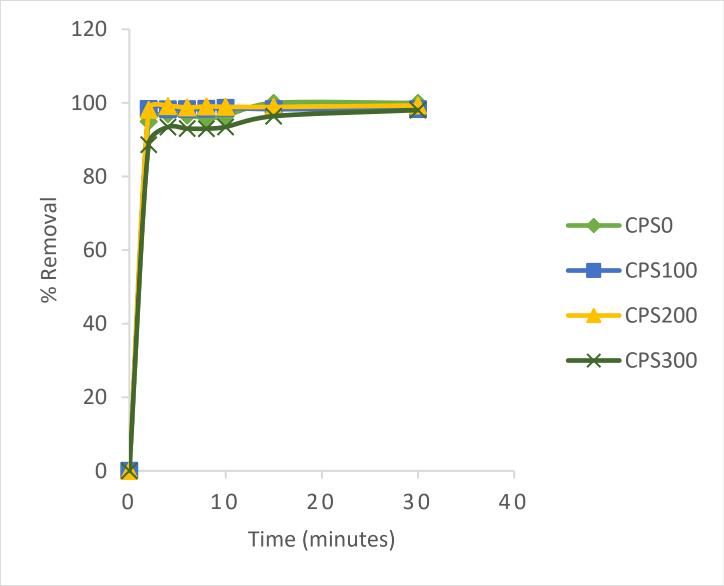


Figure 4. 28: Percentage removal for the adsorption of Methylene Blue onto CPS seeds.

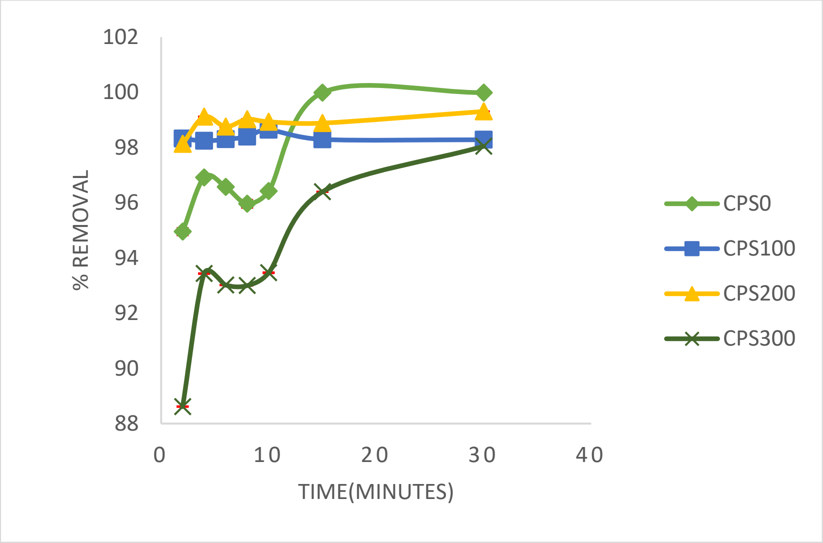


Figure 4. 29: An expanded version of percentage removal for the adsorption of Methylene Blue onto CPS seeds.

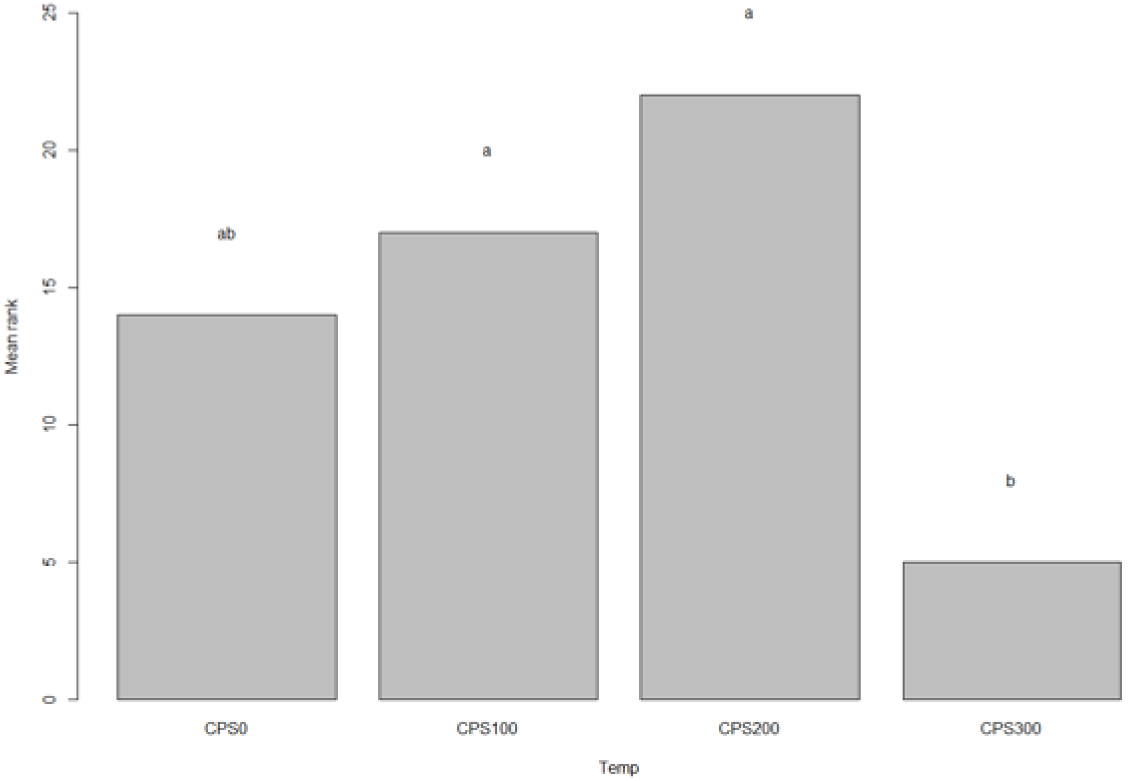


Figure 4. 30: Post hoc test for pairwise comparison (100% CPS)

(Same letters on bars indicate no significant difference)

KW test was carried out, and results (p=<0.05) indicated that the efficiency of the adsorbents was not similar. Therefore, a post-hoc test was used for pairwise comparison in order to select the best adsorbent material (Figure 4.30) test was used for pairwise comparison. Figure 4.30 shows that CPS0 has similar adsorption efficiency in comparison with calcined CPS. However, despite the similarity of adsorption efficiency, adsorbent CPS200 had the highest mean rank. Thus showing how fast the adsorption of Methylene Blue occurred when CPS200 was used. Hence, CPS200 was selected as a suitable adsorbent for this proportion.

4.3. Adsorption studies using Reactive Blue 4

4.3.1. Detection limit

Using the USEPA MDL method (USEPA, 2016), the detection limit (DL) was calculated for both dyes used for this study. For Reactive Blue 4, the detection limit is 1.30 mg/L (Figure 4.31).

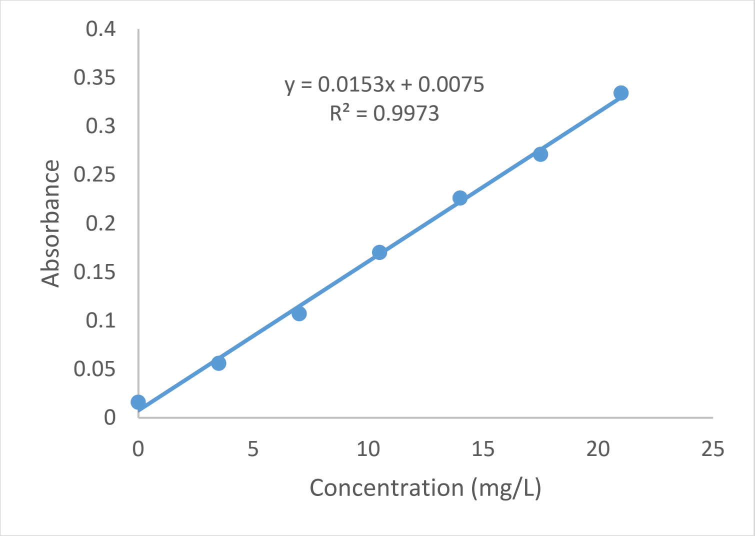


Figure 4. 31: Detection limit (DL) for Reactive Blue 4

Calculation of detection limit

x	y	$\hat{y}$	y-$\hat{y}$	(y-$\hat{y}$)^2
0	0.016	0.0075	0.0085	7.23×10^{-5}
3.5	0.056	0.0611	-0.0051	2.55×10^{-5}
7	0.107	0.1146	-0.0076	5.78×10^{-5}
10.5	0.17	0.1682	0.0019	3.4×10^{-6}
14	0.226	0.2217	0.0043	1.85×10^{-5}
17.5	0.271	0.2753	-0.0042	1.81×10^{-5}
21	0.334	0.3288	0.0052	2.70×10^{-5}
				2.23×10^{-4}

Where,
y= absorbance
a= intercept (Y_{blank})
x= concentration
n= number of standard solutions

$$\hat{y} = bx + a$$
$$\hat{y} = 0.0153x + 0.0075$$
$$\hat{y} = 0.0153 \text{ X } 0 + 0.0075$$
$$\hat{y} = 0.0075$$

To calculate the standard deviation of the regression line

$$S_{y/x} = \sqrt{\frac{\sum(y-\hat{y})^2}{n-2}}$$

$$S_{y/x} = \sqrt{\frac{2.23 \times 10^{-4}}{5}}$$

$$S_{y/x} = 0.00667$$

Calculation for detection limit

$a = Y_{blank}$

$S_{y/x} = S_{blank}$

$Y_{LD} = Y_{blank} + 3S_{blank}$

$Y_{LD} = a + 3S_{y/x}$

To calculate Y_{LD}

Y_{LD} = 0.0075+ (3 X 0.00667)

= 0.02751

Calculating L_D using the regression equation

Y= 0.0153x + 0.0075

0.02751 = 0.0153x + 0.0075

x= (0.02751 – 0.0075)/ 0.0153

x= 1.30 mg/L

L_D = 1.30 mg/L

4.3.2. Standard curve for Reactive Blue 4

A standard curve was plotted for Methylene Blue at low concentration of 10mg/L to 60mg/L (Figure 4.32). Using y=mx, the unknown concentrations of final absorbance readings were calculated.

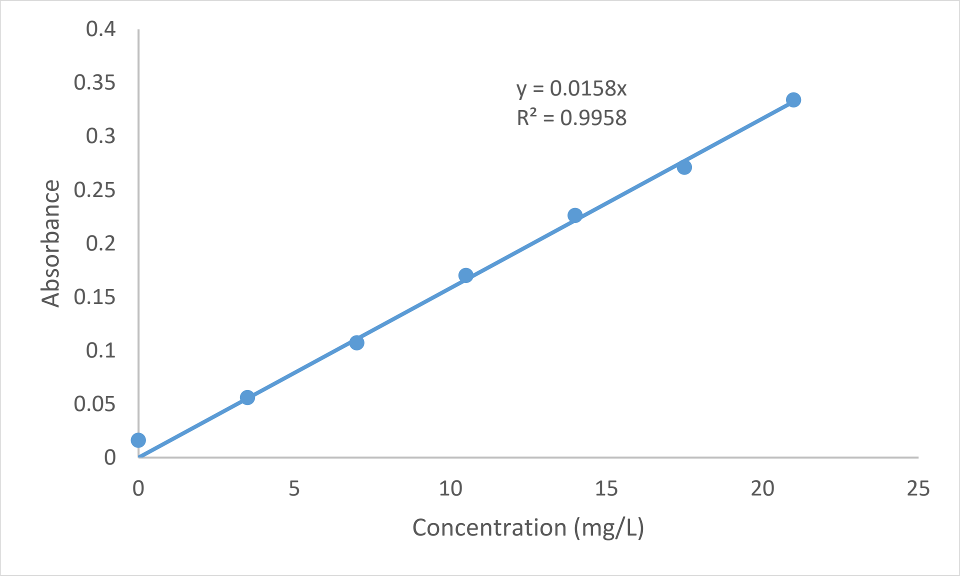


Figure 4. 32: Reactive Blue 4 standard curve

A summary of the batch experiments conducted for selecting the best adsorbents is given in Table 4.6

Table 4. 6. Summary table of the batch experiments carried out to select the best adsorbent for Methylene Blue (MB)

Subsection	Adsorbent	Calcined temperature (°C)	Conditions
4.3.3	100% Kaolinite (KC)	T0, T300, T400, T500 and T600	*Dose - 2.0 g;* *pH - neutral* *Initial conc., - 50 mg/L*
4.3.4	25% CPS/75% KC		
4.3.5	50% CPS/50% KC		
4.3.6	75% CPS/25% KC		
4.3.7	100% Bentonite (BC)		
4.3.8	25% CPS/75% BC		
4.3.9	50% CPS/50% BC		
4.3.10	75% CPS/25% BC		
4.3.11	100% CPS	CPS0, CPS100, CPS200, CPS300	

4.3.3. Adsorption process optimisation using 100% kaolinite

Using 100% kaolin calcined at 300–600°C for the adsorption of Reactive Blue 4, the percentage removal for all calcination temperature as seen in Figure 4.34 showed that calcined kaolin clay was not a high efficient, suitable adsorbent with <50% removal. In addition, results obtained showed that within 15 mins equilibrium adsorption can be achieved. With the continuous increase in contact time, which was run until 30 mins (Figure 4.33), there was no change in adsorption (absorbance value).

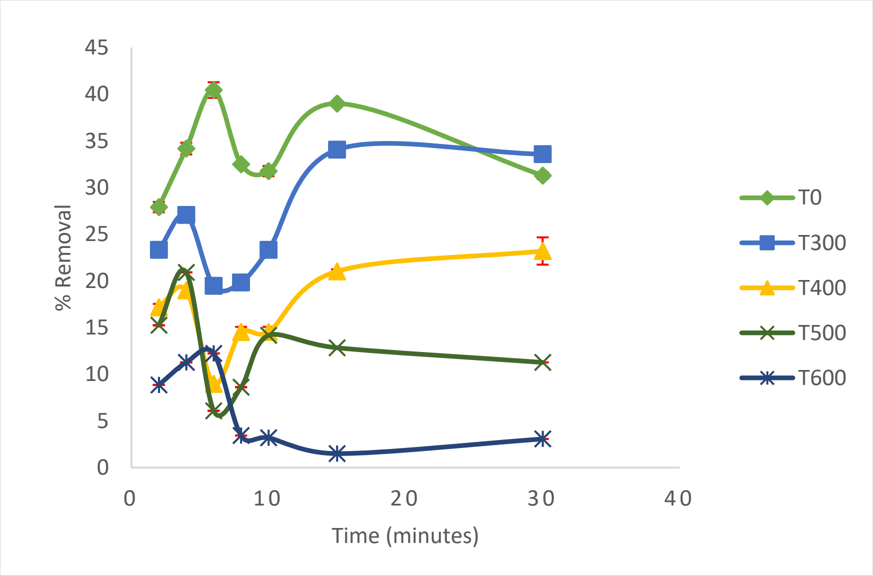


Figure 4. 33: Percentage removal for the adsorption of reactive blue using 100% kaolin

The comparison of average percentage removal of dye was done to understand and determine if there were similarities or differences in adsorption capacities of the adsorbent used. To determine which comparison statistical test to be used, it was essential to determine if the data followed the two assumptions of the parametric statistical tests. Hence, the goodness-of-fit (GOF) and homogeneity of variance (HOV) tests were done using the average percentage removal. For normality, the goodness-of-fit done using 3 different types all gave the same result, indicating that it is not a normal distribution (Table 4.7). For variance, results from Bartlett's test and Levene's Test for Homogeneity of Variance showed that the variances are equal at the 95% confidence level (Table 4.8). Following these tests, the data obtained for adsorption of Methylene Blue on kaolin calcined at selected calcination temperatures were non-parametric.

Table 4. 7. Results of various goodness of fit (GOF) tests for adsorption of Reactive Blue 4 onto kaolin using data from Figure 4.33.

Goodness of Fit test	H_O	H_1	P-value
SW	Normal distribution	Not a normal distribution	1.24×10^{-11}
SF	Normal distribution	Not a normal distribution	6.91×10^{-10}
PPCC	Normal distribution	Not a normal distribution	6.91×10^{-10}

Table 4. 8. Homogeneity of variance test for adsorption of Reactive Blue 4 onto kaolin using data from Figure 4.33.

HoV test	P-value
Bartlett's	0.7121
Levene's	0.7863

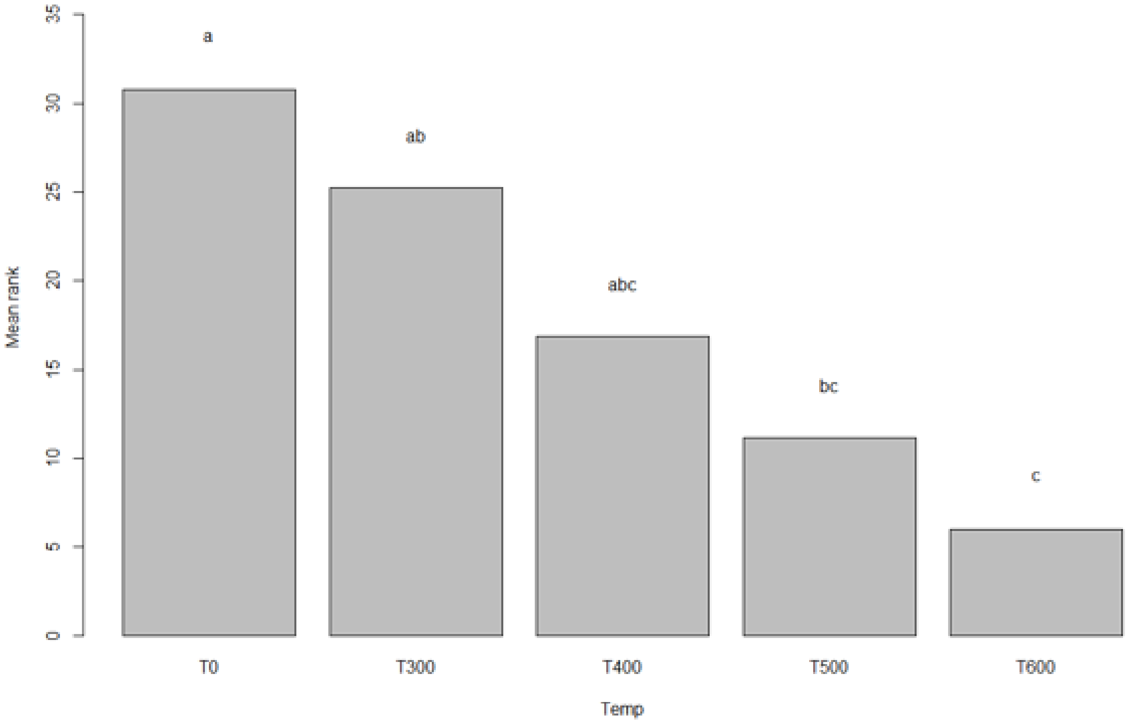


Figure 4. 34: Post hoc test for pairwise comparison (100% kaolinite)

(Same letters on bars indicate no significant difference)

KW test was used to investigate if there is a difference in the efficiency of the adsorbents used as part of this study. The test showed ($p = <0.05$) that there is a significant difference between the absorbent materials. A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.34). T0, T300, T400 and T500 have similar adsorption capacities and also showed that rapid adsorption of Reactive Blue 4 occurred (Figure 4.34). It was thus pointing out that any of these adsorbents can be used for adsorption of Methylene Blue. Also, T500 shares similar adsorption capacity with T600, which indicates that any of both can be used. It was clear that T400 could be a suitable adsorbent for this proportion as it shares similarities with prepared adsorbents. However, for this proportion, T0 was the suitable adsorbent because it rapidly removes Methylene Blue and requires no calcination to achieve the same adsorption efficiency as the calcined adsorbents (T300, T400 and T500). It was also observed that with increasing calcination temperature, there was a decline in the removal efficiency of the prepared adsorbent.

4.3.4. Adsorption process optimisation using 25% CPS/75% KC

For the adsorption of Reactive Blue 4 using 25% CPS/75% KC adsorbents, the adsorption was rapid for adsorbents T300 and T400, and no absorbance reading was obtained. The absence of absorbance reading shows that the final reading is below the detection limit. The concentration calculated for below detection limit was used for calculating the percentage removal. No change in percentage removal was observed with an increase in agitation time. For T0 and 25/75 adsorbent calcined at T500 and T600, less than 50% removal was observed (Figure 4.35). For statistical analysis, the first step was to analyse the data to determine if it was parametric or non-parametric. To do this, the variance and normality of the data were analysed. For normality, three goodness-of-fit tests were done (Table 4.9). For variance, Bartlett's test and Levene's test for homogeneity of variance were used. For variance, the results obtained showed that the variance of each percentage removal is not equal to 1; hence, indicating that the data are not equal. Both tests have shown that the results obtained for the adsorption of reactive blue using 25/75 adsorbents was non- parametric. Furthermore, it was observed that results for subsequent adsorption experiments were not normally distributed, hence, non-parametric. Thus, repeated writing of goodness-of-fit and homogeneity of variance tests was not done.

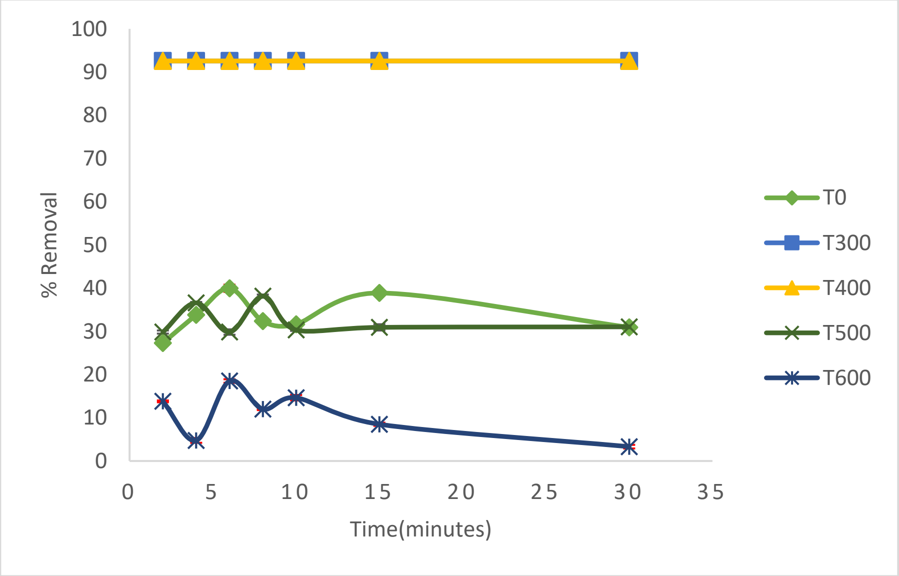


Figure 4. 35: Percentage removal for adsorption of Reactive Blue 4 using 25% CPS/75% KC.

Table 4. 9. Results of various goodness of fit (GOF) tests for adsorption of Reactive Blue 4 onto 25% CPS/75% KC using data from Figure 4.35.

Goodness of Fit test	**H_O**	**H_1**	**P-value**
SW	Normal distribution	Not a normal distribution	2.5×10^{-14}
SF	Normal distribution	Not a normal distribution	3.1×10^{-12}
PPCC	Normal distribution	Not a normal distribution	3.1×10^{-12}

Table 4. 10. Homogeneity of variance for adsorption of Reactive Blue 4 onto 25% CPS/75% KC using data from Figure 4.35

HoV test	**P- value**
Bartlett's	$2.2 \text{ X } 10^{-16}$
Levene's	$3.4 \text{ X } 10^{-5}$

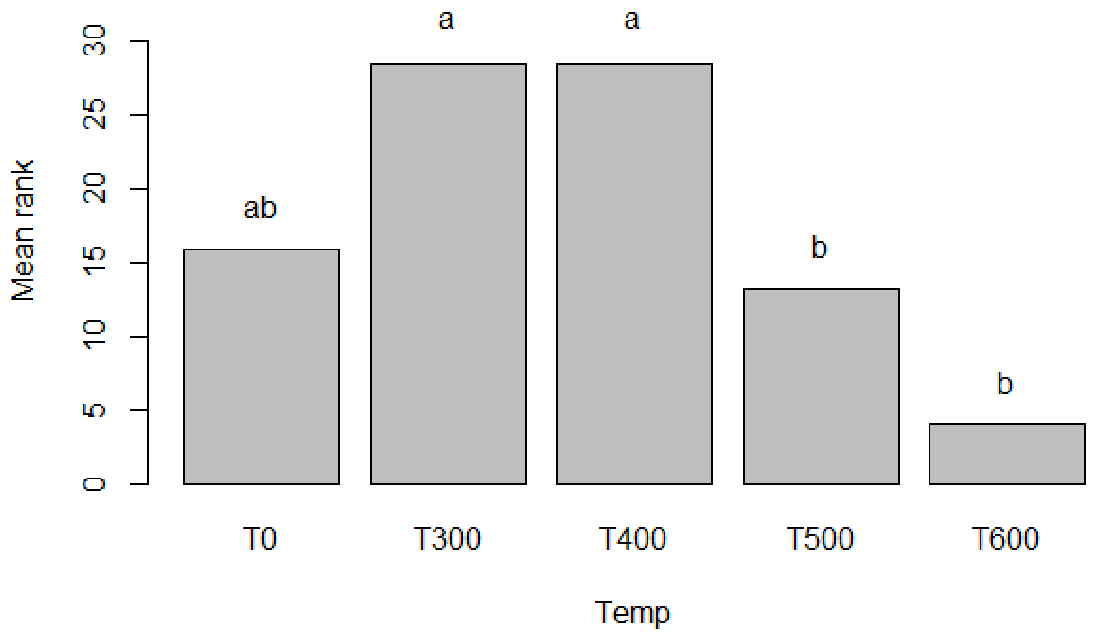


Figure 4. 36: Post hoc test for pairwise comparison (25% CPS/75% KC)

(Same letters on bars indicate no significant difference)

KW test was used to investigate if there is a difference in the efficiency of the adsorbents used as part of this study. The test showed ($p = <0.05$) that there is a significant difference between the absorbent materials. Figure 4.36 shows the pairwise comparison for adsorption of Reactive Blue 4 using 25% CPS/75% KC. T0, T500 and T600 have similar adsorption capacities and also showed low adsorption efficiency with the low mean rank observed. T300 and T400 had the highest removal efficiency and share similarities in removal efficiency compared to other adsorbents for this proportion. Hence, any of these adsorbents (T300 or T400) can be selected as the optimum adsorbent, but T300 was selected because it is lower in calcination temperature than and still as efficient as T400.

4.3.5. Adsorption process optimisation using 50% CPS/50% KC

For 50% CPS/50% KC, Figure 4.37 shows the percentage removal of dye that occurs when adsorption of Reactive Blue 4 was done using calcined 50% CPS/50% KC adsorbents and compared with uncalcined kaolin. The results showed that adsorbents T400 had rapid adsorption within 5 mins, and no reading was seen; hence, the value for detection limit for Reactive Blue 4 was used to calculate the percentage removal (Figure 4.37).

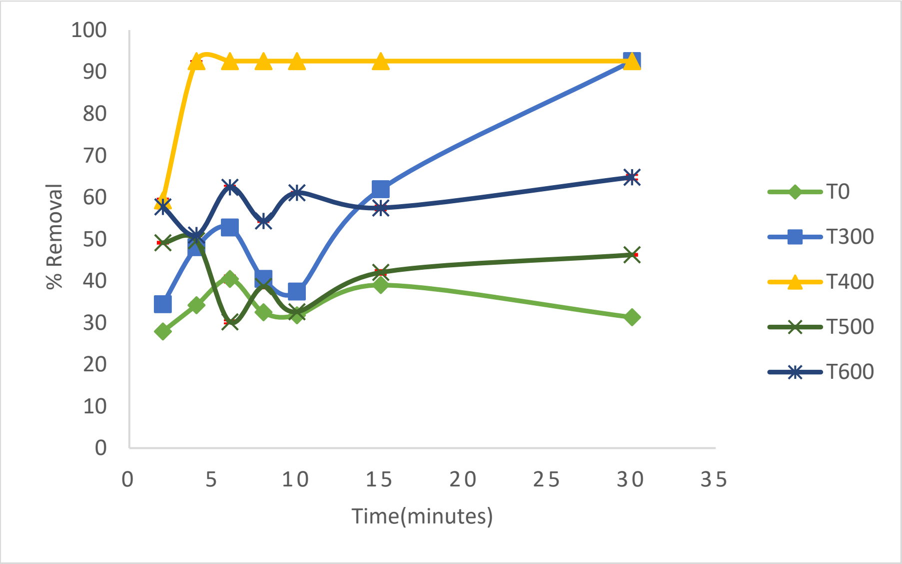


Figure 4. 37: Percentage removal for the adsorption of Reactive Blue 4 using 50% CPS/50% KC.

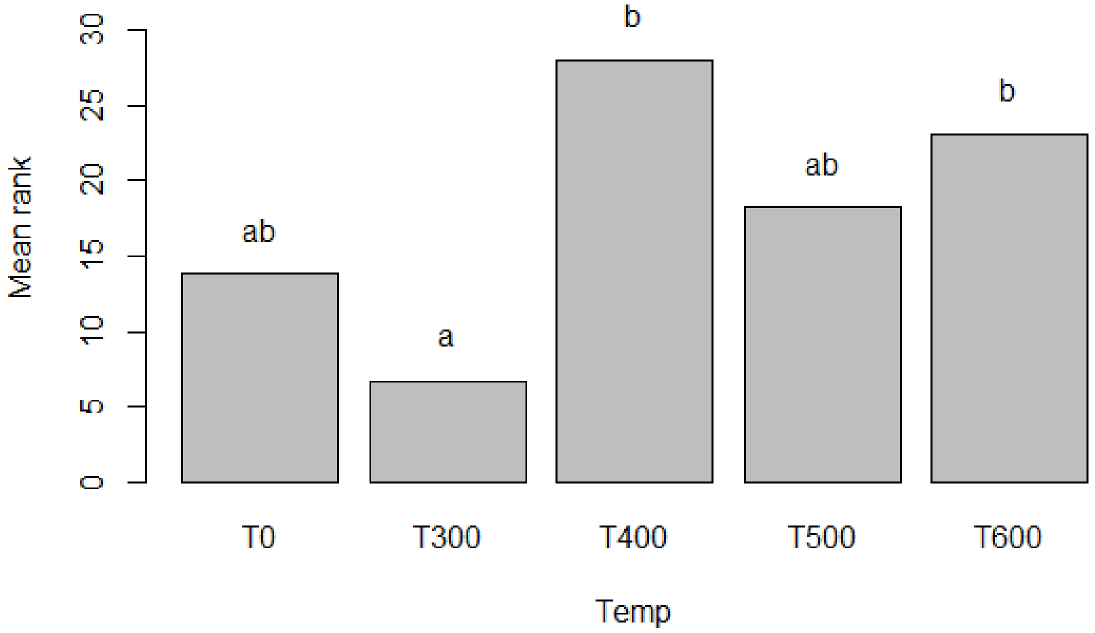


Figure 4. 38: Post hoc test for pairwise comparison (50% CPS/50% KC)

(Same letters on bars indicate no significant difference)

KW test was used to determine if there were differences in the efficiency of the adsorbents used. The test indicated (p= <0.05) that there was a significant difference between the absorbents. A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.38). Adsorbents T0, T300, and T500 share similar removal efficiency and T0, T400 and T600 share similar adsorption efficiency. Although any of the adsorbents that had similar efficiency to T400 can be used, however, T400 had the most rapid adsorption for Methylene Blue. Hence, T400 was a suitable adsorbent.

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4.3.6. Adsorption process optimisation using 75% CPS/25% KC

For adsorption of Reactive Blue 4 using 75% CPS/25% KC adsorbents, it was observed that the increase of milled CPS improved the removal efficiency of the prepared adsorbents calcined at higher temperatures. In addition, the adsorbents calcined at higher temperatures were observed to have better percentage removal of dye. For T600, maximum percentage removal of dye was seen within 5 mins. For T500, the maximum percentage removal was recorded as 2 mins, however with the increase in time, the efficiency of the adsorbent reduced which could be due to the reduction of available active sites on the adsorbent. Unlike T500, for adsorption of Reactive Blue 4 using T400, had a percentage removal that increased with an increase in agitation time. For adsorbent calcined at T300 and T0, the percentage removal of dye was lower compared to the rest for this proportion (Figure 4.39).

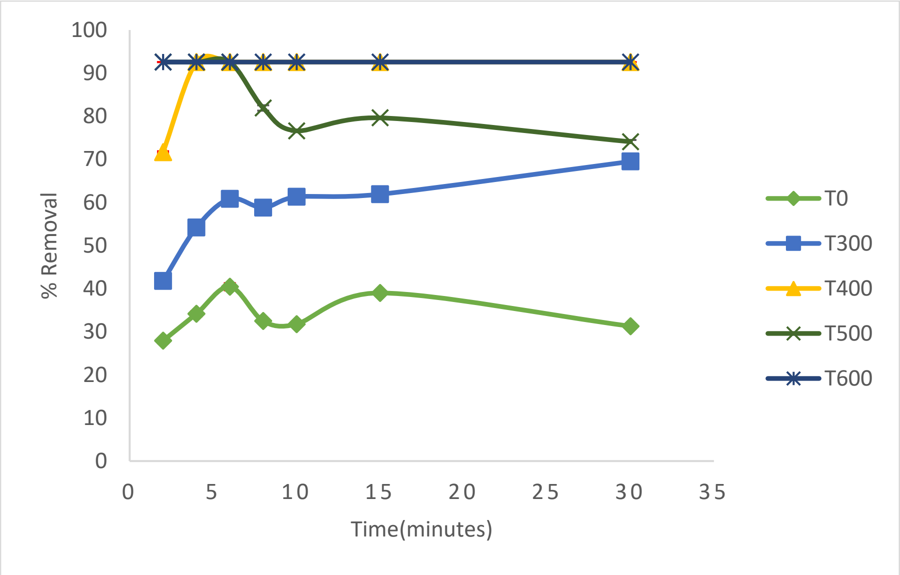

Figure 4. 39: Percentage removal for the adsorption of Reactive Blue 4 onto 75% CPS/25% KC.

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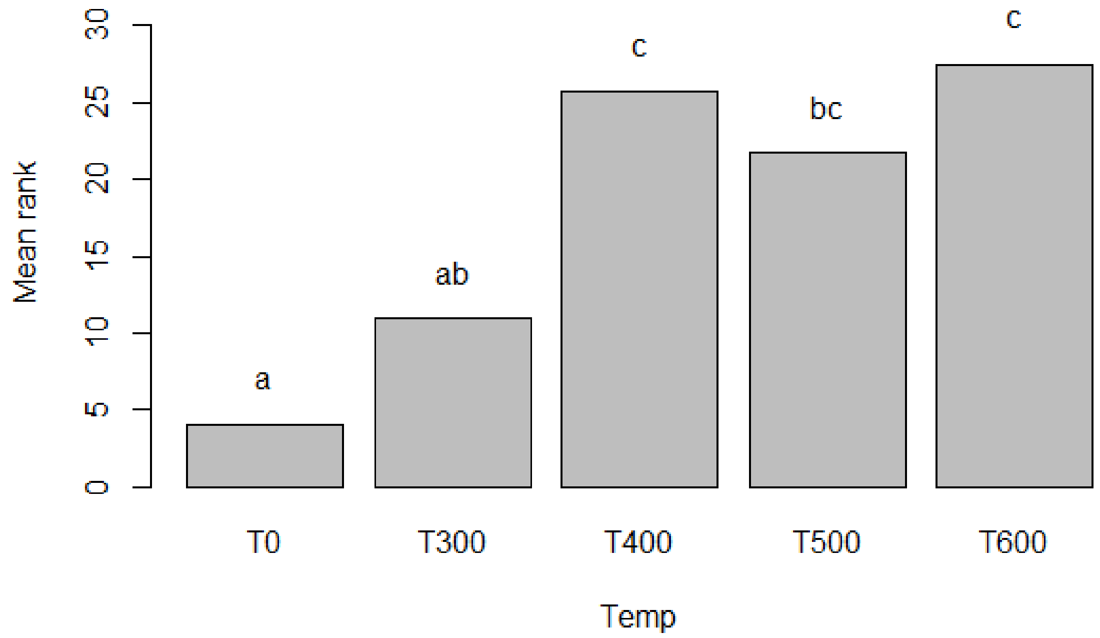

Figure 4. 40: Post hoc test for pairwise comparison (75% CPS/25% KC)

(Same letters on bars indicate no significant difference)

Kruskal-Wallis test was used to determine the relationship and comparison of the adsorbents efficient for this proportion and result ($p= <0.05$) showed that the efficiency of the adsorbents is different. A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.40), and it was observed that adsorbent T600 had a better removal efficiency than the other adsorbents calcined in this proportion. Hence, T600 was selected as a suitable adsorbent for this proportion.

4.3.7 Adsorption process optimisation using 100% bentonite

Using 100% bentonite calcined at different temperatures (300–600^{O}C) for the adsorption of reactive blue. For all adsorbent used in for this proportion had a percentage removal that was <50%. The maximum removal was seen at T300 and T400 (Figure 4.41).

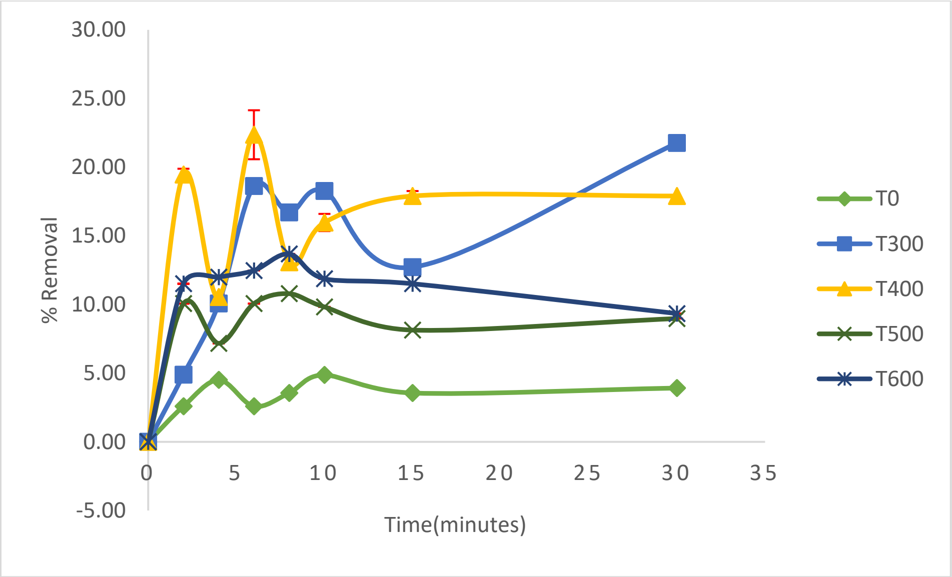

Figure 4. 41: Percentage removal for adsorption of Reactive Blue 4 onto 100% bentonite.

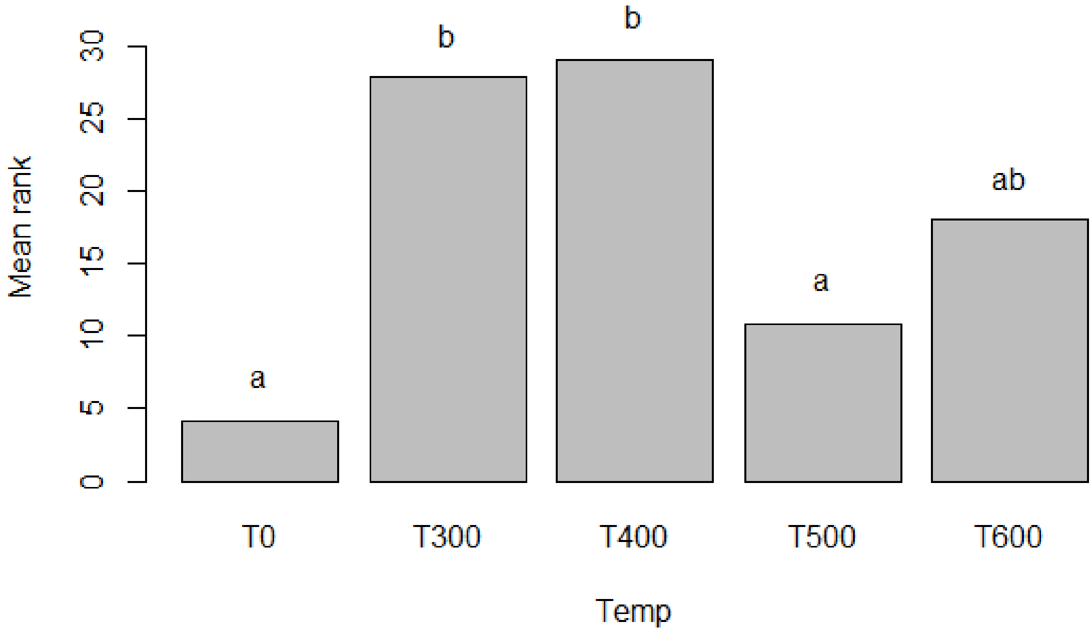

Figure 4. 42: Post hoc test for pairwise comparison (100% bentonite)

(Same letters on bars indicate no significant difference)

The Kruskal-Wallis test was used for determining if there were differences or similarities between the adsorbents used and p= <0.05 indicated that there were differences. A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.42). Figure 4.43 illustrates the removal efficiency of each adsorbent used for the adsorption of reactive blue in this proportion. T300 T400 and T600 share similarities in removal efficiency as results show that the removal efficiencies of these adsorbents were low. However, T400 was selected as a suitable adsorbent.

4.3.8. Adsorption process optimisation using 25% CPS/75% BC

Using 25% CPS/75% BC adsorbent, the adsorption was not rapid until 15 mins into the adsorption process (Figure 4.43). For T400, there was a gradual increase from and similar results were found for the adsorbent T300. The Kruskal-Wallis test was done and p= <0.05 indicated that there were differences in the efficiency of the adsorbents used for this proportion.

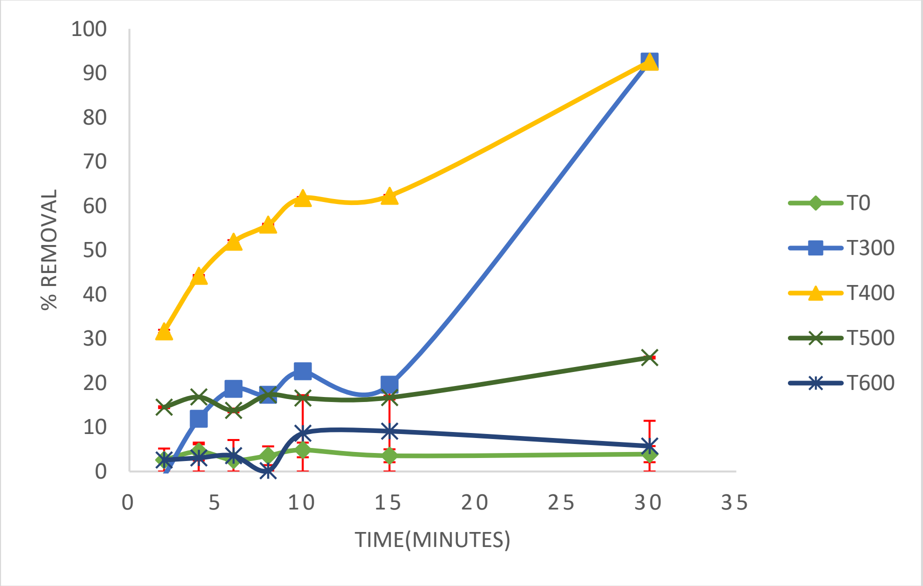

Figure 4. 43: Percentage removal for adsorption of Reactive Blue 4 onto 25% CPS/75% BC.

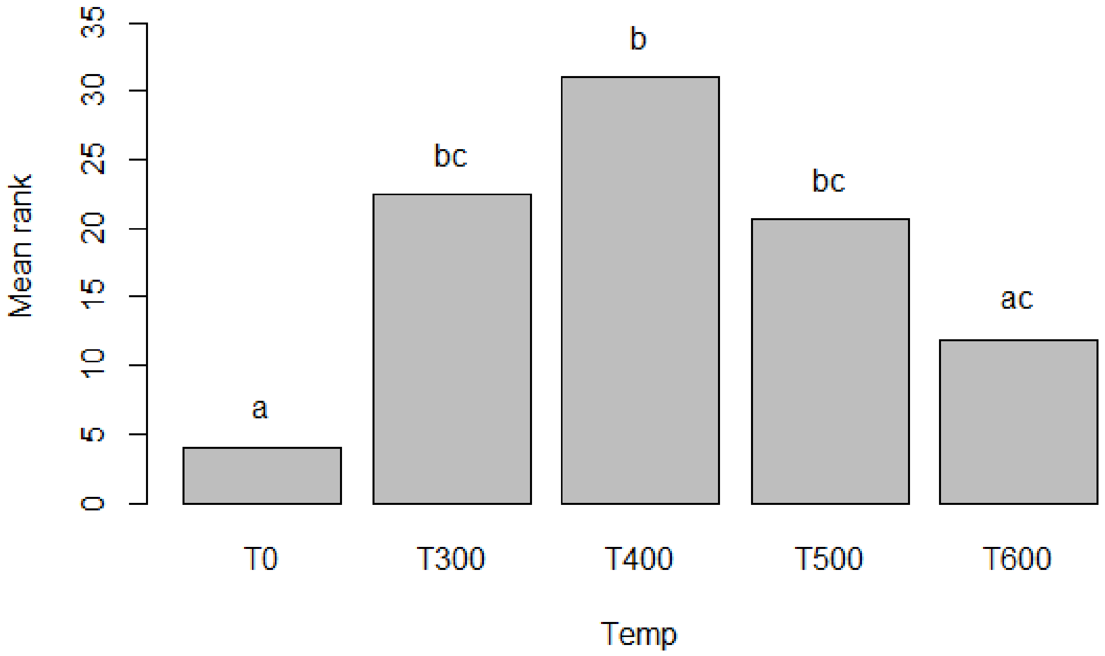

Figure 4. 44: Post hoc test for pairwise comparison (25% CPS/75% BC).

(Same letters on bars indicate no significant difference)

Post-hoc test was used for pairwise comparison in order to select the best adsorbent material (Figure 4.45). Figure 4.45 represents the removal efficiency of the adsorbent used for of 25/75(CPS/BC) used for the adsorption of Reactive Blue 4. T0 and T600 share similar removal efficiency. Also, T300 and T400 share similar removal efficiency. T400 was selected as the adsorbent that yielded the favourable removal efficiency, and the removal was seen to be rapid as well.

4.3.9. Adsorption process optimisation using 50% CPS/50% BC

For 50% CPS/50% KC adsorbents calcined at T300 and T400 showed a gradual increase in percentage removal for both adsorbents (Figure 4.45). The use of adsorbent calcined at T500, T600 and T0 resulted in low percentage removal of dye (<25%).

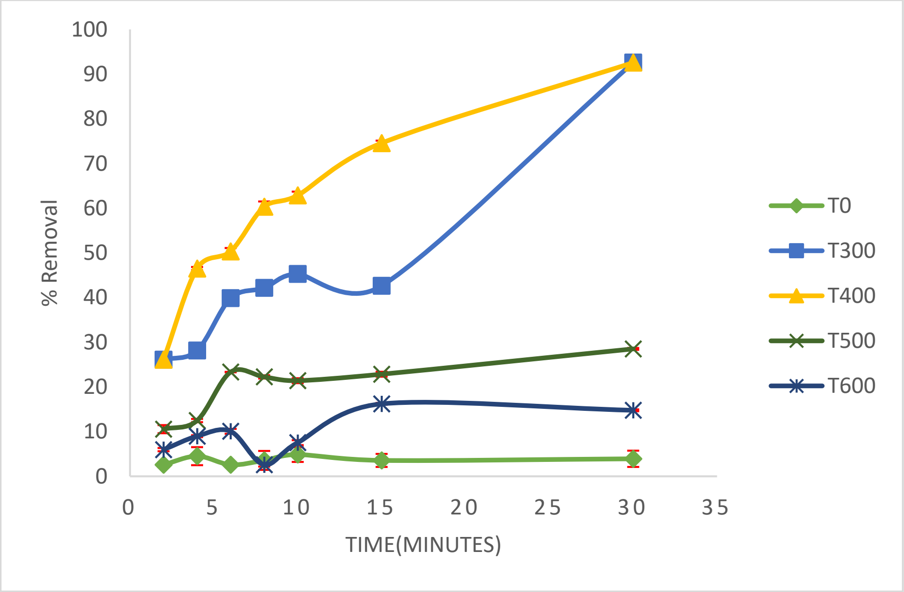

Figure 4. 45: Percentage removal for the adsorption of Reactive Blue 4 onto 50% CPS/50% BC

KW test was used to investigate if there is a difference in the efficiency of the adsorbents used in this study. The test showed (p = <0.05) that there is a significant difference between the absorbent materials. A post-hoc test was also used for pairwise comparison in order to select the best adsorbent material (Figure 4.46). Similar to adsorbent of the 25% CPS/75% BC proportion, results showed that T400 of the 50% CPS/50% BC as a suitable adsorbent.

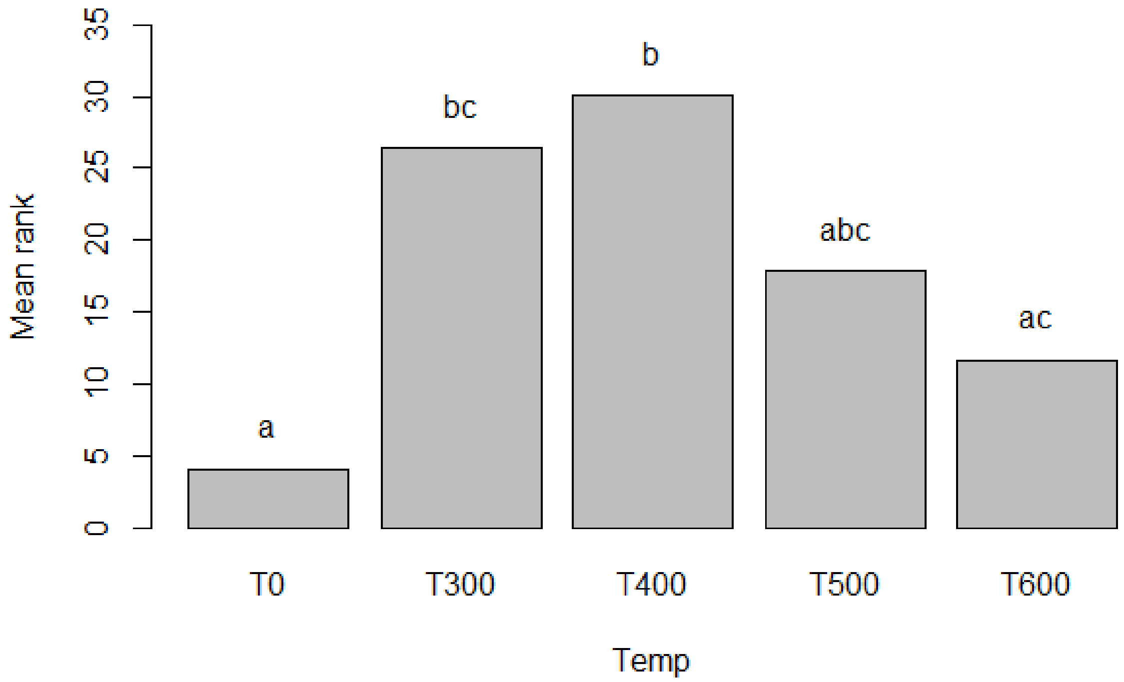

Figure 4. 46: Post hoc test for pairwise comparison (50% CPS/50% KC CPS/BC)

(Same letters on bars indicate no significant difference)

4.3.10. Adsorption process optimisation using 75% CPS/25% BC

The results obtained from adsorption of Reactive Blue 4 using 75% CPS/25% BC adsorbents was different from other proportions for the same dye. It was observed that maximum percentage removal was at 4 mins and 2 mins for adsorbents T400 and T300 and no changes were recorded for both adsorbents as agitation time increased. For T500 and T600, the maximum percentage removal was 62% and 50.9% at 2 mins (Figure 4.47). However, with an increase in agitation time, there was a decrease in percentage removal, suggesting that most actives sites on the surface of the adsorbents have been occupied.

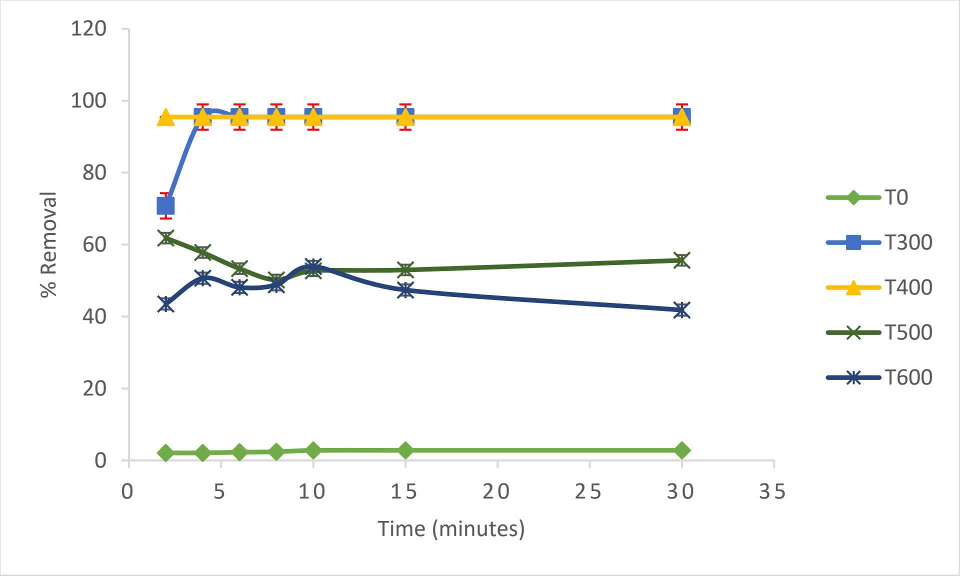

Figure 4. 47: Percentage removal for the adsorption of Reactive Blue 4 onto 75% CPS/25% BC (CPS/BC).

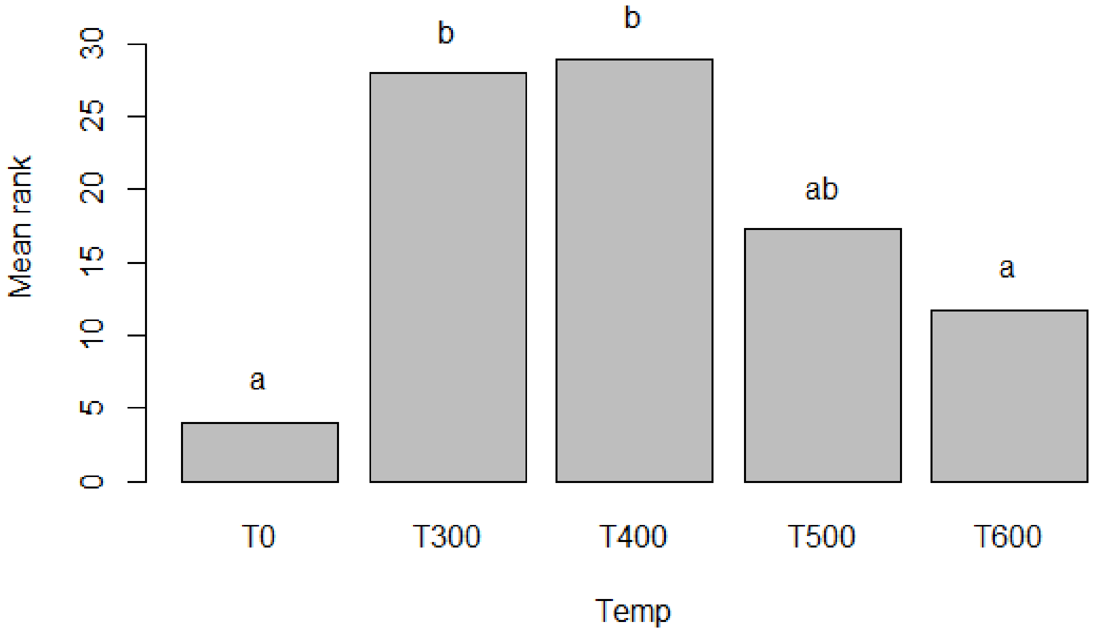

Figure 4. 48: Post hoc test for pairwise comparison (75% CPS/25% KC)

(Same letters on bars indicate no significant difference)

KW test was used to investigate if there is a difference in the efficiency of the adsorbents used as part of this study. The test showed (p = <0.05) that there is a significant difference between the absorbents. A post-hoc test was used for pairwise comparison in order to select the best adsorbent material (Figure 4.48). Figure 4.48 shows the comparison between the removal efficiency of adsorbents used for this proportion. The result indicated that T300 and T400 have similar removal efficiencies. However, the adsorption of Reactive Blue 4 using T400 was faster than the other adsorbent. Therefore, T400 was a suitable adsorbent for this proportion.

4.3.11. Adsorption process optimisation using milled *carica papaya* seeds

The results for adsorption using *carica papaya* seeds showed that the calcination of CPS did improve its removal efficiency. With CPS0, CPS100 AND CPS200, the results showed that the percentage removal of dye was significantly low. CPS300 had the maximum percentage removal of dye, and it was the suitable adsorbent for this proportion

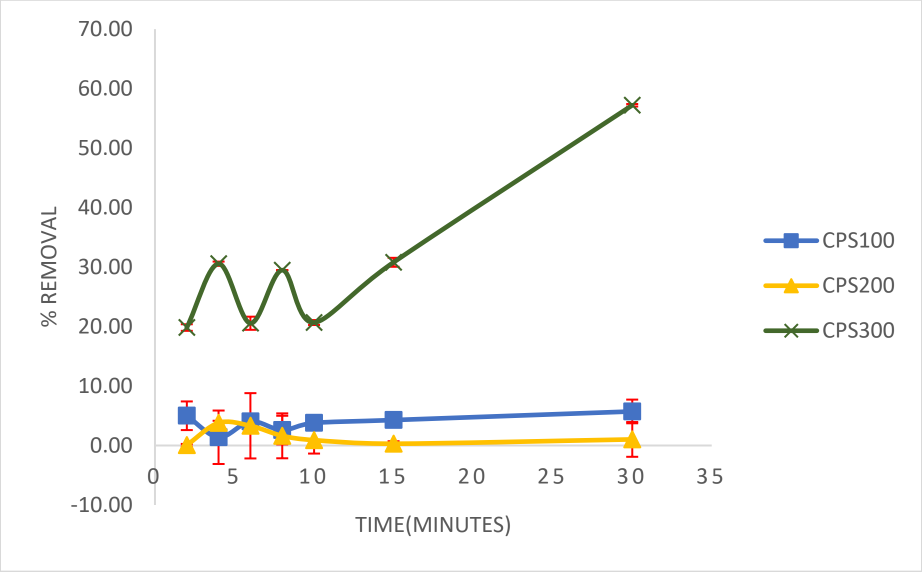

Figure 4. 49: Percentage removal for the adsorption of Reactive Blue 4 onto 100% CPS

Table 4. 11. Summary of adsorbents selected at the proportions used for this study.

Dye	Proportion	Adsorbent
Methylene Blue	100% Kaolinite (KC)	T0
	25% CPS/75% KC	
	50% CPS/50% KC	
	75% CPS/25% KC	
	100% Bentonite (BC)	T500
	25% CPS/75% BC	T300
	50% CPS/50% BC	
	75% CPS/25% BC	
	100% CPS	CPS200
Reactive Blue 4	100% Kaolinite (KC)	T0
	25% CPS/75% KC	T300
	50% CPS/50% KC	T400
	75% CPS/25% KC	T600
	100% Bentonite (BC)	T400
	25% CPS/75% BC	
	50% CPS/50% BC	
	75% CPS/25% BC	
	100% CPS	CPS300

4.4. Parameters for Methylene Blue using Uncalcined kaolin (T0)

4.4.1. Effect of adsorbent dose

The effect of adsorbent dose on the removal of Methylene Blue dye in aqueous solution was studied using T0 at a dose varying from 0.4 g to 1.8 g. Figure 4.50 shows the plot of qt (amount of dye adsorbed per gram of adsorbent) against adsorbent dose variation of adsorbent dose. From Figure 4.50, it was observed that percentage dye removal increased with increase in adsorbent dose from 0.4 g/93 % removal – 0.8 g/99.98 % removal. The uptake of Methylene Blue dye can be as a result of the increase of surface area as the adsorbent dose increased. With increasing adsorbent dose, there was no significant increase in percentage removal. The maximum adsorption capacity recorded was 11.67 mg/g the reverse was observed as increasing dose resulted in a decrease in the amount of dye adsorbed.

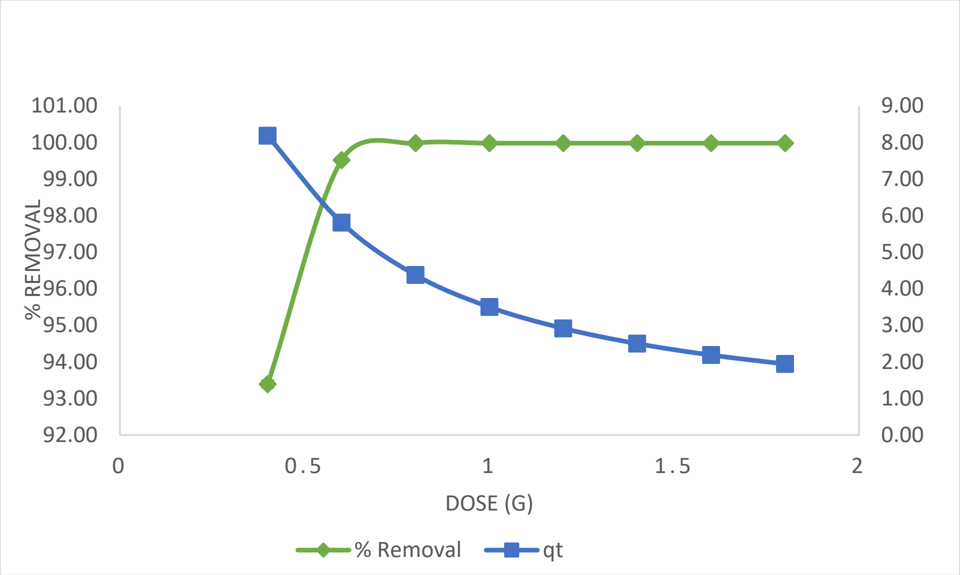

Figure 4. 50: Effect of adsorbent dose using uncalcined kaolin for the adsorption of Methylene Blue.

4.4.2. Effect of pH

Figure 4.51 shows the effect of pH on the adsorption of Methylene Blue onto T0. The sorption of dye onto an adsorbent differs when there are changes in the pH of the solution. The effect of pH on the removal of Methylene Blue in aqueous solution using T0 was studied in pH range 2-10/50 mg/L. It was found that in an acidic pH and basic pH, 99 % removal occurred.

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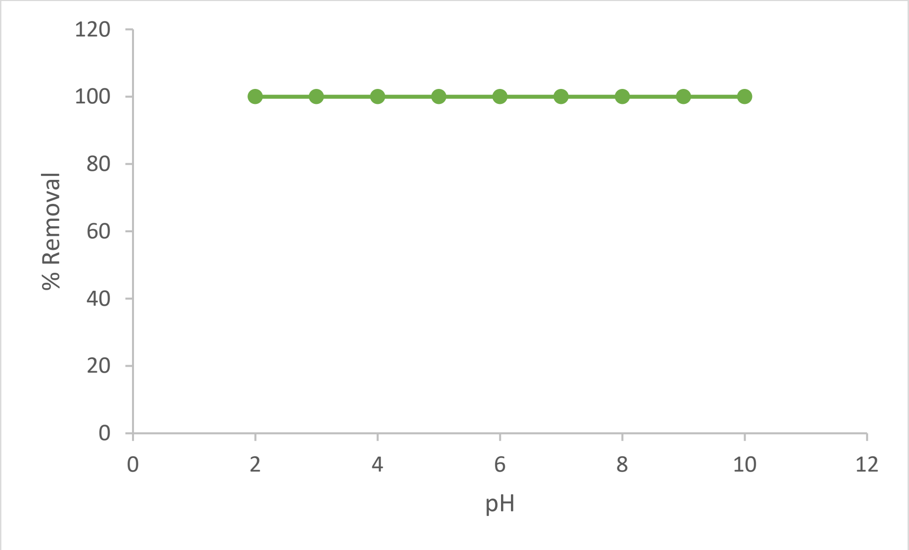


Figure 4. 51: Effect of pH using T0 for adsorption studies of Methylene Blue.

4.4.3. Effect of initial concentration

The effect of initial dye concentration on the removal of Methylene Blue onto T0 was studied, and results are plotted in Figure 4.52. The maximum adsorption capacity was 14.75 mg/g at 210 mg/L. However, the percentage removal of dye tells a different story. At 70 mg/L and 105 mg/L, 99.98 % removal was observed, and with an increase in concentration, there was a decrease in percentage removal. Hence showing that the adsorption efficiency of uncalcined kaolin is more efficient at initial concentrations lower than 105 mg/L.

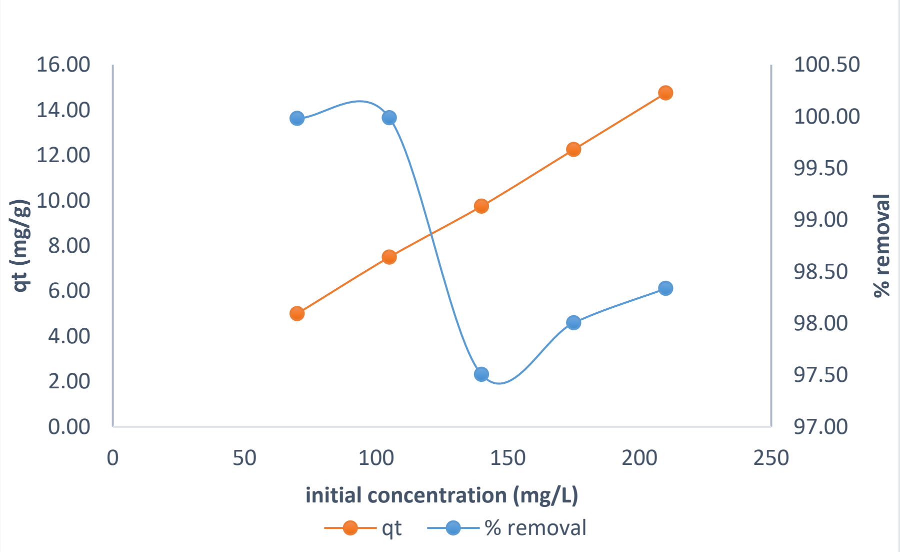


Figure 4. 52: Effect of initial concentration using T0 for adsorption studies of Methylene Blue

4.5 Parameters for Methylene Blue using Bentonite and CPS

Unlike uncalcined kaolin being the suitable adsorbent amongst all the proportion for the adsorption of Methylene Blue, the use of bentonite identified different suitable adsorbents at different proportions.

4.5.1 Effect of adsorbent dose

With T500 (Bentonite), the effect of adsorbent dose on the adsorption of Methylene Blue onto 100% bentonite clay was investigated using an adsorbent dose of 0.4-1.8 g/50 mg/L and the results obtained are shown in Figure 4.53. With increasing dosage from 0.4 g to 1.2 g, there was a slight increase in percentage removal of dye which was due to the increase of available adsorption sites on the surface of the adsorbent. The continuous increase of adsorbent dose did not yield an increase in percentage removal. For the equilibrium adsorption capacity, a decrease was observed with increasing adsorbent dosage.

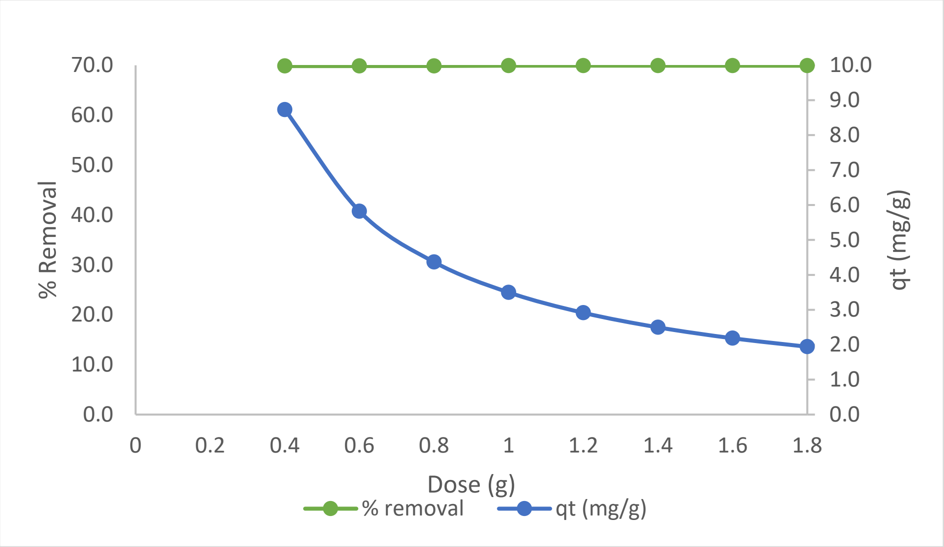


Figure 4. 53: Effect of adsorbent dose using T500 (Bentonite) for adsorption studies of Methylene Blue

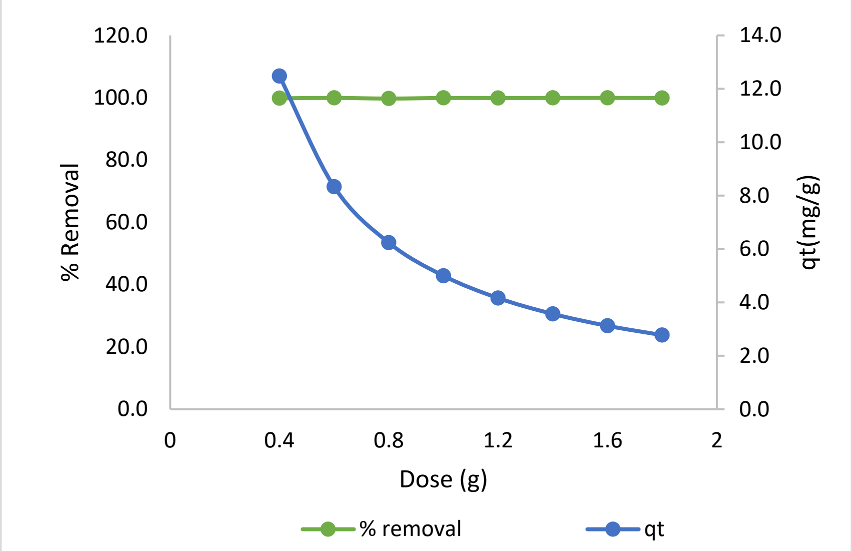


Figure 4. 54: Effect of adsorbent dose using 25% CPS/75% BC (T300) for adsorption studies of Methylene Blue

This could be a result of the overlapping of adsorption sites, thus reducing thus the availability of active sites for adsorption of Methylene Blue. For the 25% CPS/75% BC, the removal of Methylene Blue was investigated, and the adsorbent dose used range from 0.4 g to 1.8 g. It was observed that with adsorbent dose from 0.4 g to 0.6

g there was a slight increase in percentage removal, however, with a further increase to 0.8g, there was a sharp decrease (Figure 4.54). For 75% CPS/25% BC (Figure 4.55) a slight decline in percentage removal was seen as the dose increased and this was also observed for adsorption capacity. The maximum adsorption capacity for all the adsorbents used was 12.49 mg/g.

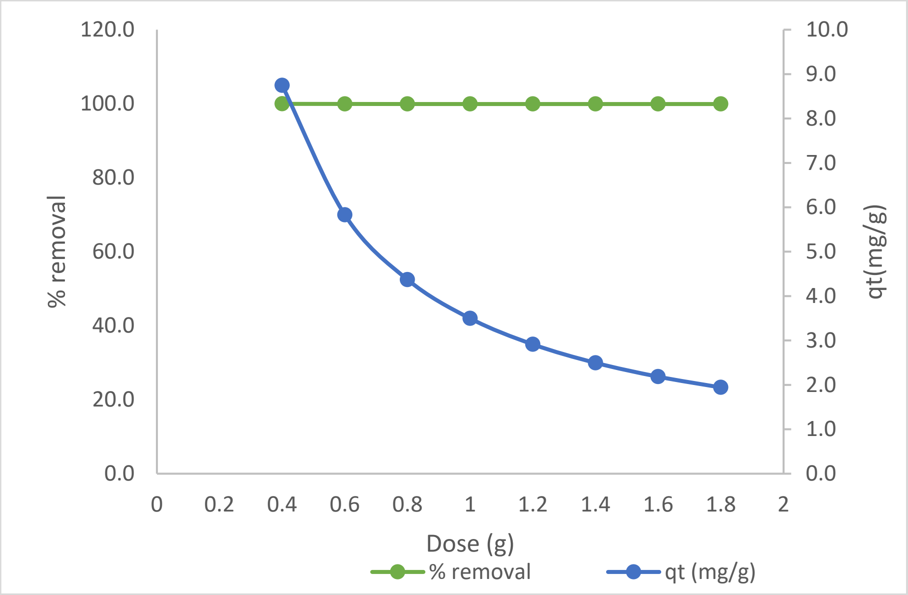


Figure 4. 55: Effect of adsorbent dose using 75% CPS/25% BC (T300) for adsorption studies of Methylene Blue

4.5.2. Effect of pH

The effect of pH for selected adsorbents for each proportion can be seen in Figure 4.56. It was observed that for T500 (100% bentonite), 99% removal was recorded at pH 2.0. However, for T300 (25% CPS/75% BC) with increasing pH from 2.0 to 5.0, there was an increase in percentage removal, which decreased after 5.0. Thus, indicating that the adsorption of Methylene Blue T300 (25% CPS/75% BC) would be more efficient in an acidic medium. However, at pH 5.0 there was an increase after which a decrease in percentage removal was recorded. For T300 (75% CPS/25% BC), an increase in pH from 2.0 top 5.0 also resulted in increased percentage removal; however, after 5.0, a decrease in percentage removal was recorded. Therefore, it was evident that for the adsorption of Methylene Blue onto calcined bentonite clay or a calcined homogenous mixture of bentonite clay and CPS, the use of an acidic medium will yield favourable results.

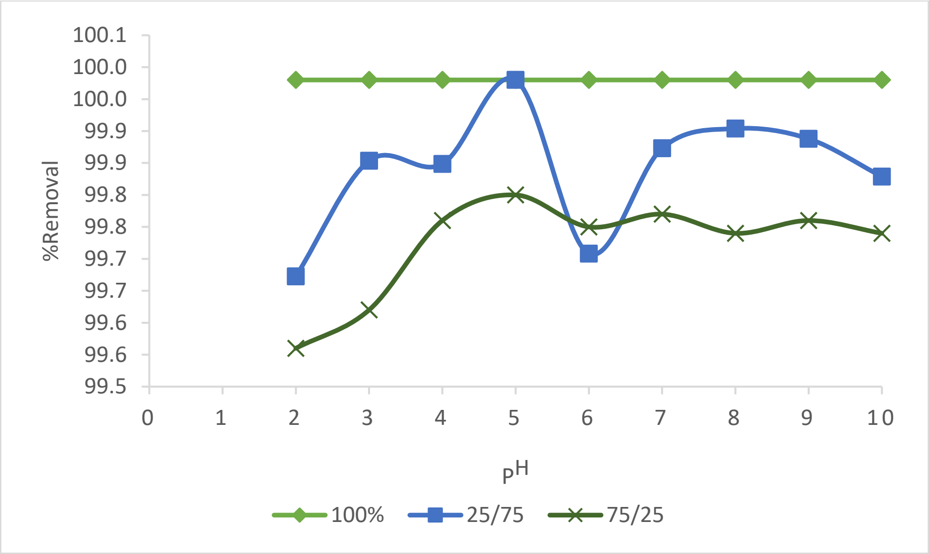


Figure 4. 56: Effect of pH on the adsorption of Methylene Blue using selected adsorbents for each proportion (CPS/BC)

4.5.3 Effect of initial concentration

Figure 4.57 shows the percentage removal of Methylene Blue at different initial concentrations (70–210 mg/L) using adsorbents of the homogenous mixture (CPS/bentonite) at different proportions. For Figure 4.57a, the adsorption of Methylene Blue onto T500 (100% bentonite) revealed results that showed high percentage removal >90% for 105 mg/L – 210 mg/L. Also, rapid removal was observed. The high percentage removal seen for this adsorbent is probably due to the adsorptive proprieties of its surface and availability of active sites. For Figure 4.57b, which was T300 (25% CPS/75% BC), it was observed that the adsorption process bears a semblance to adsorption of Methylene Blue using T500. Rapid adsorption occurred, and an increase in percentage removal was observed with an increase in agitation time for initial concentrations of 140 mg/L – 210 mg/L. Thus indicating the presence of available adsorption sites on the adsorbent irrespective of high concentration of Methylene Blue. However, for 105 mg/L, it was recorded that no change in percentage removal was observed after 30mins, which shows the equilibrium had been attained. Also, for Figure 4.57c, T300 (75% CPS/25% KC) > 90% percentage removal of dye was observed. The use of calcined bentonite and the calcined homogenous mixture of CPS and bentonite was favourable for the effect of initial concentration as all adsorbents showed favourable results.

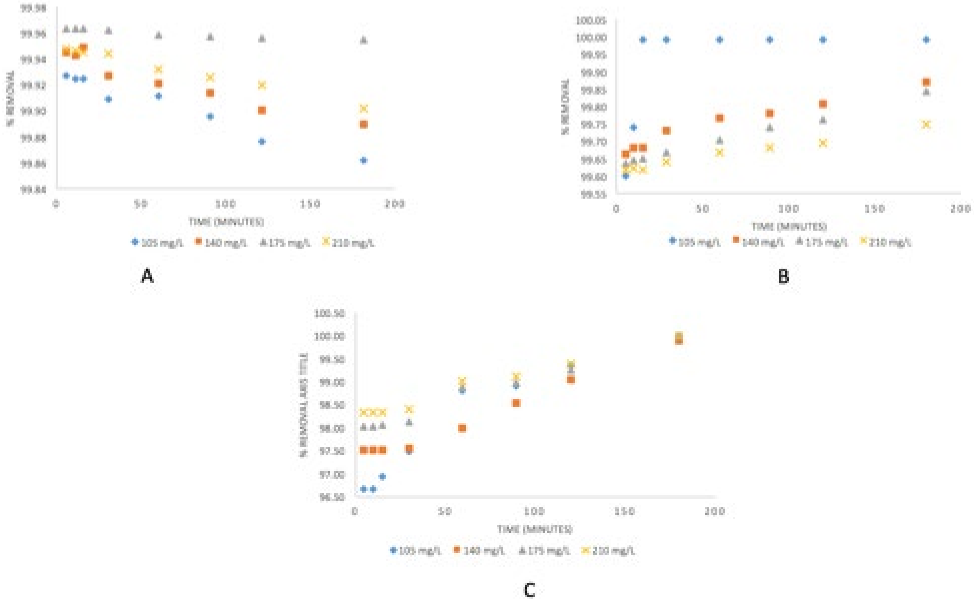


Figure 4. 57: Effect of initial concentration using T500 (100% bentonite), (b) using T300 (25% CPS/75% BC), (c) using T300 (75% CPS/25% KC).

4.6. Parameters for reactive blue using CPS and kaolin

4.6.1. Effect of adsorbent dose

From observation, it was seen that for all the proportion of adsorbents used, and the percentage removal was below 50% (Figures 4.58 and 4.59). For T0, the maximum percentage removal of 36.9% was recorded at dosage 1.8 g (Figure 4.58). Similarly, for 25% CPS/75% KC (T300) 37.5% removal was observed at 1.8 g adsorbent dosage (Figure 4.59).

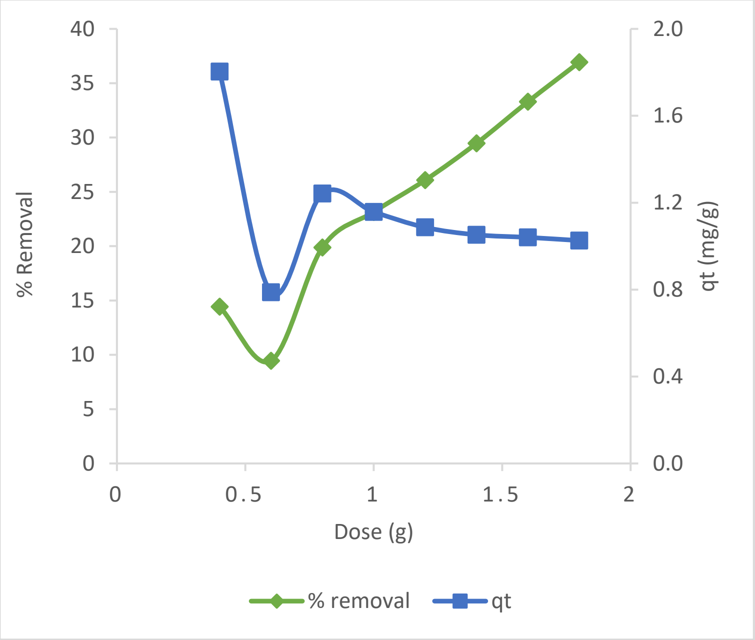


Figure 4. 58: Effect of adsorbent dose using T0 (100% kaolin) for adsorption studies of Reactive Blue 4

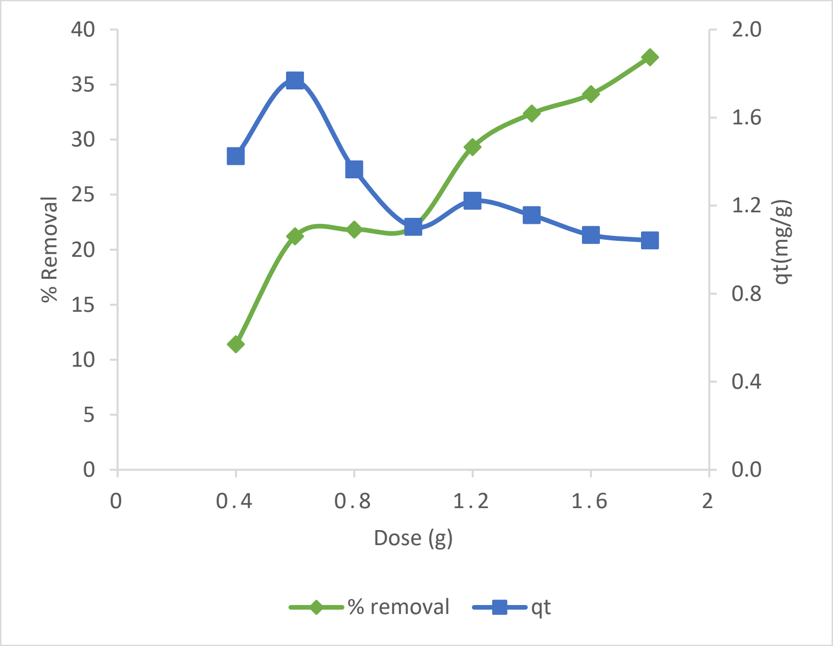


Figure 4. 59: Effect of adsorbent dose using 25% CPS/75% KC (T300) for adsorption studies of Reactive Blue 4

4.6.2 Effect of pH

The effect of pH on the percentage removal of Reactive Blue 4 dye from aqueous solution using CPS and kaolin in different proportions can be seen in Figure 4.60. For T0, the maximum percentage removal of 18.8% was recorded at pH 2.0, and a decrease to 11.9% at pH 10.0 was observed, thus, the acidic pH increase the removal of RB_4. The use of 25% CPS/75% KC had results similar to T0, whereby the maximum percentage removal of 20.1% at pH 3.0 was recorded, and with increasing pH, there was increase and decrease of percentage removal of dye and 19.5% at pH 10.0. For 75% CPS/25% KC, at pH 2.0, the maximum percentage removal was recorded and increasing the pH results in decrease with percentage removal of 12.2% at pH 10.0. From the results, it could be said that maximum removal occurs in the acidic medium and increase in pH or proportion of CPS does not increase percentage removal. As with other adsorbents in this study except 25/75, a decrease in percentage removal was observed as pH values were increased. Hence, showing that the pH medium significantly affects the removal efficiency of the adsorbents.

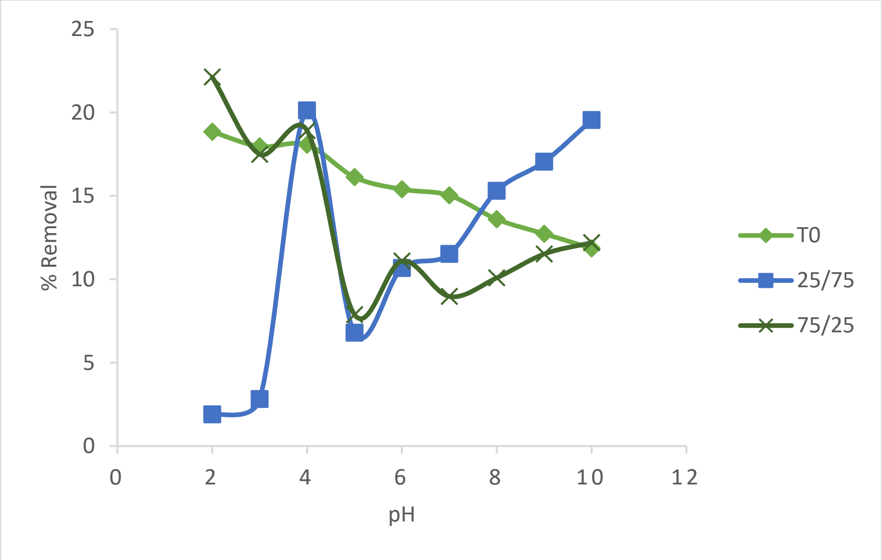


Figure 4. 60: Effect of pH using different proportions of CPS and KC for the adsorption of Reactive Blue 4

4.6.3 Effect of initial concentration

Figure 4.61 shows the effect of initial dye concentration on the adsorption of Reactive Blue 4 using selected adsorbents for each proportion. For T0(A) the maximum percentage removal for initial concentration 105–210 mg/L was seen to be

50.9%, 59.9%, 65.4% and 69% respectively. Results also indicated that there were an increase and decrease in percentage removal as agitation time increased. The results for 25% CPS/75% KC (B) had a very low percentage removal of below 20%. Hence, it is not a suitable adsorbent, and the low percentage removal could be as a result of the addition of CPS. For 75% CPS/25% KC (C), the maximum percentage removal of 36.4%, 34.6%, 33.5% and 32.8% respectively for 105–210 mg/L initial concentration at 180mins.

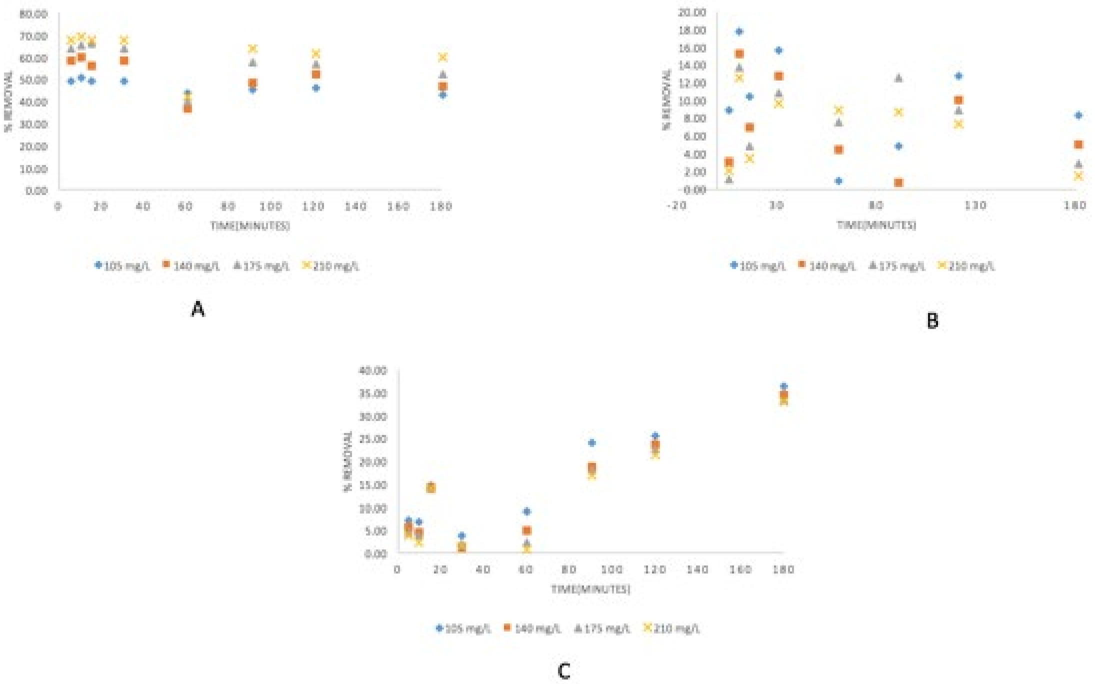


Figure 4. 61: Effect of initial concentration for the adsorption of Methylene Blue. (A) Using T0 (100% Kaolin) (B) using T300 (25% CPS/75% KC), (C) using T600 (75% CPS/25% KC).

4.7. Parameters for Reactive Blue 4 using bentonite clay and CPS

4.7.1 Effect of adsorbent dose

Using 25/75 (T400) proportion, it was observed that with increasing dosage (0.4–1.8 g) there was an increase in percentage removal (26.50% - 46.99%) which could be due to the increase of surface area and available active sites (Figure 4.62).

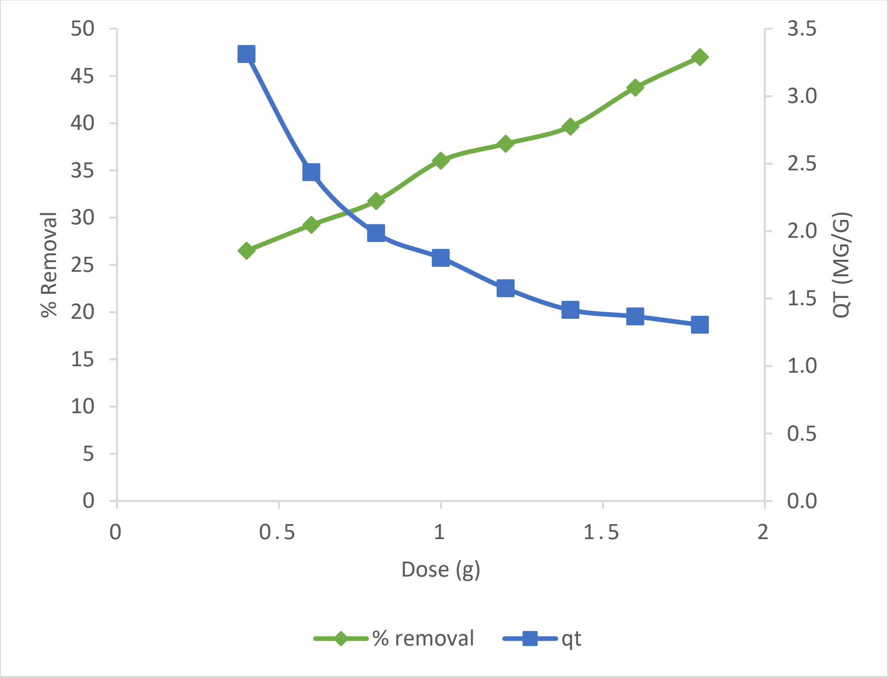


Figure 4. 62: Effect of adsorbent dose using 25% CPS/75% BC (T400) for adsorption studies of Reactive Blue 4

4.7.2. Effect of initial pH

Figure 4.63 shows the effect of pH on the adsorption of Reactive Blue 4 using selected adsorbents prepared at different proportions and calcined. For 100% bentonite (100Ben), was observed to increase with an increase in pH with maximum percentage removal of 66% seen at pH 10. Similarly, for adsorbents 25% CPS/75% BC, the highest percentage removal of 59.4% and 95.48% were respectively at pH 10. However, for adsorption using 75% CPS/25% BC adsorbent, the maximum percentage removal of 63% was recorded at pH 2, and there was a decrease with increasing pH. For the effect of pH, it was observed that the changes in pH values influenced the percentage removal of dye.

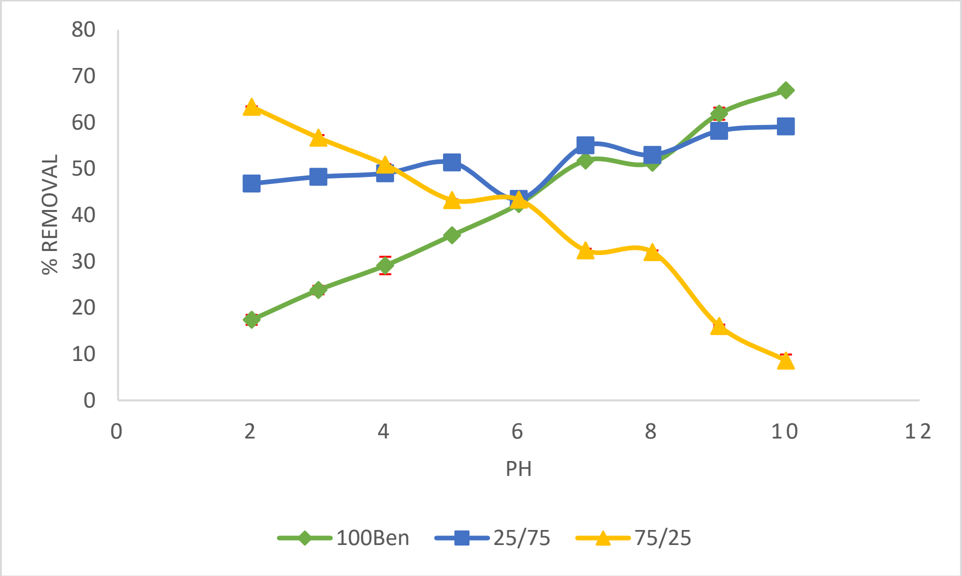


Figure 4. 63: Effect of pH on the adsorption of Reactive Blue 4 using calcined adsorbents (CPS/Bentonite)

4.7.3 Effect of initial concentration

Looking at Figure 4.64, For adsorption using 100Ben(T400), there was a continuous increase in percentage removal form 6.97% at 5 mins to 11.2% at 180mins. However, for 140–210 mg/L, a decrease in percentage removal was observed at these concentrations with an increase of agitation time. Thus indicating that the available active sites in the surface of 100Ben have been occupied, resulting in limited active sites. In addition, the percentage removal of dye recorded for the adoption of Reactive Blue 4 using 100Ben <50%. For adsorption using 25/75, it was observed that at all initial concentration, there was an increase in percentage removal with an increase in agitation time. The maximum percentage removal of 91.6% and 70.2% were seen at 180mins for 105 mg/L and 210 mg/L respectively. Although, with an increase in agitation time, there was a decrease in percentage removal as initial concentration increased. The decrease could be to the decrease of available active sites on the surface of adsorbent 25/75. For adsorption using 50% CPS/50% KC adsorbent results obtained showed that with an increase in agitation time, there was an increase in percentage removal with the maximum removal of 91.6% at 180 mins for 105 mg/L. With the increase in initial concentration, there was a decrease in percentage removal, the maximum percentage removal of dye for 140 mg/L, 250 mg/L and 300 mg/L was found to be 80.9%, 74.4%, 70.1% respectively. For adsorption using 75% CPS/25% KC adsorbent, the results obtained for all initial concentration, the percentage removal of dye was <50%.

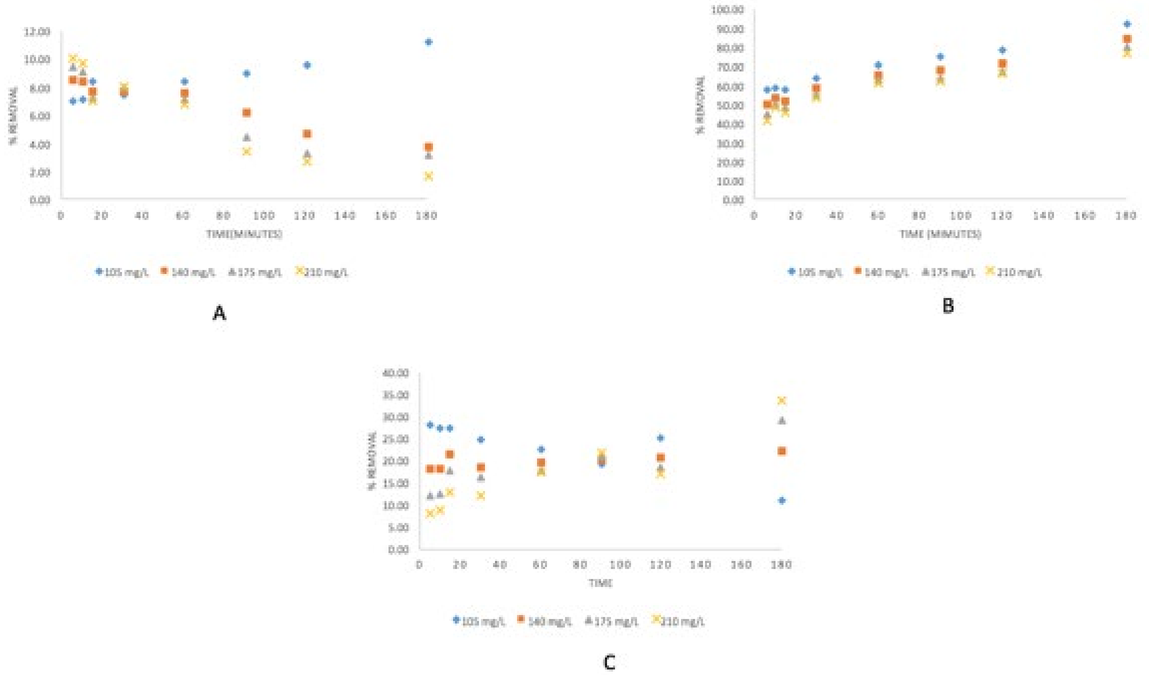


Figure 4. 64: Effect of initial concentration for the adsorption Methylene Blue. (A) Using T400 (100% Bentonite), (B) using T400 (25% CPS/75% BC), (C) using T500 (75% CPS/25% BC).

Furthermore, it was observed that the use of bentonite without the addition of milled CPS yielded less than 50% removal. However, the addition of milled CPS for 25/75 adsorbent, an increase of percentage removal of 50% was at all initial concentration of Reactive Blue 4 used. Although the expectation would be a continuous increase of milled CPS will result in increased percentage removal, but that was not the case for 75% CPS/25% KC adsorbent used for the adsorption of Reactive Blue 4. Hence, showing that 25*% CPS*/75*% BC* is a suitable adsorbent to be used.

4.8. Adsorption isotherms

Langmuir and Freundlich's isotherms were used to describe the mechanism and favorability of the adsorbents for the adsorption of Methylene Blue and Reactive Blue 4 dyes. For adsorption isotherms, the correlation coefficient was used to determine the best fitting isotherm to the experimental data. In addition, using the Langmuir isotherm model, the adsorption process is considered favourable when the dimensionless separation factor (R_L) (Eq. 9) value is between 0 and 1. In this study, the initial concentration used was 100-300 mg/g. Also, to calculate R_L, the Langmuir constant (K_L) with the best fit was used. Furthermore, Table 4.12 shows the linear forms of isotherm models and plots for calculation isotherm parameters using the slope and intercept.

$$R_L = \frac{1}{1+K_L+C_O} \qquad (9)$$

Table 4. 12. Linear forms of isotherm models used for the analysis of experimental data of adsorption studies for Methylene Blue and Reactive Blue 4

Isotherm model	Linear form	Plot	Slope	Intercept
Langmuir isotherm 1	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	$C_e/q_e \ vs \ C_e$	$m = \frac{1}{q_m}$	$c = \frac{1}{q_m K_L}$
Langmuir isotherm 2	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m.K_L} . \frac{1}{C_e}$	$1/q_e \ vs \ 1/C_e$	$m = \frac{1}{q_m.K_L}$	$c = \frac{1}{q_m}$
Langmuir isotherm 3	$q_e = q_m - (\frac{1}{K_L}) \frac{q_e}{C_e}$	$q_e \ vs \ q_e/C_e$	$m = \frac{1}{K_L}$	$c = q_m$
Langmuir isotherm 4	$\frac{q_e}{C_e} = K_L q_m - K_L q_e$	$q_e/C_e \ vs \ q_e$	$m = K_L$	$c = K_L q_m$
Freundlich isotherm	$log \ q_e = \log K_f + \frac{1}{n} \log C$	$\log q_e \ vs \log C_e$	$m = \frac{1}{n}$	$c = \log K_f$

Adapted from Chen (2015).

q_m= Maximum adsorbent capacity (mg/g)

K_L= Langmuir constant (L/mg)

Kf= Freundlinch constant

C_e= Equilibrium concentration (mg/L)

q_e= Adsorption capacity at equilibrium (mg/g)

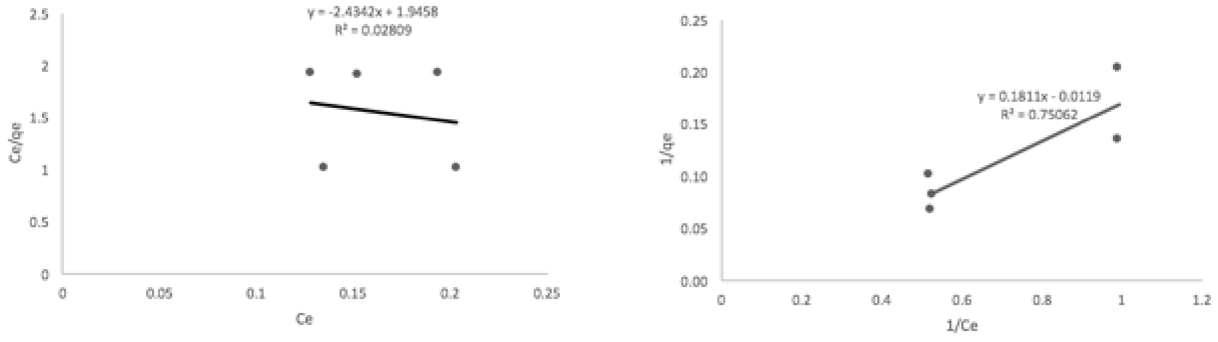
C_O= Initial concentration (mg/L)

4.8.1. Methylene Blue

4.8.1.1. Using 75% CPS/25% BC

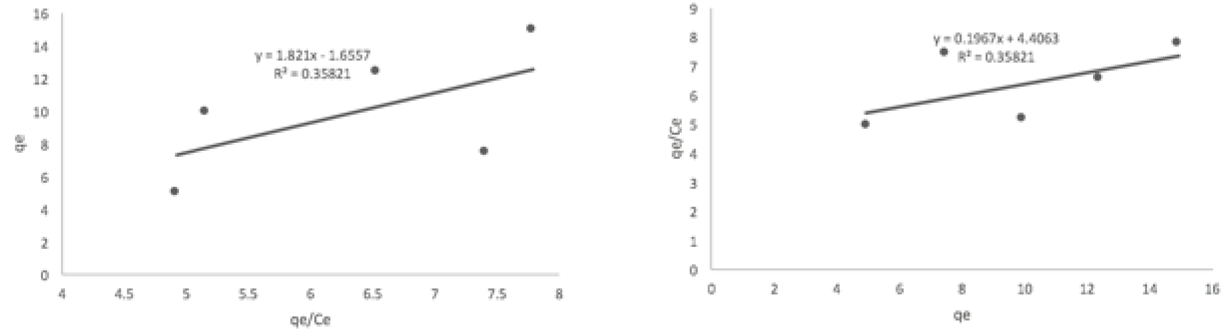
Figure 4.65 and 4.66 shows the linear fittings of Langmuir and Freundlich adsorption isotherms for 75% CPS/25% BC. Table 4.13 summarises the isotherm parameters obtained from the linear fittings and their correlation coefficients (r^2). According to the r^2 seen for the parameters in Table 4.12, the Freundlich model fitted the experimental data best by linear analysis and Langmuir did not fit the experimental data.

For the dimensionless factor (R_L), R_L values were between -0.132 to -0.053 with an increasing initial concentration of dye from 100 mg/L to 300 mg/L(Table 4.13) which, indicates that the adsorption of Methylene Blue onto 75% CPS/25% BC was not favourable.



Langmuir isotherm 1

Langmuir isotherm 2



Langmuir isotherm 3

Langmuir isotherm 4

Figure 4. 65: Linear fitting plots of Langmuir isotherms for adsorption Methylene Blue onto 75% CPS/25% BC adsorbent.

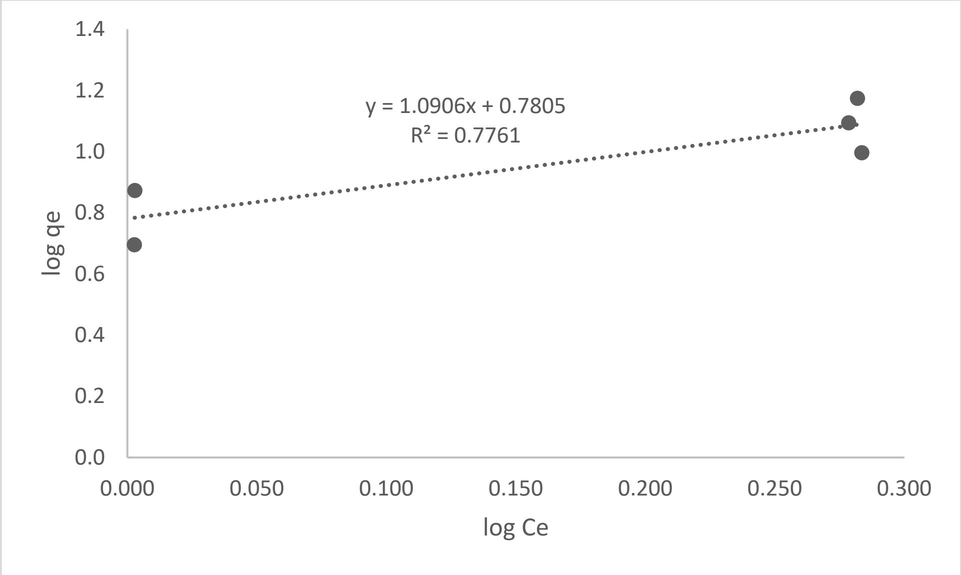


Figure 4. 66: Linear fitting plot of Freundlich isotherm model plot for Methylene Blue onto 75% CPS/25% BC adsorbent.

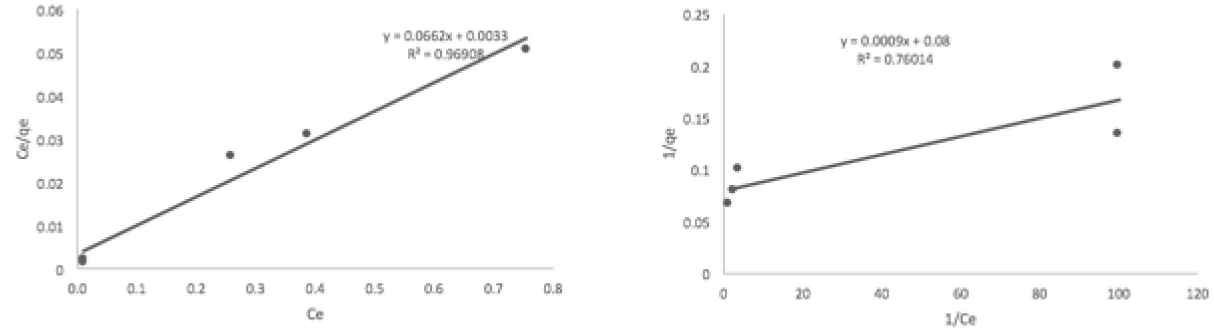
Table 4. 13. Langmuir and Freundlich isotherm parameters obtained by linear fittings of 75% CPS/25% BC adsorbent.

Isotherm models	
Langmuir 1 qm= -0.411mg/g K_L = -1.250L/mg r^2= 0.0228	Freundlich K*f*= 6.0325mg/g n= 0.917 R^2= 0.7761
Langmuir 2 q_m= 8.4x104 K_L= -0.0657L/mg r^2= 0.751	
Langmuir 3 q_m= -1.65mg/g K_L= 0.55L/mg r^2= 0.358	
Langmuir 4 q_m= 22.4mg/g K_L= 0.19L/mg r^2=0.358	
Separation factor (R_L) 100 mg/L= -0.132 150 mg/L = -0.11 200 mg/L = -0.081 250 mg/L = -0.065 300 mg/L = -0.053	

4.8.1.2. Using 25% CPS/75% BC

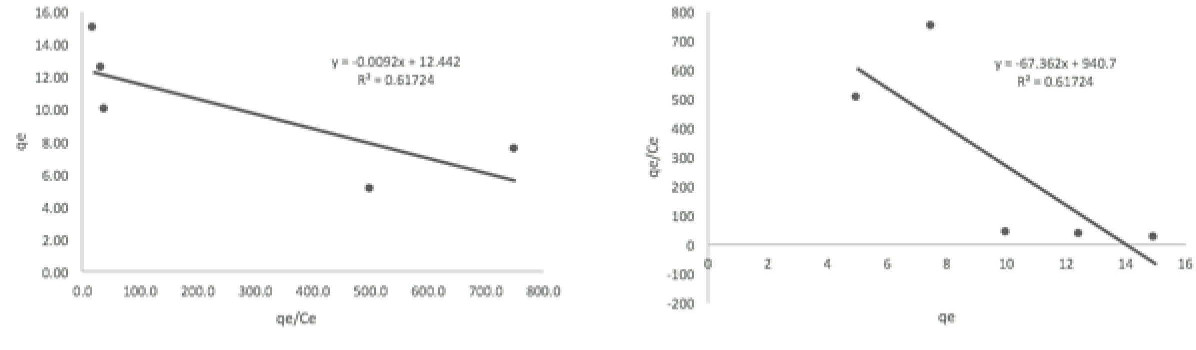
Figure 4.67 and 4.68 shows the linear fittings of Langmuir and Freundlich adsorption isotherms for 25% CPS/75% BC. Table 4.14 summarises the isotherm parameters obtained from the linear fittings and their correlation coefficients (r^2). According to the r^2 seen for the parameters in Table 4.14, the Langmuir 1 model fit the experimental data best by linear analysis and Freundlich did not fit the experimental data.

For the dimensionless factor (R_L), R_L[2] values were between 4.98 x 10^{-4} and 1.66x 10^{-4} with an increase in the initial concentration of dye from 100 mg/L to 300 mg/L (Table 4.14). Hence, indicating the favorability of the adsorption of Methylene Blue onto 25% CPS/75% BC.



Langmuir isotherm 1

Langmuir isotherm 2



Langmuir isotherm 3

Langmuir isotherm 4

Figure 4. 67: Linear fitting plots of Langmuir isotherms for adsorption Methylene Blue onto 25% CPS/75% BC adsorbent.

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[2] It was observed that increase of initial concentration of dye resulted in decrease of RL value. The RL value moves closer to zero. With R_L, R_L= 0 (Linear); R_L>1 (Unfavourable adsorption process); 0>R_L<1= Favourable adsorption.

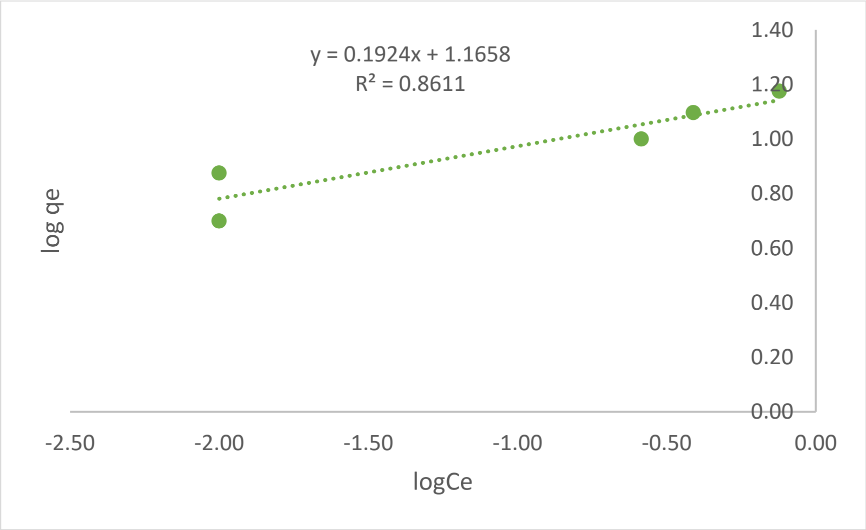


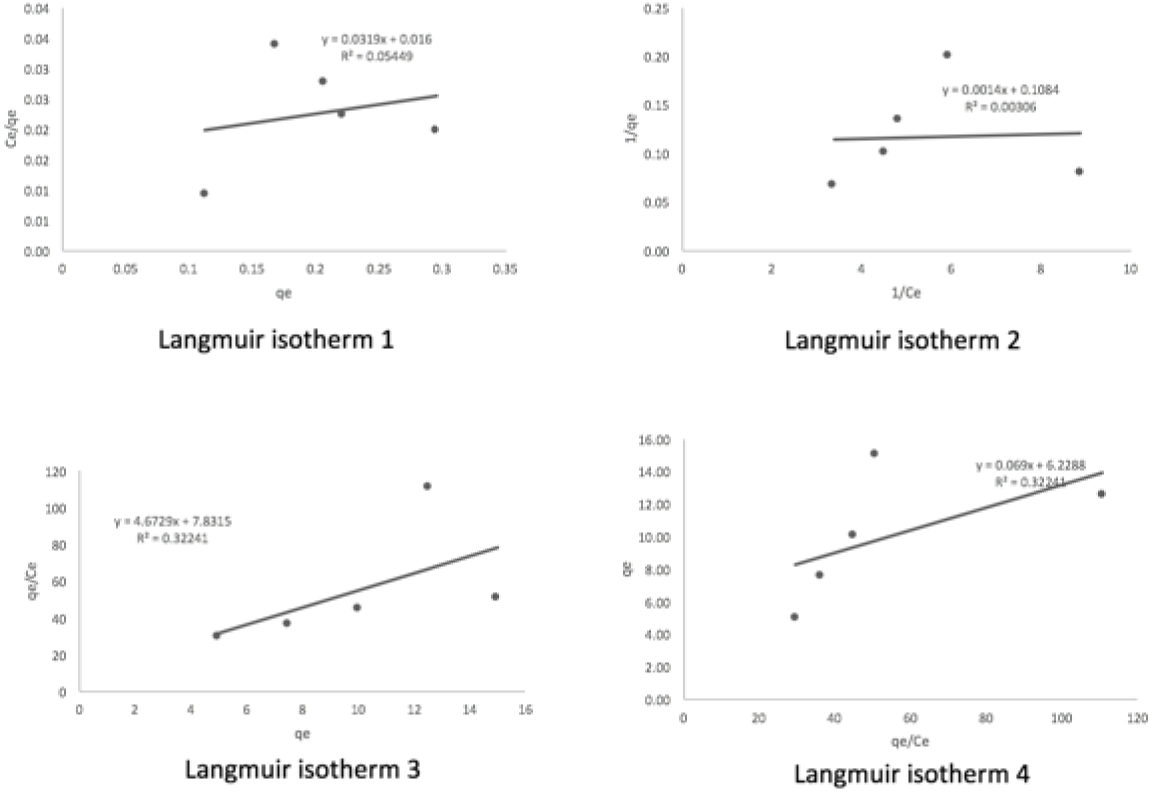
Figure 4. 68: Linear fitting plots of Freundlich isotherm for adsorption Methylene Blue onto 25% CPS/75% BC adsorbent.

Table 4. 14. Langmuir and Freundlich isotherm parameters obtained by linear fittings of 25% CPS/75% BC adsorbent.

Isotherm models	
Langmuir 1 q_m= 15.10 mg/g K_L = 20.06 L/mg r^2= 0.969	**Freundlich** K*f*= 14.09 mg/g n= 6.92 R^2= 0.8724
Langmuir 2 q_m= 12.5 mg/g K_L= 88.8 L/mg r^2= 0.7601	
Langmuir 3 q_m= 12.44 mg/g K_L= -108.69 L/mg r^2= 0.6172	
Langmuir 4 q_m= -67.36 mg/g K_L= -13.96 L/mg r^2=0.6172	
Separation factor (R_L) 100 mg/L= 4.98×10^{-4} 150 mg/L = 3.3×10^{-4} 200 mg/L = 2.49×10^{-3} 250 mg/L = 1.99×10^{-4} 300 mg/L = 1.66×10^{-4}	

4.8.1.3. Using 100% bentonite (T400)

Figure 4.69 and 4.70 shows the linear fittings of Langmuir and Freundlich adsorption isotherms for 100% bentonite. Table 4.15 summarises the isotherm parameters obtained from the linear fittings and their correlation coefficients (r^2). According to the r^2 seen for the parameters in Table 4.15, the Langmuir model was the best fit for the experimental data by linear analysis, and Freundlich did not fit the experimental data. For the dimensionless factor (R_L), R_L values calculated (Table 4.15) indicated that the adsorption of Methylene Blue onto 100% bentonite was favourable.



Langmuir isotherm 1

Langmuir isotherm 2

Langmuir isotherm 3

Langmuir isotherm 4

Figure 4. 69: Linear fitting plots of Langmuir isotherms for adsorption Methylene Blue onto 100% Bentonite adsorbent.

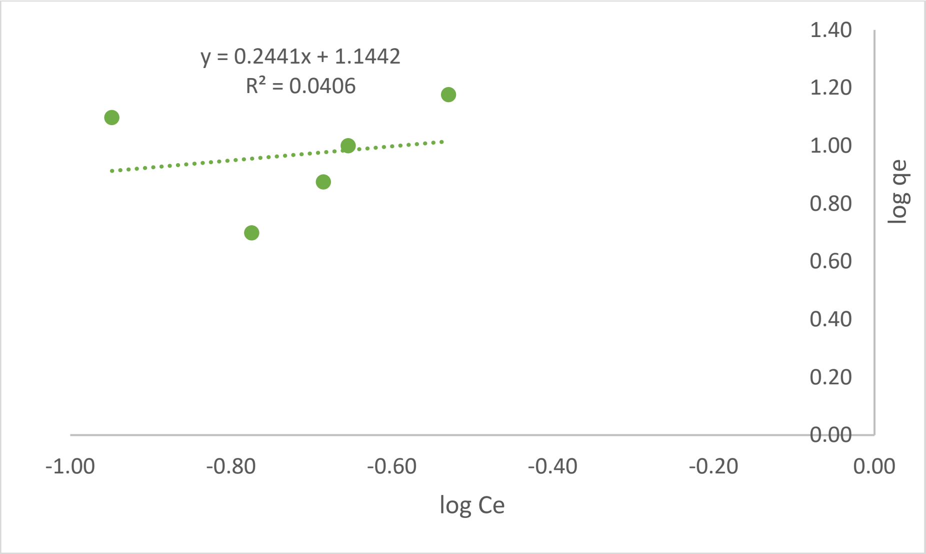


Figure 4. 70: Linear fitting plot of Freundlich isotherm model plot for Methylene Blue onto 100% Bentonite adsorbent.

Table 4. 15. Summary of adsorption isotherm results for Methylene Blue onto 100% Bentonite adsorbent.

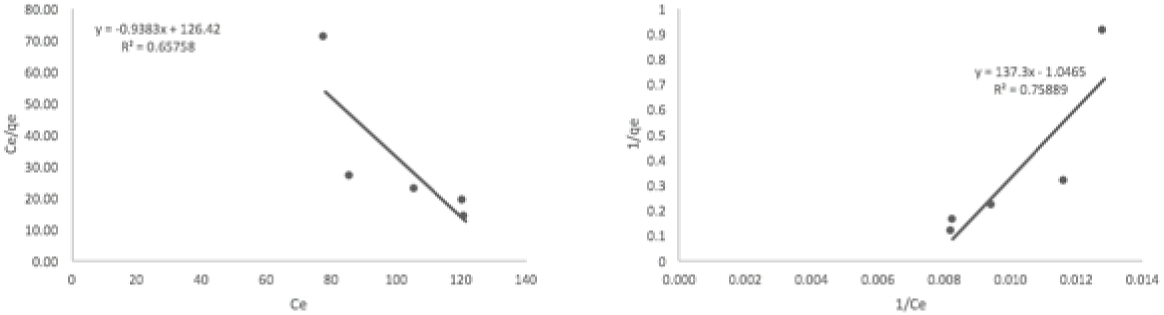
Adsorption Isotherm models	
Langmuir 1 qm= 31.34 mg/g K_L = 1.99 L/mg r^2= 0.9616	**Freundlich** K_f= 14.09 mg/g n= 6.92 R^2= 0.8724
Langmuir 2 q_m= 9.23 mg/g K_L= 77.42 L/mg r^2= 0.0031	
Langmuir 3 q_m= 6.23 mg/g K_L= 14.49 L/mg r^2= 0.322	
Langmuir 4 q_m= 1.68 mg/g K_L= 4.67 L/mg r^2=0.322	
Separation factor (R_L) 100 mg/L= 5×10^{-3} 150 mg/L = 3.33×10^{-3} 200 mg/L = 2.5×10^{-3} 250 mg/L = 2.01×10^{-3} 300 mg/L = 1.67×10^{-3}	

4.8.2. Reactive Blue 4

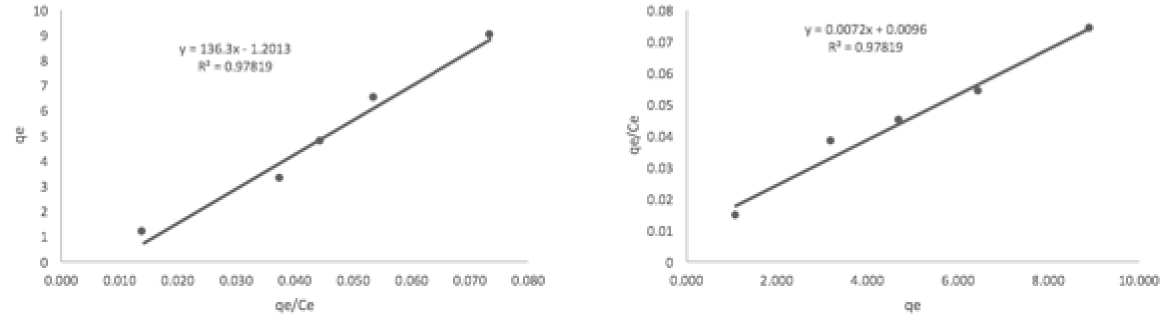
4.8.2.1 Using 75% CPS/25% KC

Figure 4.71 and 4.72 shows the linear fittings of Langmuir and Freundlich adsorption isotherms for 75% CPS/25% KC. Table 4.16 summarises the isotherm parameters obtained from the linear fittings and their correlation coefficients (r^2). According to the r^2 seen for the parameters in Table 4.15, the Freundlich model fitted the experimental data best by linear analysis and Langmuir did not fit the experimental data.

However, despite the lack of fit with Langmuir model, R_L was calculated, and its values were between 0.484-0.7380 (Table 4.16) which indicates that the adsorption of Reactive Blue 4 onto 75% CPS/25% KC was favourable.



Langmuir isotherm 1 Langmuir isotherm 2



Langmuir isotherm 3 Langmuir isotherm 4

Figure 4. 71: Linear fitting plots of Langmuir isotherms for adsorption Reactive Blue 4 onto 75% CPS/25% KC adsorbent.

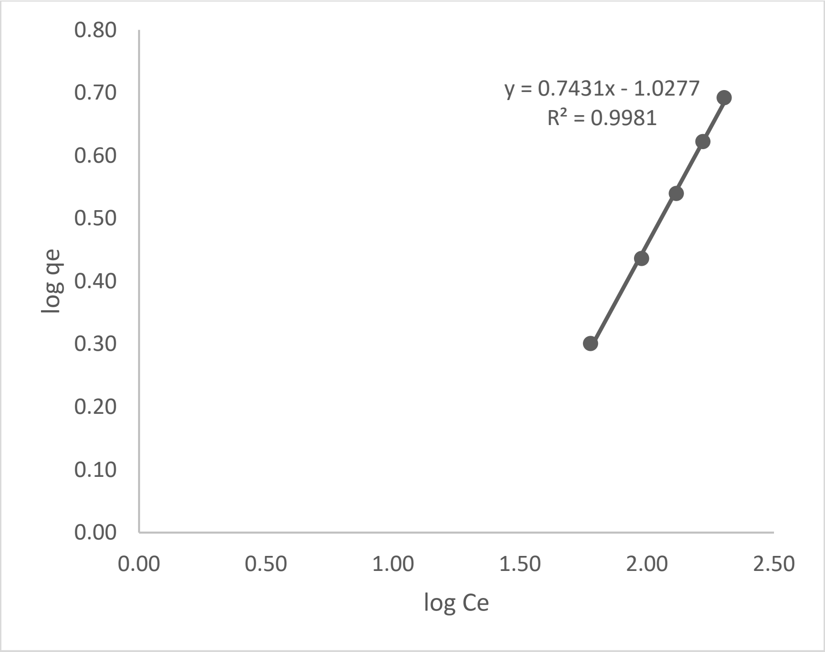


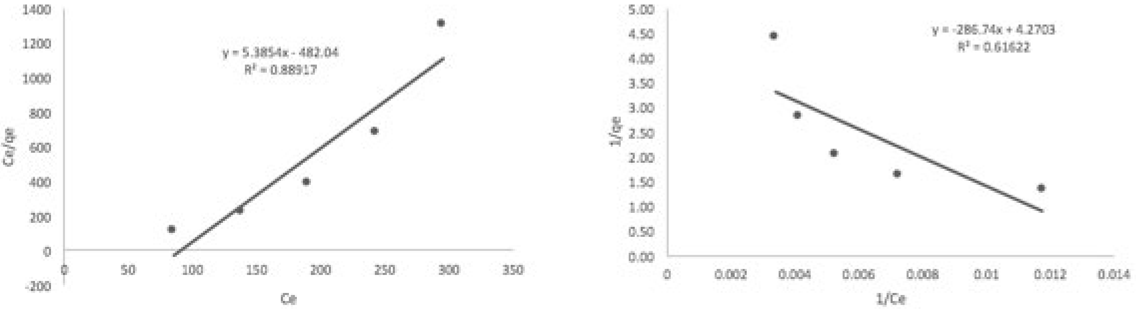
Figure 4. 72: Linear fitting plot of Freundlich isotherm for adsorption of Reactive Blue 4 onto 75% CPS/25% KC

Table 4. 16. Langmuir and Freundlich isotherm parameters obtained by linear fittings of 75% CPS/25% KC adsorbent

Isotherm models	
Langmuir 1 q_m= 13.29 mg/g K_L = 2.8x10-3 L/mg R^2= 0.9355	**Freundlich** K*f*= 0.093 mg/g n= 1.34 R^2= 0.999
Langmuir 2 q_m= 11.19mg/g K_L= 3.55x10-3L/mg R^2= 0.9926	
Langmuir 3 q_m= 11.90 mg/g K_L= -3.26x10-3 L/mg R^2= 0.888	
Langmuir 4 q_m= -12.96 mg/g K_L= -0.0029 L/mg R^2=0.888	
Separation factor (R_L) 100 mg/L= 0.738 150 mg/L = 0.653 200 mg/L = 0.584 250 mg/L = 0.529 300 mg/L = 0.484	

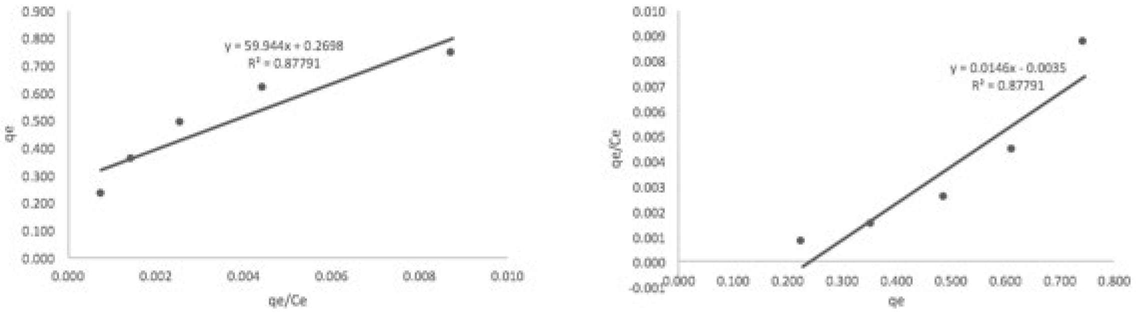
4.8.2.2. Using 25% CPS/75% KC

Figure 4.73 and 4.74 shows the linear fittings of Langmuir and Freundlich adsorption isotherms for 25% CPS/75% KC. Table 4.17 summarises the isotherm parameters obtained from the linear fittings and their correlation coefficients (r^2). According to the r^2 seen for the parameters in Table 4.17, the Langmuir model fit the experimental data best by linear analysis and Freundlich model did not fit the experimental data. For the dimensionless factor (R_L), R_L values were between 0.23 to 0.47 (Table 4.17), which indicates that the adsorption of Methylene Blue onto 25% CPS/75% KC was favourable.



Langmuir isotherm 1

Langmuir isotherm 2



Langmuir isotherm 3

Langmuir isotherm 4

Figure 4. 73: Linear fitting plots of Langmuir isotherms for adsorption of Reactive Blue 4 onto 25% CPS/75% KC adsorbent

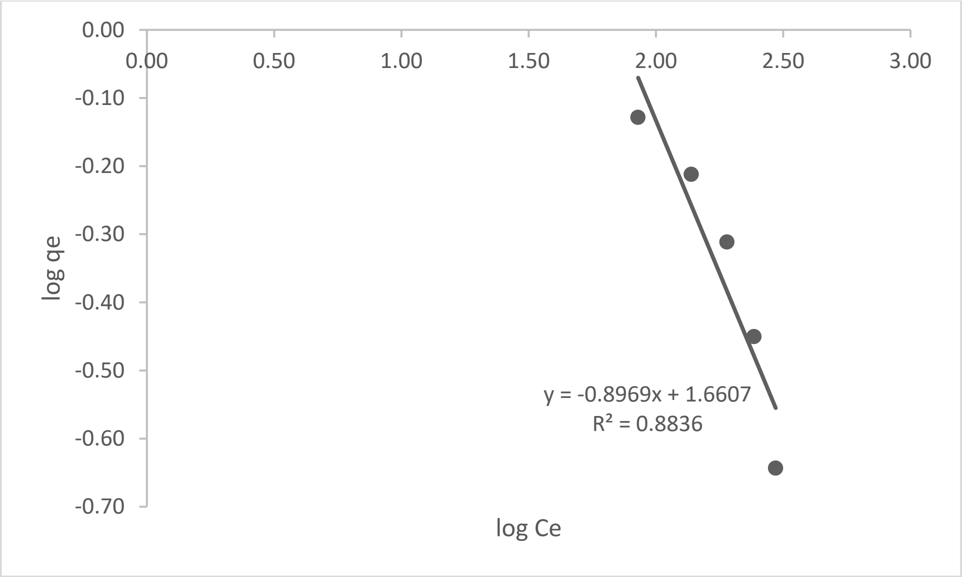


Figure 4. 74: Linear fitting plot of Freundlich isotherm model plot for adsorption of Reactive Blue 4 onto 25% CPS/75% KC adsorbent

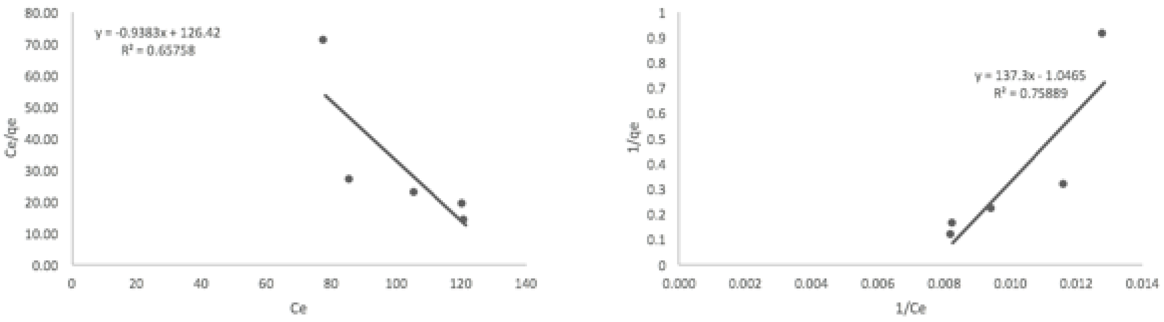
Table 4. 17. Langmuir and Freundlich isotherm parameters obtained by linear fittings of 25% CPS/75% KC adsorbent

Isotherm models	
Langmuir 1 q_m= 0.186 mg/g K_L = 0.011 L/mg R^2= 0.889	Freundlich K_f= 45.78 mg/g n= -0.103 R^2= 0.88
Langmuir 2 q_m= 0.234 mg/g K_L= -67.14 L/mg R^2= 0.616	
Langmuir 3 q_m= 0.269 mg/g K_L= 0.016 L/mg R^2= 0.877	
Langmuir 4 q_m= 0.239 mg/g K_L= 0.014 L/mg R^2=0.877	
Separation factor (R_L) 100 mg/L= 0.47 150 mg/L = 0.38 200 mg/L = 0.31 250 mg/L = 0.26 300 mg/L = 0.23	

4.8.2.3. Using 100 % kaolin (T0)

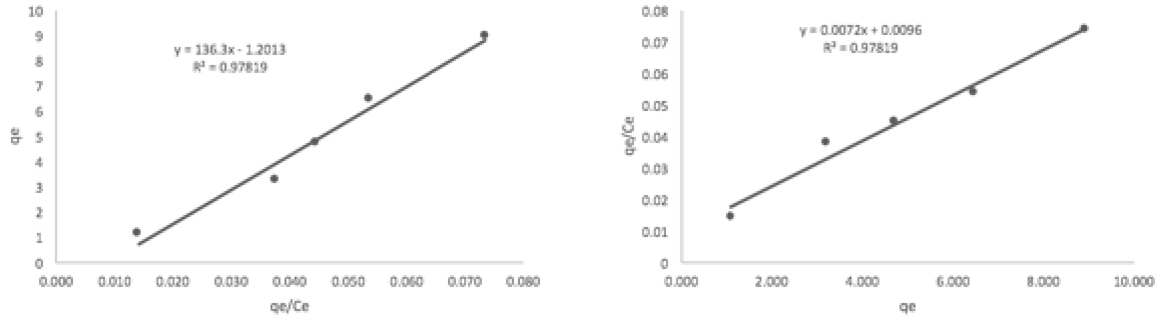
Figure 4.75 and 4.76 shows the linear fittings of Langmuir and Freundlich adsorption isotherms for 100% kaolin (T0). Table 4.18 summarises the isotherm parameters obtained from the linear fittings and their correlation coefficients (r^2). According to the r^2 seen for the parameters in Table 4.18, the Freundlich model fitted the experimental data best by linear analysis and Langmuir did not fit the experimental data.

For the dimensionless factor (R_L), R_L values were between 0.23 to 0.47 (Table 4.18), which indicates that the adsorption of Methylene Blue onto 100% kaolin (T0) was favourable.



Langmuir isotherm 1

Langmuir isotherm 2



Langmuir isotherm 3

Langmuir isotherm 4

Figure 4. 75: Linear fitting plots of Langmuir isotherms for adsorption of Reactive Blue 4 onto T0 (KC) adsorbent

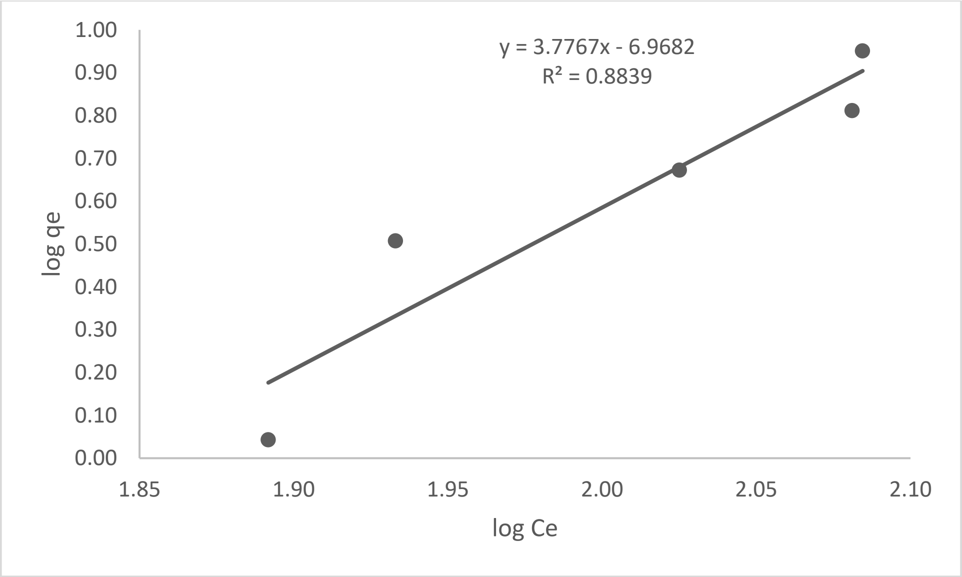


Figure 4. 76: Linear fitting plot of Freundlich isotherm for adsorption of Reactive Blue 4 onto T0 (KC*) adsorbent.*

Table 4. 18. Langmuir and Freundlich isotherm parameters obtained by linear fittings of Reactive Blue 4 onto T0 (KC) adsorbent.

Isotherm models	
Langmuir 1 q_m= -0.1065 mg/g K_L = -134 L/mg r^2= 0.657	**Freundlich** K*f*= 1.07×10^{-7} mg/g n= 0.264 R^2= 0.88
Langmuir 2 q_m= -0.955 mg/g K_L= -67.14 L/mg r^2= 0.7588	
Langmuir 3 q_m= -1.20 mg/g K_L= 7.33×10^{-3} L/mg r^2= 0.9781	
Langmuir 4 q_m= 1.3 mg/g K_L= 0.0072 L/mg r^2= 0.9781	
Separation factor (R_L) 100 mg/L= 0.47 150 mg/L = 0.38 200 mg/L = 0.31 250 mg/L = 0.26 300 mg/L = 0.23	

4.9. Adsorption kinetics

Kinetic models are used to know the rate of an adsorption process. For this research work, two kinetic models were used pseudo-first-order and pseudo-second-order. To determine the best kinetic model for the experimental data, the correlation coefficients of linear plots were taken into account.

4.9.1. Methylene Blue

Figure 4.77 shows the pseudo-first and second order for adsorption of Methylene Blue using kaolin and bentonite clay. For kaolin, 75% CPS/25% KC, the correlation coefficient for pseudo-first-order and pseudo-second-order was 0.965 and 1, respectively. Using these values obtained, the experimental data fit both kinetic orders. However, the kinetic order with the highest correlation coefficient (pseudo-second-order) was a better fit.

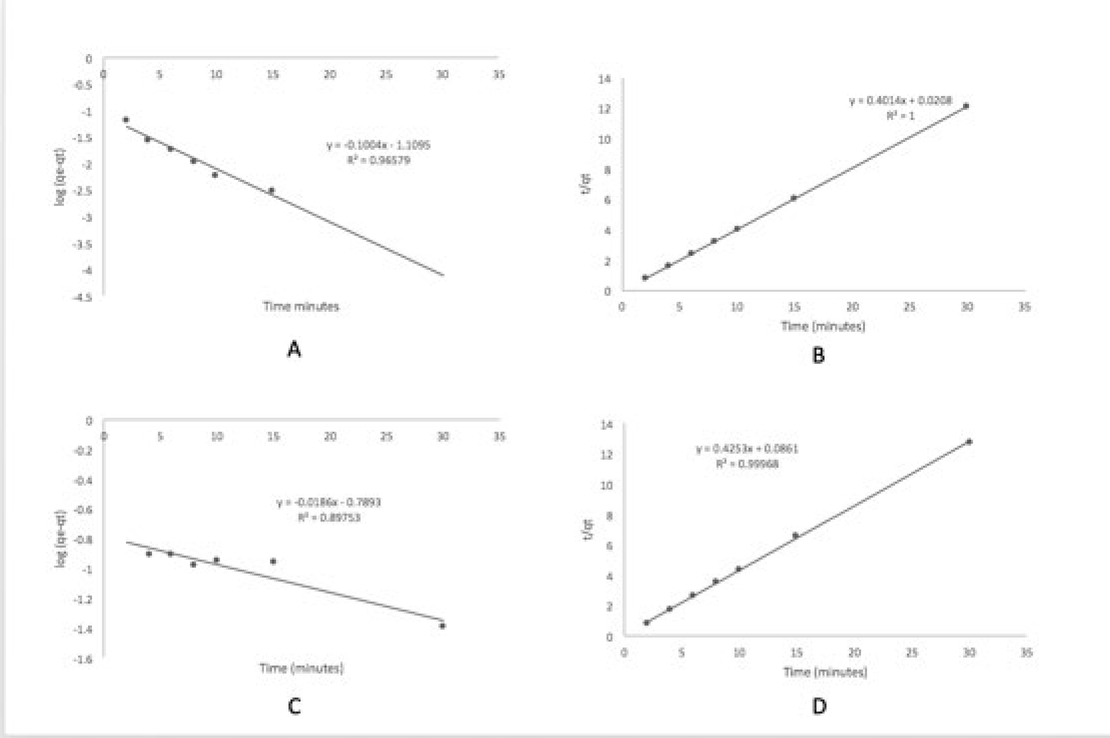


Figure 4. 77: Adsorption kinetics for Methylene Blue using kaolin and bentonite clay. A and B are for pseudo-first and second order for kaolin clay (75% CPS/25% KC). C and D are for pseudo-first and second order for 100 % Bentonite.

In addition, the calculated adsorption capacity at equilibrium (qe_{cal}) and experimental adsorption capacity (qe_{exp}) was closer to each other for pseudo-second-order than pseudo-first-order (Table 4.18). Similarly, for adsorption using 100% Bentonite clay, the experimental data fit the pseudo-second-order (0.99) better than the pseudo-first-order (0.8753). It was also observed that the calculated adsorption capacity at equilibrium (qe_{cal}) and experimental adsorption capacity (qe_{exp}) was closer to each other for pseudo-second-order than pseudo-first-order (Table 4.18).

4.9.2. Reactive Blue 4

Fig 4.78 illustrates the adsorption kinetics for adsorption of reactive blue using kaolin and bentonite clay. The correlation coefficient of the first and second-order was seen to be 0.67 and 0.99, respectively. Therefore, indicating that pseudo-second-order was a better fit for the experimental data obtained. Similarly, for adsorption using bentonite clay, the experimental data fit the pseudo-second-order (0.854) better than the pseudo-first-order (0.094) (Table 4.18).

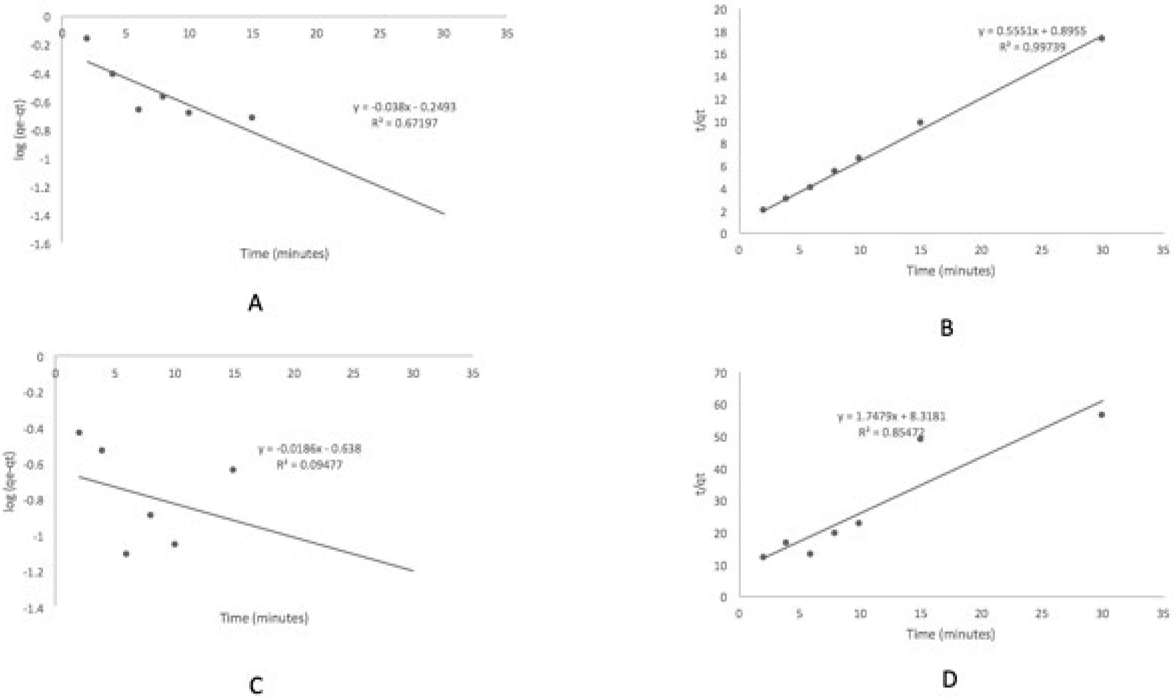


Figure 4. 78: Adsorption kinetics for adsorption of Reactive Blue 4 onto kaolin and bentonite clays. A and B Pseudo 1 and 2 for kaolin clay (75% CPS/25% KC), C and D for pseudo 1 and 2 for bentonite clay.

In addition, the calculated adsorption capacity at equilibrium (qe_{cal}) 0.533 and experimental adsorption capacity (qe_{exp}) was closer to each other for pseudo-second-order (0.572) than pseudo-first-order (0.230) (Table 4.19). Based on the observation made in this, pseudo-second-order is the most applicable kinetic model for determining the adsorption process of Methylene Blue and Reactive Blue 4 unto selected adsorbents used.

Table 4. 19. Kinetic data calculated for the adsorption of Methylene Blue and Reactive Blue 4 onto selected adsorbents

Dye		**Methylene Blue**		**Reactive Blue 4**	
Adsorbent		**75% CPS/25% KC (CPS/KC)**	**100Ben (300)**	**75% CPS/25% KC (CPS/KC)**	**100Ben (300)**
	qe (exp)	4.958	2.389	1.733	0.533
Pseudo 1st order	qe cal (mg/g)	0.160	0.162	0.5632	0.230
	K_1 min− 1	-0.0267	-0.043	-0.087	0.048
	R^2_1	0.86196	0.897	0.6717	0.094
Pseudo 2nd order	qe cal (mg/g)	4.970	2.351	1.801	0.572
	K_2 (g mg^{-1} min^{-1})	0.389	2.10	0.344	0.210
	R^2_2	0.999	0.999	0.99	0.854

4.10. Surface characterisation

4.10.1. SEM analysis

The morphology of selected adsorbents was characterised using SEM analysis. The SEM images shown in Figure 4.79 revealed the porous nature of uncalcined and what happens after it had been used for adsorption of Methylene Blue and Reactive Blue 4. For uncalcined CPS, there were uneven edges and porosity was observed on the surface. The SEM images for uncalcined CPS after use for the adsorption of Methylene Blue as in seen in Figure 4.79. Although the image showed a reduction in porosity, there were still some available active sites on the adsorbent. The SEM images of uncalcined CPS after adsorption with Reactive Blue 4 revealed some part that was covered, flat with rough edges and were not porous. In addition, some parts of the adsorbent were porous.

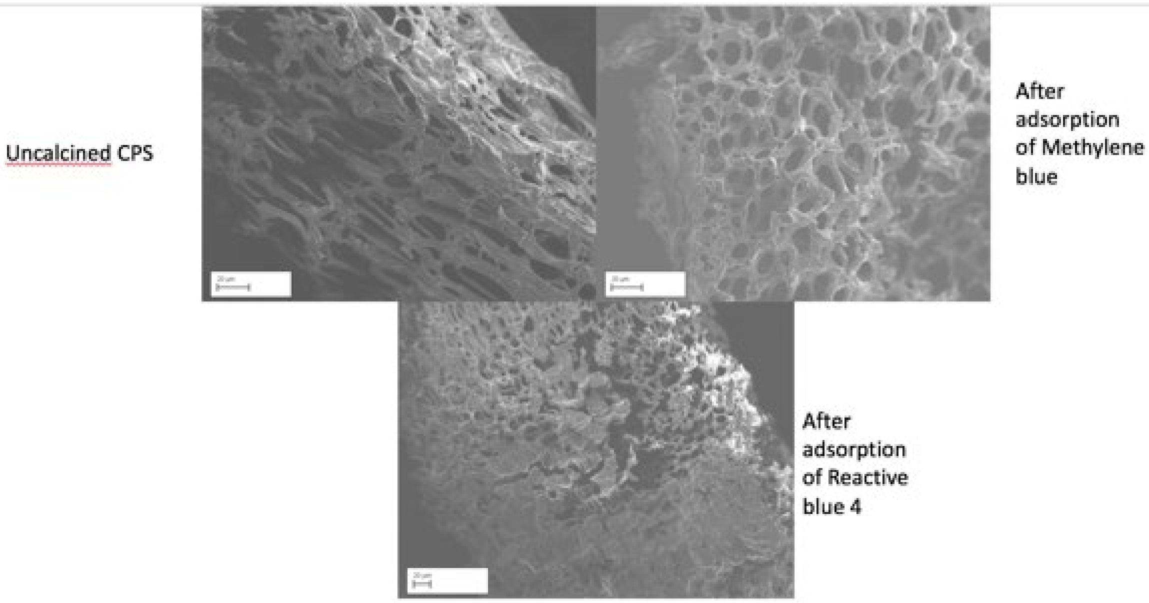


Figure 4. 79: SEM images for uncalcined CPS after adsorption of Methylene Blue and reactive blue4.

After calcination of CPS, SEM images showed a good distribution of pore structure. This increase in porosity could be as a result of calcination hence resulting in increased maximum adsorption capacity. The large pore in calcined CPS may have aided the movement and diffusion of dye molecules into the pores, therefore, resulting in high adsorption. Figure 4.80 shows that SEM images calcined CPS after it was used for the adsorption of Methylene Blue. The images showed a change in the pores of calcined CPS due to its use for adsorption of Methylene Blue. Although the image showed that the pores had been filled, it also showed that there were available sites for adsorption on the surface of the adsorbent used. For the adsorption of Reactive Blue 4 onto calcined CPS, the SEM images showed less porosity after adsorption (Figure 4.80).

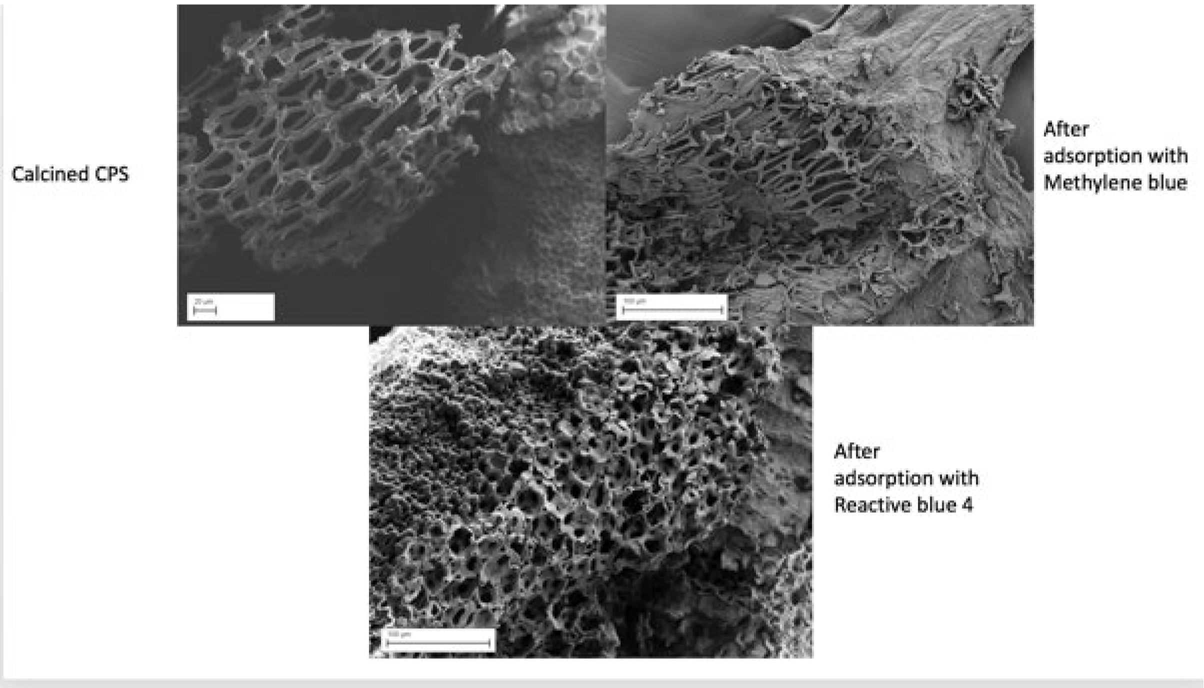


Figure 4. 80: SEM images calcined CPS after adsorption of Methylene Blue and Reactive Blue 4.

The SEM images of 75% CPS/25% KC before and after its use for adsorption of Methylene Blue and Reactive Blue 4 was captured (Figure 4.81). Image of before adsorption showed that the adsorbent porous and some part of its surface was flat with no pores. The SEM image of 75% CPS/25% KC after Methylene Blue adsorption, shows particles with rough edges and low porosity. For Reactive Blue 4, low porosity was observed.

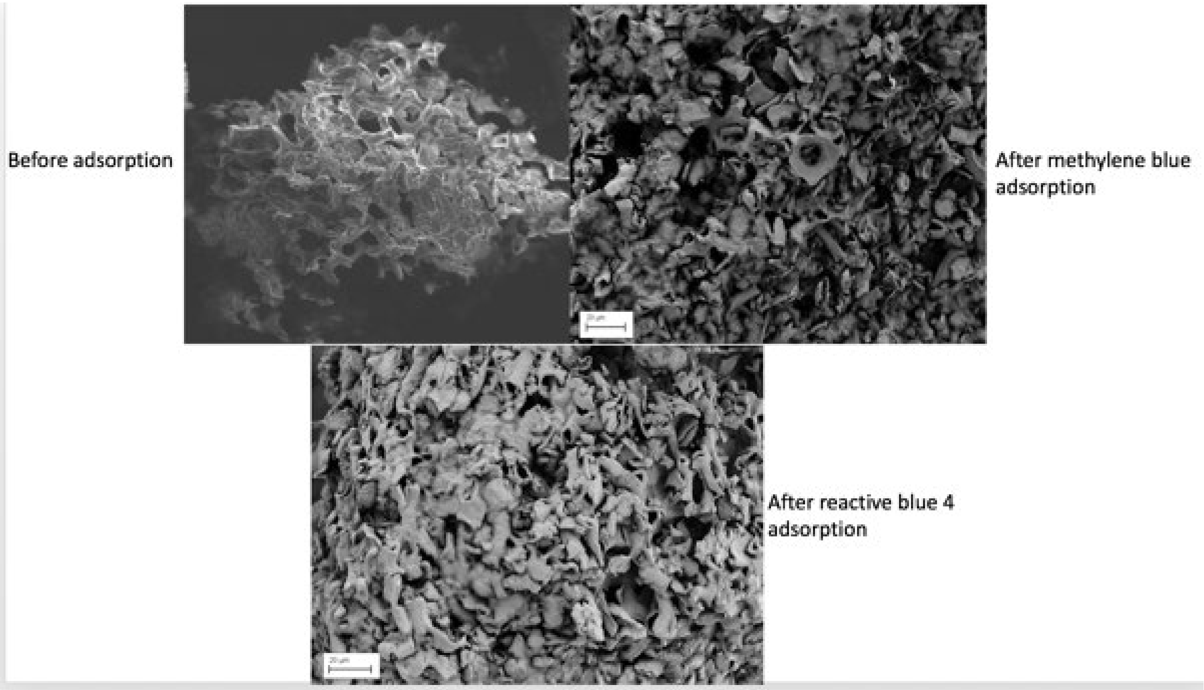


Figure 4. 81: SEM images of 75% CPS/25% KC before and after its use for adsorption of Methylene Blue and Reactive Blue 4

4.10.2. EDX analysis

EDX analysis was done using the SEM, and the elemental analysis of different adsorbents are shown in Figure 4.82, Table 4.19 and Table 4.20. The EDX spectrum of uncalcined milled carica papaya seeds (CPS), calcined milled CPS and the calcined homogenous mixture of kaolin and milled CPS showed that changes occurred in per cent weight of elements as a result of calcination and mixing of two materials.

The elemental analysis showed that the presence of carbon and oxygen had the highest percentage weight before and after adsorption. The increase in %weight of carbon after adsorption of Methylene Blue and Reactive blue 4 showed that some amount of dye was adsorbed by the adsorbents used. Before adsorption UnCPS had 63.21%w, CaCPS had 68.01%w, and 75% CPS/25% KC(CPS/KC) had 68.85%w. After adsorption of Methylene Blue and Reactive Blue 4 dye, there was an increase in carbon content on the surface of UnCPS (78.40%w:MB; 67.55%w:RB4) and CaCPS (72.21%w:MB; 70.79%w:RB4) However, for 75% CPS/25% KC(CPS/KC) there was a decrease in carbon content (55.20%w:MB; 44.64%w:RB4). For oxygen, before adsorption UnCPS had 59.58%w, CaCPS had 26.67%w, and 75% CPS/25%

KC(CPS/KC) had 21.30%w. After adsorption using Methylene Blue and Reactive Blue 4 dye, there was a decrease in oxygen content on the surface of UnCPS(16.25%w: MB; 23.92%w: RB4) and CaCPS (18.83%w: MB; 9.82%w: RB4) However, for 75% CPS/25% KC(CPS/KC) there was an increase and decrease in oxygen content (35.87%w: MB; 16.74%w: RB4)

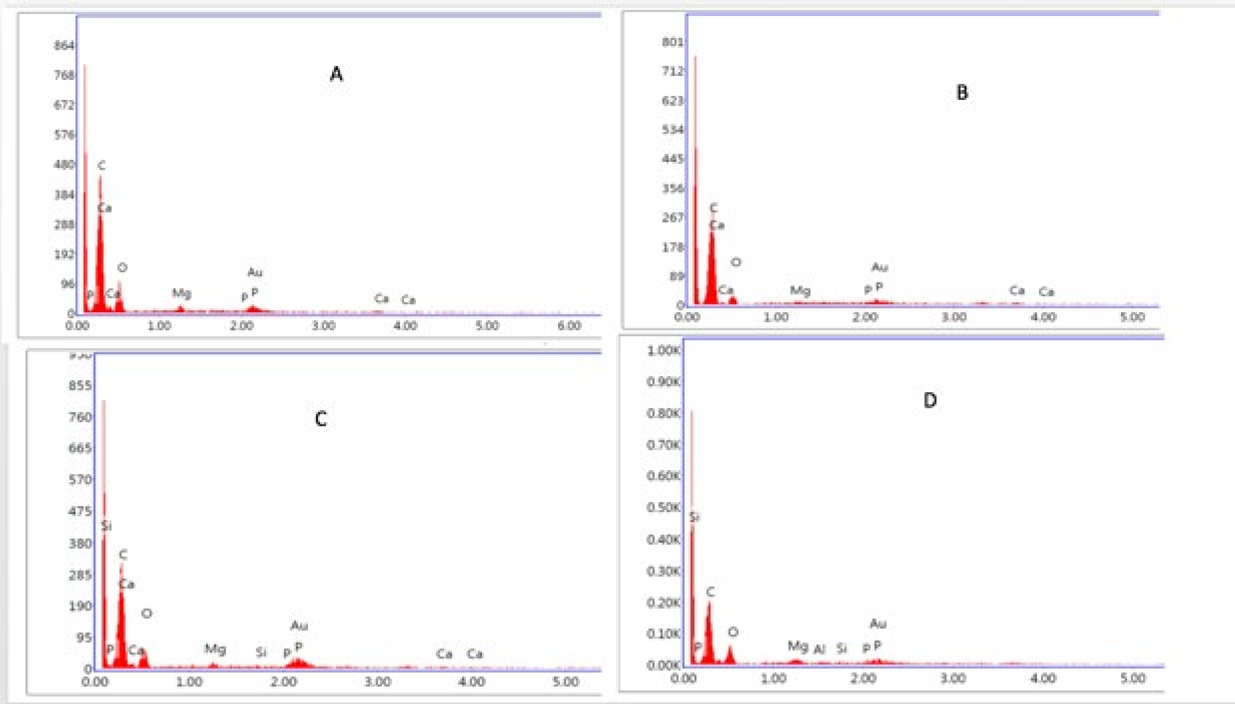


Figure 4. 82: EDX spectra of (A) uncalcined CPS, (B) uncalcined CPS after adsorption with Methylene Blue, (C) uncalcined CPS after adsorption using Reactive Blue 4, (D) Calcined CPS.

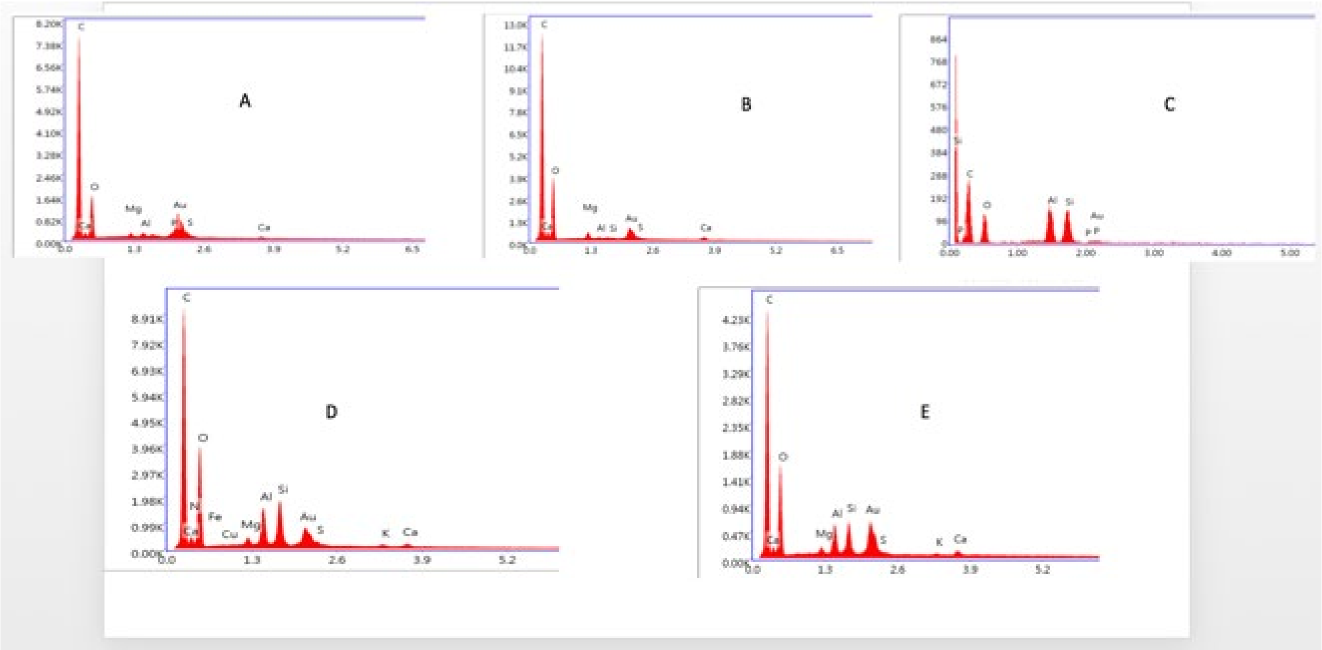


Figure 4.83. EDX spectra of (A) After adsorption of Methylene Blue onto calcined CPS, (B) After adsorption of Reactive Blue 4 onto calcined CPS, (C) Calcined 75% CPS/25% KC (CPS/KC), (D) After adsorption of Methylene Blue onto calcined 75% CPS/25% KC (CPS/KC), (E) After adsorption of Reactive Blue 4 onto calcined 75% CPS/25% KC (CPS/KC).

Table 4. 19. Elemental proportion on selected adsorbents use for the adsorption of Methylene Blue and Reactive Blue 4

Element (%w)	**UnCPS**	**UnMB**	**UnRB$_4$**	**CaCPS**	**CaMB**	**CaRB$_4$**
C	63.91	78.40	67.55	68.01	72.21	70.79
O	59.58	16.25	23.92	26.67	18.83	9.82
Mg	2.17	0.46	0.81	1.13	0.15	0.55
Ca	0.95	1.36	0.48	0.81	0.29	0.89

Table 4. 20. Elemental proportion on selected adsorbents use for the adsorption of Methylene Blue and Reactive Blue 4

Element (%w)	75% CPS/25% KC (CPS/KC)	75% CPS/25% KC (MB)	75% CPS/25% KC (RB_4)
C	68.85	55.20	44.64
O	21.03	35.87	16.74

UnCPS- Uncalcined CPS
UnMB- Uncalcined CPS after adsorption with Methylene Blue
$UnRB_4$- Uncalcined CPS after adsorption with Reactive Blue 4
CaCPS- Calcined CPS
CaMB- Calcined CPS after adsorption with Methylene Blue
$CaRB_4$- Calcined CPS after adsorption with Reactive Blue 4
75% CPS/25% KC (CPS/KC) - Calcined proportion
75% CPS/25% KC (MB) - Calcined proportion after adsorption with Methylene Blue
75% CPS/25% KC (RB_4) - Calcined proportion after adsorption with Reactive Blue 4

4.10.3. FTIR analysis

The FTIR spectra for calcined CPS, uncalcined CPS and 75/25 (CPS/KC) was before and after adsorption using methylene blue and reactive blue dye is shown in figure 4.83 – figure 4.85. The FTIR spectra gotten showed that there were different functional groups detected on the surface of the adsorbents before and after adsorption. It was observed that some peaks shifted slightly and some disappeared after adsorption. As seen in Figure 4.83, three there are three bands that are quite similar among the adsorbents used were 3285& 3277 cm^{-1}, 2922 cm^{-1}, and 1744 cm^{-1} which indicated bonded -OH group, C-H group and C=O stretching group. The presence of these bands indicate the possible role of the functional groups on the surface of the adsorbents during adsorption. In addition, it was seen that the FTIR spectra for CaCPS and UnCPS have similar bands. This similarity could probably indicate that the calcination of CPS is not necessarily required. Furthermore, the FTIR spectra of 75/25 (CPS/KC) has a strong band at 3687 cm^{-1} and this could be as a result of kaolin clay present in the adsorbent as this band was not observed in the other adsorbents analyzed.

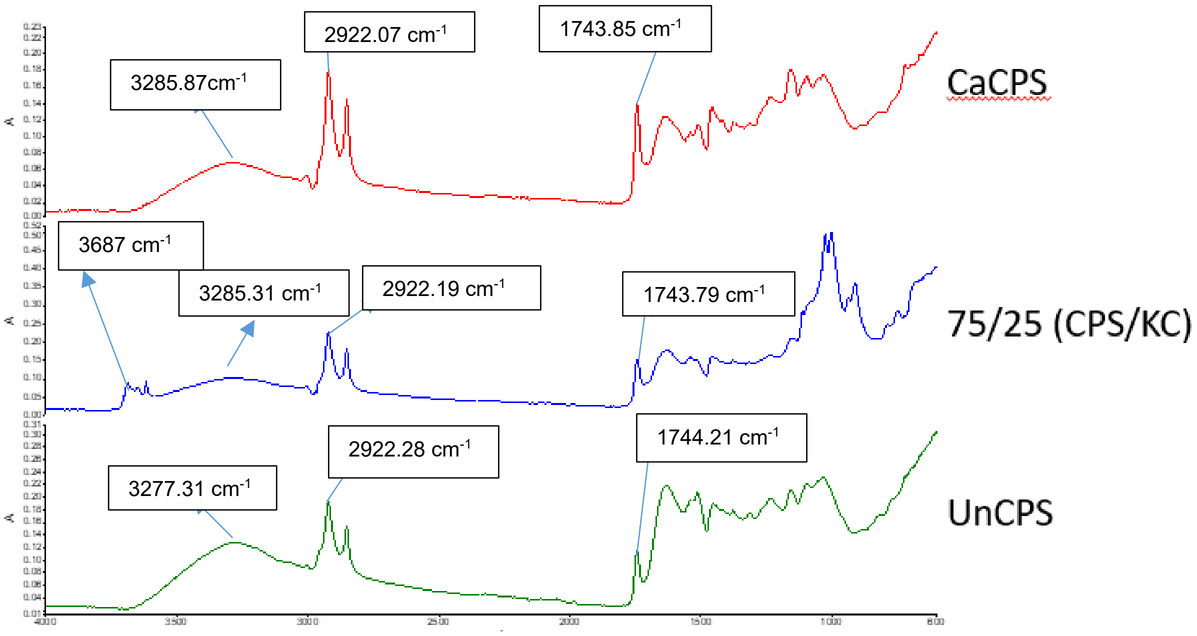


Figure 4. 83: FTIR analysis for UnCPS, CaCPS and 75% CPS/25% KC (CPS/KC)

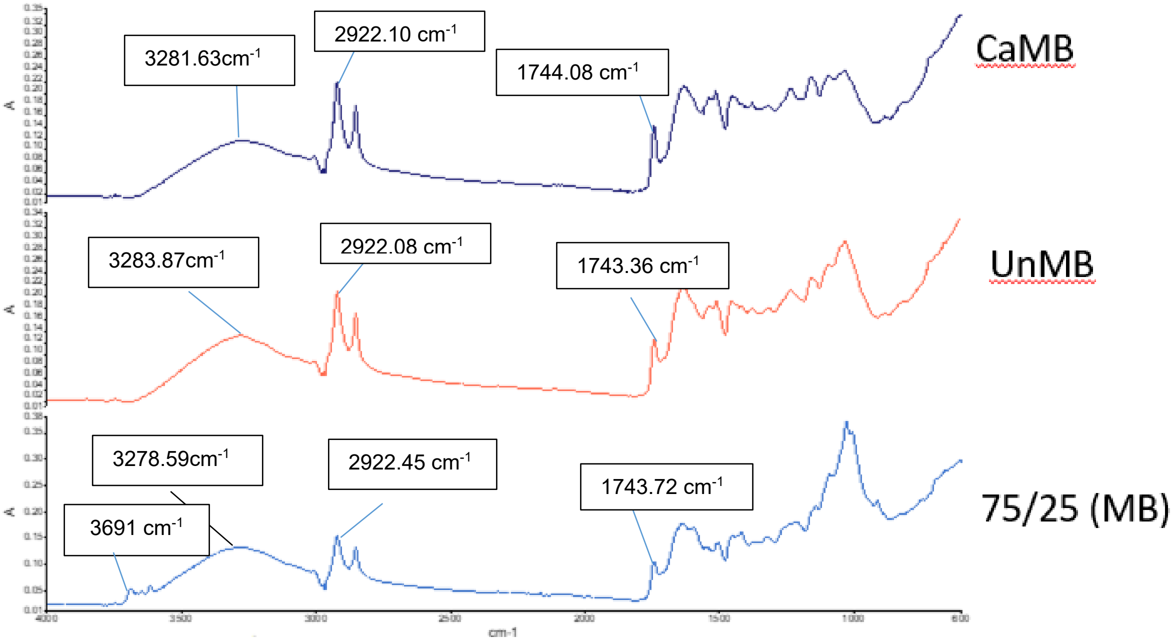


Figure 4. 84: FTIR analysis for CaMB, UnMB and 75% CPS/25% KC (MB)

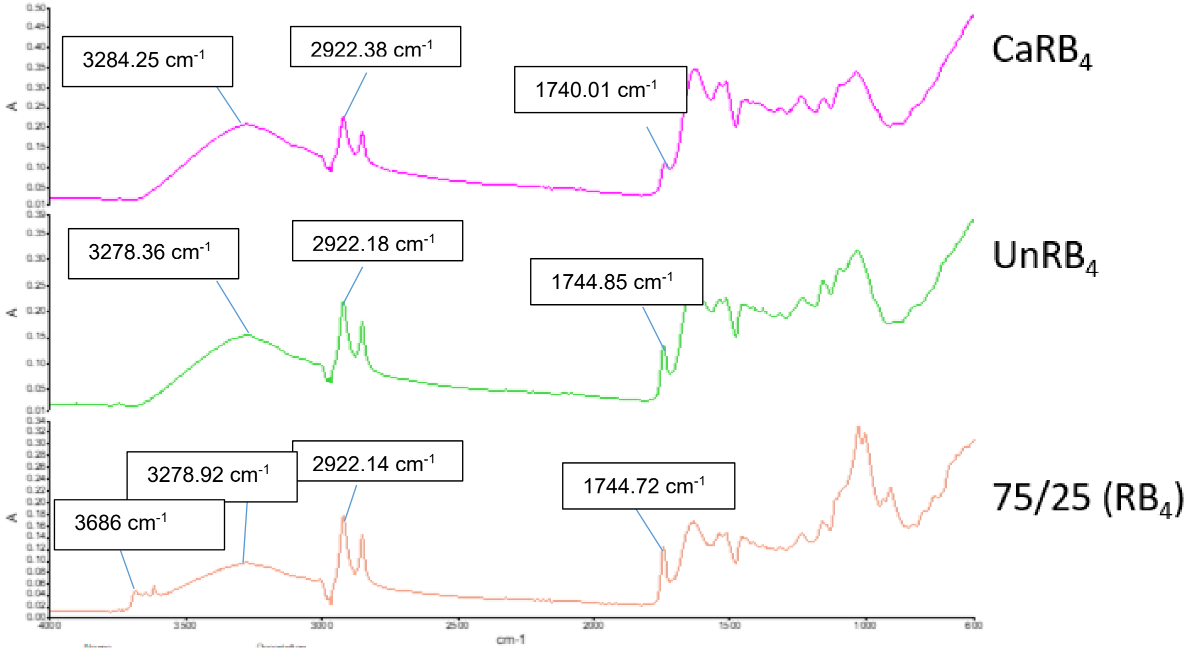


Figure 4. 85: FTIR analysis for $UnRB_4$, $CaRB_4$ and 75% CPS/25% KC (RB_4)

After adsorption of Methylene blue dye onto the adsorbents, slight changes were observed in the bands (Figure 4.84). Using UnCPS, there was a slight increase in the bonded -OH group to 3283 cm-1, no change in intensity was observed for the C-H group at 2922 cm^{-1} and a slight increase in intensity for C=O stretching group. After adsorption of Methylene Blue, there was a slight decrease in the bonded -OH group to 3281cm^{-1} and no change was seen for the C-H group at 2922 cm^{-1}. For 75% CPS/25% KC, there was a slight decrease in the OH group to 3278cm^{-1} and no change was seen for the C-H group at 2922cm^{-1}

Similarly, adsorption of Reactive Blue 4 onto the adsorbents, little changes were seen in the bands observed (Figure 4.85). For UnCPS, there was a slight increase of band in the bonded -OH group 3278 cm^{-1}, no change in the C-H group (2922 cm^{-1}) and a slight increase of band for C=O stretching group to 1744 cm^{-1}. With calcined CPS, there was a slight decrease in the bonded -OH group 3284cm^{-1}, no change in the band for C-H group (2922 cm^{-1}) and a slight decrease in the band for C=O stretching group to 1740 cm^{-1}. For 75% CPS/25% KC, there was a slight decrease in the bonded -OH group (3278cm^{-1}), no change in the C-H group (2922 cm^{-1}) and no change in band for C=O stretching group 1744 cm^{-1}.

CHAPTER 5

Discussions

Dyes are used in different industries such as plastics, paper, leather, textile and food industry. In this study, the focus was on the textile industry, and the wastewater discharged into water bodies. The textile industry discharged a significant amount of textile wastewater which leads to water pollution (Begum *et al*., 2018; Mohebali *et al.,* 2018; Mouni *et al.,* 2018). To combat water pollution caused, different wastewater treatment methods are used, and adsorption is one of them. For most industries, the use of activated carbon, silica gel and alumina for adsorption is effective. However, the downside to using activated carbon is the cost of purchasing it and the high cost of manufacturing it. Hence, the increased need to find cheaper and efficient adsorbents). Therefore, materials such as clay minerals, agricultural and food waste have been used and studied by researchers to produce adsorbents which could potentially replace the use of activated carbon. The use of adsorbents made from alternative sources is a good one for small and medium scale textile industries in developing countries (Pollard *et al.,* 1992; Sanghi and Bhattacharya, 2002; Rafatullah *et al.,* 2010; Hasan *et al.,* 2019). In this study, adsorbents were prepared using clay minerals (bentonite and kaolin clay) and an agriculture waste called *carica papaya* seeds, also known as pawpaw seeds. However, most agriculture or food waste are used individually as adsorbents. Little study has been done on mixed adsorbents with regards to producing low-cost adsorbents.

Some studies have highlighted the necessity of modifying low-cost materials when used as adsorbents as these improve the efficiency of the adsorbent material (Crini, 2006; Ogata *et al.,* 2015; Kausar et al., 2018; Ali, 2018). In this study, the calcination and mixing proportions of adsorbents used had a significant influence on adsorbent efficiency. Aside from these, physical colour changes were observed with an increase in calcination temperature. The adsorption capacity of adsorbents prepared at different temperatures (100-600^{o}C) was investigated. The parameters considered were percentage dye removal, calcination temperature, adsorbent dose and contact time, initial concentration and pH. Results obtained were used to optimise the proportion, calcination temperature and adsorbent that was most efficient.

5.1. Calcination of adsorbents

5.1.1. 100% kaolin

The calcination of clay minerals and its use for adsorption dyes has been widely investigated and reported (Ghosh and Bhattacharyya, 2002; Alkan *et al.*, 2005; Vimonses *et al.*, 2009; El Mouzdahir *et al.*, 2010). The effect of calcination temperature on adsorption of Methylene Blue and reactive blue 4 onto kaolin was studied at calcination temperature varying between 300-600^{O}C, this was done at an initial concentration of 50 mg/L and quantity of adsorbent was 2.0 g. Although studies have indicated that the increasing calcination temperature reduces the percentage removal (Ghosh and Bhattacharyya, 2002; Karaoglu *et al.*, 2009; Mouni *et al.*,2018), however, in this study the adsorption of Methylene Blue onto calcined kaolin had results that showed 90% removal at all calcination temperatures (Figure 4.3a). El Mouzdahir e*t al.* (2010) investigated the removal of Methylene Blue using thermally activated clay minerals and discovered that the adsorptive capacity varied based on the temperature used. Authors found out that thermal treatments of kaolin done at a temperature higher than 300^{O}C reduced the adsorption capacity of the clay mineral. Similarly, the adsorption of reactive blue 4 onto calcined kaolin results showed the maximum percentage removal at 300^{O}C. With increasing calcination temperature, there was a decrease in percentage removal of Reactive blue 4 (El Mouzdahir e*t al.*, 2010). In comparison, the difference in adsorption efficiency when the same adsorbents were used for both dyes could be as a result of the ionic state of the dyes. The surface charge on calcined kaolin might have been more negatively changed. Hence, the higher affinity for Methylene Blue dye which resulted in better adsorption compared with reactive blue 4 (Hu and Liu, 2003; Uddin, 2017).

Furthermore, adsorption of both dyes onto calcined kaolin was compared with adsorption onto uncalcined kaolin. For Methylene Blue, there no significant difference and thus suggesting that to conduct the adsorption of Methylene Blue onto kaolin, calcination is not necessarily required. With reactive blue 4, a significant difference was seen, and uncalcined kaolin had a higher percentage removal. Therefore, like Methylene Blue, the adsorption of reactive blue using kaolin does not require the calcination with the assumption that it would increase the removal efficiency of kaolin

5.1.2. 100% bentonite (Calcined)

For bentonite, with increasing temperature there was an increase in percentage removal of above 90% and equilibrium was reached quickly with 10 mins. However, despite the close percentage removal calculated, the statistical analysis pointed out that the adsorption of Methylene Blue onto calcined bentonite at 500°C was the most suitable adsorbent. Studies have shown that the calcining bentonite beyond 500°C results in a reduction of adsorption efficiency and results in dehydroxylation (Noyan *et al.,* 2006; Bayram *et al.,* 2010; dos Santos *et al.,* 2019). However, the adsorption of reactive blue 4 onto calcined bentonite compared to Methylene Blue did not give impressing results as maximum percentage removal was less than 30%.

5.2. Calcination on mixed adsorbents (CPS and kaolin)

The use and role of agricultural waste in treating textile effluent has been done extensively; however, in most cases, these waste materials have to be modified. Most modifications are done using chemical, physical methods and the combination of both methods for the producing a cheaper version of activated carbon (Nafiza *et al.*, 2018; Bestani and Benderdouche, 2018; Wang *et al.*, 2018; Khan and Khan, 2018). However, despite the favourable adsorption capacity seen using modified agricultural waste, the combination of agricultural waste and clay minerals is yet to be explored deeply. In this study, the combination and calcination of kaolinite clay and *carica papaya* at different proportion for adsorption of Methylene Blue and reactive blue 4 showed that increasing or decreasing proportion of each material could affect the removal efficiency of prepared adsorbents.

5.2.1. Methylene Blue

For adsorption of Methylene Blue using 25/75, > 90% colour removal was observed within 15 mins and remained that way, thus indicating that equilibrium is attained within 15mins. In comparison with 100% kaolin, both proportions shared similar result which could be as a result of the high percentage of kaolin in 25/75. With the increase in the percentage of CPS to 50%, it was seen that the percentage removal was all the same at 300–500°C calcination temperature (Figure 4.10). Hence, highlighting the value of milled CPS brings to the adsorption capacity of the homogenous mixture with kaolin clay. Thus, it could be said that the calcination of kaolin with papaya seeds could improve the adsorption efficiency of kaolin clay. However, the adsorbent calcined at 600°C did not adsorb any adsorbate and analysis of the filtrate could not be read by the UV. Thus suggesting that the increase of papaya seeds does not necessarily improve the adsorption efficiency when it is calcined above 500°C. In addition, this could also have been as a result of the presence of kaolin (Mouni *et al.*,2018). Similarly, for 75/25 (CPS/KC) there was a decrease in percentage removal, and there was no absorbance reading for adsorption studies of Methylene Blue using adsorbent calcined at 600°C (Mouni *et al.*,2018). However, despite the results obtained highlighting the advantage of adding milled CPS to kaolin to increase its adsorption efficiency after calcination at the selected temperature, the adsorption of Methylene Blue using uncalcined kaolin was better statistically (Olu-Owolabi et al., 2016).

5.2.1. Reactive blue 4

For Reactive blue 4, the addition of milled CPS to kaolin clay was seen to result in improvement of adsorption efficiency. At 25% addition of milled CPS, the maximum percentage removal of dye was obtained with 5 mins into adsorption process for adsorbent calcined at 300°C and 400°C, and less than 40% removal for the adsorbents calcined at 500°C and 600°C. Therefore, indicating the adsorption of RB4 using 25/75 calcined at 500°C and 600°C (or calcined above 400°C) does reduce the efficiency of the adsorbents. The increase in the percentage of CPS to 50%, adsorbent calcined at 400°C had the highest percentage removal, and equilibrium was reached within 5 mins as well. Then the increase of CPS proportion to 75% resulted in adsorbent calcined at 600°C to become the most efficient adsorbent with the highest percentage removal. For adsorption of reactive blue 4, it was clear that the continuous addition of milled CPS would result in different calcination temperature as being the preferred at the proportions used. Thus the use of a homogenous mixture of kaolin and milled CPS for adsorption of reactive blue 4 would solely lie on the availability of each material and energy for calcination. Unlike the adsorption of Methylene Blue, the comparison of adsorption studies of reactive blue onto the homogenous mixture of kaolin and milled

CPS (calcined) with uncalcined kaolin showed that using uncalcined kaolin was not favourable.

5.3. Calcination of mixed adsorbents (CPS and bentonite)

5.3.1. Methylene Blue

Using bentonite, the addition of milled CPS to bentonite clay at 25/75, 50/50 and 75/25 all calcined at 300–600^{O}C had similar percentage removal when used for the adsorption of Methylene Blue dye and showed rapid removal of Methylene Blue dye. Therefore, suggesting that increasing the percentage of milled CPS with bentonite does not increase or decrease the removal efficiency of adsorbents prepared. In comparison with uncalcined bentonite, the adsorption of Methylene Blue had a lower percentage removal which could mean that to increase the removal efficiency of bentonite for adsorption of Methylene Blue calcination should be done. Although the addition of papaya seeds at different proportions had improved the adsorption efficiency of prepared adsorbents after calcination, the addition of papaya seeds did not increase or decrease the efficiency of prepared adsorbents at each proportion used. In addition, in comparison with kaolin, there seemed to be a higher tolerance for thermal modification for bentonite (600^{O}C) than kaolin (300^{O}C). Thus suggesting that dehydroxylation did not occur with an increase in calcination temperature, which points out the stability of bentonite over kaolin.

5.3.2. Reactive blue 4

Using bentonite, the addition of milled CPS did improve the removal efficiency of adsorbents as the percentage proportion increased. For 25/75, adsorbents calcined at 400^{O}C and 300^{O}C had the maximum percentage removal, and the adsorbents calcined at higher temperatures were not improved. However, it was observed that with an increase 50% and 75% CPS, there was an increase in percentage removal of reactive blue 4. In comparison, the adsorption of reactive blue 4 onto uncalcined bentonite was not favourable. Hence, indicating that the combination of bentonite and milled CPS improved the adsorption qualities of bentonite clay.

5.4. Calcination of CPS

The results obtained showed that the percentage removal of Methylene Blue was rapid at CPS 200 as seen in figure 4.19. It was observed that the increase in calcination temperature reduces the adsorption capacity of milled CPS for the decolourisation of Methylene Blue. However, for reactive blue 4, CPS300 was the suitable adsorbent. Thus, indicating that the calcination of CPS increases its removal efficiency when used for the adsorption of reactive blue. Studies have been done supporting the calcination of agricultural waste can be done in higher temperatures (Gurses *et al.,* 2006; Aworn *et al.,* 2009; Nasrullah *et al.,* 2019).

5.5 Using kaolin batch adsorption studies

The adsorbent dose has an effect on the percentage removal of dye and the adsorption capacity. In this adsorption study, the adsorption of Methylene Blue and reactive blue 4 were done using the 44 adsorbents samples. For the purpose of optimizing the suitable adsorbent for each dye Kruskal-Wallis test was done and the adsorbents that showed rapid adsorption were used to determine the effect of dosage, pH and initial concentration on adsorption of Methylene Blue and reactive blue 4.

5.5.1. Effect of dosage

For adsorption of Methylene Blue onto kaolin, there was an increase in percentage removal of dye as dosage was increased which is consistent with research done by Toumi *et al*., (2019) which investigated the effect of dosage on the removal of Methylene Blue onto olive cake waste. Similarly, for the adsorption of Methylene Blue onto bentonite at different proportions, there was a gradual increase in percentage removal of dye with increasing dosage of T500 (100% Bentonite) and 25/75 (T300), a gradual decrease when 75/25 (T300) was used. The number of available adsorption sites increases with an increase in dosage which resulted in the increase in the amount of dye adsorbed. For reactive blue 4, it was observed that an increase in T0 (100% Kaolinite) and 25/75 (T300) dosage resulted in an increase in percentage removal of dye. (Malik *et al.,* 2007, Yener et al., 2006; Balarak *et al.,* 2015; Tahir *et al.*, 2016; Hameed *et al.,* 2017).

5.5.2. Effect of pH

The pH of a solution is important to an adsorption process, and it increases or prevents the removal of dyes on the solution (Kausar *et al.,* 2018; Aichour *et al.,* 2019). For Methylene Blue using T0 (kaolin), there was no change in percentage removal as pH increased which could be that the adsorption of Methylene Blue in aqueous solution can be done in a basic or acidic state. For reactive blue 4, it was noticed for T0 and 75/25(T600) that the maximum percentage removal of dye occurred at pH 4. The search for a study for comparison of reactive blue 4 using similar conditions as this study was futile. However, in comparison to adsorption of anionic dyes using alkali-soluble polysaccharide of CPS, the continuous increase of pH resulted in a reduction of percentage removal of dyes (Fatombi *et al.,* 2019).

5.5.3. Effect of initial concentration

It is known that the effect of initial concentration relies on the relationship between the concentration of dye used and the binding sites that are available on the surface of the adsorbent (Sallah *et al.,* 2011; Bharathi and Ramesh, 2013). For Methylene Blue, the decrease in percentage removal of dye as initial concentration was observed. For Reactive Blue 4, increasing initial concentration also resulted in an increase in percentage removal of dye in some adsorbents used, and there was a decrease in other adsorbents (Fatombi *et al.,* 2019). Hence, the result obtained for both dyes could be due to increasing dye molecules as concentration increases and rapid saturation of accessible and active sites on the surface of adsorbents used. In addition, the decrease in percentage removal of dye stems from the fact that the dosage is fixed irrespective of the initial concentration uses. Therefore, the amount of dye adsorbed would be the quantity that the weight of dosage can adsorb (Sallah *et al.,* 2011; Bharathi and Ramesh, 2013). However, for adsorbent that showed an increase in percentage removal of dye (Reactive Blue 4), this could be as a result of unsaturated sites on the surface of the adsorbent. For such cases as this, the increase observed is due to the high initial dye concentration allows mass transfer driving force for adsorption to occur (Zhou et al., 2019). Therefore, the percentage removal of dye relies on initial concentration (Sallah *et al.,* 2011; Bharathi and Ramesh, 2013; Mohebali *et al.,* 2018; Toumi *et al.*, 2019).

5.6 Using bentonite batch adsorption studies

5.6.1. Effect of dosage

For adsorption of Methylene Blue onto bentonite, an increase in percentage removal of dye was observed, and it was similar in all adsorbents used. Results presented showed that 99% of dye was removed with increasing dosage and the remained that way till 1.8g. For adsorption of Reactive Blue 4 onto 25/75 (CPS/BC) similar result was obtained and the maximum percentage removal of 47% at 1.8 g. Vimonses *et al.* (2009) had a similar result while studying the removal of anionic dyes using clay material combined with calcium hydroxide. However, it was noticed that the adsorption capacity reduces with increasing dosage for all adsorbents used (Tahir *et al.*, 2016; Hameed *et al.,* 2017).

5.6.1. Effect of pH

The initial pH of a dye solution is vital to an adsorption process and it (Kausar *et al.,* 2018; Aichour *et al.,* 2019). For Methylene Blue, a slight increase in percentage removal of dye, but generally, amongst the adsorbents, >90% removal of dye was observed. However, the maximum removal of dye was seen in pH 5.0 for 25/75 (T300) and 75/25(T300) and pH 2.0 for 100% bentonite (T500). Although some authors have suggested that maximum adsorption of Methylene Blue is in the neutral, however, in this study, the high percentage removal of dye recorded at pH 2.0-10.0 suggested that the efficiency of these adsorbents for adsorption of Methylene Blue is not dependent on changing pH. However, for reactive blue 4, the increase and decrease in percentage removal of dye suggested that the adsorption process relies on pH. Although Chinoune *et al.,* (2016) and Gharbani (2018) stated that the maximum adsorption of reactive dyes is achieved at acidic pH, the results in this study did not align with that. The maximum percentage removal of dye using 25/75 and 100% bentonite was at pH 10.0, which suggests that the surface of the adsorbents has a negative charge. However, for 75/25 (T300), the maximum percentage removal of dye was achieved at pH 2 (Chinoune *et al.,* 2016; Chowdhury and Saha, 2016; Gharbani, 2018).

5.5.3. Effect of initial concentration

In this study, results obtained for the effect of initial concentration of Methylene Blue onto bentonite showed a slight increase and decrease in percentage removal of dye (> 90% removal) using the selected adsorbents, viz: 100% Bentonite (T500), 25/75(T300) and 75/25 (T300). For Reactive Blue 4, increasing initial concentration resulted in an increase in percentage removal of dye in some adsorbents used [25/75 (T400)], and there was a decrease in other adsorbents [100% Bentonite (T400)] (Fatombi *et al.,* 2019). Hence, the result for both dyes could be due to increase of dye molecules as concentration increases and rapid saturation of active sites on the surface of adsorbents. Also, the decrease in percentage removal of dye could be due to the constant dosage used irrespective of the initial concentration of dye. Therefore, the amount of dye adsorbed would be the quantity that the weight of dosage can adsorb (Bharathi and Ramesh, 2013). However, for adsorbent that showed an increase in percentage removal of dye (Methylene Blue and Reactive Blue 4), this could be as a result of unsaturated sites on the surface of the adsorbent. Therefore, the percentage removal of dye relies on initial concentration (Bharathi and Ramesh, 2013; Mohebali *et al.,* 2018; Toumi *et al.*, 2019)

5.6. Adsorption isotherms and kinetics

It was important to understand the relation between adsorbent and adsorbate as well as the distribution of adsorbate between the solution and the adsorbent. Adsorption isotherms aided the understanding of the interaction that occurs. In addition, the isotherms provided information on the optimum use of the adsorbents and their capacities. There are different isotherms used for adsorption studies, but Langmuir and Freundlich isotherm models are mostly used (Hameed and Ahmad, 2009; Ahmed and Dhedan, 2012; Ghasemi et al, 2014; Ruthiraan *et al,* 2018). The isotherm data were analysed by fitting them into linear forms of Langmuir and Freundlich isotherm models (Almeida *et al.,* 2009; Fouodjouo *et al.,* 2017; Vahidhabanu *et al.,* 2017). Langmuir model assumes that the adsorbent is a monolayer and the surface is homogenous while Freulinch assumes that the adsorbent is multi-layer with a heterogeneous surface (Boukhemkhem and Rida, 2017; Khanday *et al.*, 2017).

For this study, four linear derivatives of Langmuir isotherm and Freundlich isotherm were used (Kumar and Sivanesan, 2005). For both isotherms, two parameters are observed to determine if the adsorption was favourable and fits into the isotherm models, namely; correlation coefficient for both isotherms, the dimensionless separation factor (R_L) for Langmuir isotherm and n for Freundlich isotherm (Tran *et al.*, 2017). In this study, the adsorption of Methylene Blue using 75/25, due to the correlation coefficient obtained Freundlich isotherm (0.776) was a better fit, thus suggesting that the adsorbent and adsorbate interact during adsorption. However, the adsorption of Methylene Blue using 25/75 and T400(Ben) showed that Langmuir 1 was the best fit for the experimental data for both adsorbents based on the correlation coefficient 0.969 and 0.9616 respectively. In addition, the maximum adsorption capacity was seen to be 15.10 mg/g and 31.34 mg/g. Furthermore, the RL value showed that the Langmuir isotherm was favourable. With most adsorption studies, it has been found that the experimental data fit the Langmuir isotherm better than the Freundlich isotherm, and it was evident in this study as well.

5.7. Adsorption kinetics

Furthermore, to determine the rate of the adsorption process, kinetic models were used to examine the experimental data obtained. The adsorption rate was crucial for determining suitable adsorbent. Most adsorption studies of dyes have used pseudo-first and second-order to study the adsorption kinetics, and for this study, these kinetic models were used as well. For pseudo-first-order, the correlation coefficient was observed to range from 0.094 – 0.861 and the calculated qe values did not show good agreement with the experimental qe values. Hence, the experimental data did not fit the pseudo-first model. Consequently, studies have shown that in most adsorption studies of dye, pseudo-first-order is not always a good fit for experimental data (Salleh *et al.,* 2011; Singh *et al.,* 2017). Aljebree *et al.* (2017) investigated the adsorption of textile dyes using coconut shells activated carbon and experimental data obtained did not fit pseudo-first-order. Similarly, Stavrinou *et al.* (2018) explored the adsorption of cationic and anionic dyes onto waste peels of banana, cucumber and potato. Authors found that for adsorption kinetics study, the experimental data did not fit pseudo-first-order for all adsorbent material used. However, there are adsorptions studies whereby the experimental data fit the pseudo-first-order model, but they are not common (Hameed and El-Khaiary, 2008). As with most adsorption of dyes studies, pseudo-second-order was the best fit in this research. Kallel *et al.,* (2016), used garlic peel for the adsorption of methylene and found that the experimental data fit pseudo-second-order best. Degermenci *et al.,* (2019) compared pseudo-first degree, pseudo-second degree, Weber-Morris (intraparticle diffusion model), Bangham, Elovich and Boyd kinetic models for the adsorption of reactive dyes and authors found that pseudo-second-order best fit the experimental data. In this study, pseudo-second-order for all adsorbents used had correlation coefficient ranging from 0.854 – 0.99 and the calculated qe was in good agreement with the experimental qe for all adsorbents as well. Therefore, showing that the pseudo-second-order model is the experimental data better. Thus signifying the assumption that the rate-controlling step could be chemisorption (Salleh *et al.,* 2011; Ashaine *et al.,* 2018)

CHAPTER 6

Conclusion

In this project, mixed adsorbents using two clay minerals (kaolin and bentonite) and *carica papaya* seeds (CPS) were prepared and used for adsorption of Methylene Blue and Reactive Blue 4 from aqueous solution. This study has explained the sample preparations, proportions and calcination temperature are necessary parameters required to produce an adsorbent which is suitable for adsorbing synthetic dyes used in this research work. Some differences observed with the efficiency of prepared adsorbents were mainly due to the different proportion of adsorbents material used and the calcination temperature (100-600^{O}C).

Although, calcination of adsorbents was done to improve adsorption efficiency; however, it was observed that calcination was not necessary for some proportion, and it was important for some adsorbents.

- The use and comparison of natural kaolin clay, calcined kaolin and combined adsorbents (CPS/Kaolin) for adsorption of Methylene Blue showed that natural kaolin was the suitable adsorbent.
- The use and comparison of natural bentonite clay, calcined bentonite and combined adsorbents (CPS/Bentonite) for the adsorption of Methylene Blue showed that the addition of CPS and the calcination of bentonite clay improved its adsorption efficiency.
- For Reactive Blue 4, the calcination of natural kaolin and bentonite was found to be necessary to increase the percentage removal of dye.
- The combination of kaolin and bentonite clay with CPS also improved the removal efficiency of these clay minerals. However, the calcination of adsorbents should be done, preferably at 400^{O}C.

Table 6.1 shows the adsorption capacities of adsorbents used for adsorption of methylene blue and reactive blue 4. The table shows varying adsorption capacities which could be due to the difference in materials, combination of materials and preparation of adsorbents.

Table 6. 1. Adsorption capacities for adsorbents used for adsorption of Methylene Blue and Reactive Blue 4

Dyes	Adsorbents	Maximum adsorption capacity (mg/g)	Dosage (g)
Methylene blue	Kaolin	15.55	Ghosh and Bhattacharyya (2002)
	Corn husk	30.3	Malik et al., (2016)
	Almond shell	66.67	Çiğdem Sarici-Özdemir & Fatih Kiliç (2018)
	Bark of cactus fruit	222.22	Benderdouche et al,. (2017)
	T0 (Kaolin)	11.67	Present stu dy
	T500 (Bentonite)	12.49	
	T300 (25% CPS/75% BC)		
	T300 (75% CPS/25% BC)		
Reactive Blue 4	Red seaweed	55.6	Hii et al., (2011)
	T300 (25% CPS/75% KC)	1.77	Present study
	T400 (25% CPS/75% BC)	3.31	
	T0 (Kaolin)Red seaweed	1.8	

The techniques used for surface characterisation of prepared adsorbents showed that was used to understand the impact of calcination of adsorbents.

- SEM was used to get the pictorial image of adsorbents materials and it showed that adsorbent materials were porous. However, after adsorption was done, there was a decrease in porosity.
- EDX was used to determine the elements present in the adsorbents. It showed that the calcination and adsorption process had a considerable impact on the percentage weight of elements in selected adsorbents.

- FTIR spectra pointed out the functional group (O-H and C-H group) present on the adsorbent. However, it showed that with calcination and adsorption, there were slight increases in the intensity of the peaks.

Overall, this study has shown that the preparation of a suitable adsorbent for adsorption of synthetic dyes can be done using low-cost adsorbent (CPS) available in Nigeria.

Future work

The following will be done for future adsorption studies:

- The use of other low cost waste materials to compare adsorption capacities of these materials to *carica papaya* seeds.

- The prepared adsorbents were used in a controlled environment or conditions and further studies will be done to determine the efficiency of prepared adsorbents using real textile effluent.

- Also investigations will be done to determine if batch or column process is suitable for large scale application. For large scale implantation, a proper CPS collection system from the market sellers will be designed.

- Furthermore, regeneration of prepared adsorbent will also be studied extensively, as this will inform on how many times the adsorbents can be used. Hence, this will provide more information on the cost effectiveness of these adsorbents.

Glossary of terms

BC- Bentonite clay

BIS - Bureau of Indian Standards

CaCPS- Calcined CPS

CaMB- Calcined CPS after adsorption with Methylene Blue

$CaRB_4$- Calcined CPS after adsorption with Reactive Blue 4

CCME - Canadian Council of Ministers of the Environment

C_e- Equilibrium concentration (mg/L)

CM- Clay mineral

C_O- Initial concentration (mg/L)

COD- Chemical oxygen demand

CP- *Carica papaya*

CPS- *Carica papaya*

CPS0- Uncalcined *Carica papaya*

CPS100- *Carica papaya calcined at* $100^{O}C$

CPS200- *Carica papaya calcined at* $200^{O}C$

CPS300- *Carica papaya calcined at* $300^{O}C$

EDX- Energy- dispersive x-ray spectroscopy

EPA - Environmental Protection Agency (United States)

FTIR- Fourier Transform Infrared

FMENV- Federal Ministry of Environment (Nigeria)

KC- Kaolin/Kaolinite lay

K_f- Freundlinch constant

K_L- Langmuir constant (L/mg)

K_1 - Pseudo-first order rate constant of adsorption

MB- Methylene Blue

q_e- Adsorption capacity at equilibrium (mg/g)

q_t- Amount of dye adsorbed per unit of adsorbent (mg/g)

RB_4- Reactive Blue 4

r^2- Correlation coefficient

SEM- Scanning electron microscope

t - Time

T0- No calcination done

T300- Calcined at $300^{O}C$

T400- Calcined at $400^{O}C$

T500- Calcined at $500^{O}C$

T600- Calcined at $600^{O}C$

UnCPS- Uncalcined CPS

UnMB- Uncalcined CPS after adsorption with Methylene Blue

$UnRB_4$- Uncalcined CPS after adsorption with Reactive Blue 4

V= Volume of adsorbate

W= Weight of adsorbent

qe = Amount of dye adsorbed (mg/g)

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