DEVELOPMENT AND CHARACTERIZATION OF POROUS GEOPOLYMER PELLETS FOR DYE ADSORPTION

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Development and Characterization of Porous Geopolymer Pellets for Dye Adsorption

by

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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
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Approved by,

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September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

GUILLES, ARIELAINE FE CRUZAT

ABSTRACT

Apart from being a water-intensive process, the textile industry also poses problems in wastewater generation. The dyeing section alone contributes to about 15-20% of total waste water that is generated in an average sized textile mill. Various techniques for dye removal have been employed and some of these are physical separation method, biological treatment, and chemical method. However, these techniques suffer from flaws one way or another and are still not widely used in the industry for reasons like economical, disposal or availability of raw material. This project aims to develop a novel method of converting raw fly ash to porous geopolymer pellets for the purpose of dye wastewater treatment by adsorption. The porous geopolymer pellets were prepared from mixing raw fly ash and 10M of NaOH as alkali activator. Various amounts of sodium silicate were added as desired in order to vary the Si/Al ratio. It has been found that parameters such as curing temperature of the pellets, Si/Al ratio and pH of the dye solutions greatly affect the dye adsorption capacity of the samples. The geopolymer pellets that were cured at 70°C with 1.8 Si/Al ratio and pellets that were cured at 60°C with Si/Al ratio of 2.0/1 show the most promising adsorption capacity without compromising the mechanical properties of the sample. Also, at lower pH, the adsorption of all samples have decreased which is due to the presence of H^+ ions in the dye which gets selectively adsorbed by the geopolymer pellets. After analyzing the plot of kinetic models and adsorption isotherms, pseudo-second order and two-site Langmuir isotherm models were identified as the best-fit curves for the acquired experimental data. The results imply that the geopolymer pellets have a high potential to be packed in a column which can provide an alternative means of treating dye wastewater in an industrial scale.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

People have always been attracted to various colors and it has indeed become a vital part of fashion to wear colorful and patterned clothes to suit everyone's desire to look good whether for personal satisfaction or to please others. There have been historical records that date back as early as 3500 BC wherein it was found that the use of natural dyes from flowers, vegetables and fruits as well as animals like insects and fishes had been employed in order to enhance people's self-appearance and to add color to the world. During the early centuries, clothes were being dyed by natural means but because of the dull colors that they give, people were driven to look for alternatives that will provide bright colors on fabrics as well as refrain from fading even when exposed to sunlight and frequent washing (Kant, 2012). As a result, the very first synthetic dye called Mauveine was discovered by W.H. Perkins in 1856 which started to revolutionize the dye industry (Hunger, 2003).

Since synthetic dyes have adverse effects to people as well as highly toxic, the search for ways to utilize natural dyes are still popular. However, even natural dyes have its own disadvantages due to the mordants, substances like chromium, which are used to permanently "fix" the color into the fabric. These make the natural dyes highly toxic and results to a highly negative effect on the wastewater quality. Apart from that, natural dyes require water that is almost equal or double of the fiber's own weight which amounts to large quantities of water being used for dyeing alone. From this dyed water, only 80% gets absorbed by the fabric and the rest has to go down the drain (Kant, 2012).

Various techniques for dye removal have been employed and some of these are physical separation method, biological treatment, and chemical method. However, these techniques suffer from flaws one way or another and are still not widely used in the industry for reasons like economical, disposal or availability of raw material.

On the other hand, fly ash, which comes from coal-fired power stations, gives a tremendous impact on the environment and economy if not disposed properly. This is because only a relatively small percentage of fly ash is being used as a primary ingredient in products like cement and other construction materials while the rest of generated ash are being held in various dumps. As a result, the land used remains unproductive and maintenance becomes a problem due to the costs that it entails (Iyer & Scott, 2001).

This project aims to find yet another possible way to utilize fly ash by taking advantage of its porous properties and using this to adsorb dye in wastewater systems. By doing so, this project does not just solve the problem of utilizing wastes like fly ash, but also, this project aspires to help wastewater management in the dye industry.

1.2 Problem Statement

The environmental issue as well as health hazards that the dye-polluted wastewater imposes to the society has become one of the primary focus of today’s study and experimentation. Various technologies have been investigated in order to remove dye from wastewater but in one way or another, they suffer from disadvantages like process complexity, handling difficulty, lifetime unpredictability due to biodegradable components, expensive process due to hard to obtain raw materials, sludge disposal issues, etc.

This project will take advantage of using fly ash based geopolymer which are abundant, readily available materials and are environmentally friendly when disposed which gives lower incurred costs. The raw materials used in this project will be fly ash collected from the waste of coal fired power stations which primarily consists of SiO_2 and Al_2O_3 and will then be mixed with an alkali activator (NaOH) to form geopolymer pellets. Different formulations of porous geopolymer pellets will then be developed and characterized by varying the curing temperature and Si/Al ratios, respectively. It is important to note that although this project's focus is the use of fly ash as raw material, any other industrial waste that contains a large amount of amorphous silica such as meta-kaolin, rice husk, or blast furnace slag can be utilized.

1.3 Objectives

i. Develop and characterize porous geopolymer pellets (composition, setting time, porosity)
ii. Establish dye adsorption characteristics of the geopolymer pellets by using Langmuir, Freundlich and Temkin models
iii. Study the effect of varying parameters like curing temperature, Si/Al ratio, pH of the dye solution, initial dye concentration and contact time on the dye adsorption capacity of geopolymer pellets

1.4 Scope of Study

The components of the raw fly ash were analyzed using XRF (X-ray fluorescence) in order to determine the initial Si/Al ratio and varied as desired. A set of samples with constant Si/Al ratio were also prepared and cured at various temperatures. Several images of the respective samples' porosity will be taken using Scanning Electron Microscope (SEM). Also, the setting time will be measured for each sample using the Vicat needle under the standards of ASTM C191.

Moreover, the results of the dye adsorption will be kinetically modeled in order to find the equilibrium time and used for building the Langmuir and Freundlich adsorption isotherm models. Comparisons of dye adsorption when varying curing temperature, Si/Al ratio, pH and initial dye concentrations will also be analyzed.

CHAPTER 2
LITERATURE REVIEW

2.1 Dye Pollution

Unlikely as it may seem, the textile dyeing and treatment processes amount to almost 20% of global industrial water pollution according to the World Bank(World Bank Group., United Nations Environment Programme., & United Nations Industrial Development Organization., 1999). Today, the industry manufactures more than 3600 individual textile dyes and more than 8000 chemicals are being introduced in all kinds of processes that are involved in textile manufacture which includes dyeing and printing. Many of these chemicals are highly toxic and give adverse side effects to humans whether directly or indirectly (Kant, 2012).

Apart from being a water-intensive process wherein for a daily production of 8000kg of fabric in an average-sized textile mill, 1.6million liters of water are consumed, and depending on the type of dye that is being used, the water consumption requirement varies from 30-50 liters per kg of cloth, the textile industry also poses problems in wastewater generation. The dyeing section alone contributes to about 15-20% of total waste water that is generated in a textile mill. There are about 72 toxic chemicals that have been identified in the wastewater that comes from textile dyeing. As a result, the world is faced with a dreadful environmental problem that is caused by human’s superficial need to wear clothes that have attractive colors and designs (Kant, 2012).

For instance, in China’s Guangdong province lays the denim capital of the world where one in three pairs of jeans sold globally is made from this town. Despite its impressive statistics in production which amounts to 300 million denim articles per year and providing jobs to 220,000 people, the city faces a potentially catastrophic problem which is due to the water in the East River in Xintang turning blue (Figure 2.1) because the factories who are in the business of dyeing denim discharge their wastewater directly to the East River. Apart from the health of those living in the wastewater directly to the East River. Apart from the health of those living in the immediate area, another concern is the potential lack of drinking water for the people who are living downstream of the river. Furthermore, the threat of the polluted water scattering and flowing to other nearby cities like Dongguan and Shenzhen is highly feared (Guang et al., 2013).

FIGURE 2.1 Untreated waste water that are pouring out directly to the river from dyeing factories (Guang, Mingzhuo, & Guang, 2013)

Apart from that, the world’s second leading exporter (after China) in the clothing industry, Bangladesh, also suffers from the same water pollution resulting from dyeing factories. In a town called Savar where Genda Government Primary School is located, teachers say that there are days when the pupils could not

FIGURE 2.2 Untreated waste water which are poured directly into the canal (Yardley, 2013)

concentrate due to the suffocating reek that drifts from the polluted canal nearby (Figure 2.2). The factories which are mostly composed of textile mills and dyeing plants simply dump their wastewater to the canal where the students can figure out the current fashion depending on the current color of the canal (Yardley, 2013).

As a result, all these dyeing business which heavily supports the textile industries generate effluents that carry various impurities like salt, surfactants and heavy metals that leads to be one of the causes of public health problem and pollutants to source and treated water (Lewinsky, 2007). These heavy metals and dyes that are discharged into aquatic systems are non-biodegradable which results to accumulation in living organisms as well as causing various human diseases and disorders (Al-Ghouti et al., 2010). Moreover, the colored effluents obstruct the light transmission that occurs in the bodies of water and as a result, it causes direct destruction of aquatic ecosystems by upsetting its biological metabolism process (Lewinsky, 2007).

2.2 Dye removal techniques

To curb the increasing contamination of water bodies which results to increasing biochemical oxygen demand (BOD) as well as disruption of ecosystems, various dye removal techniques have been studied and developed. However, these techniques suffer from various flaws that may range from use of expensive technology, raw materials that are hard to obtain or expensive, lifetime unpredictability and disposal issues.

With that said, there are currently different technologies available for removal of dye from effluents. Biological treatment, for example, may be efficient in treating polluted waters due to microorganisms that can degrade various pollutants (Crini, 2006) but its large land area requirement is a disadvantage (Bhattacharyya & Sarma, 2003) as well as its inability to totally eliminate the color of dyes in the water (Crini, 2006). Other techniques include physical separation using membrane filtration but this method suffers from limited lifetime caused by fouling of the membrane which results to highly incurred maintenance costs (Crini, 2006). In addition to that, chemical methods which include coagulation or flocculation are usually deemed as an expensive process and even though it can remove the dyes, its accumulated sludge poses its own disposal problem. Also, one of the advanced oxidation process (AOP) that is commonly applied in the industry, the Fenton oxidation process, is regarded as a simple process because it does not require special equipment and has high efficiency when removing organic pollutants (Zhou, Yu, Lei, & Barton, 2007). As a result, due to reasons like high cost of technology, raw materials that are hard to obtain or expensive, as well as problems in disposal, these conventional methods for dye removal are not being applied in the whole industry (Ghoreishi & Haghighi, 2003).

In Table 2.1 below, the current techniques used in removal of dye from wastewater is summarized and compared. It can be seen that several technologies are now being employed as dye removal techniques. However, processes like the conventional method suffers from disadvantages like sludge disposal, expensive regeneration and high maintenance requirements while membrane and oxidation processes either require high pressures or high energy cost during operation. Moreover, there are some processes that are currently emerging wherein they take advantage of biomass which gives a low operating cost but can prove to be a slow process and is highly dependent on external factors like pH and salt content of the dye wastewater.

TABLE 2.1 Summarized list of current methods of dye removal (Crini, 2006)

	Technology	**Advantages**	**Disadvantages**
Conventional treatment processes	Coagulation Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favourable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

Another physical separation method that is widely used is adsorption and it may be one of the cheapest and easiest techniques for dye removal but finding an inexpensive and readily available adsorbent material continuously proves to be a challenge. One of the commonly used dye removal methods in the industry that uses adsorption technique is the use of commercial activated carbons (CAC). It is more ideal compared to other treatment options due to its great capacity to absorb dyes and are commonly thought to be the most effective adsorbents available in the market. This is because CAC has porous characteristics and large surface area in addition to having an easily modified chemical nature so that it can be treated to optimize its properties further. However, with good quality comes high cost where it has been found that the regeneration of saturated carbon is not straightforward which means that there will be big losses in the adsorbent used (Crini, 2006).

Therefore, a low-cost adsorbent which requires little processing, abundant in nature, considered by many as waste, as well as environmentally safe to dispose without the need of expensive treatments are important to keep in mind as some of the criteria to consider when investigating ways to remove dye from wastewater. With that in mind, fly ash is considered as abundant in nature, requires little processing. comes as industrial waste and after utilizing it for dye adsorption, its sludge can be considered as a non-hazardous waste (no environmental or human health impact) upon disposal.

2.3 Utilization of biomass for wastewater treatment

The search for ways to utilize biomass has been increasing not only due to its economic potential but also due to the environmental impact that arise upon its disposal. One of the most promising uses for biomass is for wastewater treatment, particularly wastewater that is mixed with dye. Due to the risks that dye wastewater poses to the environment and to human health and the lack of economically viable and environmental-friendly means of treating dye wastewater, various studies have been conducted in order to utilize biomass for this application.

2.3.1 Date pits as solid adsorbents for removing dyes from aqueous solutions

Raw date pits (RDP), one of the possible sources of inexpensive solid adsorbent for dyes (methylene blue – MB) that are present in aqueous solutions was investigated by conducting a study on the adsorption mechanism of MB onto the RDP wherein it was found that its maximum adsorption capacities was reached after 72 hours. Factors that affect adsorption, namely pH, particle size and initial solute concentration were focused upon this research. It was seen that the increase in pH of the solution affected the adsorption capacity for MB directly. Also, it was found that the particle size of RDP did not have significant effect on the MB adsorption when the initial solute concentrations are low but if the concentrations are higher, a slight effect was observed. After building the adsorption isotherms, it was found that there exists a heterogeneous surface binding between RDP and MB. It was also seen that the surface functional groups present in the RDP have greatly impacted its adsorption characteristics (Al-Ghouti et al., 2010).

2.3.2 Pineapple waste as source of activated carbon for dye removal

In this study, the pineapple waste biomass was converted to activated carbon by saturating them with $ZnCl_2$ then undergoing pyrolysis at 500°C for 1 hour. Various pieces of pineapple leaves, stems and crowns that are disposed by the pineapple agriculture industry were utilized. Factors which affect adsorption for the methylene blue (MB) dye like contact time, initial concentration of MB and the dose of adsorbent used were investigated. At the initial period of contact, the MB removal was rapid until it reaches a saturation point wherein the system is in equilibrium and no additional dye was adsorbed while initial concentration of MB meant that longer contact time was required. The study also found that the increase in adsorbent dosage also led to a decrease in the contact time required to remove MB in the solution which is because of the increased binding sites in the surface that are available for adsorption (Mahamad, Zaini, & Zakaria, 2015).

2.3.3 Chitosan matrix fabricated with cellulose nanocrystals to make nanoporous membranes

In this study, the preparation of cellulose nanocrystals (CNCs) were done by sulfuric acid hydrolysis of sludge in the form of non-dried cellulose residue. For chitosan, it was dissolved in acetic acid then deionized water was added to the solution. The chitosan solution was mixed with the concentrated CNCs which were then subjected to freeze drying. The resulting porous composites were placed between aluminum plates to form compacted nanoporous membranes. Some of the samples underwent the crosslinking process while the others did not. As a result, the crosslinked nanocomposite was more mechanically and dimensionally stable in moist environments as well as it possesses less pore size and surface area compared to its counterpart. The effect of pH on dye removal was also investigated and it was found that as the pH of the solution increases, the surface charge potential of the adsorbent decreases which means that the electrostatic attraction between the dyes that are positively charged vs. the adsorbent's surface was also lowered and as a result, the rate of adsorption has also decreased. Furthermore, it was found that the increase in dye concentration results to a lower composite membrane adsorption capacity (Karim, Mathew, Grahn, Mouzon, & Oksman, 2014).

The following table shows the summarized list of the studies outlined above as well as their key limitations.

TABLE 2.2 Limitations of the research studies

Research Study	Limitations
Use of date pits	• Limited to countries/places that have an abundant amount of dates • Most useful only during the months that dates are available
Activated carbon from pineapple waste	• Limited to countries/places that have abundant amount of pineapples • Process involves pyrolysis at 500°C which will make regeneration an expensive process
Nanoporous membranes with chitosan matrix	• The use of membrane poses problems in fouling and maintenance costs • Expensive and not widely available raw material
Activated carbon from sludge and sugarcane bagasse	• Costly pre-treatment of sludge before turning it into an adsorbent material • Preparation of raw materials is complex and expensive

2.4 Geopolymer from waste

Coal-fired power stations have their own share in the economic and environmental problems due to the issue of the disposal of fly ash. Majority of this fly ash find their way to ash dams while a small percentage is used as a cement ingredient and other products for construction. As a result, studies have been led in order to minimize the dumping of waste in lands which will further impact costs in maintenance of such dumps (Li, Wang, & Zhu, 2006).

The search for ways in utilizing fly ash is fairly new and one of the discoveries have found that through hydrothermal conversion, fly ash can produce aluminosilicate network in amorphous form. This is commonly referred to as geopolymers (Li et al., 2006). Also, the process of geopolymerization is friendly to the environment and only needs a moderate energy to produce. There are certain mix compositions and reaction conditions for Al_2O_3/SiO_2 which can significantly influence the geopolymer properties and formation (Khale & Chaudhary, 2007).

2.5 Geopolymer as adsorbent

The chemical reaction that takes place during polymerization of a geopolymer is relatively fast and consists of the following steps which are hard to isolate from each other because they may overlap and occur simultaneously (Chanh, Trung, & Tuan, 2008):

- Dissolution of Si and Al atoms from the source material through the action of hydroxide ions
- Transportation, orientation or condensation of precursor ions into monomers
- Setting, polycondensation or polymerization of monomers into polymeric structures

The figure below shows the three basic forms that geopolymer can take (Figure 2.3).

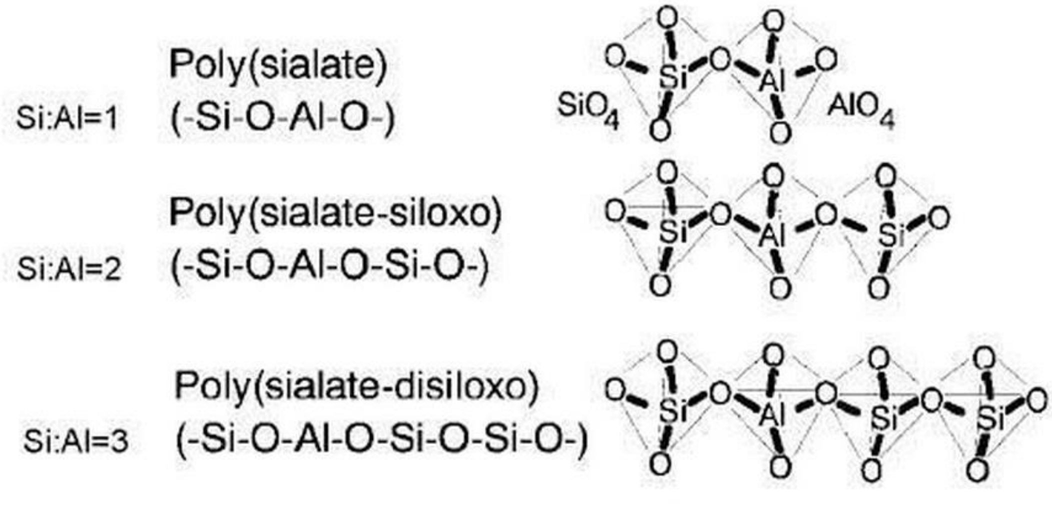


FIGURE 2.3 Chemical structure of geopolymer (Chanh et al., 2008)

Amorphous aluminosilicate geopolymers can be formed from fly ash and used for applications like wastewater treatment. It is considered to be a good adsorbent material due to the possibility of hydrogen bonding and presence of amorphous regions that make it porous and suitable for various applications. It has been reported that geopolymers can adsorb heavy metals that are present in wastewater systems like copper ions (Mužek, Svilović, & Zelić, 2013), cesium ions (Lopez, Sugita, & Kobayashi, 2014), and arsenic ions that can possibly poison the drinking water systems (Lewinsky, 2007).

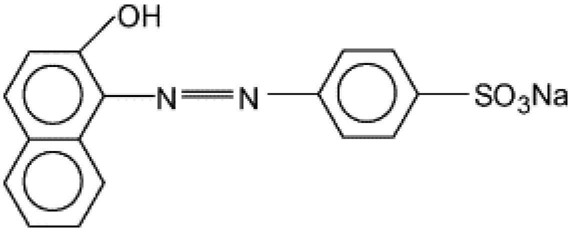


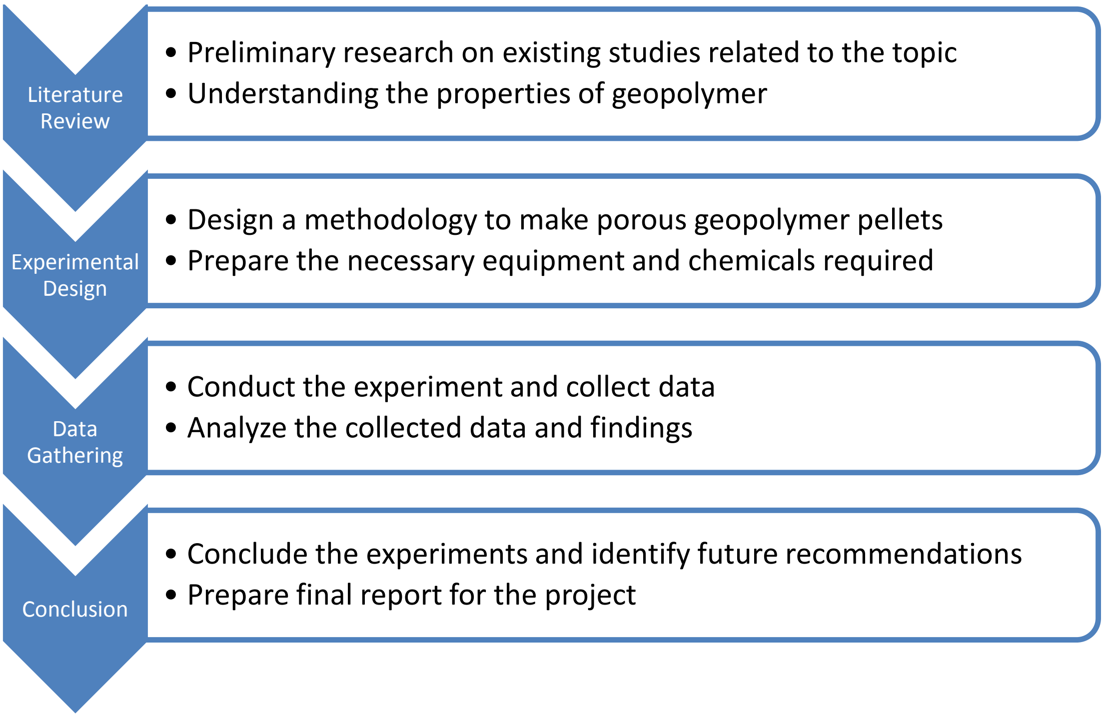
FIGURE 2.4 Chemical structure of orange II dye (Daneshvar, Rasoulifard, Khataee, & Hosseinzadeh, 2007)

Furthermore, there have been ongoing investigations as to how well geopolymers can adsorb dye that is present in wastewater. However, these studies use crushed geopolymer adsorbents in powder form (Zhang & Liu, 2013), (Li et al., 2006). For this study, the adsorption kinetics and characteristics of porous geopolymer in pellet form was used as dye adsorbent. The dye that will be used is orange II which has the following chemical structure (Figure 2.4).

CHAPTER 3

METHODOLOGY AND PROJECT WORK

3.1 Project Flow Chart



- Preliminary research on existing studies related to the topic
- Understanding the properties of geopolymer

- Design a methodology to make porous geopolymer pellets
- Prepare the necessary equipment and chemicals required

- Conduct the experiment and collect data
- Analyze the collected data and findings

- Conclude the experiments and identify future recommendations
- Prepare final report for the project

FIGURE 3.1 Project process flow

3.2 Methodology

3.2.1 Adsorbent materials

Coal fly ash that was collected from coal-fired power stations and the alkali activator, sodium hydroxide (NaOH) was obtained from R and M chemicals. Various samples of porous geopolymer pellets were produced by preparing 10M of NaOH solution using NaOH pellets from R and M chemicals which was mixed with distilled water in a volumetric flask. Then, as a reference adsorbent, used paper, a common biomass, was left to soak for a few days then dried and crushed before using them for adsorption tests.

3.2.2 Synthesis of geopolymer

For the first batch of samples, a known amount of fly ash was added to the desired amount of NaOH to produce porous geopolymer pellets that has a constant solid/liquid ratio of 3:1 (Asif, Man, Azizli, Nuruddin, & Ismail, 2014) and then cured at various temperatures (60°C, 70°C, 80°C, 90°C). Then for the second batch, Si/Al ratio was varied (2.0/1, 2.2/1, 2.5/1) by adding sodium silicate (Na_2SiO_3) to the slurry mixture while keeping the solid/liquid ratio set to 3:1.

3.2.3 Characterization techniques

The composition of raw fly ash was determined by X-ray fluorescence (XRF) data analysis that was taken from a previous study conducted which utilizes the same raw fly ash (Asif et al., 2014). Also, the setting time of each formulation was determined using a Vicat needle (Figure 3.2) and tested under the standards of ASTM C191 in order to identify the amount of working window before the slurry sets and is deemed unusable. To do so, the penetration of the 1 mm needle was first determined after allowing the slurry mixture to set for a few minutes and subsequently tested for the penetration amount for every couple of minutes. The time when the needle penetration is at 25 mm will be interpolated from the data and will be deemed the setting time of the mixture. Additionally, Scanning Electron Microscope (SEM) images were taken in order to characterize the outer surface of the samples.

FIGURE 3.2 Vicat needle penetration at 25mm

3.2.4 Adsorption of dye on geopolymer pellets

Adsorption tests were conducted in batch systems in order to identify the rate and equilibrium data for the respective samples. An anionic orange II dye was selected for the study which was obtained from Acros Organics. About 0.50 ± 0.05 g of geopolymer pellet was placed in a 50 mL of known initial concentration of orange II dye which was left to agitate in a shaker (Innova 3100 from New Brunswick Scientific – Figure 3.3) at 150 rpm and 25°C for the desired time periods. To determine the final concentrations of the dye solutions after adsorption tests, known concentrations of dye were tested on the UV-VIS Spectrophotometer (Figure 3.3) and their respective absorbance at $\lambda = 485nm$ were recorded in order to generate a calibration curve. Then, the amount of adsorption capacity by the samples is calculated using the following equation:

$$q_t = \frac{C_o - C_t}{C_o}\left(\frac{V}{m}\right) \qquad (1)$$

wherein V is the amount of dye solution in liters and m is the dosage amount of porous geopolymer pellet in grams and C_o and C_t are the initial and final dye concentrations, respectively.

FIGURE 3.3 Innova 3100 water bath shaker and UV-VIS Spectrophotometer

3.2.4.1 Effect of curing temperature

In order to investigate the effect of curing temperature, a constant amount of geopolymer pellet samples that were cured with varying temperatures were left to agitate in a 50 mL of 10ppm dye solution for 24 hours.

3.2.4.2 Effect of Si/Al ratio

The effect of Si/Al ratio on the dye adsorption was tested by adding a constant amount of geopolymer pellet samples that have different Si/Al ratios and left to agitate in a 50 mL of 10ppm dye solution for 24 hours.

3.2.4.3 Effect of contact time

The effect of contact time was studied by adding a constant amount of geopolymer pellet samples and left to agitate in a 50 mL of 10ppm dye solution for the desired time periods.

3.2.4.4 Effect of pH

For this study, the pH of the dye solutions was varied by addition of 1.0M hydrochloric acid wherein a constant amount of geopolymer pellet samples were left to agitate in a 50 mL of 10ppm dye solution for 24 hours.

TABLE 3.1 Summarized list of experiment conditions

Investigated Parameter	Curing Temperature (°C)	Si/Al ratio	Contact Time (min)	Initial Dye Concentration (ppm)	pH
Curing temperature	60 70 80 90	1.8:1	1440 (24 hours)	10	8
Si/Al Ratio	60	2.0:1 2.2:1 2.5:1	1440 (24 hours)	10	8
Contact time	60	1.8:1	5 15 30 60 120 180 240 300	10	8
pH	60	1.8:1	1440 (24 hours)	10	2 3 4 8

3.2.5 Kinetic modelling and adsorption isotherms

In order to study the rate and constants of adsorption, kinetic models were plotted and tested for their suitability with experimental data. The two most widely used models are Lagergren's pseudo-first order (Lagergren, 1898) as well as Ho's pseudo-second order kinetic models (Ho, 2006). For the adsorption isotherms, the Langmuir, Freundlich and Temkin (Temkin & Pyzhev, 1940) isotherms were graphed and the parameters were calculated using Origin® graphing software.

3.2.5.1 Pseudo-first order model

The differential equation that describes this model is given by:

$$\frac{\partial q_t}{\partial t} = k_1(q_{e1} - q_t) \tag{2}$$

After integrating Equation 2 above using boundary conditions of $t = 0$ to $t = t$ and $q_{t=0} = 0$ to $q_{t=t} = q_t$ gives the integrated rate law for the pseudo-first order reaction

$$\log\left(\frac{q_{e1}}{q_t}\right) = \frac{k_1}{2.303}t \tag{3}$$

wherein: q_{e1} and q_t is the amount of dye sorbed at equilibrium and at time t (mg/g), respectively and k_1 is the equilibrium rate constant of pseudo-first order sorption (1/min). To linearize equation 3, the following equation arises:

$$\log(q_{e1} - q_t) = \log(q_{e1}) - \frac{k_1}{2.303}t \tag{4}$$

In order to obtain the constants of equation 4, a linear plot of $\log(q_{e1} - q_t)$ vs. t for different samples and experimental conditions are analyzed wherein the variance (R_1^2) value will be analyzed.

3.2.5.2 Pseudo-second order model

This model can be described by the equation:

$$\frac{\partial q_{e2}}{\partial t} = k_2(q_{e2} - q_t)^2 \tag{5}$$

After integrating Equation 5 above using boundary conditions of $t = 0$ to $t = t$ and $q_{t=0} = 0$ to $q_{t=t} = q_t$ gives the integrated rate law for the pseudo-second order reaction:

$$\frac{1}{(q_{e2}-q_t)} = \frac{1}{q_{e2}} + k_2 t \qquad (6)$$

wherein: q_{e2} and q_t is the amount of dye sorbed at equilibrium and at time t (mg/g), respectively and k_2 is the equilibrium rate constant of pseudo-first order sorption (g mg^{-1} min^{-1}). To linearize equation 6, the following equation arises:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_{e2}}^2} + \frac{1}{q_{e2}} t \qquad (7)$$

Similar to the previous model, in order to obtain the constants of equation 7, a linear plot of $\frac{t}{q_t}$ vs. t for different samples and experimental conditions are analyzed wherein the variance (R_2^2) value will be analyzed.

3.2.5.3 Intraparticle diffusion model

The intraparticle diffusion equation can be expressed as:

$$q_t = k_i t^{0.5} \qquad (8)$$

wherein k_i is the rate constant for intraparticle diffusion (mg/g $min^{0.5}$). The linear plot of q_t against $t^{0.5}$ gives the calculated value for k_i.

3.2.5.3 Langmuir adsorption isotherm

This type of isotherm takes into account the fact that a monolayer adsorption occurs only at specific homogeneous sites within the adsorbent. The general equation for Langmuir isotherm can be expressed by:

$$Q_e = \sum_{i=1}^{n} \frac{a_i b_i C_e}{1 + b_i C_e} \qquad (9)$$

where $Q_e$is the adsorbed amount of dye (mg dye/g geopolymer pellet) at equilibrium, C_e is the equilibrium concentration of the dye in solution and a_i is the monolayer adsorption capacity, b_i is the constant related to the free energy of adsorption, respectively and together, they are taken as the parameters of Langmuir isotherm.

3.2.5.4 Freundlich adsorption isotherm

This type of isotherm is most commonly used to describe the adsorption characteristics of a heterogeneous surface. The equation can be expressed by:

$$Q_e = KC_e^{1/n} \tag{10}$$

where K and n indicates an approximation of adsorption capacity and strength of adsorption during the adsorption process.

3.2.5.5 Temkin adsorption isotherm

This isotherm differs from other isotherms in such a way that it takes into account the interactions between adsorbate and adsorbent during the adsorption process. The equation implies that there is a uniform distribution of binding energies until it reaches a certain maximum value. The equation for this model is given by:

$$Q_e = \frac{RT}{b_T} ln(A_T C_e) \tag{11}$$

where $R = 8.314 \frac{J}{mol\ K}$, $T = 298K$, A_T is the Temkin isotherm equilibrium binding constant (L/g) and b_T is the Temkin isotherm constant.

3.3 Gantt Chart

Table 3.2 Gantt Chart for FYP II

	Detailed Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Familiarization with geopolymer preparation	■●														
2	Conversion of fly ash to geopolymer		■	■●												
3	Preparation of different samples of porous geopolymer pellets			■	■●											
4	Test for dye adsorbent ability of the samples and effect of different parameters					■	■●									
5	Submission of Progress Report							■●								
6	Characterize the samples using BET Surface Area Analysis and check the porosity using SEM							■	■●							
7	Build the Langmuir-Freundlich models								■	■●						
8	Pre-SEDEX										■●					
9	Submission of Draft Final Report											■●				
10	Submission of Dissertation (Soft Bound)												■●			
11	Submission of Technical Paper												■●			
12	Viva													■●		
13	Submission of Project Dissertation (Hard Bound)															■●

CHAPTER 4

RESULTS AND DISCUSSION

For the isotherm studies, all samples were tested under the same conditions as described in the previous chapter and three experimental data for each testing condition were taken in order to minimize experimental errors. For simplification purposes, the various samples will be coded hereinafter and the list is shown below in Table 4.1.

TABLE 4.1 Properties of porous geopolymer pellets prepared

Sample Name	**Curing Temperature (°C)**	**Si/Al ratio**
S1	60	1.8/1
S2	70	1.8/1
S3	80	1.8/1
S4	90	1.8/1
S5	60	2.0/1
S6	60	2.2/1
S7	60	2.5/1

FIGURE 4.1 Geopolymer pellets before (left) and after (right) addition of Na_2SiO_3

4.1 Characterization of porous geopolymer pellets

The XRF data of raw fly ash given in the table below was crucial to determine its initial Si/Al ratio and to help guide when estimating the varying Si/Al ratio parameter.

Table 4.2 XRF data analysis of fly ash (Asif et al., 2014)

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	SO_3 (%)	Na_2O (%)	TiO_2 (%)	P_2O_5 (%)	BaO (%)	SrO (%)	MnO (%)
43.34	20.77	12.41	11.13	3.75	1.98	1.45	0.95	0.88	0.32	0.17	0.12	0.11

Sample calculations for calculating the Si/Al ratio:

Initial Si/Al ratio – 1.8/1 (from original composition of fly ash shown in Table 3)

For every 100g of fly ash – there exists 43.34g of SiO_2 and 20.77g of Al_2O_3. To identify the amount of Si and Al present in the fly ash:

$$\frac{43.34\text{g SiO}_2}{60.08\frac{\text{g}}{\text{mol}}\text{SiO}_2} * \frac{1\text{ mol Si}}{1\text{ mol SiO}_2} * 28\frac{\text{g}}{\text{mol}}\text{Si} = 20\text{g Si}$$

$$\frac{20.77\text{g Al}_2\text{O}_3}{101.96\frac{\text{g}}{\text{mol}}\text{Al}_2\text{O}_3} * \frac{2\text{ mol Al}}{1\text{ mol Al}_2\text{O}_3} * 27\frac{\text{g}}{\text{mol}}\text{Al} = 11\text{g Al}$$

$$\frac{20\text{g Si}}{11\text{g Al}} = \frac{1.8}{1} = 1.8:1\ (\text{Si/Al ratio})$$

Varying the ratio to 2.0:1 (Si/Al ratio) requires the addition of sodium silicate (Na_2SiO_3) and in order to calculate the amount of Na_2SiO_3 that is required, the following calculations were done:

$$\frac{\text{M Si}}{11\text{g Al}} = \frac{2.0}{1}$$

$$\text{M} = 22\text{g Si}$$

Keeping in mind that there exists 20g Si in the original fly ash composition, therefore the required additional Si becomes M_{Si}= (22-20) g = 2g Si. This required amount of Si will be taken from the sodium silicate solution that was supplied by R and M Chemicals and has 40% Si concentration. This means that the amount of sodium silicate to be added in order to make the geopolymer will be:

$$\frac{100\mathrm{g\ Na_2SiO_3}}{40\ \mathrm{g\ Si}} = \frac{\mathrm{M_{req}}}{2\ \mathrm{g\ Si}}$$

$$\mathrm{M_{req}} = 5\mathrm{g\ Na_2SiO_3}$$

The same method of calculation is applied for Si/Al ratios of 2.2:1 and 2.5:1 in order to identify how much sodium silicate must be added in order to meet the desired respective ratios.

Moreover, the setting time was determined to identify how much working time window is there for every formulation and to ensure that the slurry does not set before it is ready for curing process. It can be seen in the table below that the setting time decreases dramatically upon the addition of Na_2SiO_3 and decreases further as the Si/Al ratio increases due to the further addition of Na_2SiO_3.

TABLE 4.3 Setting time of each formulation

S1	23 hours
S5	35 minutes
S6	24 minutes
S7	11.5 minutes

Additionally, images with 3000x magnification from SEM were taken for each sample in order to characterize their respective surface as well as the amount and size of the samples' respective pores. It can be seen that there is a significant amount of clusters formed in S3, S4, S6 and S7 which may be deemed undesirable in terms of the distribution of mechanical strength properties of the samples. This becomes an important factor if the samples are placed in a packed bed column because a more equal distribution of compressive strength and amount of crushing is more desirable for such application.

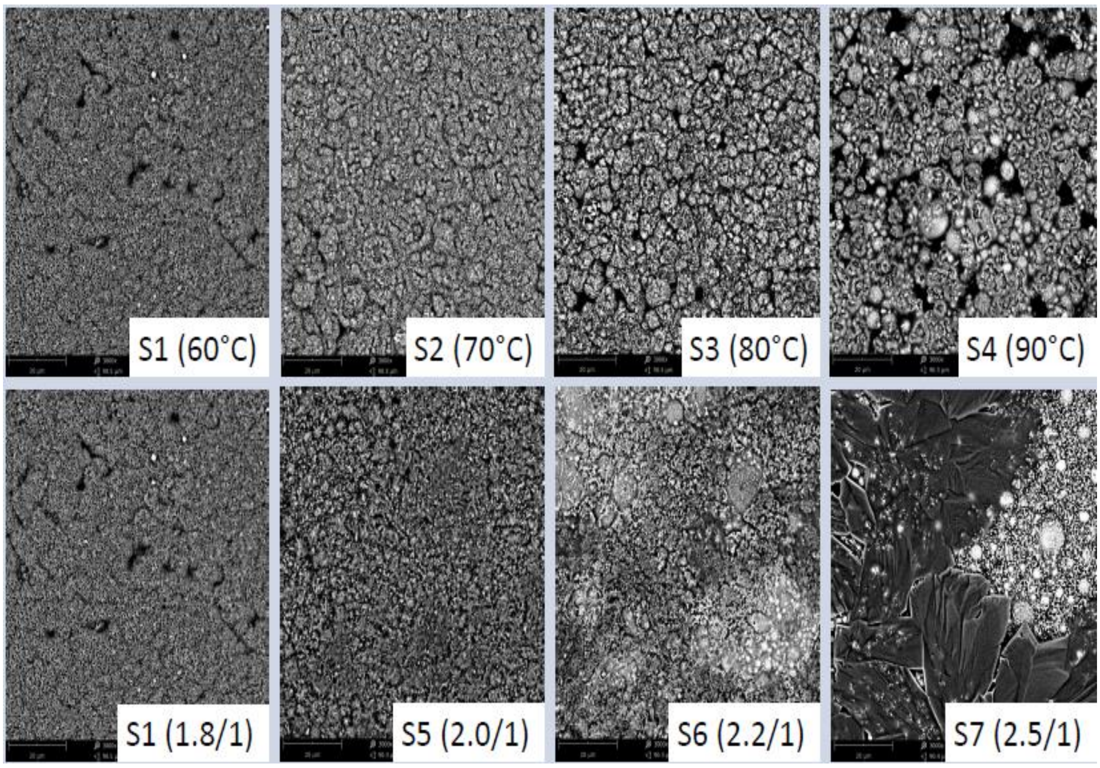


FIGURE 4.2 SEM images with 3000x magnification

4.2 Dye adsorption on geopolymer pellets

A calibration curve was generated by adding known amounts of dye to distilled water to make various solutions with known concentrations. The absorbance of these solutions are then measured using the UV-VIS Spectrophotometer at $\lambda = 485\ nm$. The calibration curve generated, shown in the figure below, will then be used to calculate the final concentrations of various dye solutions after exposing them to various samples porous geopolymer pellets at different conditions.

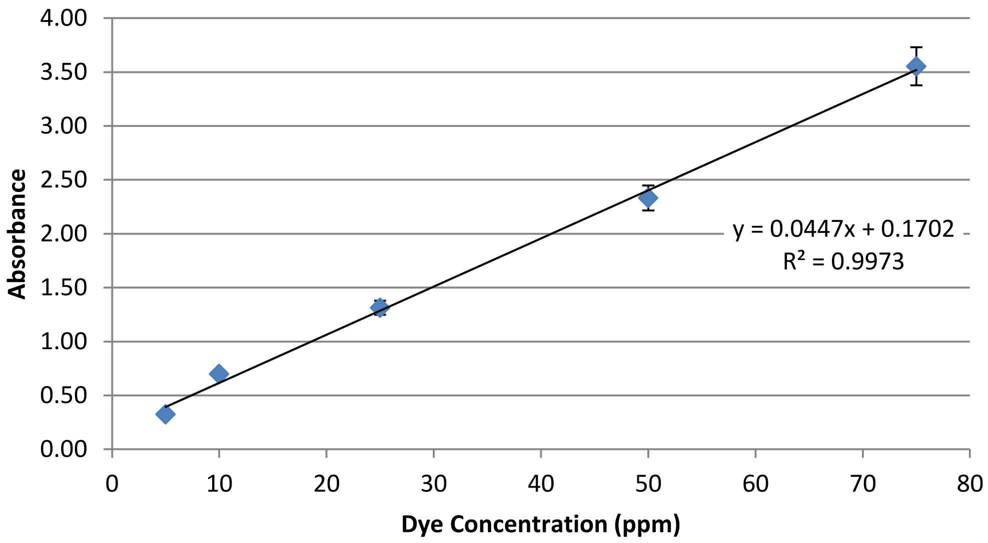


FIGURE 4.3 Calibration curve for orange II dye

Shown in the graph above (Figure 4.3) is the equation (12) that relates absorbance with the dye concentration. It is safe to say that this relation is valid due to the high value of variance (0.9973) and the graph also shows the 5% error on the data points which can also be deemed negligible in this case.

$$y = 0.0447x + 0.170 \tag{12}$$

4.2.1 Effect of contact time

The figure below shows a representative graph for the effect of contact time in the dye adsorption of geopolymer pellet sample S1. The rest of the graphs for the other samples are available in Appendix I. The contact time plays an important role in the dye adsorption which reaches equilibrium at about 24 hours (Li et al., 2006). Also, as a means of comparison, the adsorption of used paper was compared with the adsorption of geopolymer and it can be seen that initially, used paper has better performance but starts to plateau while the geopolymer pellets' adsorption capacity continue to significantly increase. With that said, the rest of the experiments will mainly focus on the porous geopolymer pellets alone.

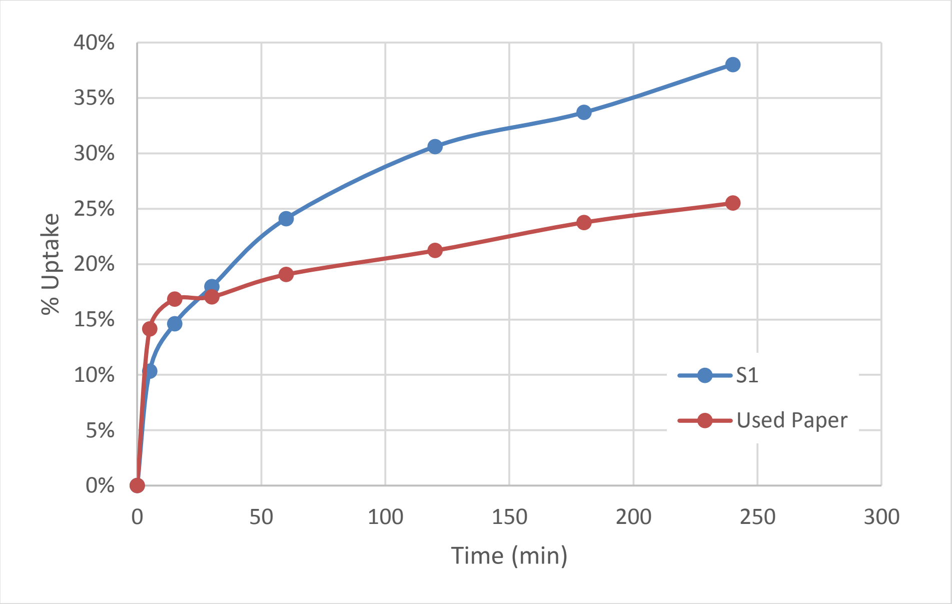


FIGURE 4.4 Effect of contact time on dye removal of S1

4.2.2 Effect of curing temperature

The graph below shows the effect of curing temperature in the dye uptake of the geopolymer pellets. It can be seen that increasing the curing temperature generally increases the dye adsorption of the geopolymer pellets which may be due to a higher conversion of fly ash to geopolymer (Li et al., 2006). However, the plot also shows that there is a slight decrease on the percent uptake when the sample was cured at 80°C and 90°C, respectively. As seen in Figure 4.2, this may be due to the increase in pore size which may have reduced the overall surface area of S3 and S4 when compared to S2.

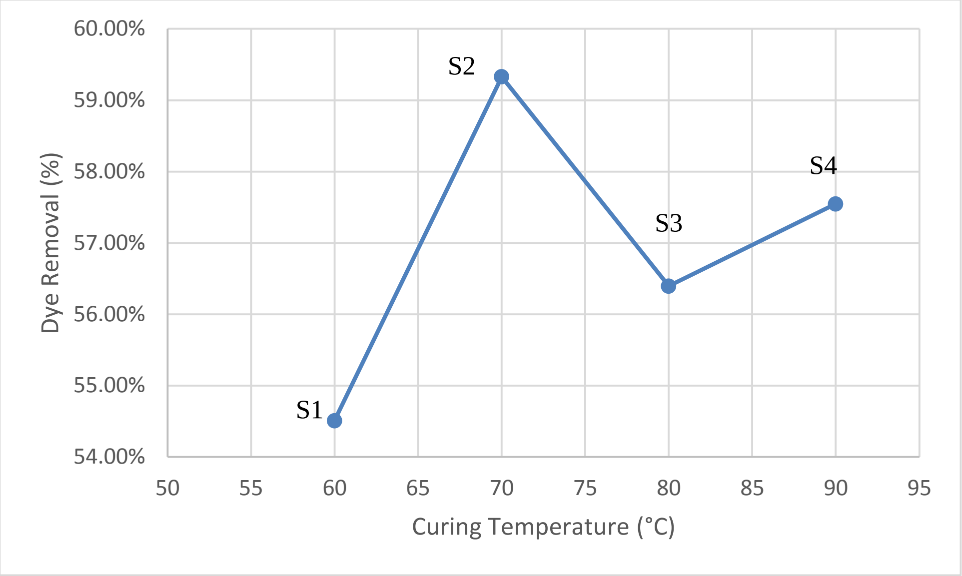


FIGURE 4.5 Effect of curing temperature on dye removal

4.2.3 Effect of Si/Al ratio

The graph below shows the influence of Si/Al ratio on the dye removal of porous geopolymer pellets. It can be seen that there is a general increase in the percent of dye removed when the Si/Al ratio was increased. However, a slight decrease happened when the Si/Al ratio were at values 2.2/1 and 2.5/1 for S6 and S7, respectively. It has been found that increasing the Si/Al ratio of geopolymers results to a more amount of larger pores present in the sample which in turn, shifts its pore volume distribution (Zheng, Wang, & Shi, 2010). This finding is supported by the SEM images that was obtained for the geopolymer pellets wherein it can be seen from Figure 4.2 that the pore sizes of samples S5, S6 and S7 have increased with respect to S1 upon the addition of Na_2SiO_3 to increase Si/Al ratio.

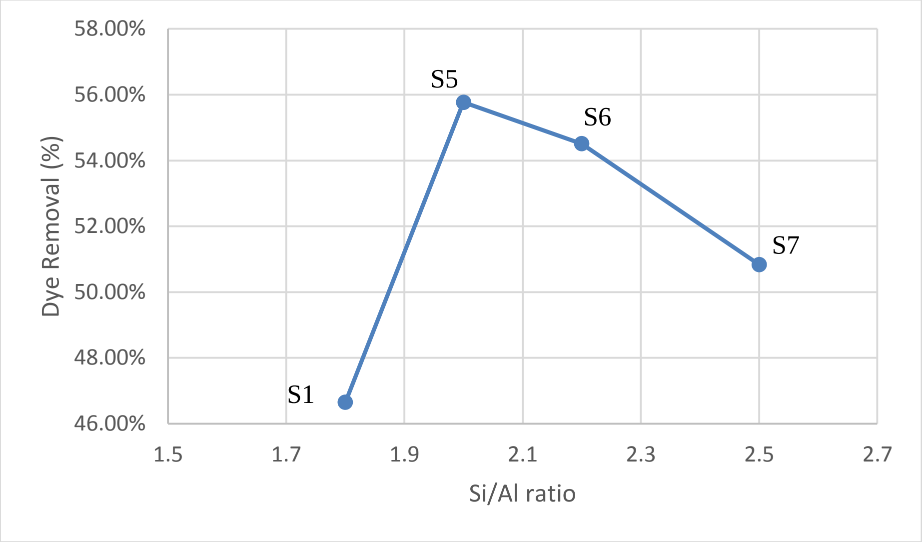


FIGURE 4.6 Effect of Si/Al ratio on dye removal

4.2.4 Effect of pH

The graph below shows that there is a significant decrease on the samples' dye adsorption when the pH of the dye solutions was lowered. This is because a decrease in pH means that there is more concentration of H^+ ions in the solution which increases the tendency of the geopolymer sample to selectively adsorb only H^+ ions (Cheng, Lee, Ko, Ueng, & Yang, 2012). Kamel et al. also found that the adsorption efficiency of fly ash based geopolymer increases drastically as the pH of the solution is increased from 1 to 5 (Al-Zboon, Al-Harahsheh, & Hani, 2011).

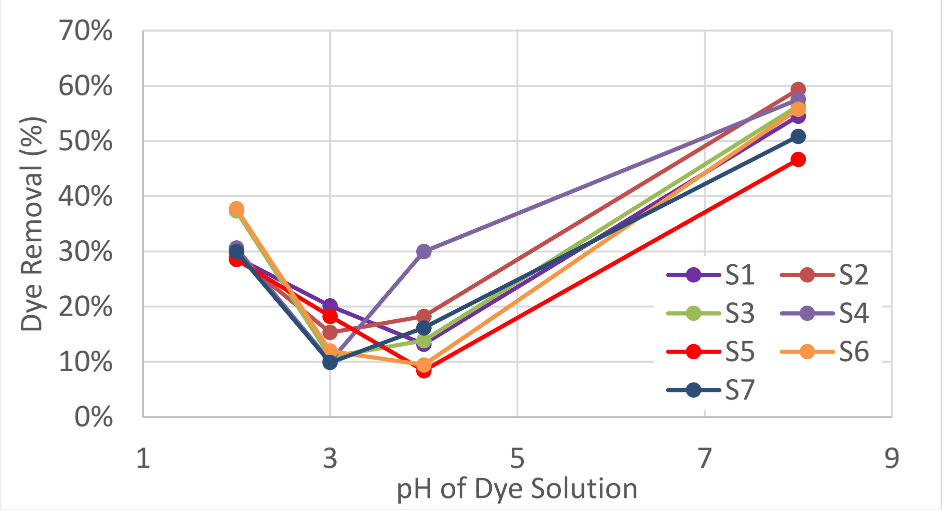


FIGURE 4.7 Effect of pH of dye solution on dye removal

4.3 Kinetic Modelling

The tabulated results below show that the pseudo-second order model best fits the experimental data with correlation coefficients that range from 91-99%. The calculated parameters of each geopolymer pellet sample are given as follows:

TABLE 4.4 Parameters for kinetic models

Sample Name	Pseudo-second order			Pseudo-first order			Intraparticle diffusion	
	q_2	k_2	R^2	q_1	k_1	R^2	k_p	R^2
S1	0.3523	0.1194	0.9919	0.4113	0.0039	0.9434	0.0203	0.9803
S2	0.6360	0.0594	0.9861	0.4795	0.0097	0.9821	0.0369	0.9054
S3	0.4678	0.1116	0.9826	0.3843	0.0062	0.9725	0.0239	0.9777
S4	0.4715	0.0850	0.9133	2.3856	0.0071	0.8690	0.0238	0.8904
S5	0.4925	0.0680	0.9840	0.3303	0.0191	0.7949	0.0310	0.9296
S6	0.5876	0.0882	0.9914	0.3258	0.0173	0.8685	0.0351	0.8480
S7	0.4615	0.2270	0.9983	0.2703	0.0069	0.8010	0.0215	0.8652

4.4 Adsorption isotherms

The figure below shows a representative isotherm plot for sample S1 which was analyzed using Origin® graphing software. The isotherm plots for various samples are shown in Appendix II. It can be seen from the plot that the two-site Langmuir isotherm best explains the experimental data. The calculated parameters for Langmuir, Freundlich and Temkin isotherms are shown in Figure 4.8 and Table 4.5 and 4.6. The variance *(R^2)* values show that two-site Langmuir isotherms give the best fit on the experimental data.

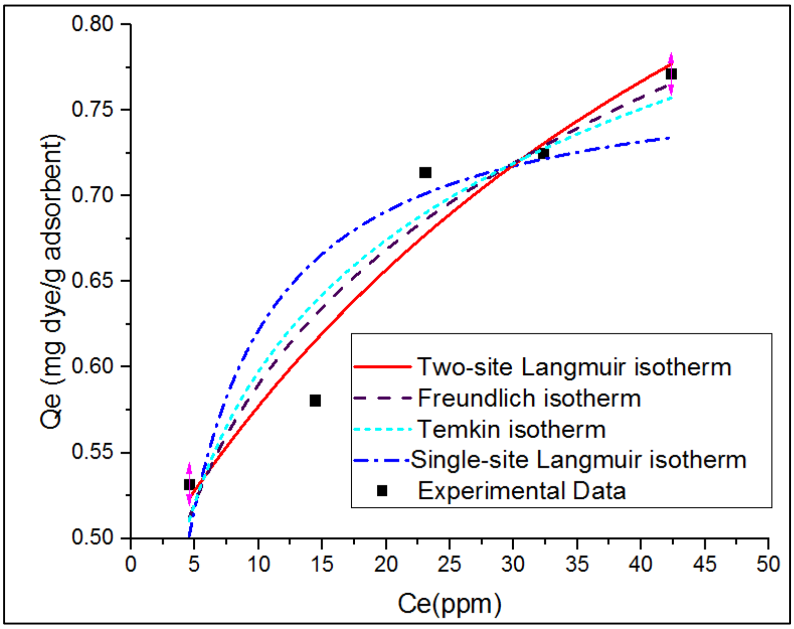


FIGURE 4.8 Adsorption isotherm plots for S1

TABLE 4.5 Parameters for two-site and single-site Langmuir isotherms

Sample Name	Two-site Langmuir			Single-site Langmuir		
	q_m	K_L	R^2	q_m	K_L	R^2
S1	0.757	0.267	0.991	0.778	0.399	0.782
S2	2.241	0.054	0.931	2.107	0.018	0.917
S3	2.731	0.051	0.944	2.589	0.057	0.926
S4	2.012	0.084	0.976	3.356	0.034	0.939
S5	3.856	0.024	0.985	3.828	0.024	0.967
S6	3.839	0.031	0.981	3.560	0.021	0.921
S7	0.613	0.152	0.982	0.582	0.198	0.884

TABLE 4.6 Parameters for Freundlich and Temkin isotherms

Sample Name	Freundlich Model Parameters				Temkin Model Parameters		
	K_f	1/n	n	R^2	A_T	b_T	R^2
S1	0.390	0.180	5.545	0.912	22.110	22382.979	0.892
S2	0.243	0.513	1.948	0.917	0.698	5553.351	0.915
S3	0.258	0.548	1.825	0.938	0.540	4264.764	0.927
S4	0.214	0.608	1.645	0.976	0.502	4108.811	0.917
S5	0.145	0.706	1.416	0.975	0.315	3567.829	0.966
S6	0.149	0.779	1.283	0.914	0.381	3163.921	0.918
S7	0.212	0.248	4.027	0.960	3.827	23740.629	0.942

Shown in Table 4.5 are the parameters for two-site Langmuir isotherm where it can be seen that the maximum uptake of the geopolymer pellets happens for samples S5 and S6 respectively. However, it is important to note that there is a limit to the compressive strength increase in the sample when the Si/Al ratio increases because after certain ratio values, approximately above the ratio of 2.1, the strength tends to decrease again (Zheng et al., 2010). With respect to the samples involved in this study, S5 is a better choice even if it exhibits a slightly less maximum capacity compared to S6 because it has better mechanical properties which plays an important role in packed bed systems type of application.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

To conclude, this project has found a more economical way of dye removal technique as the ones available in the industry are either considered as an expensive process or the raw materials are hard to find. Contrary to the widely used techniques of dye removal, the project used cheap and readily available fly ash as raw material which is considered by many as waste and also solves environmental and economic issues that arise upon disposal. Even though this project utilizes raw fly ash alone, other industrial wastes that are rich in amorphous silica such as meta-kaolin, rice husk, or blast furnace slag can also be used for the same application.

In addition to that, this project has found a novel method of converting fly ash to geopolymer pellets which has the potential of being applied to packed bed systems as opposed to the current method of crushing the samples into powder form. It has been found that the pseudo-second order kinetic and two-site Langmuir isotherm models fit the kinetics and adsorption mechanism of the porous geopolymer pellet samples, respectively.

The author hopes that the study will be beneficial not just in a research setting but also applicable in the industry as a whole. This can be done by further applying the research study in continuous systems and placing the porous geopolymer pellets in a packed bed column in order to simulate a more realistic industrial approach.

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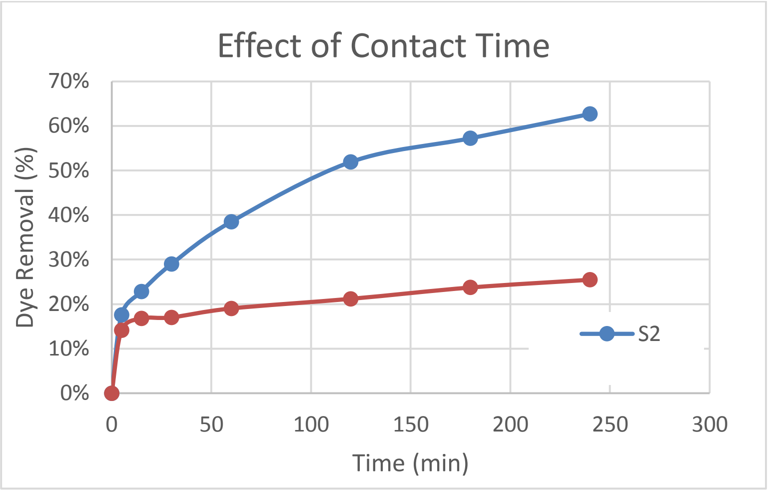
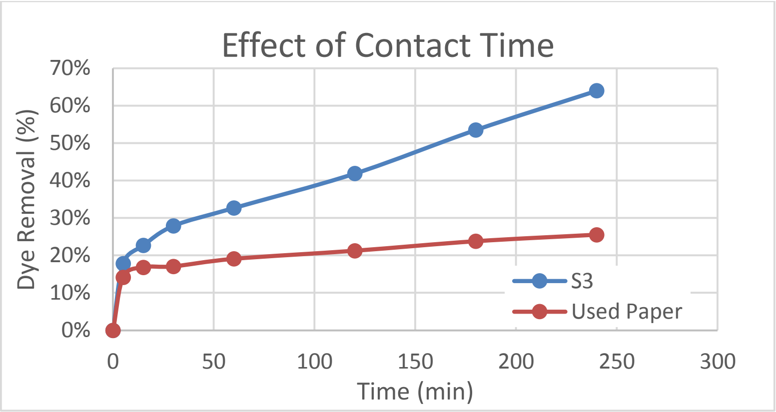
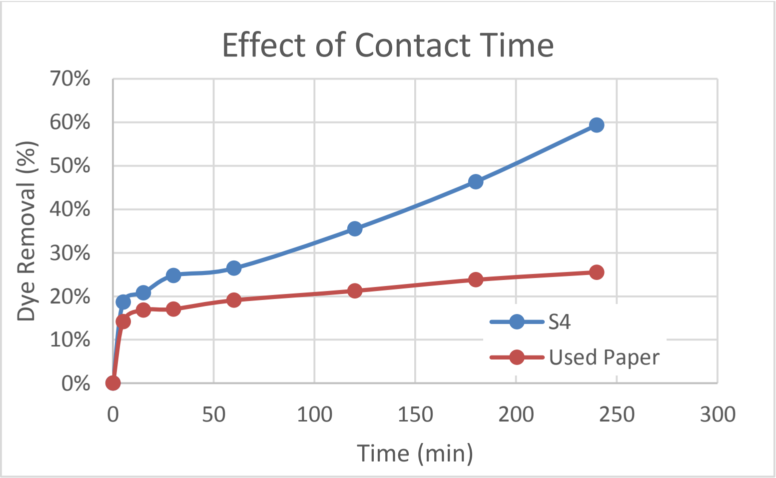
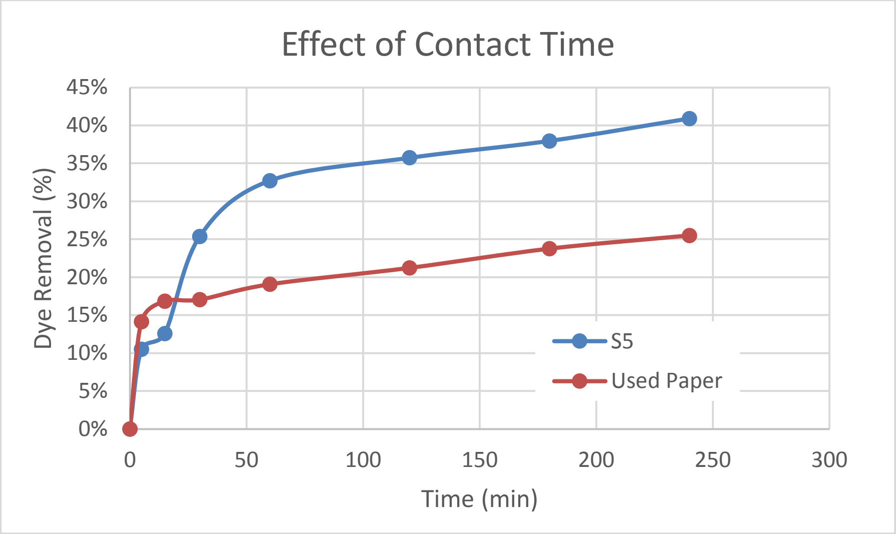
APPENDICES

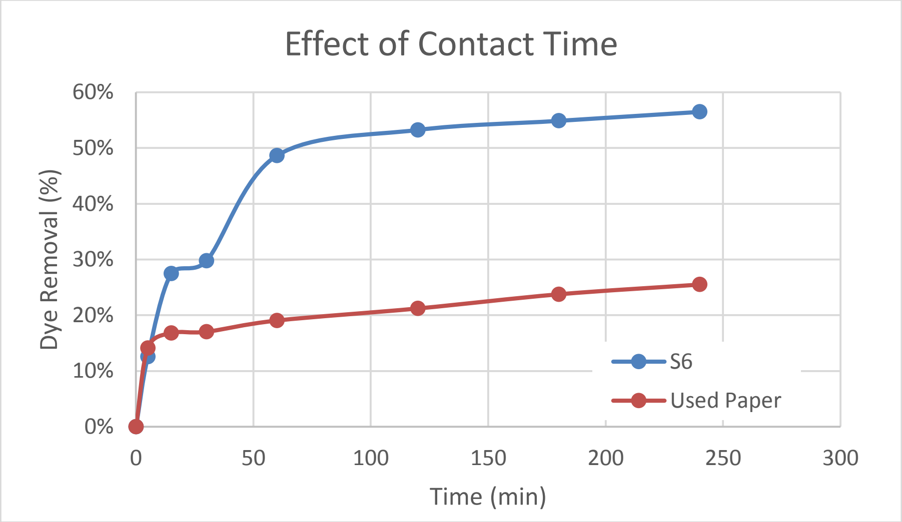
I. Effect of contact time on dye adsorption of various samples, with used paper as reference

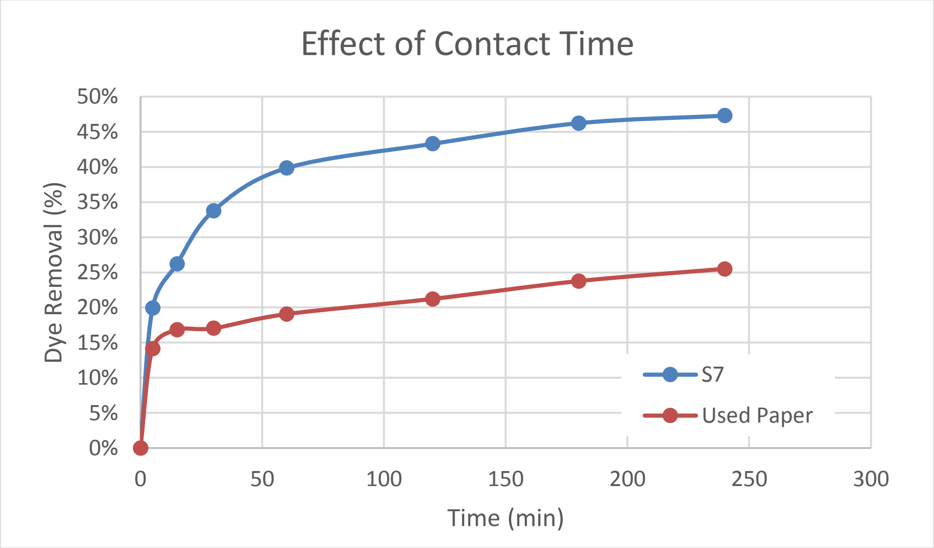




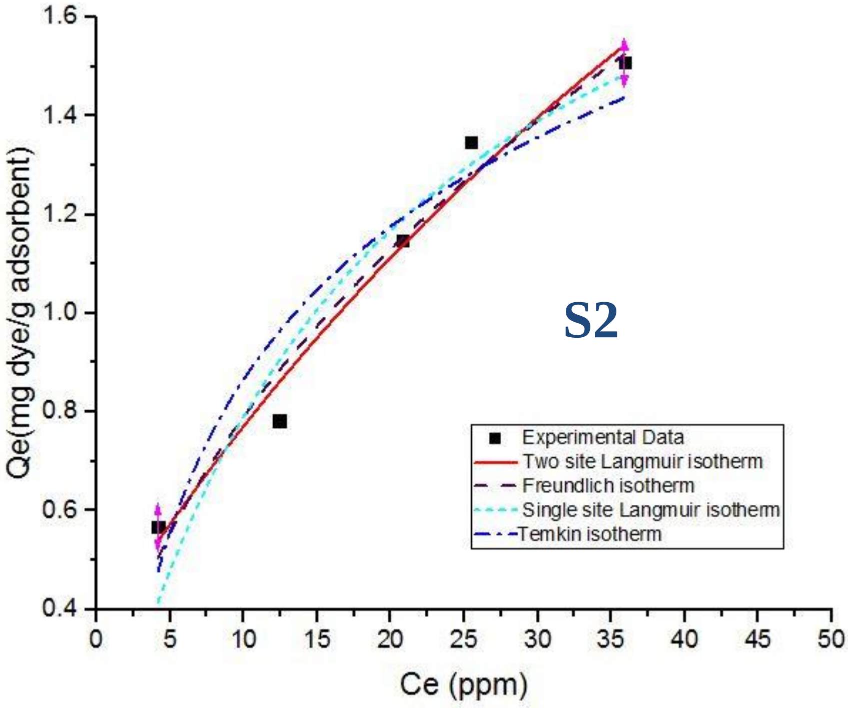


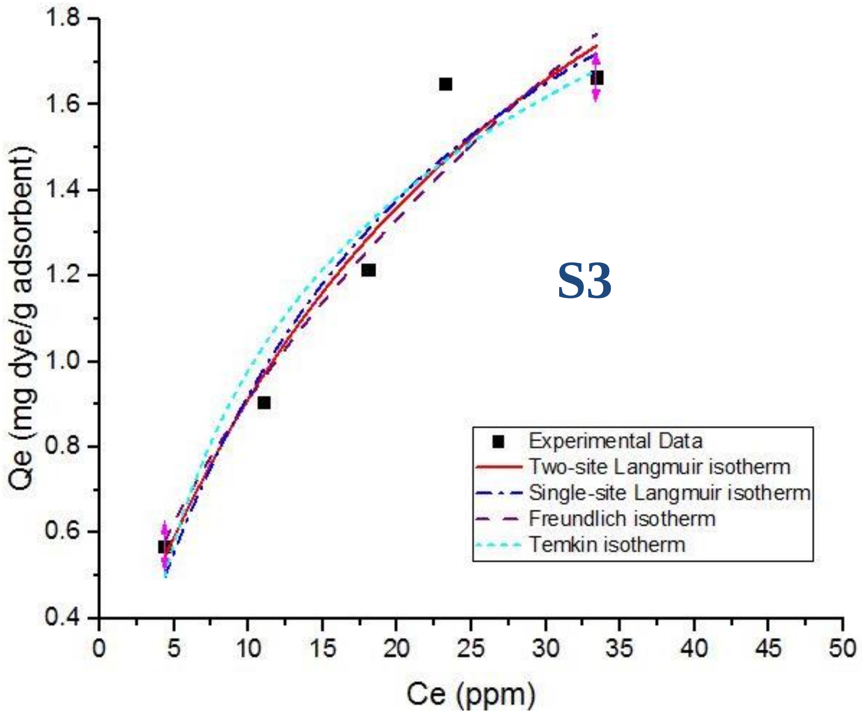

Effect of Contact Time
Dye Removal (%)
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
0
50
100
150
200
250
300
Time (min)
S5
Used Paper

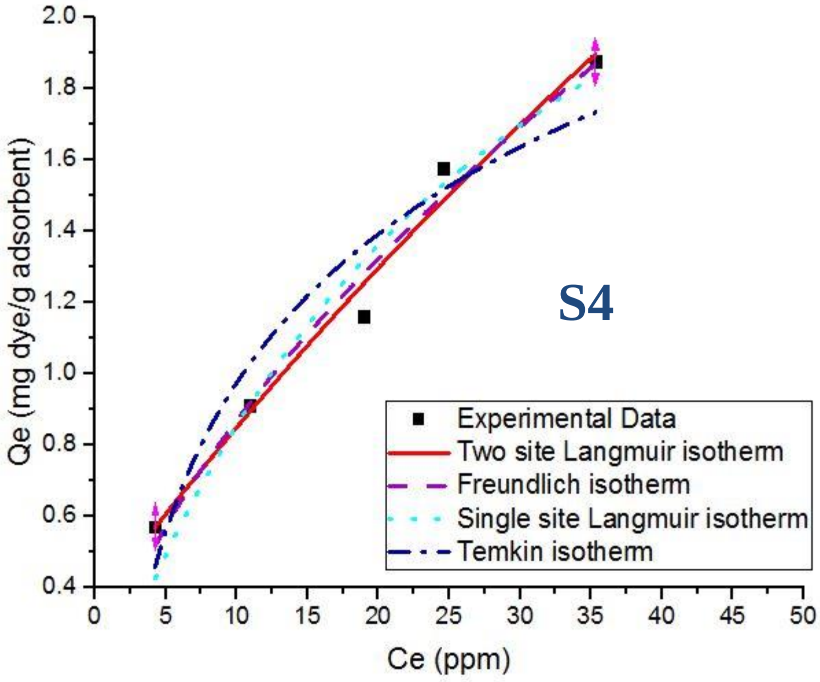

Effect of Contact Time
Dye Removal (%)
60%
50%
40%
30%
20%
10%
0%
0
50
100
150
200
250
300
Time (min)
S6
Used Paper

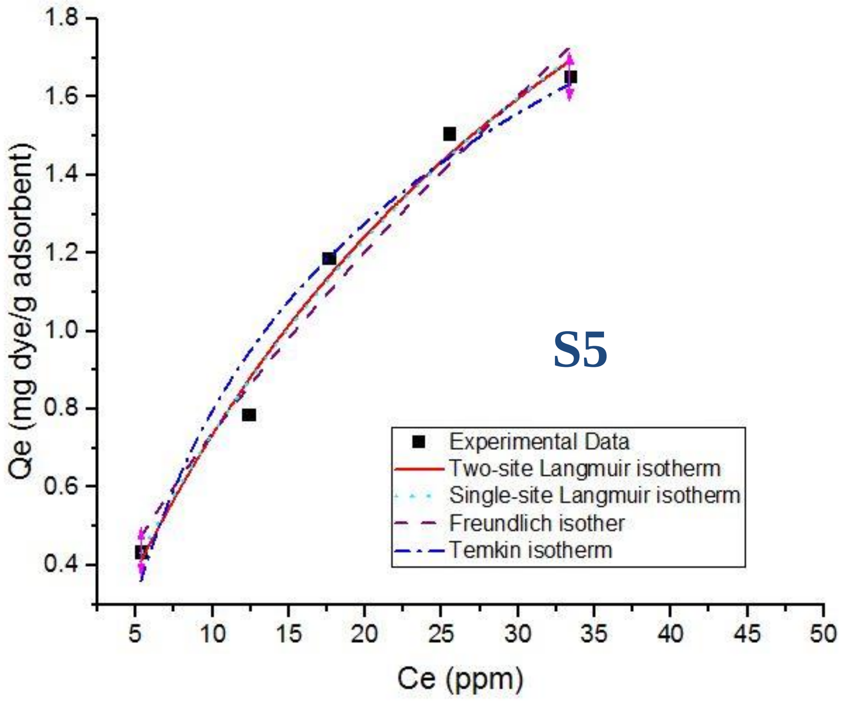

Effect of Contact Time
Dye Removal (%)
50%
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
0
50
100
150
200
250
300
Time (min)
S7
Used Paper

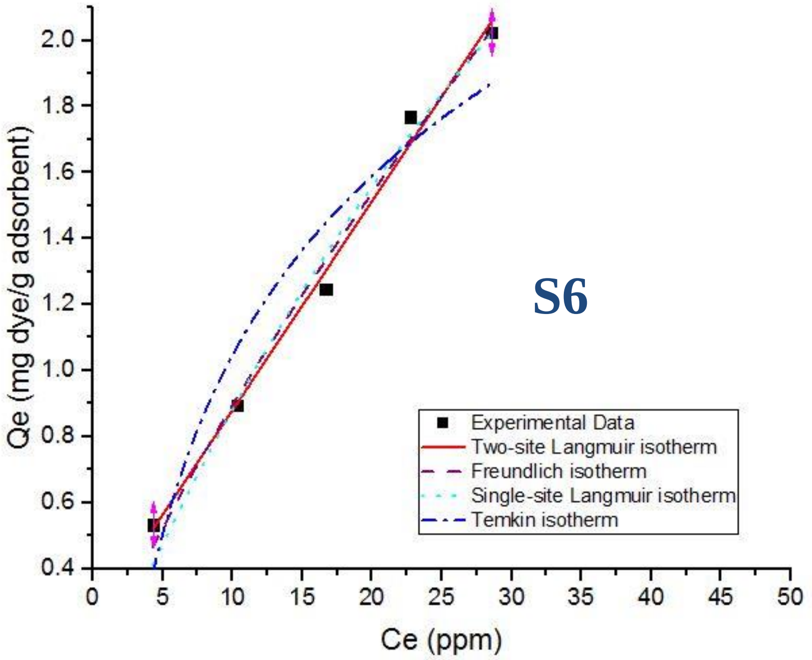
II. Adsorption isotherms



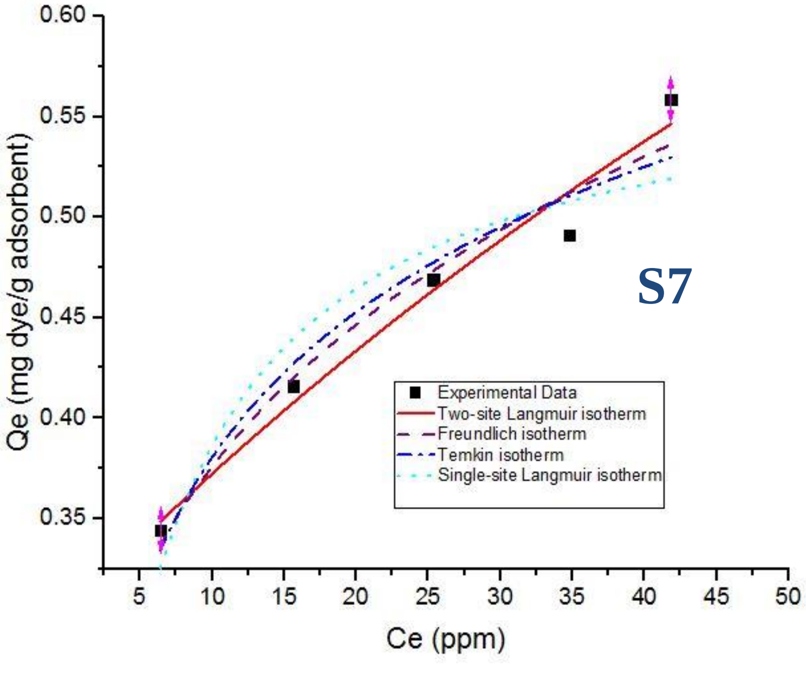



S4
Qe (mg dye/g adsorbent)
Ce (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0
5
10
15
20
25
30
35
40
45
50
Experimental Data
Two site Langmuir isotherm
Freundlich isotherm
Single site Langmuir isotherm
Temkin isotherm


S5
Qe (mg dye/g adsorbent)
Ce (ppm)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
5
10
15
20
25
30
35
40
45
50
Experimental Data
Two-site Langmuir isotherm
Single-site Langmuir isotherm
Freundlich isother
Temkin isotherm


Qe (mg dye/g adsorbent)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0
5
10
15
20
25
30
35
40
45
50
Ce (ppm)
■ Experimental Data
Two-site Langmuir isotherm
Freundlich isotherm
Single-site Langmuir isotherm
Temkin isotherm

S6


Qe (mg dye/g adsorbent)
0.60
0.55
0.50
0.45
0.40
0.35
5
10
15
20
25
30
35
40
45
50
Ce (ppm)
■ Experimental Data
Two-site Langmuir isotherm
Freundlich isotherm
Temkin isotherm
Single-site Langmuir isotherm

S7