ADSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING TEA WASTE IN A CONTINUOUS STIRRED TANK REACTOR (CSTR)

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AHMAD SHAFIQ BIN HASHIM

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering

Signature :
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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedication

In the name of Allah, our Lord, my Lord;

the Most Gracious, the Most Merciful;

Him who provided me with dedication;

Him who bestowed me with everlasting strength;

Whilst the inevitable end for this study period approaches.

Also, with love, I dedicate this work;

To my most beloved, caring and ever-inspiring parents;

Munahwar Sultanah and Hashim Suleman

For which without, I would never have been;

To not be forgotten,

My supervisor, Dr.Md Maksudur R. Khan;

Whom with immense criticism; only to improve, never to dismiss;

From the depths of my heart, I thank all of you.

Thank You

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ABSTRACT

In these past few decades, huge numbers of technologies have been developed for wastewater treatment. The scale of these technologies is also very diverse, from a basic aeration pond, to a more sophisticated nanotechnology based treatment system. In this research, dye removal from aqueous solution by adsorption was studied in batch and continuous mode. The main objective of this study was to develop a continuous stirred tank reactor (CSTR) type adsorption unit for continuous dye removal from aqueous solution. The investigated parameters are the effect of adsorbent dose, and residence time on the performance of CSTR in treating synthetic Methylene Blue (MB) wastewater by using tea waste (TW). The equilibrium batch and kinetic study has been performed to characterize the adsorbent-adsorbate system. For the CSTR adsorption test, the adsorbent was added at suitable time intervals while the residence time and adsorbent dosage is varied. The Langmuir isotherm data obtained with varying MB concentrations fits the isotherm with an R^2 of 0.99. The Langmuir parameters from the experiment were a Q (mg/g) of 68.02 and K (L/mg) of 0.385 while the R_L value was 0.017, assuring a favourable adsorption. Next, the kinetics data were fitted with Unified Approach Model and the adsorption and desorption rate constants were determined to be 1.00E-8 ± 3.00E-9 and 2.60E-8 respectively. It was also found that the kinetic rate constants were initial concentration independent. Lastly, the CSTR adsorption study data was very comparable to the theoretical line predicted with the CSTR model, with very minute offsets from theoretical predictions. The maximum achievable utilization coefficient, η_{max} was found to be 78% for TW-MB system, where higher utilization coefficient attributes to the higher adsorption capacity and better performance.

***Keyword**: Camellia sinesis, CSTR, Methylene Blue, Tea waste, Adsorption*

ABSTRAK

Sejak kebelakangan ini, terdapat kemunculan pelbagai teknologi yang telah dibangunkan spesifik untuk sistem rawatan air kumbahan. Skala kemajuan teknologi-teknologi ini juga amatlah luas, merangkumi teknologi rawatan yang lebih mudah, seperti menggunakan sistem kolam kumbahan atau “aeration ponds” kepada sistem-sistem yang jauh lebih maju, mengaplikasikan teknologi nanoteknologi dan sebagainya. Skop utama dalam kajian ini adalah untuk mengeluarkan bahan perwarna dari air kumbahan sintetik menggunakan sistem “batch” dan “continuous”. Objektif utama kajian ini pula adalah untuk menghasilkan teknologi baru yang menggunakan “Continuously Stirred Tank Reactor” atau CSTR untuk merawat air kumbahan berwarna ini. Parameter yang dikaji adalah kesan dos “adsorbent”, dan “residence time” keatas prestasi CSTR tersebut menggunakan sistem perwarna “Methylene Blue (MB)” dan hampas daun teh (TW) sebagai “adsorbent” atau singkatannya, sistem MB-TW. Kajian yang telah dilakukan untuk mengenalpasti kualiti sistem MB-TW tersebut adalah “batch and kinetic equilibrium tests”. Untuk kajian yang melibatkan aplikasi CSTR pula, “adsorbent” telah dimasukkan pada jangka masa yang sesuai semasa jumlah keseluruhan “adsorbent” dan “residence time” dimanipulasikan. Data dari “batch study” telah memenuhi kehendak “Langmuir isotherm” dengan ketepatan R^2 0.99. Parameter “Langmuir” daripada eksperimen tersebut adalah 68.02 untuk Q (mg/g) dan 0.385 untuk K (L/mg). Seterusnya, data kinetik telah dimuatkan pada model “Unified Approach” dengan nilai “adsorption” dan “desorption” 1.00E-8 ± 3.00E-9 and 2.60E-8. Nilai kinetik yang ditemui tidak berubah dengan perubahan kepekatan MB. Data “adsorption” CSTR yang dikaji telah dikenalpasti, dan nilai yang diperolehi tidak berubah jauh dari yang telah dijangka oleh model CSTR. Akhir sekali, “maximum achievable utilization coefficient” atau “η_{max}” telah dikenal pasti sebagai 78% untuk sistem MB-TW tersebut.

Kata kunci: *Hampas teh (TW), Methylene Blue (MB), CSTR*

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NOMENCLATURE

TW	Tea Waste
$C_{A,L}$	Industrial authority limit, ppm
C_i	Initial concentration, ppm
C_e	Equilibrium concentration, ppm
CSTR	Continuous stirred tank reactor
MB	Methylene Blue
k_1	Adsorption rate constant, L/mg.min
k_2	Desorption rate constant, min^{-1}
K	Langmuir empirical constant, L/g
q	Amount adsorbed, mg/g
q_e	Amount of dye adsorbed at equilibrium, mg/g
q_{max}	Maximum capacity adsorption, mg/g
q_t	Amount adsorbed at time t, mg/g
q_∞	Maximum adsorption capacity for Langmuir model, mg/g
R	Percentage removal, %
t	Time, min
u	Volumetric flow rate, L/min
V	Reactor volume, L
w_a	Adsorbent dosage, g/L

1 INTRODUCTION

1.1 *Motivation, problem statement and background*

Today, Malaysia is at the peak of industrial growth. What used to be countryside is now a massive economic landmark, churning billions in revenues per year. While all this is great in bringing more work opportunities and modernization to the masses, it's taking a toll on the well-being of our surrounding nature. One of many contributors for this rampant pollution problem is an uncontrolled release of industrial wastewaters to the seas and rivers. Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, a considerable amount of colored wastewater are produced and disposed to the environment. These dyes, if not properly treated, are considered toxic and carcinogenic, making it inhabitable by aquatic life and hazardous for human consumption. In these last few years, more information on the environmental consequences of dyestuff usage has become available and the dye manufacturers, users and government themselves are taking substantial measures to treat the dye containing wastewaters Dye contamination could affect plant life and thusly destroy entire ecosystems (Wang, Zhu, Coomes, Haghseresht, & Lu, 2005). Malaysia also houses a plethora of Asian food manufacturers that contributes a massive US$ 3.5 trillion in profits per annum (Industries in Malaysia: Food Industry, 2012). However, these multitudes of food manufacturing plants are also generating a lot of wastes, both solid and liquid from the production, preparation and consumption of these foods. Thus, an optimized system must be developed for the management of these wastes (Mahapatra, Ramteke, & Paliwal, 2012).

There are more than 100,000 commercially available dyes with production amounts exceeding 70,000 tons annually. Dyes are expected to be resistant to fading from sunlight, chemicals and water exposure. This is done by using different types of dyes, suited to different types of materials and expected product. Such dyes are for example, acidic, basic, dispersed, azo, diazo, anthroquinone and metal based complex dyes (Hameed, Din, & Ahmad, Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies, 2007).

According to (Hameed & Auta, Preparation of waste tea activated carbon using potassium acetate as an activating agent for adsorption of Acid Blue 25 dye, 2011), MB is the most common dye in Malaysian batik industry as a coloring agent for the final products. However, since dyes have a synthetic origin and complex aromatic molecular structures, they are inert and difficult to biodegrade, making it highly hazardous when discharged into water streams without any prior treatment. From an environment standpoint, the degradation of these synthetic dyes proves to be potent as the byproducts may possess carcinogenic properties and under acute exposures, MB could cause vomiting, shock, jaundice, and tissue narcosis in humans.

The solution in averting this plague that is pollution is by simply applying wastewater treatment techniques to these wastes, deeming it safe for release back into the rivers and seas. Biological treatment processes such as aerated lagoons and conventional activated sludge processes are frequently used in treating dye-bearing wastewater. However, these processes are ineffective in removing dyes from wastewater due to the non-biodegradable nature of most dyes (Attia, Girgis, & Fathy, 2008). Physico-chemical processes used to treat dyes laden wastewater include coagulation, flocculation, electro-flotation, chemical precipitation, electro-kinetic coagulation, ion exchange, membrane filtration, electrochemical destruction, irradiation, and ozonation. The down sides to these treatment methods are however, all these processes are costly and cannot be used by small industries to treat the wide range of dye wastewater (Indra, Vimal, Nitin, & Indra, 2005). On the other hand, adsorption is considered to be one of the most effective treatment methods, especially in the case of natural adsorbents, as it is cheap, environmentally friendly, and widely available worldwide. The most effective adsorbent available nowadays is activated carbon, due to its highly porous structure, but, it is unsuited to a low cost operation due to the high price compared to natural adsorbents. In more recent times, research on natural adsorbents as dye removal agents have been at an all-time high, utilizing materials such as bagasse, barley husk, water hyacinth, olive pits, rattan sawdust and more.

There are three basic types of sorption contact systems used in industrial wastewater treatment processes, namely, packed-bed, fluidized-bed and completely mixed system. Packed-bed columns are the most applied system at industrial scales, although, it cannot handle suspension, requires column alternation due to breakthrough time, need for unit multiplications for scale-up and is highly sensitive to pressure drops (Vilar, Botelho, & Boaventura, 2008). In contrast, a

Continuous-Stirred Tank Reactor (CSTR) type adsorption unit is free from all the drawbacks that plague the column type adsorption unit. Also, a CSTR would not only take up less space than a similarly yielding Batch process, but also would allow a more continuous and easily automated process (Crowl & Louvrar, 2002). In a research conducted by (Dahlke, Chen, Franzeb, & Holl, 2006), continuous removal of copper ions from diluted feed streams using magnetic weak-base anion exchangers in a CSTR was studied. The Cu^{2+} containing stream was added to the CSTR continuously while resin was simultaneously added to the reactor. The effect of operation parameters such as liquid and resin flow rate, CSTR volume and resin properties on adsorption process is studied. From the research, a theoretical model which allows the prediction of the CSTR performance was also proposed. Other such researches are by (Menoud, Cavin, & Renken, 1998) for adsorption of Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} by a chelating resin in a CSTR and (Vilar, Botelho, & Boaventura, 2008) for Lead and Copper bio-sorption by marine red algae and algal composite in a CSTR. However, at the time this research was conducted, the number of researches relating to dye removal process in CSTRs via adsorption with natural adsorbents are very rare.

In Malaysia, like many other countries, tea is the traditional drink of most Malaysian adults. Usually, the locally produced tealeaves are sold in disposable bags. The normal practice after the brewing of tea is to dispose of it as waste. These wastes usually constitute part of the household waste. However, little did we know, this disregarded waste was actually precious all along. Tea waste, with very little processing could act as a very viable adsorbent that is proven to eliminate a multitude of wastes, from dyes to heavy metal toxics. Such discoveries are the removal of Pb (II) ions, which is a heavy metal by (Mondal, 2009), Chromium (VI) removal by (Malkoc & Nuhoglu, 2007) and Acid Blue 25 (AB25) dye by (Hameed & Auta, Preparation of waste tea activated carbon using potassium acetate as an activating agent for adsorption of Acid Blue 25 dye, 2011). This discovery could very well change the course of wastewater treatment, as tea waste is something that is in abundance. This could very well benefit Malaysia itself, with its BOH Tea Plantations that spans over 3000 acres and Bharat Tea Plantations at about 800 acres, both situated in Cameron Highlands. These tea wastes could be sold with a good premium to those countries lacking in such commodities and hence, what used to be a waste is now precious beyond belief. In the present study a CSTR type adsorption unit has been designed and fabricated for the continuous removal of dye from wastewater. The dye solution was fed to the

CSTR continuously, but a definite amount of adsorbent was fed to the system periodically to maintain the desired adsorbent density in the reactor. TW has been used to evaluate their adsorption capacity to remove MB from aqueous solution. Effects of feed flow rate, residence time and adsorbent dosing rate on the dye removal efficiency in the CSTR unit have been studied. Finally the maximum achievable utilization coefficient ($\eta_{\max}$) for a specific amount of dye removal was evaluated for Continuous Stirred Tank Reactor (CSTR) type adsorption unit.

1.2 Objectives

This study aims to evaluate and predict the performance of CSTR using a Methylene Blue – Tea Waste system by varying:

1) Residence Time
2) Adsorbent Dosage

1.3 Scope of Study

The scope of this study is firstly, to analyze the MB-TW system in a batch study environment, and later, fit the data using the Langmuir adsorption isotherm. Next, the kinetics of the MB-TW system was investigated. From these available data, the Unified Approach Model suggested by (Islam, Khan, & Mozumder, Adsorption Equilibrium and Adsorption Kinetics: A Unified Approach, 2004) was applied to gauge the viability of the model in predicting the kinetics for the MB-TW system. Once the batch tests were completed, the CSTR was rudimentarily fabricated from locally sourced material and a performance study was conducted to assess the characteristics of the reactor. Next, after the reactor performance was established, the main parameter for the MB-TW system were investigated, which were the adsorbent dose and residence time. Lastly, the obtained data, combined with the data obtained from the batch study, all come together at the end in the CSTR model suggested by (Islam, Khan, & Mozumder, Performance Equation for a Reactor Type Adsorption Unit, 2009). All analysis was done with a UV-Vis Spectrophotometer, and the batch study was conducted in an isothermal orbital shaker.

1.4 Significance of Study

In this study, the removal of MB by using TW in a CSTR was researched. MB is a synthetic dye that is resistant – to a degree – of biodegradation. The by-product of MB degradation and MB itself causes significant damage to both humans and the environment. The need to conduct this study had arisen due to the large volume of effluent leaving industries that involves dyes and pigments in its processes. Due to the high cost of carbonaceous adsorbents, such as AC, many industries forgo treatment all together, placing many individuals at risk along the process. With the implementation of the über low cost and readily available TW, more industries – big or small – could easily adopt this process. Furthermore, due to the high volume of effluents leaving these industries, there is also a need for a true continuous wastewater treatment system, and there's where the CSTR chimes in. By implementing a CSTR, several benefits are garnered in comparison to the PBR, the best which allows any form of wastewater to be treated, be it with or without suspended material in addition to the increase in efficiency due to the completely continuous nature.

2 LITERATURE REVIEW

2.1 Wastewater and its Treatment Techniques

Wastewater is defined as any water that has been adversely affected in quality by influence from human activities. Wastewater is the liquid waste discharged by domestic residences, commercial properties, industrial sites and agricultural farms, which often contains some contaminants those results from the mixing of wastewater from different sources. Industrial wastewaters however contain contaminants such as suspended solids, biodegradable organics, pathogens, heavy metals and more (Peavy, Rowe, & Tchobanoglous, 1985). Wastewater contaminants adversely affects the environment, human health and impede day-to-day activities. These contaminants are non-biodegradable and can spread easily by means of food, water and air. A further example of wastewater, which lies in the scope of this research are dyes and pigments. Azo dyes are widely used in a multitude of products, ranging from textiles, to papers, foodstuffs and even leather. Releasing these dyes into the environment causes major threats to the environment and many azo dyes – and their broken down counterparts – are known to be toxic and/or mutagenic. Examples of such dyes are C.I. Disperse Blue 79, C.I. Disperse Blue 183, C.I. Disperse Red 82, C.I. Disperse Red 65 and C.I. Disperse Orange 25 (Sahin, Demir, & Gucer, 2007).

There are several methods that could be employed when dealing with the treatment of wastewaters. In a typical municipal wastewater treatment plant, the process of treating wastewater is divided into three major categories, namely, primary treatment, secondary treatment and lastly, sludge treatment. In primary treatment, most common processes involve mechanical screening, grit and grease removal, flow measurement and primary sedimentation. Moving on to the secondary treatment, more advanced systems are implemented such as an advanced culture system, rotating biological contactors, activated sludge, ponds, lagoons, chemical oxidation, foam flotation, electrolysis, biodegradation, adsorption, chemical coagulation and photo-catalysis (Peavy, Rowe, & Tchobanoglous, 1985). As observed from the plethora of methods listed above, a major portion of these methods involves biological processes, which are deemed inefficient in removing dyes in wastewater. The most effective and reliable method in removing dyes is via adsorption (Berrios, Martin, & Martin, 2012). Activated carbon is an excellent adsorbent due to its porous nature, thus resulting in a high surface area to volume ratio (Wang, Zhu, Coomes, Haghseresht, & Lu, 2005). Although highly effective, activated carbon is very costly, mainly due to the need for regeneration – with methods such as thermal reactivation – of the carbon after dye removal. Although the dyes may have been effectively removed, industries still face the problem of the disposal of this concentrated sludge (Robinson, Chandran, Naidu, & Nigam, 2002).

2.2 Methylene Blue

Methylene Blue, a heterocyclic aromatic compound with the molecular formula $C_{16}H_{18}N_3SCl$, is diversely used throughout different fields, spanning from medical to chemical applications. The physical properties of methylene blue are a color index (C.I.) of 52015, CAS number of 61-73-4, a molecular weight of 319.85 g/mol, maximum absorbance of 664 nm and solubility in water of 1g/25 mL. Methylene blue is also a cationic dye (Ghaedi, Ghazanfarkhani, Khodadoust, Sohrabi, & Oftade, 2014). In more recent years, as experimented by (Orth, Beck, Genze, & Ruck, 2000), MB has proven to be very effective in enhancing the percentage of tumor destruction in Photodynamic Cancer Therapy. Furthermore, MB has been the dye of choice for medical professionals in sample tissue staining for colonoscopic polypectomy (Munakata & Uno, 1994). The use of MB doesn’t just end there; it also branches into analytical chemistry as a Redox Indicator. In an oxidizing environment, the MB solution maintains a blue hue. However, once a reducing agent is added, the MB will decolorize, leaving a clear, transparent solution, easing differentiations between reducing and oxidizing reactions (Hulanicki & Glab, 1978). The textile industries also greatly benefits from MB as a coloring agent. Even here in Malaysia, the batik industry uses MB as a dye in their products. The problem arises when these dye-polluted effluents are released into the water streams. Even though MB is not highly toxic, the effects if inhaled or consumed may be quite severe, ranging from confusion all the way to vomiting and painful micturition (Hameed, Ahmad, & Latiff, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, 2007). In order to solve this conundrum, wastewaters must be treated before releasing them into natural water streams. Furthermore, methylene blue are widely used worldwide for the evaluation of adsorbents as this dye can be viewed as a model for visible pollution and as an indicator for mesoporosity (Bestani, Benderdouce, Benstaali, Belhakem, & Addou, 2008).

2.3 Synthetic and Natural Adsorbents – The Impacts

Synthetic adsorbents are commonly composed of polymers with ligands containing anchor sites such as nitrogen, oxygen or sulfur. By using these polymers and varying production technologies, such as with the applications of ion-based resins, the surface area of these adsorbents could be as high as 800 to 1500 m^2g^{-1} (Shemsadi, Arvand, Effendiev, & Zeynalov, 2012). The most common adsorbent used in wastewater treatments, such as with the Powdered Activated Carbon Treatment (PACT) system, as the name implies, is activated carbon. It is classified into two main forms, which are the powdered and granular activated carbon (Suhas & Gupta, 2009). The fixed bed adsorption column for wastewater treatment commonly utilizes the granular form of activated carbon, mainly due to the size of the granules, which is more suited as a column packing material. However, in batch processing of wastewater, powdered activated carbon is preferred. This is mainly due to the larger surface area provided by the powdered activated carbon in comparison to the granular activated carbon.

Adsorption processes using synthetic adsorbents are widely used to remove pollutants from wastewaters in today's day and age. Adsorption process begins when firstly; the adsorbate migrates through the solution to the exterior surface of the synthetic adsorbent particles, or natural adsorbents such as oil palm kernels, olive stones, rattan sawdust, jute fiber, bagasse, rice husks and tea waste (Hameed, Din, & Ahmad, Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies, 2007). Next, molecular diffusion takes place in the in the boundary layer where solutes are moved from the particle surface into the interior site by pore diffusion and finally, the adsorbate is adsorbed into the active sites of the adsorbent particle (Berrios, Martin, & Martin, 2012). This research focuses mainly on tea waste due to several critical aspects that helps differentiates tea waste to the other available alternatives. Firstly, the surface area of tea waste is very reasonable for adsorption to occur, as researched by (Amarasinghe & Williams, 2007) found that the surface are of tea waste is 0.79 m^2/g, in contrast to the surface area of Granular Activated Carbon, which is at 683.14 m^2/g. Even though the surface area of tea waste isn't as high as activated carbon, from an economic standpoint however, a reduction in surface area is well worth due to the almost non-existent price tag for tea waste. However, the research also proved that the pore size for tea waste – which is a very important criterion in an adsorption process – is almost similar to activated carbon, at 1.92 and 2.28 nm respectively. This correlates well with the second reasoning of why tea waste is the better alternate option, which is the product availability. In Malaysia, tea waste could be obtained directly from the canned drink industries. Such industries are, to name a few, is Yeo's Malaysia and Delite or Amoy Canning Sdn. Bhd. These companies purchase tea leaves directly from tea plantations and use them to produce tea-based drinks such as canned ice lemon tea and milk tea. The tea waste produced by these factories contains almost zero percent of tea, making it easier to adapt the waste as an adsorbent. However, the applicability of these materials has been found to be quite limited due to leaching of organic substances into the solution. To overcome such problems, chemical treatment – such as acid washing and alkali washing – on solid adsorbents has been used as a technique in improving the physical and chemical properties of these adsorbates thusly improving their adsorption capacity (Mondal, 2009).

2.4 Tea, or Camellia sinesis

Camellia sinesis or tea plant is a member of the Theaceae family whose leaves are used to produce the ever-popular aromatic beverage, tea. Besides water, tea is the second most consumed fluid worldwide (MacFarlane & MacFarlane, 2004). This is simply due to the fact that tea contains many medicinal properties, such as its stimulating and detoxifying properties, improved blood and urine flow and joint-pain reliever (Balentine, Wiseman, & Bouwens, 1997). For the past several thousand years, tea is only harvested for their leaves. However, in more recent years, it is discovered that tea wastes, that consists of woody overgrown shoots are used as an alternative adsorbent for wastewater treatment (Malkoc & Nuhoglu, 2007). Since tea waste is classified as an agricultural waste, which often end up unused, it poses as a very good candidate in replacing the more costly synthetic adsorbents due to its natural abundance, renewability, cost effectiveness and its eco-friendly characteristics (Hameed & Auta, Preparation of waste tea activated carbon using potassium acetate as an activating agent for adsorption of Acid Blue 25 dye, 2011).

2.5 Adsorption Technologies

In an industrial scale adsorption process, the two most preferable methods are with the usage of either a batch reactor unit, or a fixed bed column (PBR). Both the batch and PBR have their own strengths and weaknesses. While the batch reactor has lower construction cost, and is easier to control, a PBR system is however able to process more wastewater at any given time due to its continuous nature. However, eventually, even the PBR will cease to function as the adsorbent reaches its breakthrough point, where from there onwards, the efficiency of the unit will greatly decrease. This is where the CSTR type of reactor comes in handy. The advantage that CSTR provides over the batch and PBR process lies in the absence of breakthrough time for the reactor. As the adsorbate is constantly being supplied and removed from the system, for a truly continuous wastewater treatment system (Robinson, Chandran, Naidu, & Nigam, 2002). However, as pointed by (Papadimitriou, Samaras, & Sakellaropoulus, 2009), an efficient pollutant removal capacity was observed in both batch and CSTR systems; however, the performance of the batch reactor system, was better than the continuous one. For the experimental data acquisition, (Berrios, Martin, & Martin, 2012) suggested in their research that the batch study should be done with a variance in temperature and agitation speed in the equilibrium and kinetic batch study. However, (Hameed, Din, & Ahmad, Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies, 2007) with (Yang & Qiu, 2010) suggested that the temperature and agitation speed were left to be constant while varying the concentration of adsorbate instead. This helps in acknowledging the performance of tea waste as an adsorbent in multiple sets of concentrations and at different points in time, for the case of kinetic batch study. The main objective for a batch study is to obtain the effect of initial concentration and dose adsorbent. However, for a CSTR, there are more variables at play, such as pointed by (Yang, Wang, & Tseng, 2013), where the retention time of the wastewater must be at an optimum value to increase the efficiency of the CSTR. Also, for a CSTR system, the reactor design must be fully optimized to discourage problems such as Bypassing and formation of Dead Volume in the system (Fogler, 2010). Furthermore, in order to be qualified for a CSTR type process, the adsorbent must fulfill several requirements: (i) the particles must be resistant to mechanical wear, (ii) the settling of the particles during the solid–liquid separation step must be fast enough, and (iii) the particles must have a high selectivity for substances to be adsorbed. These are the challenges that must be faced for the success of this comparatively rare CSTR adsorption process (Dahlke, Chen, Franzeb, & Holl, 2006).

2.7 UV-Vis Spectrophotometry

Ultraviolet-visible spectroscopy or spectrophotometry which often is abbreviated to UV-Vis is a device used in measuring the absorption or reflectance spectroscopy for the ultraviolet-visible spectral region. Between different compounds, an obvious difference normally would be their colour, such as green chlorophyll, yellow quinine and then some. Chemicals too changes in colours as the structures change (such as the difference is double bond conjugations), whereby colours for aldehydes and ketones range from bright yellow to deep red. As a general guideline for the visible spectrum, violet ranges from 400-420 nm, indigo from 420-440 nm, yellow from 570-585 nm and more. Wavelengths lower than 400 nm constitutes the ultraviolet range while a wavelength higher than 800 nm lies in the infrared range (William Reusch, 2013). The theoretical principle for absorbance, as stated in Beer Lambert’s Law is absorbance is directly proportional to the path length and concentration of the species. Different molecules absorb radiation of different wavelengths. An absorption spectrum, such as UV-Vis will display a number of adsorption bands corresponding to structural groups within the molecule (UV-Vis Absorption Spectroscopy: Theoretical Principles). The applications of UV-Vis spectroscopy include quantitative determination of concentrations in analytical chemistry, and also for determination of biological macromolecules.

2.8 Chapter Summary

To conclude, in this stream of modernization, a great balance is essential in ensuring a proper well-being of our mother nature. Although methylene blue is a crucial colouring and biological staining agent, without proper safety measures, a series of catastrophic side effects could arise. Thus, a proper system is essential in treating these wastes, and is further improved with the use of organically sourced adsorbents. Such examples of adsorbents are of cheaper, agricultural byproducts and a drastically more expensive and less effective, enzymatic matter. The tea waste is a rather unexplored opportunity in the long list of available natural adsorbents. Since tea is the worlds’ second most consumed fluid, tea waste poses as an interesting alternative to the general adsorbents due to its mass abundance and since it is a waste material, there are no cost barriers too. Finally, a need has arisen for a true continuous wastewater treatment system, and the CSTR based adsorption is the answer. Since it has all the cons of the PBR system, without the cumbersome breakthrough time and multiple column setups, it is definitely much more efficient in dealing with large amounts of wastewater.

3 METHODOLOGY

3.1 *Materials*

Methylene blue, an analytical grade cationic dye purchased from Fischer Scientific Malaysia is chosen as the targeted adsorbate without further purification prior to use in this study. Methylene Blue has a molecular weight of 319.85 g/mol, with a molecular formula of $C_{16}H_{18}ClN_3S{\cdot}xH_2O$. Hydrochloric Acid (HCL) used in this researched was sourced from Fischer Scientific Malaysia with a concentration of 37.7% wt/wt. All dilutions are done with ultrapure water to prevent unwanted interference in the adsorbate.

3.2 *Adsorbent Preparation*

The tea waste used in this research was synthetically manufactured from black tea that is sourced from BOH Fairley Plantations Malaysia located in Cameron Highlands, Pahang, Malaysia. The leaves were first boiled repeatedly with deionized water until all soluble and coloured components are removed to an extent. For further cleansing, the leaves were boiled with 1 M of HCl, thus causing all tea solutes to be perfectly leached from the leaves. Finally, the leaves were boiled again until it achieves a pH reading of 7 ± 0.1. The leaves were then dried in an oven for 24 hours at 120^{o}C, before being grinded and sieved to 315 μm.

3.3 *Adsorbent Characterization*

Before the adsorbent is ready to be used, it must first be characterized to find the adsorbent surface area, average pore diameter, pore volume, functional group identifications and more.

3.3.1 *Brunauere Emmette Teller (BET-N_2) test*

The BET-N_2 test, which is the most standard procedure used in characterizing an adsorbent or catalyst, was carried out at 77 K (-196◦C) using a Surfer Turbo (Thermo Scientific, USA). This test is used in identifying the surface area, average pore diameter and pore volume of the adsorbent. Prior to the experiment, all samples are degassed overnight at 120°C (Wang, Zhu, Coomes, Haghseresht, & Lu, 2005).

3.3.2 *Fourier Transform Infrared Spectroscopy (FTIR)*

Next, a Fourier Transform Infrared Spectroscopy (FTIR) was done on the adsorbent. The FTIR measures the spectral range of the adsorbent before and after adsorption allowing for qualitative identification of functional groups. The spectrum is measured from 4000cm^{-1} to 400cm^{-1}.

3.3.3 *Field Emission Scanning Electron Microscopy (FESEM)*

A Field Emission Scanning Electron Microscopy (FESEM), JSM-7800F (Jeol, Japan) is then prepared to help in determining the surface morphology of the tea waste adsorbent. FESEM allows in a near-atomic resolution of the topographical features on the adsorbent surface before and after an adsorption process (Yang & Qiu, 2010).

3.3.4 *X-Ray Diffraction (XRD)*

An X-ray Diffraction Spectroscopy (XRD) is also done on the particles to help in identifying the atomic structure, molecular structure and presence of inorganic constituents in the adsorbent. The XRD is carried out with a Miniflex II (Rigaku, Japan) tabletop XRD in the range of two theta (2θ) from 1 to 80 (Mahapatra, Ramteke, & Paliwal, 2012)

3.4 *Calibration curve*

A calibration curve is essential in the correlation of raw UV-Vis data to a usable concentration data. Firstly, a set of methylene blue solution is prepared, with concentrations ranging from 1 to 10 ppm. Each sample is then placed in a UV-Vis Spectrophotometer (Hitachi U-1800, Japan) and the absorbance readings are then recorded. Lastly, the absorbance is plotted against the concentration to obtain a straight line at a y-intercept of 0. This line can now be used to predict methylene blue solutions based on absorbance values. The calibration data – shown in **Figure 2** – used in this research have a R^2 value of 0.9988. Also, based on **Figure 1**, the concentration correlation data proves that the peak for MB exists as 664 nm, as discussed by (Berrios, Martin, & Martin, 2012). However, the peak for MB can show some discrepancy, whereby the peak for MB used in the research done by (Wang, Zhu, Coomes, Haghseresht, & Lu, 2005) and (Hameed, Ahmad, & Latiff, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, 2007) was at 665 nm and 668 nm respectively. This is related to the difference of vendor for MB, where each make could use a slightly different hue, causing shifts at the maximum absorbance value.

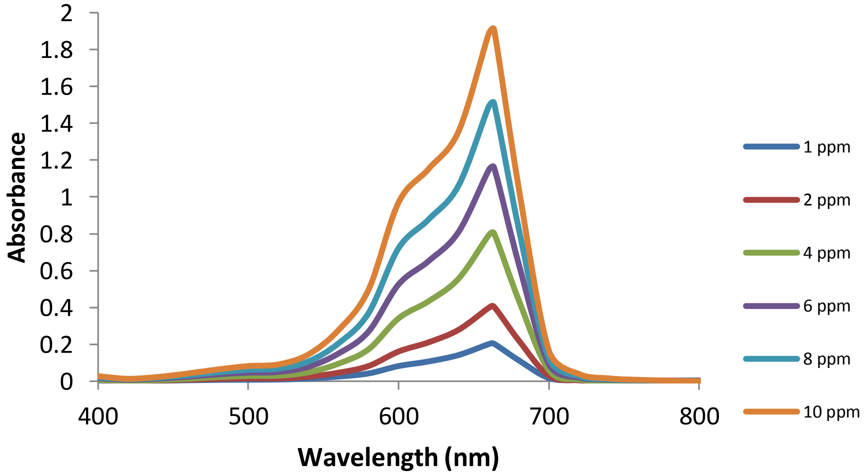

Figure 1: Concentration correlation for MB for concentrations of 1, 2, 4, 6, 8 and 10 ppm

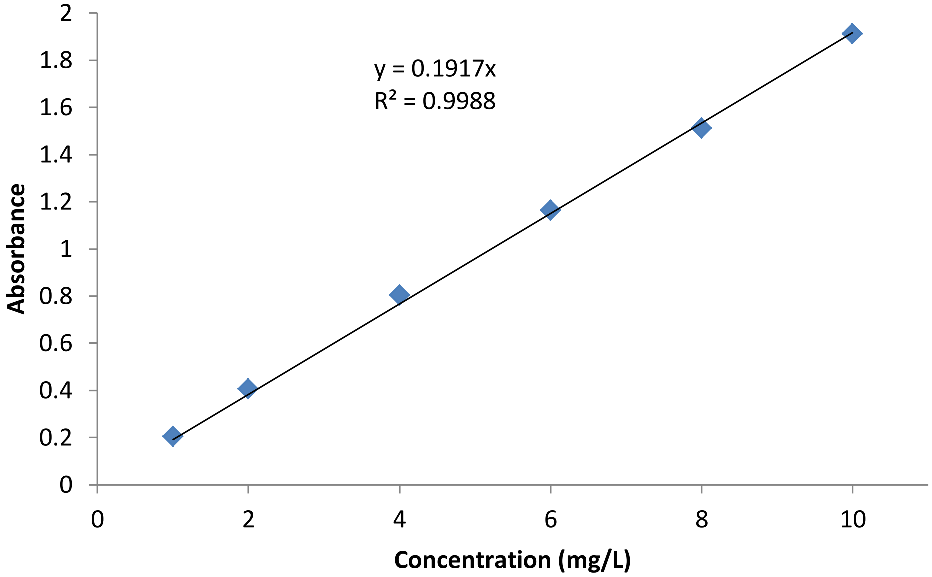

Figure 2: MB calibration curve for concentrations of 1, 2, 4, 6, 8 and 10 ppm

3.5 Batch adsorption test

3.5.1 Equilibrium study

The equilibrium study is conducted in a set of 250 mL Erlenmeyer flasks with varying concentrations of 100 mL synthetic methylene blue wastewater (50, 75, 100, 125 and 150 ppm). Next, the 0.01 g tea waste adsorbent is added to each of the flasks, before being placed in an isothermal shaker (Multitron, Infors HT) at 30 ± 2°C and 300 rpm until equilibrium is reached. After the time has elapsed, the samples were centrifuged (Kubota, Japan) at 5000 rpm for 15 minutes and the concentration of dye left is determined with a UV-Vis Spectrophotometer (Hitachi U-1800, Japan). The amount of dye absorbed is calculated with respect to time, t, at equilibrium, q_e (mg/g), using:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

Where C_o and C_e (mg/L) are the liquid-phase concentration of the dye at the initial and equilibrium respectively; V is the volume (L) of the solution; and W is the mass (g) of the dry adsorbent used.

3.5.2 Kinetic study

Adsorption kinetic experiments were conducted at 30 ± 2 °C. For each experimental run, 250 ml of MB solution of known concentration, and 0.08 g of adsorbent were taken in a 500 mL conical flask and was shaken continuously using an isothermal shaker (Multitron, Infors HT) at 300 rpm. Samples were withdrawn at appropriate time intervals and were centrifuged and the concentration of the dye left in the supernatant solution was analyzed using a UV-VIS spectrophotometer (Hitachi U-1800, Japan) by monitoring the absorbance changes at a wavelength of 664 nm.

3.6 Mathematical modeling

3.6.1 Langmuir Isotherm

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}k_L} \tag{2}$$

Langmuir isotherm assumes a surface with homogeneous binding sites, equivalent adsorption energies, and no interaction between adsorbed species. A Langmuir isotherm is done with obtaining a straight line by plotting C_e/q_e versus C_e. Lastly, the $q_{\max}$ and k_L determined respectively from the intercept and the slope. $q_{\max}$ and k_L represents the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively (Li, et al., 2013).

3.6.2 Unified Approach Model

According (Islam, Khan, & Mozumder, Adsorption Equilibrium and Adsorption Kinetics: A Unified Approach, 2004), their studies developed a new kinetics model named Unified Approach Model to characterize the adsorbent-adsorbate system using both equilibrium and kinetic concepts.

$$\frac{1}{a(\alpha - \beta)} ln \frac{(q-\alpha)\beta}{(q-\beta)\alpha} = k_1 t = Y \tag{3}$$

$$q = (\alpha - \beta) \frac{(\beta/\alpha)e^{(\beta-\alpha)ak_1 t}}{(\beta/\alpha)e^{(\beta-\alpha)ak_1 t} - 1} + \beta \tag{4}$$

Where,

$$\alpha = \frac{b + \sqrt{b^2 - 4ac}}{2a} \tag{5}$$

$$\beta = \frac{b - \sqrt{b^2 - 4ac}}{2a} \tag{6}$$

$$a = w_a\,, b = C_0 + w_a q_\infty + \frac{1}{K}\,, c = q_\infty C_0$$

k_1 is determined from the slope of **Eq. (3)** and k_2 is determined from the relation $k_2 = \frac{k_1}{K}$**.** The k_1 and k_2 values are found to be independent of different initial concentrations and adsorbent dosages.

3.7 CSTR Fabrication

In this research, the main aspect of concern is with regards to evaluate and predict the performance of CSTR using Methylene Blue – Tea Waste system. To do so, a scale model of a functioning CSTR should be fabricated. The key feature of the CSTR include a pump capable of delivering desired flow rates, a variable speed mixer with a 2 bladed rotor, and a 2L working volume. The test will be done repeatedly with varying amount of adsorbate and flow rate. The flow rate of entering wastewater is controlled with an aquarium water pump. Before this CSTR is deemed usable, a CSTR Performance Study shall be conducted to assess the viability of the design. The study is done by filling methylene blue into the CSTR up to the overflow level, and collecting the effluent at a constant time interval throughout the whole time period while flowing in clean water. At each interval, the effluent is analyzed with a UV-Vis Spectrophotometer and the concentrations obtained are plotted against time. From this plot, the performance of the CSTR can be predicted accordingly.

3.8 CSTR Adsorption Test

In the CSTR adsorption test, a fixed amount of adsorbate will be added to the system at varying time intervals to assure the adsorbent density throughout the test period remains at a desirable level. The test will be done repeatedly with varying amount of adsorbate and flow rate. When the flow rate of the inlet wastewater decreases, the residence time in the CSTR increases and vice versa. The concentrations will be recorded at suitable time intervals until the desired concentration levels are reached, and results obtained will be plotted against time. The available data will be then compared to the theoretical data predicted by the model suggested by (Islam, Khan, & Mozumder, Performance Equation for a Reactor Type Adsorption Unit, 2009).

3.9 Modeling of the CSTR system

Recently (Islam, Khan, & Mozumder, Performance Equation for a Reactor Type Adsorption Unit, 2009) developed the design cum performance equation for a CSTR type adsorption unit which is presented below.

3.9.1 Design of Reactor Type Adsorption Unit

In this section, the design and performance equation of CSTR type adsorption unit is derived. Unlike the conventional design procedure, the proposed method is completely based on the results obtained from the characterization of the adsorbent by an approach recently developed by (Islam, Khan, & Mozumder, Adsorption Equilibrium and Adsorption Kinetics: A Unified Approach, 2004). It is considered that the adsorption process could be described by a physico-chemical interaction of the type:

$$A + ac \underset{k_2}{\overset{k_1}{\Leftrightarrow}} acA, \; K = \frac{k_1}{k_2} \tag{7}$$

Where A, ac & acA represent respectively the pollutant, active sites and active complexes, and k_1 & k_2 represent the rate constant for adsorption and desorption respectively. These two rate constants together with another Langmuir parameter q_∞ characterizing the capacity of the adsorbent form the fundament for the proposed design procedure. The three parameters k_1, k_2 & q_∞ are determined by conventional batch adsorption experiment.

3.9.2 *Design and Performance Equation for CSTR Type Adsorption Unit*

The mode of operation of a CSTR is presented in **Figure 3** below.

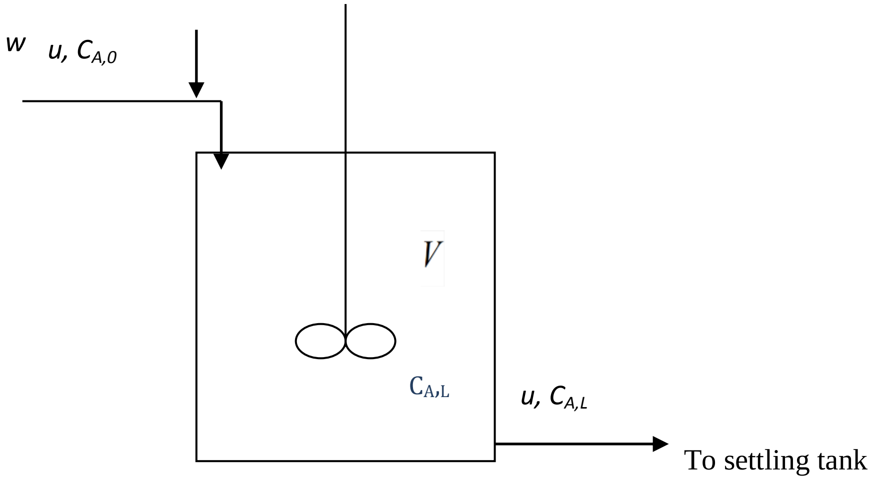

Figure 3: Mode of operation of a CSTR type adsorption unit. The meanings of the symbols are described in the text below

Let u (m^3/min) be the volumetric flow rate entering and exiting the reactor operating at steady state. Let $C_{A,0}$ (kg/m^3) be the concentration of the pollutant in the wastewater and $C_{A,L}$ (kg/m^3) be the limit imposed to the industrial authority. Let w (kg/min) be the dosage rate of the adsorbent into the reactor. Then if V (m^3) be reactor volume (in fact, this is the design parameter, which is to be determined yet), then the following relations express the material balance with respect to the components A, ac and acA:

$$uC_{A,0} - uC_{A,L} = (k_1 C_{A,L} C_{ac} - k_2 C_{acA})V \tag{8}$$

$$wq_{\infty} - uC_{ac} = (k_1 C_{A,L} C_{ac} - k_2 C_{acA})V \tag{9}$$

$$-uC_{acA} = -(k_1 C_{A,L} C_{ac} - k_2 C_{acA})V \tag{10}$$

By combining Eq. (8) to Eq. (10);

$$C_{ac} = \frac{wq_{\infty}}{u - (C_{A,0} - C_{A,L})} \quad \& \quad C_{acA} = C_{A,0} - C_{A,L} \tag{11}$$

and

$$\frac{V}{u} = \frac{C_{A,0} - C_{A,L}}{k_1 C_{A,L}\left[wq_{\infty} / u - (C_{A,0} - C_{A,L})\right] - k_2 (C_{A,0} - C_{A,L})} \tag{12}$$

Now defining a term 'Coefficient of Utilization of the adsorbent η (eta)' as that in the Eq. (13), the Eq. (12) may be rearranged as the Eq. (14).

$$\eta = \frac{uC_{acA}}{wq_{\infty}} = \frac{u(C_{A,0} - C_{A,L})}{wq_{\infty}} \tag{13}$$

$$u / V = k_1 C_{A,L}(1/\eta) - (k_1 C_{A,L} + k_2) \tag{14}$$

The u/V vs. $1/\eta$ plot is a straight line. The utilization coefficient η would be chosen depending on the cost of the adsorbent, and the design parameter V would be determined from the straight line. In a technological process, the operational parameter u and $C_{A,0}$ could vary.

3.9.3 Maximum Achievable η and the Minimum Dosage Rate for CSTR

The eq. (14) shows that as the volume V increases, the utilization coefficient η also increases. This is reasonable as with the increase in the reactor volume V, the residence/reaction time for the adsorbent increases attaining the maximum value of $\eta = \eta_{max}$ for $V \rightarrow \infty$. Thus, for $V \rightarrow \infty$ the Eq. (14) reduces to the Eq. (15).

$$\eta_{max} = \frac{KC_{A,L}}{1 + KC_{A,L}} \tag{15}$$

Combining the Eq. (13) and Eq. (15), for the minimum dosage rate w_{min}, we obtain

$$w_{min} = \frac{u(C_{A,0} - C_{A,L})}{\eta_{max} q_{\infty}} = \frac{u(C_{A,0} - C_{A,L})}{q_{\infty}} \left(\frac{1 + KC_{A,L}}{KC_{A,L}} \right) \tag{16}$$

3.9.4 Dosage Rate Calculation in Operational Conditions

In the stage of designing, the volume V of a unit is calculated based on an assumed flow rate u_o and influent concentration $C_{A,o}$. The dosage rate w_0 is also fixed. In operational condition, however, the flow rate u and influent concentration C_A differ from the design flow rate u_o and the design influent concentration $C_{A,o}$. In that case, the dosage rate, w should be recalculated in order to achieve the same performance as planned during design.

3.9.5 Dosage Rate in an Operating CSTR

Re-writing the equation for design and operating condition we have:

$$u_0 / V = k_1 C_{A,L} (1/\eta_0) - (k_1 C_{A,L} + k_2) \tag{17}$$

$$u / V = k_1 C_{A,L} (1/\eta) - (k_1 C_{A,L} + k_2) \tag{18}$$

The dosage rate for the operating CSTR can be written as:

$$w = \frac{w_0 (C_A - C_{A,L})}{u_0 (C_{A,0} - C_{A,L})} u - \frac{C_A - C_{A,L}}{V k_1 C_{A,L} q_{\infty}} (u_0 - u) u \tag{19}$$

Now the Eq. (19) would give the dosage rate for a CSTR type adsorption unit for which the imposed pollutant limit would be met.

4 RESULTS AND DISCUSSIONS

4.1 Adsorbent Characterization

Figure 4: Dried, grinded and sieved TW, ready to be used in characterization (Before liquid nitrogen pre-treatment)

The figure above shows TW, which is the sample used throughout this research. However, before the experiment could be conducted; there are several tests that should be conducted in order to assess the viability of TW as an adsorbent. These tests are classified as adsorbent characterization, and it is done using three most common methods in adsorbent characterizing. These methods are the Brunauere-Emmette-Teller (BET) nitrogen physisorption isotherm, Fourier Transform Infrared Spectroscopy (FT-IR) and lastly, Field Emission Scanning Electron Microscopy (FESEM). Lastly, before characterizations can be made, the TW sample is pulverized to create fine TW particles by soaking the sample in liquid nitrogen and grinding it with a mortar and pestle. The sample was then placed in an oven for 12 hours at 120^{o}C to ensure there isn't any moisture or liquid nitrogen residue left in the sample.

4.1.1 *Brunauere-Emmette-Teller (BET-N_2)*

The textual characteristics of the TW was carried out by applying the Brunauere Emmett Teller analysis to give a BET surface area of 59.969 m^2/g, Langmuir surface area of 201.7 m^2/g, an average pore diameter of 5.3303 nm and a cumulative pore volume of 0.0309 cm^3/g. The latter two results are obtained via the Barrett-Joyner-Halenda (BJH) method. Lastly, the average pore diameter (L=5.3303 nm) suggests that TW is a mesoporous adsorbent.

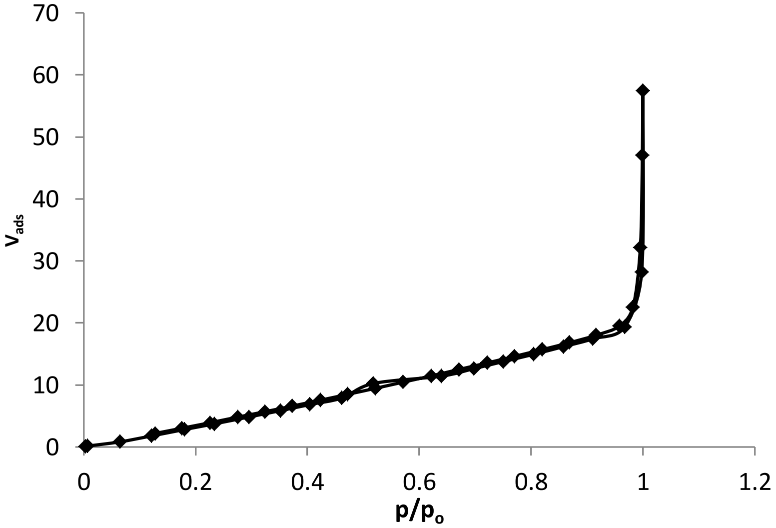

Figure 5: Nitrogen physisorption isotherm for TW (Thermo Scientific, USA)

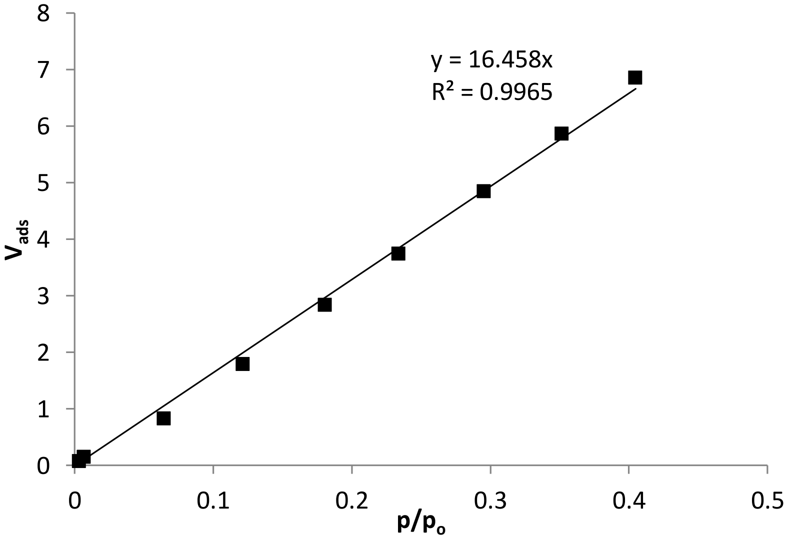

Figure 6: Linearized isotherm plot of BET from p/p_o 0.005 to 0.4

Sample name	**BET Surface Area (m^2/g)**	**Average Pore Diameter (nm)**	**Pore Volume (cm^3/g)**
Tea Waste (TW)	59.9	5.33	0.031
Rattan Sawdust (RS)[1]	1083	2.77	0.64
Activated Carbon (AC)[2]	1688	2.5	1.04
Graphene Oxide (GO)[2]	32	17.3	0.11
Carbon Nanotubes (CNT)[2]	177	12.1	0.54

Table 1: Description and characterization of sample (TW) in comparison to carbonaceous samples (AC, GO, CNT) using BET-N_2

From the data available in **Table 1**, it is very clear that while TW does not have a very high surface area as compared to the more expensive alternatives of Activated Carbon (AC) and Carbon Nanotubes (CNT) or even Rattan Sawdust (RS); it is still reasonably higher than the more expensive Graphene Oxide (GO) based adsorbent. The pore diameter for TW is also very reasonable. However, the surface area, pore diameter and volume only tells us the physical characteristic of the adsorbate; it doesn't necessarily reflect the adsorbents' efficiency as different chemicals adhere to different set of requirements for adsorption to occur efficiently (Mangun, Daley, Braatz, & Economy, 1998). Furthermore, TW is still a better alternative in comparison to sawdust mainly due to its worldwide availability, in contrast to the very locational based availability of RS. The pore size of TW, which is 5.33 nm, is classified as a mesopore, and mesoporous adsorbents are greatly sought for in adsorption processes due to the faster rate of adsorption and high maximum amount of solute adsorbed quantities.

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[1] (Hameed, Ahmad, & Latiff, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, 2007)

[2] (Li, et al., 2013)

4.1.2 Field Emission Scanning Electron Microscopy (FESEM)

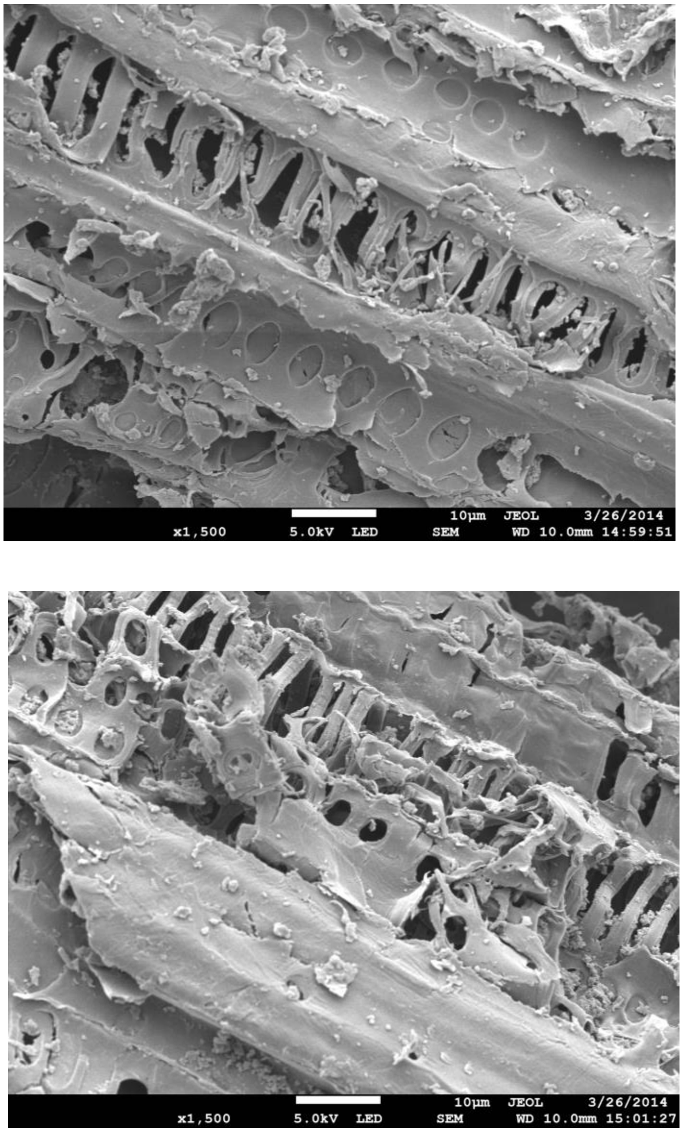

Figure 7: FESEM images of TW adsorbent at 1,500x magnification (Jeol, Japan)

From **Figure 7**, the morphology of TW before adsorption of MB could be observed. It could be seen that the surface of TW at 1,500x magnification is very rough with many pores and crevices, making it very suitable for adsorption to occur. However, there are signs of shearing and damage at the leaves, which could be a result from the grinding process in reducing the TW size to 315 µm.

4.1.3 Fourier Transform Infrared Spectroscopy (FT-IR)

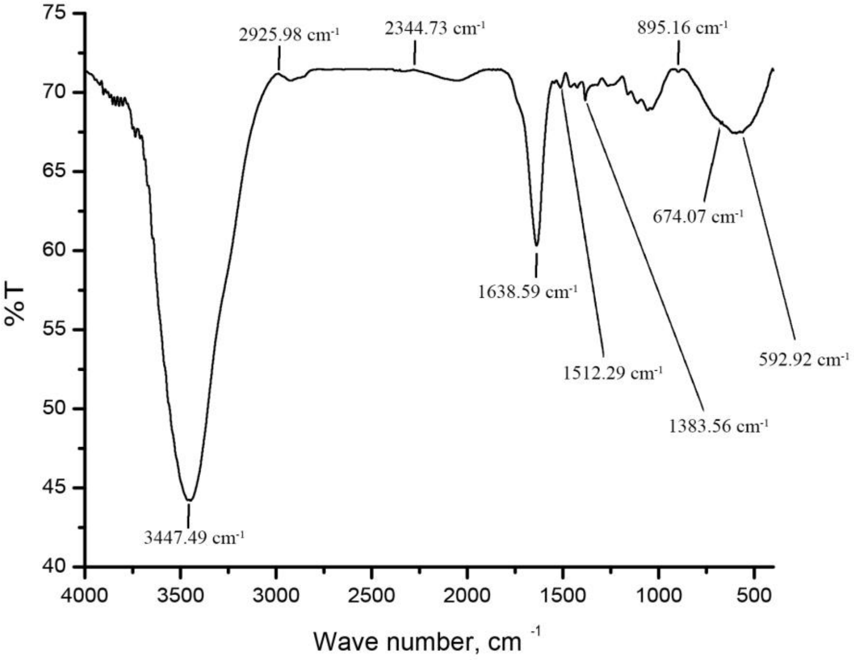

Figure 8: FT-IR spectrum for the waste tea before adsorption

The infrared spectrum of TW was recorded in KBr pellets at the region of 400-4000 cm^{-1} and was conducted at room temperature and pressure. The reference for interpreting this spectrum was obtained from (B.S., S.K., & Seema, 2006), (University of California, Los Angeles, 1997), (Larsen, 2007) and (Hameed & Auta, Preparation of waste tea activated carbon using potassium acetate as an activating agent for adsorption of Acid Blue 25 dye, 2011).

The FT-IR spectrum for waste tea before adsorption is presented in **Figure 8** above. The spectrum revealed the presence of several peaks and functional group. The sample presented a peak at 3447.49 cm^{-1}, indicating presence of O-H functional group. A peak at 2925.98 cm^{-1} signifies presence of sp^3 C-H (alkane) group while a peak at 2344.73 cm^{-1} indicates NH stretching vibrations. Next, C=C groups were located at 895.16 cm^{-1} and 1638.59 cm^{-1} while at 1512.29 cm^{-1}, the peak suggest presence of conjugated cyclic C=N. There was also presence of β(C-H) aldehydic at a peak of 1383.56 cm^{-1}. Lastly, presence of alkyl C-Cl was recorded ranging from 674.07 cm^{-1} and 592.92 cm^{-1}. The observed spectrum showed that TW consists of several surface functional groups which positively reflect on its efficiency as a colour removing agent. **Figure 32** provides an FT-IR spectrum with each peak labeled.

4.1.4 X-Ray Diffraction (XRD)

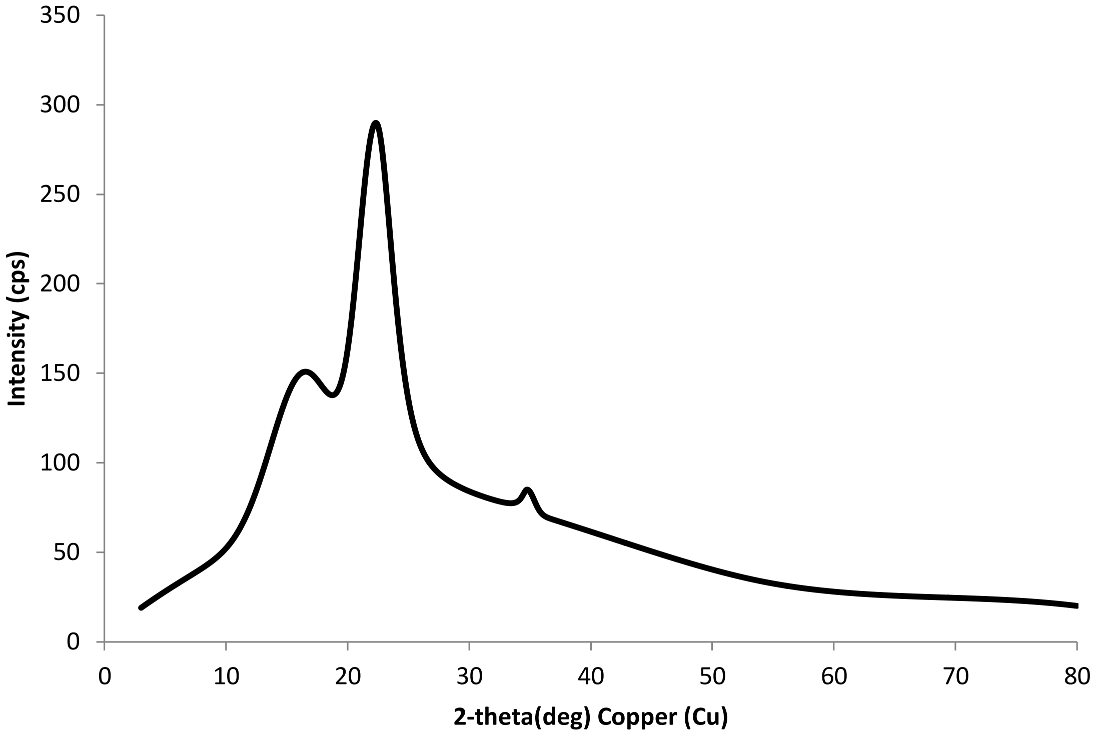

Figure 9: XRD of tea waste (Position is in 2-theta (Degree) Copper (Cu)

The crystallinity of the TW was examined by powder X-ray diffraction (MiniFlex II, Rigaku, Japan). All patterns were obtained in the range of two theta (2θ) from 1 to 80 at a scan rate of 1^{o}/min using Cu Kα 1 radiation (λ= 0.154056 nm) with a voltage and current of 30 kV and 15 mA, respectively. The results as shown in **Figure 9**, shows three main peaks at 2θ = 16.35, 22.36 and 34.8 with d spacing of 5.42^{o}A, 3.973^{o}A and 2.578^{o}A respectively. The sharp diffraction peaks indicates a high crystallinity of TW. The obtained results show high similarities when compared to the findings of (Wankhade & Ganvir, 2013).

4.2 Batch Study

The adsorption equilibrium or batch study was performed to describe the adsorption of an adsorbate in the adsorbent completely. The analysis of adsorption isotherm data is useful for design purposes. The adsorption system is described completely by three system parameters which are;

q_∞ the maximum adsorption capacity (mg adsorbate/g adsorbent)

K adsorption equilibrium constant (L/mg)

4.2.1 Equilibrium Study

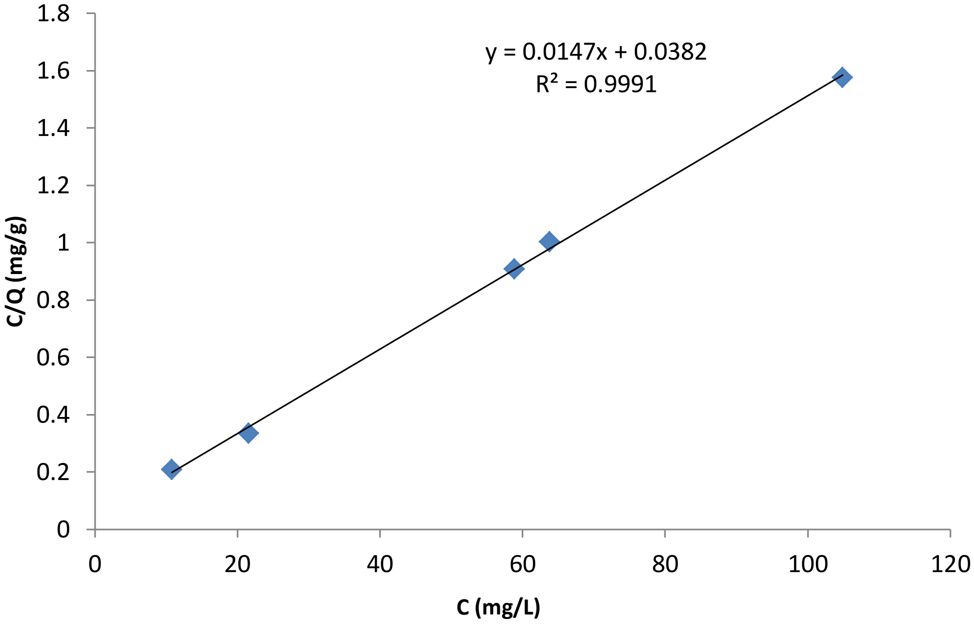

Figure 10: Langmuir isotherm plot of MB adsorption using TW

Sample	**Q (mg/g)**	**k (L/mg)**	**R^2**
TW	68.02	0.385	0.9991
AC[3]	270.27	1.23	0.9958
GO[3]	243.90	1.32	0.9907
RS[4]	294.12	0.131	0.9990

Table 2: Equilibrium parameters of Langmuir adsorption isotherm models for MB adsorbed between different types of adsorbents

The Langmuir adsorption isotherm is valid for monolayer adsorption onto a surface containing a finite number of ideal sites. This model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. **Figure 10** presents the Langmuir adsorption isotherm of MB at pH 7.0 ± 0.1 as the relationship between the amount of dye absorbed per unit mass of a given sample adsorbent and the equilibrium concentration of MB in solution. We could observe that the adsorption process of MB using TW perfectly fits the Langmuir isotherm with an R^2 of 0.9991. Furthermore, from the results obtained, a comparison was between common adsorbent choices was construed in **Table 2**. From these results, maximum amount of solute adsorbed, Q (mg/g) for TW isn't as high as the more expensive alternatives of AC and GO. RS also posed a very high Q, but, TW still edges out as rattan isn't as widely available worldwide as TW. Lastly, the adsorption constant, k of TW is significantly higher than RS. This signifies that the adsorption rate of TW is higher than of RS. This proves that TW is more suited to faster paced adsorption process, such as with the CSTR. However, the fastest adsorption process could be conducted by using GO, but as it is highly expensive, TW still poses as a better alternative in contrast to AC and GO.

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[3] (Li, et al., 2013)

[4] (Hameed, Ahmad, & Latiff, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, 2007)

4.2.2 Kinetic Study

Effects of contact time on adsorption of dye were studied for different initial concentration of dye with fixed adsorbent dosage. The amount adsorbed q (mg/g) vs. time (min) curves for two different initial concentrations are shown in **Figure 11** and **Figure 12**. **Figure 11** represents MB-TW system at 75 ppm initial concentration while **Figure 12** represents MB-TW system at 100 ppm initial concentration. The points are designated as experimental values and the dense lines represent theoretical values calculated from **Eq. (4)**. The corresponding data are given in the appendix section. It is seen from the figures that the initial rate of adsorption is acceptable for this system and 50-60% of dye is removed within first 50 min of adsorption. After that the rate is decreasing gradually leading to equilibrium. This decreasing removal rate towards the end suggests formation of monolayer coverage of dye molecules on the outer surface of the adsorbent and pore diffusion onto the inner surface of the adsorbent particles through the film due to continuous agitation maintained during the experiments.

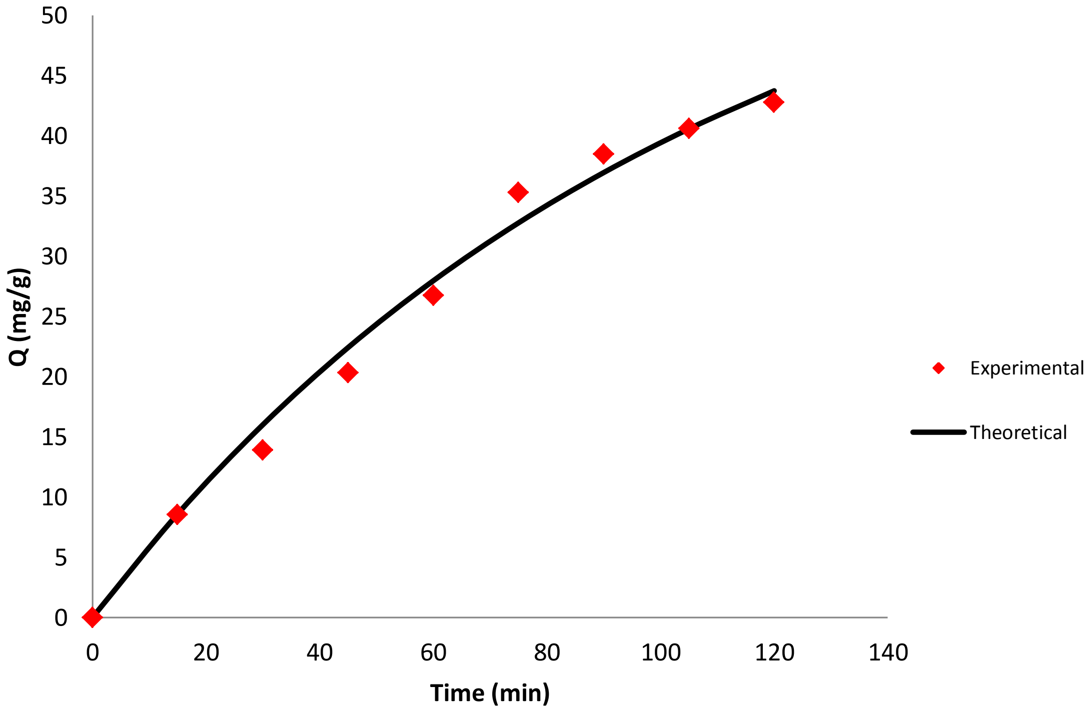

Figure 11: Kinetics of MB adsorption on TW (initial concentration = 75 ppm, time = 120 min, shaker speed = 300 rpm, w = 0.08 g)

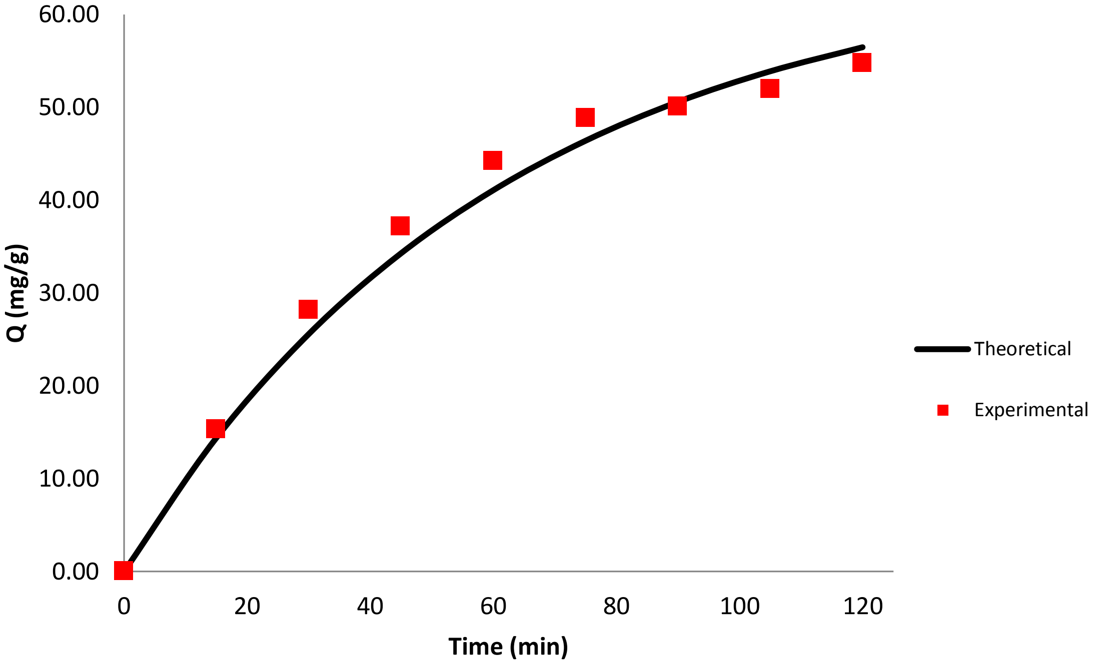

Figure 12: Kinetics of MB adsorption on TW (initial concentration = 100 ppm, time = 120 min, shaker speed = 300 rpm, w = 0.08 g)

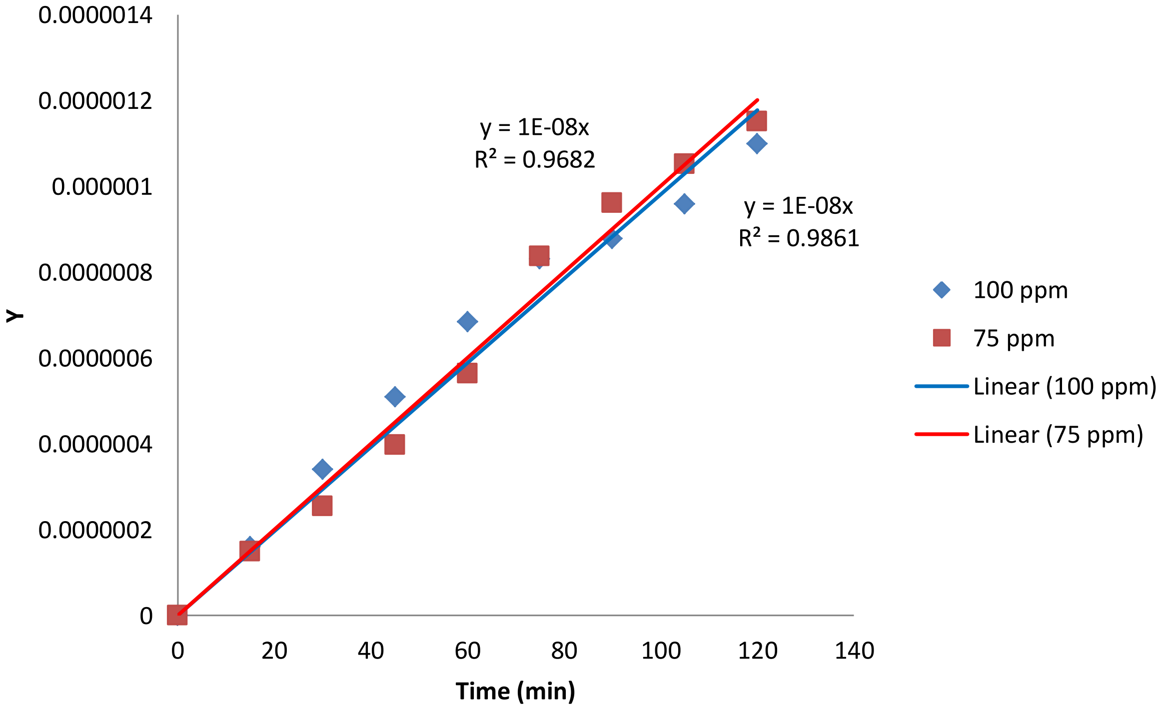

Figure 13: Unified Approach Model fitting for TW-MB system (time = 120 min, shaker speed = 300 rpm, w = 0.08 g)

To evaluate the effectiveness of the TW as an adsorbent, the plot of the amount of MB adsorbed at 75 ppm and 100 ppm as a function of time is presented in **Figure 11** and **Figure 12**. The initial adsorption stage is rapid, due to the bonding of molecules at the external surface of the adsorbent. This is followed by a slower adsorption process, as the MB seeps through the pores of the TW (Li, et al., 2013). Furthermore, from **Figure 13**, as calculated by using **Eq. (3)**, the prediction for the theoretical line given by the Unified Approach model suggested by (Islam, Khan, & Mozumder, Adsorption Equilibrium and Adsorption Kinetics: A Unified Approach, 2004) fits the experimental data with an overall R^2 greater than 0.94. The error for prediction of maximum amount of adsorbed solutes (Q) is also very acceptable, with very low errors. The kinetic parameters for MB adsorption on TW with several comparisons are listed in **Table 3** below.

Adsorption Systems	**C_o(ppm)**	**k_1(L/mg.min)**	**k_2(min^{-1})**	**Correlation Coefficient (R^2)**
MB-TW	75	1.00E-8 ± 3.00E-9	2.60E-08	0.986
MB-TW	100	1.00E-8 ± 3.00E-9	2.60E-08	0.968
MB-AC[5]	100	4.30E-4	1.21E-4	0.869
MB-WH[5]	100	3.23E-4	8.62E-4	0.965

Table 3: Kinetic parameters for MB adsorption on Tea Waste (TW), Water Hyacinth (WH) and Activated Carbon (AC)

The initial rate of adsorption was reasonably high for MB-TW systems where 60-70% of dye was removed within the first 40-50 min of adsorption. After that, the rate gradually decreases, leading towards equilibrium. This decreasing removal rate towards the end suggests formation of monolayer coverage of dye molecules on the outer surface of the adsorbent and pore diffusion onto the inner surface of the adsorbent particles through the film due to continuous agitation maintained during the experiments. k_1 was determined from the slope of **Eq. (3)** and k_2 was determined from the relation $k_2=(k_1/K)$. k_1 and k_2 values were found to be independent of different initial concentrations and adsorbent dosages (Islam, Khan, & Mozumder, Performance Equation for a Reactor Type Adsorption Unit, 2009).

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[5] (Islam, Khan, & Mozumder, Adsorption Equilibrium and Adsorption Kinetics: A Unified Approach, 2004)

4.3 *CSTR Diagnostic Study*

The performance for the CSTR unit was observed by filling the reactor up to the overflow level with dye. Water was then fed to the CSTR continuously at flow rates resulting in a 60 minute and 120 minute residence times. As water flows in, the concentration of MB decreases with time. The manipulated flow rates results in differences between the times needed to bring the concentration down to the specified concentration. The plots for these tests are as the following. In all the plots of **Figure 14** and **Figure 15** the experimental data are designated as points and the dense line represents the theoretical data which are calculated from **Eq. 20.**

$$C = C_0 e^{-\frac{u}{V}t} \tag{20}$$

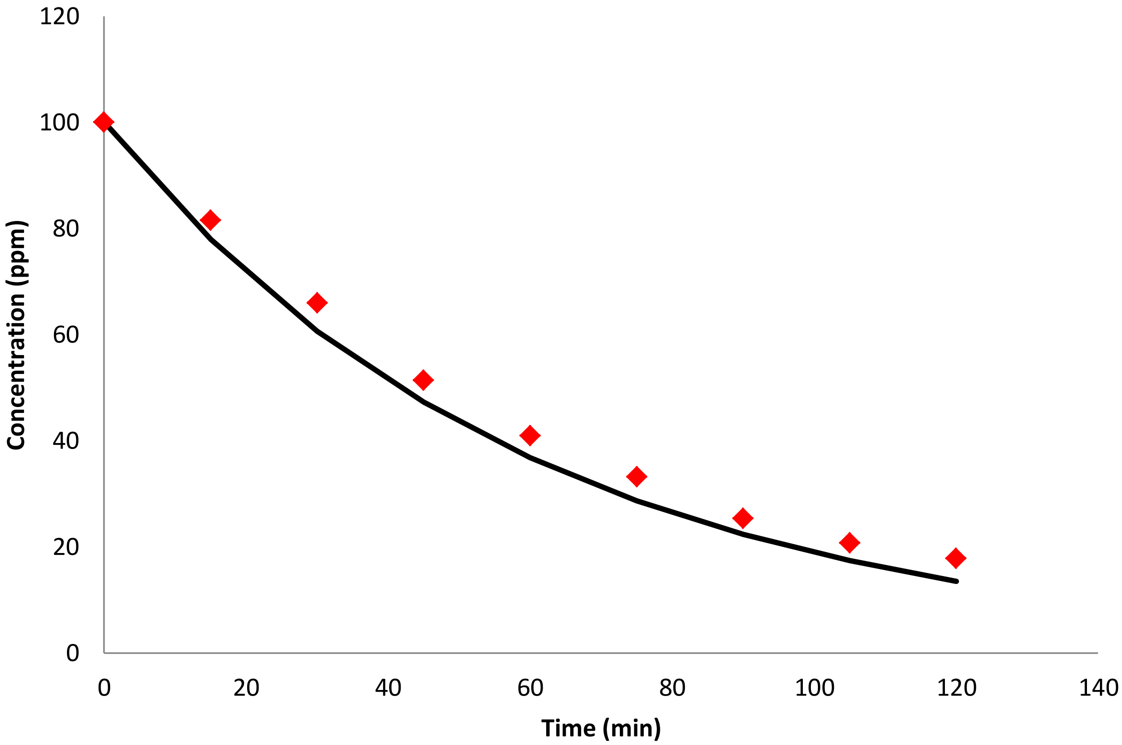

Figure 14: CSTR Performance Study (Residence time: 60 minutes; Flow Rate: 33.33 mL/min; Sampling Interval: 15 minutes)

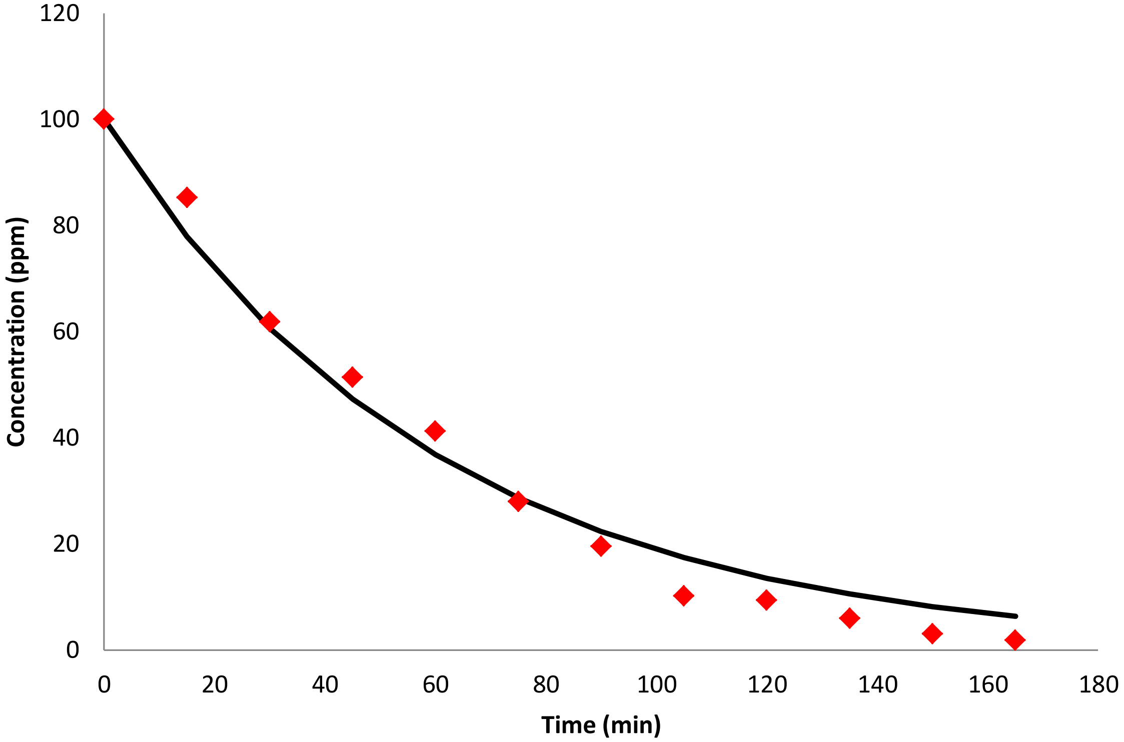

Figure 15: CSTR Performance Study (Residence time: 120 minutes; Flow Rate: 16.67 mL/min; Sampling Interval: 15 minutes)

From the above plots it was seen that for the flow rate of 33.33 mL/min (**Figure 14**) the experimental point correlates well with the theoretical line. That is at that flow rate the adsorbent concentration decreases exponentially with time. As the flow rate decreases, deviation of the experimental points from the theoretical line increases. This is likely caused by the fact that the pump used in this CSTR system is capable in supplying a maximum flow rate of 2000 L/hr. Thus, by throttling the flow rate to a very low 16.67 mL/min (**Figure 15**), the flow rate error margin increases, providing for an uneven flow rate throughout the experiment. As the time tends to reach the space time the amount of disturbance is increased for all flow rates, again due to the accumulated error from the flow rate supplied by the pump, contributed further by the omission of a rotameter in a continuous flow rate measurement and verification. In all tests, the flow rate reading is averaged between three reading during the start of all studies, using a stopwatch and a measuring cylinder. Thus, minute decimal error might have also contributed to the deviation of this CSTR from an ideal condition.

4.4 *Effect of Dosage on the Removal of Dye in CSTR*

At first, the effect of adsorbent dosage on the dye removal was studied for different flow rates. The initial concentration of the dye solution was same for all flow rates which is 100 ppm. The result displayed in **Figure 16** depicts that the outlet concentration was reduced with time and reached to a certain value for a dosage rate of w_1. As the dosage rate was changed to w_2 ($w_1<w_2$) the outlet concentration again started to drop and after a certain time it again reached to a steady level. The dosage rate in the CSTR was then consecutively changed to w_3, w_4 and w_5, until the outlet concentration reached to the desired level (40 ± 3 ppm). For each adsorbent dosage rate w, there was a minimum fixed value of outlet concentration. This is the equilibrium state of the adsorbate – adsorbent system. Here the dye solution is fed to the CSTR continuously, but a definite amount of adsorbent was fed to the system periodically to maintain the adsorbent concentration in the CSTR within a certain range. A qualitative sketch is shown below which helps to understand the process of maintaining the adsorbent concentration within a certain limit.

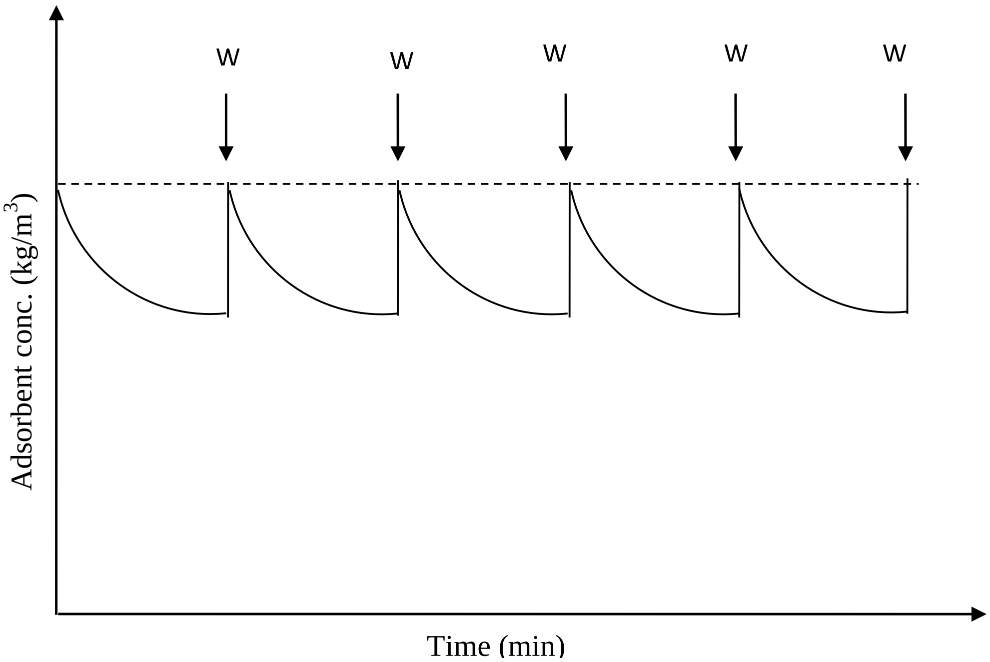

Figure 16: Qualitative sketch representing the adsorbent makeup process. Dashed line indicates a constant adsorbent concentration

In the figure above, it can be seen that as time passes, the adsorbent concentration decreases exponentially. At a certain time, adsorbent dose is added to counter the lost adsorbent. The amount added periodically can be calculated. As the makeup dose is added, the overall adsorbent dose once again reaches the set point (represented as dashed line in **Figure 16**). Thus periodical addition of calculated amount of adsorbent can keep the adsorbent concentration at a certain desired level.

Figure 17, **Figure 19** and **Figure 21** represent the effect of adsorbent dosages at different flow rates or residence times to bring the initial concentration of MB from 100 ppm to a set concentration of 46 ppm. **Figure 18**, **Figure 20** and **Figure 22** explains the relationship between difference in outlet and inlet concentration of the CSTR versus the adsorbent dosages. It can be seen that, as adsorbent doses increase, the outlet concentration decreases. Residence time affects the amount of adsorbent dosage whereby the amount needed to lower the concentration of effluent to the desired set point increases as the flow rate increases. This is due to the increased adsorbent demand in the system to treat the increased amount of wastewater that enters the CSTR. To conclude, an increase in flow rate causes the efficiency of the CSTR to decrease.

All the plots show that the outlet concentration reduces with time. As the adsorbent dose increases the outlet concentration decreases. Here in each plots 4 adsorbent dosages are used; each higher than the latter. For the first dose, the outlet concentration sets to an average value after a certain time of operation and there is no further change in the outlet concentration without addition of adsorbent. To reduce the outlet concentration further the dose is increased. As the dose is increased, the outlet concentration again starts to drop and after a certain time it again reaches a constant value. The dose in the CSTR is changed until the outlet concentration reaches to the desired level. For each adsorbent dose W, there is a minimum fixed value of outlet concentration. These characteristics are clearly exhibited in the plots below.

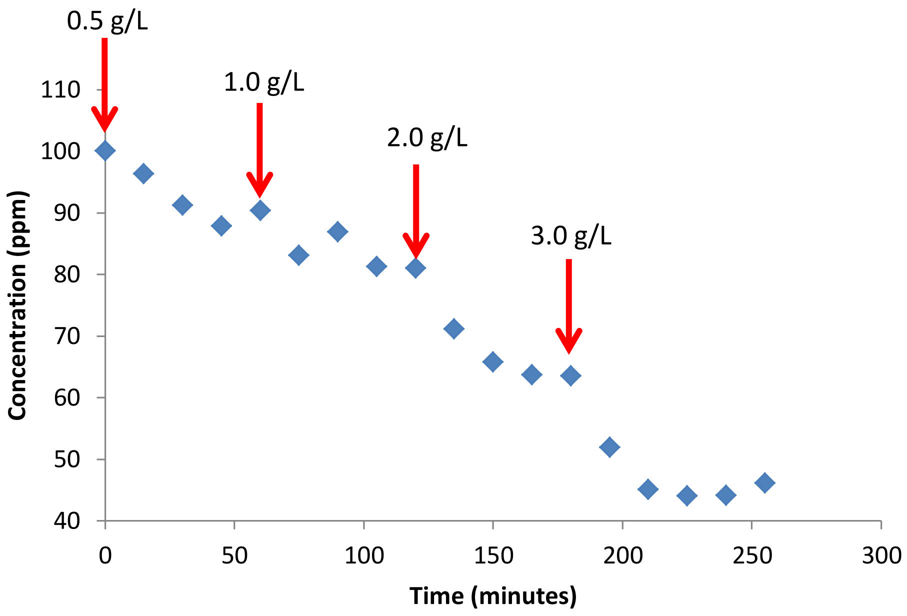

Figure 17: Plot of concentration (ppm) vs. time (min) for MB-TW system in CSTR. (Residence time: 120 minutes, Initial concentration = 100 ppm)

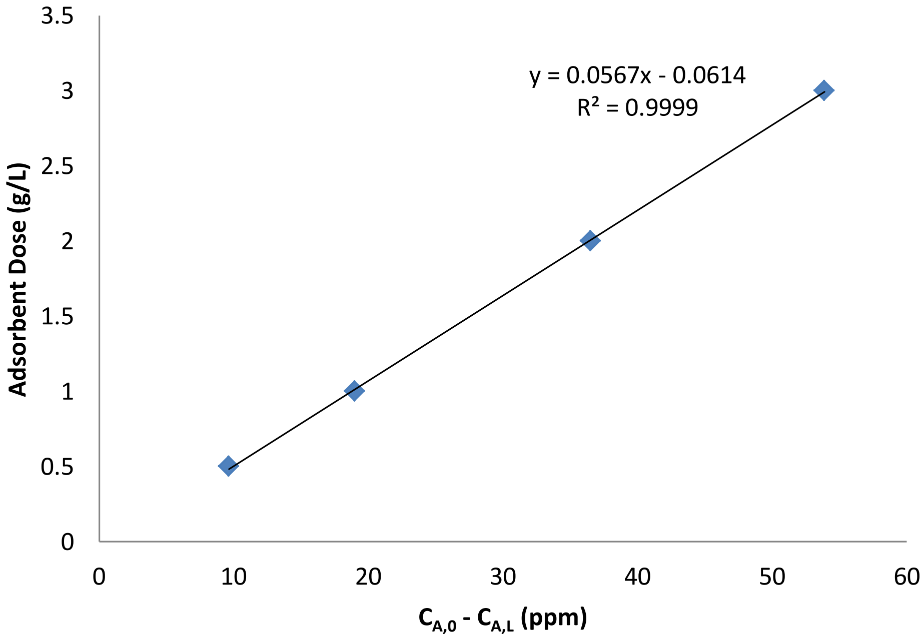

Figure 18: Correlation between adsorbent dose (g/L) and concentration difference (ppm) for 120 minutes residence time

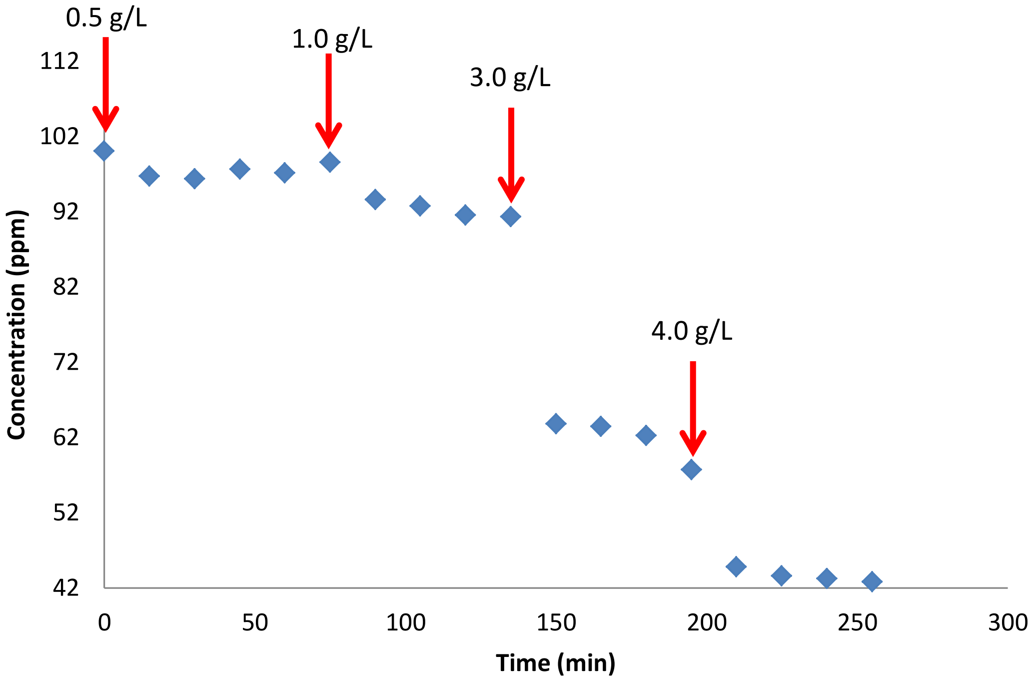

Figure 19: Plot of concentration (ppm) vs. time (min) for MB-TW system in CSTR. (Residence time: 60 minutes, Initial concentration = 100 ppm)

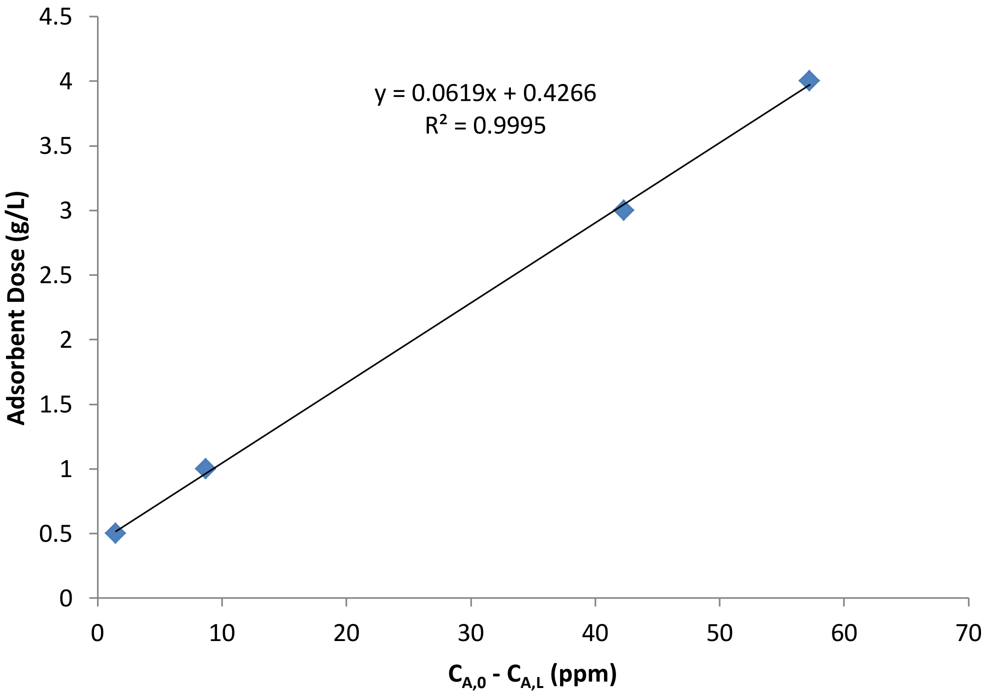

Figure 20: Correlation between adsorbent dose (g/L) and concentration difference (ppm) for 60 minutes residence time

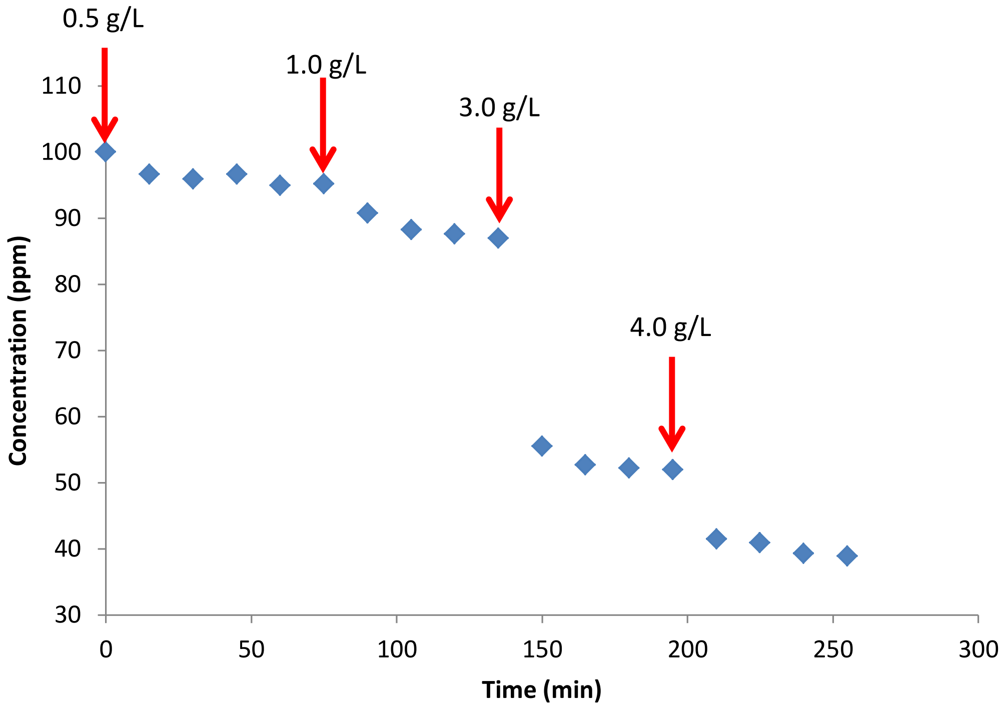

Figure 21: Plot of concentration (ppm) vs. time (min) for MB-TW system in CSTR. (Residence time: 75 minutes, Initial concentration = 100 ppm)

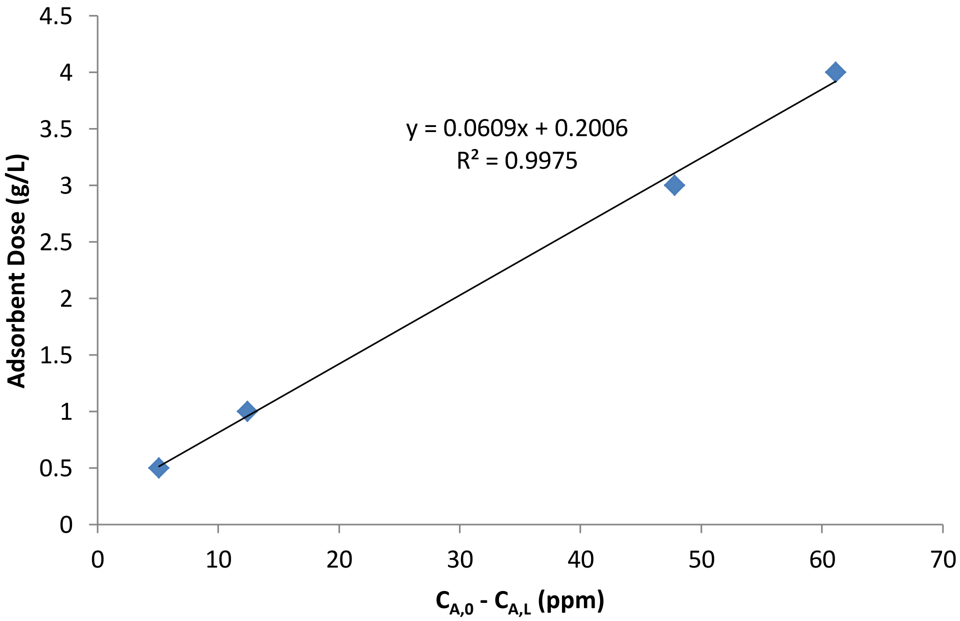

Figure 22: Correlation between adsorbent dose (g/L) and concentration difference (ppm) for 75 minutes residence time

During the last test, as shown in **Figure 19**, at a residence time of 60 minutes, the concentration of MB failed to reach an average after the addition of the first dose. There are several probable reasons as why did this scenario occur, such as the malfunction of the CSTR unit, weighing error during adsorbate measurement and the malfunction of the UV-Vis Spectrophotometer itself. However, the most plausible explanation is that, as the flow rate is too high, the minute amount of adsorbent added to the system is unable to give an observable effect. This means that, while the adsorption is proceeding, more MB dye is entering the system, negating the effect of the adsorption that just took place in the system. This is verified to be the reason, as after the next adsorbent dosage, the system shows good experimental results throughout.

4.5 *Modeling of the CSTR System*

The plot of u/V vs. 1/η for MB-TW system is shown in **Figure 23**. Here the experimental data are designated as points and the dense line represents the theoretical data calculated from **Eq. (6)**. **Figure 23** shows that for the MB-TW system, the theoretical line deviates slightly from the experimental data. This deviation from the theoretical line might be due to its greater particle size and also higher heterogeneity of the surface of TW adsorbents which contradicts the basic assumptions of the theoretical line (Islam, Khan, & Mozumder, Performance Equation for a Reactor Type Adsorption Unit, 2009).

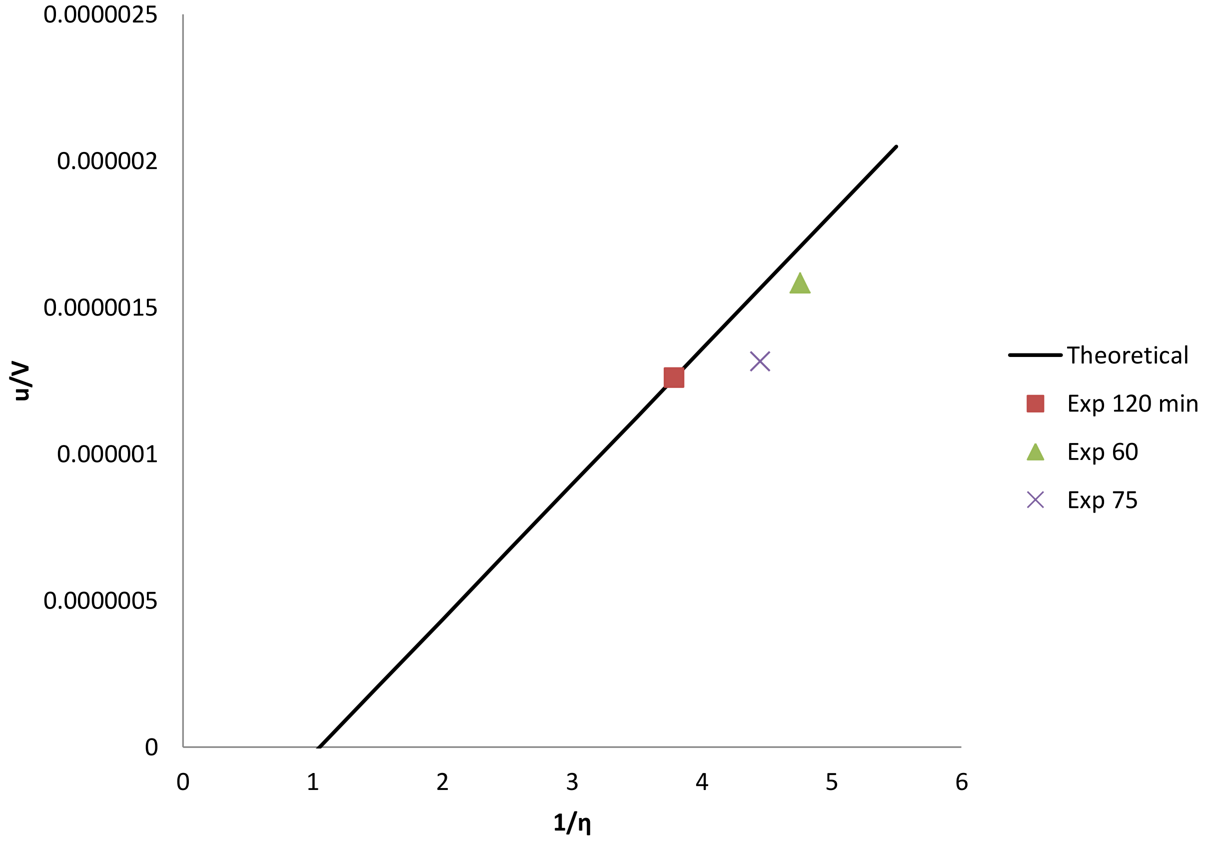

Figure 23: Plot of u/V vs. 1/ η for the CSTR system of MB-TW

From the data available in **Figure 23**, the first point lies directly on the theoretical line. This is due to the fact that the data used for the prediction of the u/V vs. 1/η theoretical line originates from the CSTR test with a residence time of 120 minutes, similar to the one for the first point. The latter points are merely predictions based on the models calculations. In the next point, the prediction of the model did very slightly veer off as this is an experimental data for the residence time of 60 and 75 minutes whereas the theoretical line is based off on prediction from the data available from the 120 minutes CSTR study. From this simple comparison, it could be seen that the model has a relatively high accuracy in the prediction for the behavior of a CSTR system even though it was initially developed for a different adsorbent-adsorbate system by (Islam, Khan, & Mozumder, Performance Equation for a Reactor Type Adsorption Unit, 2009). Lastly, by observing the plot, it can be seen that the theoretical line intersects 1/η axis when u/V is zero or the reactor volume V is infinite. This point indicates the maximum achievable utilization coefficient for a specific amount of removal. Here for the MB-TW system, $1/\eta_{max}$ was found to be 1.2798, thus giving a theoretical maximum coefficient of utilization of 78.14%.

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The present study indicates that a CSTR type adsorption unit can be used effectively for wastewater treatment with a MB-TW system. Dye removal efficiency of the CSTR type adsorption unit increases with adsorbent dosage and decrease with increase in feed flow rate or decrease in contact time. The maximum utilization coefficient η_{max} of an adsorbent depends on the adsorption system parameters q_∞, K and k_1 of that adsorbent. Higher value of these parameters attributes to a higher η_{max}. The selection of the utilization coefficient η would be chosen depending on the cost of the adsorbent and once it is set, the CSTR volume necessary for a definite amount of dye removal can be predicted from the design cum performance curve of the CSTR. The theoretical approaches used in this study can successfully predict the adsorption of methylene blue by natural adsorbents in both batch and continuous mode. Also the adsorption system parameters determined from batch study can effectively be applied to predict the CSTR performance. Furthermore, from the kinetic study, the data obtained fits the Unified Approach model and it has been proven to be effective in predicting the maximum amount of solute adsorbed at any given time by using the Langmuir isotherm data as a reference in the prediction. Lastly, from the CSTR study, the theoretically maximum coefficient of utilization of the adsorbent was found to be 78%.

5.2 Recommendations

Some recommendations that could have been done to improve the results and accuracy of this research are:

1) Add the effect of initial concentrations to the CSTR study, while maintaining the current parameter of adsorbent dosage and flow rate or residence time

2) A comparison study between the more popular AC and TW or other naturally sourced adsorbent could also be done to increase the viability of the research

3) Rather than a rudimentarily constructed CSTR, a better alternative is to utilize a bench scale CSTR unit to allow for a more controlled and repeatable results

4) The usage of a milli-pipette is strongly advisable to allow for a lesser error margin during the dilutions of sample before analysis

5) To allow for a lesser interference during tests, it is very advisable for all dilutions and samples to be prepared with ultrapure water instead of normal tap or distilled water

REFERENCES

Industries in Malaysia: Food Industry. (2012, September 18). Retrieved November 21, 2013, from Malaysian Investment Development Authority: http://www.mida.gov.my

Ahmad, A., Harris, W., Syafiee, & Seng, O. (2002). Removal of dye from wastewater of textile industry using membrane technology. *Jurnal Teknologi 26(F)*, 31-44.

Amarasinghe, B., & Williams, R. (2007). Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal 132*, 299-309.

Attia, A. A., Girgis, B. S., & Fathy, N. A. (2008). Removal of methylene blue by carbons derived from peach stones by H3PO4 activation: Batch and column studies. *Dyes and Pigments 76*, 282-289.

B.S., Y., S.K., T., & Seema. (2006). Study of vibrational spectra of 4-methyl-3-nitrobenzaldehyde. *Indian Journal of Pure & Applied Physics Vol. 44*, 644-648.

Balentine, D., Wiseman, S., & Bouwens, L. (1997). The chemistry of tea flavonoids. *Critical Reviews in Food Science and Nutrition 37*, 693-704.

Berrios, M., Martin, M., & Martin, A. (2012). Treatment of pollutants in wastewater: Adsorption of methylene blue onto olive-based activated carbon. *Journal of Industrial and Engineering Chemistry 18* , 780-784.

Bestani, B., Benderdouce, N., Benstaali, B., Belhakem, M., & Addou, A. (2008). Methylene blue and iodine adsorption onto an activated desert plant. *Bioresource Technology 99*, 8441-8444.

Crowl, D. A., & Louvrar, J. F. (2002). *Chemical Process Safety: Fundamentals with Application.* Pearson College Division.

Dahlke, T., Chen, Y., Franzeb, M., & Holl, W. (2006). Continuous removal of copper ions from dilute feed streams using magnetic weak-base anion exchangers in a continuous stirred tank reactor (CSTR). *Reactive & Functional Polymers 66*, 1062-1072.

Fogler, H. (2010). *Elements of Chemical Reaction Engineering (4th Edition).* Michigan: Pearson Education International.

Foo, K., & Hameed, B. (2011). Microwave-assisted preparation of oil palm fiber activated carbon for methylene blue adsorption. *Chemical Engineering Journal 166* , 792-795.

Foo, K., & Hameed, B. (2011). Preparation of activated carbon from date stones by microwave induced chemical activation: Application for methylene blue adsorption. *Chemical Engineering Journal 170* , 792-795.

Gargouri, B., Karray, F., Mhiri, N., Aloui, F., & Sayadi, S. (2011). Application of a continuously stirred tank bioreactor (CSTR) for bioremediation of hydrocarbon-rich industrial wastewater effluents. *Journal of Hazardous Materials 189*, 427-434.

Ghaedi, M., Ghazanfarkhani, M., Khodadoust, S., Sohrabi, N., & Oftade, M. (2014). Acceleration of methylene blue adsorption onto activated carben prepared from dross licorice by ultrasonic: Equilibrium, kinetic and thermodynamic studies. *Journal of Industrial and Engineering Chemistry 20*, 2548-2560.

Hameed, B., & Auta, M. (2011). Preparation of waste tea activated carbon using potassium acetate as an activating agent for adsorption of Acid Blue 25 dye. *Chemical Engineering Journal 171*, 502-509.

Hameed, B., Ahmad, A., & Latiff, K. (2007). Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. *Dyes and Pigments 75*, 143-149.

Hameed, B., Din, A., & Ahmad, A. (2007). Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. *Journal of Hazardous Materials 141*, 819-825.

Hulanicki, A., & Glab, S. (1978). Redox Indicators. Characteristics and Applications. *International Union of Pure and Applied Chemistry*, 463-498.

Indra, D., Vimal, C., Nitin, K., & Indra, M. (2005). Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon: Kinetic study and equilibrium isotherm analysis. *Colloids Surf. 264*, 17-28.

Islam, M., Khan, M., & Mozumder, M. (2004). Adsorption Equilibrium and Adsorption Kinetics: A Unified Approach. *Chemical Engineering and Technology*, 1095-1098.

Islam, M., Khan, M., & Mozumder, M. (2009). Performance Equation for a Reactor Type Adsorption Unit. *Journal of Scientific Research*, 450-460.

Larsen, D. (2007). *IR Spectroscopy: Practical Problems*. Retrieved 6 20, 2014, from ChemWiki: The Dynamic Chemistry E-textboox: http://chemwiki.ucdavis.edu

Li, Y., Du, Q., Liu, T., Peng, X., Wang, J., Sun, J., et al. (2013). Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. *Chemical engineering research and design 91* , 361-368.

MacFarlane, A., & MacFarlane, I. (2004). *The Empire of Tea: The Remarkable History of the Plant that took over the World.* Overlook Press.

Mahapatra, K., Ramteke, D., & Paliwal, L. (2012). Production of activated carbon from sludge of food processing industry under controlled pyrolysis and its application for methylene blue removal. *Journal of Analytical and Applied Pyrolysis 95*, 79-86.

Malkoc, E., & Nuhoglu, Y. (2007). Potential of tea factory waste for chromium (VI) removal from aqueous solutions: Thermodynamic and kinetic studies. *Separation and Purification Technology 54*, 291-298.

Mangun, C., Daley, M., Braatz, R., & Economy, J. (1998). Effect of pore size on adsorption of hydrocarbons in phenolic-based activated carbon fibers. *Carbon Vol. 36*, 123-131.

Menoud, P., Cavin, L., & Renken, A. (1998). Modelling of heavy metals adsorption to a chelating resin in a fluidized bed reactor. *Chemical Engineering Processes 37*, 89-101.

Mondal, M. (2009). Removal of Pb (II) ions from aqueous solution using activated tea waste: Adsorption on a fixed-bed column. *Journal of Environmental Management 90*, 3266-3271.

Munakata, A., & Uno, Y. (1994). Colonoscopic Polypectomy with Local Injection of Methylene Blue. *Tohoku J. Exp. Med.*, 377-382.

Orth, K., Beck, G., Genze, F., & Ruck, A. (2000). Methylene blue mediated photodynamic therapy in experimental colorectal tumors in mice. *Journal of Photochemistry and Photobiology 57*, 186-192.

Papadimitriou, C., Samaras, P., & Sakellaropoulus, G. (2009). Comparative study of phenol and cyanide containing wastewater in CSTR and SBR activated sludge reactors. *Bioresource Technology 100*, 31-37.

Peavy, H., Rowe, D., & Tchobanoglous, G. (1985). *Environmental Engineering.* McGraw-Hill International Inc.

Robinson, T., Chandran, B., Naidu, G., & Nigam, P. (2002). Studies on the removal of dyes from a synthetic textile effluent using barley husk in static-batch mode and in a continuous flow, packed-bed reactor. *Bioresource Technology 85*, 43-49.

Sahin, S., Demir, C., & Gucer, S. (2007). Simultaneous UV-vis spectrophotometric determination of disperse dyes in textile wastewater by partial least squares and principal component regressions. *Dyes and Pigments 73,* 368-376.

Shemsadi, R., Arvand, M., Effendiev, A. A., & Zeynalov, N. A. (2012). Application of synthetic polymers as adsorbents for the removal of cadmium from aqueous solutions: Batch experimental studies. *Caspian Journal of Environmental Science 10*, 1-8.

Suhas, & Gupta, V. (2009). Application of low-cost adsorbents for dye removal: A review. *Journal of Environmental Management 90*, 2312-2342.

University of California, Los Angeles. (1997). *Introduction to IR Spectra*. Retrieved 06 20, 2014, from WebSpectra: Problems in NMR and IR Spectroscopy: http://chem.ucla.edu

UV-Vis Absorption Spectroscopy: Theoretical Principles. (n.d.). Retrieved June 10, 2014, from Sheffield Hallam University: http://teaching.shu.ac.uk

Vilar, V. J., Botelho, C. M., & Boaventura, R. A. (2008). Lead and Copper biosorption by marine red algae Gelidium and algal composite material in a CSTR ("Carberry" type). *Chemical Engineering Journal 138*, 249-257.

Wang, S., Zhu, Z., Coomes, A., Haghseresht, F., & Lu, G. (2005). The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *Journal of Colloid and Interface Science 284*, 440-446.

Wankhade, A. A., & Ganvir, V. (2013). Preparation of Low Cost Activated Carbon from Tea Waste using Sulphuric Acid as Activating Agent. *International Research Journal of Environmental Sciences*, 53-55.

William Reusch. (2013, May 05). *Visible and Ultraviolet Spectroscopy*. Retrieved June 06, 2014, from Michigan State University: http://www2.chemistry.msu.edu

Yang, C.-F., Wang, C.-C., & Tseng, C.-H. (2013). Methylamine removal using mixed bacterial strains in a continuous stirred tank reactor (CSTR) system. *International Biodeterioration & Biodegradation*, 1-4.

Yang, J., & Qiu, K. (2010). Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal. *Chemical Engineering Journal 165*, 209-217.

APPENDICES

Appendix A1: Documentations

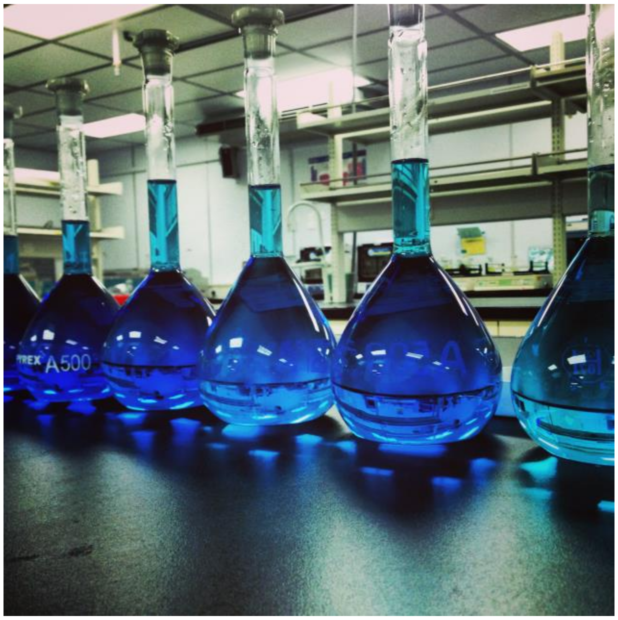

Figure 24: Stock solutions for MB calibration curve (1, 2, 4, 6, 8, 10 ppm)

Figure 25: A panoramic look on the CSTR workstation during a CSTR adsorption study

Appendix A1: Documentations (Cont'd)

Figure 26: Apparatus used throughout this research

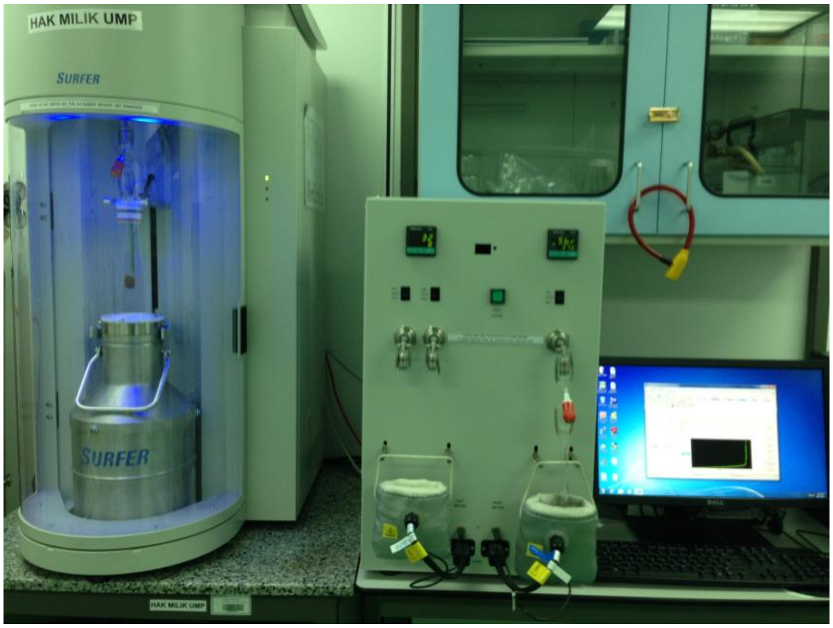

Figure 27: BET-N2 (Surfer Turbo, Thermo Scientific, USA)

Appendix A1: Documentations (Cont'd)

Figure 28: FESEM (JSM-7800F, Jeol, Japan)

Figure 29: Sieve Shaker (315 microns sieve tray attached)

Appendix A1: Documentations (Cont'd)

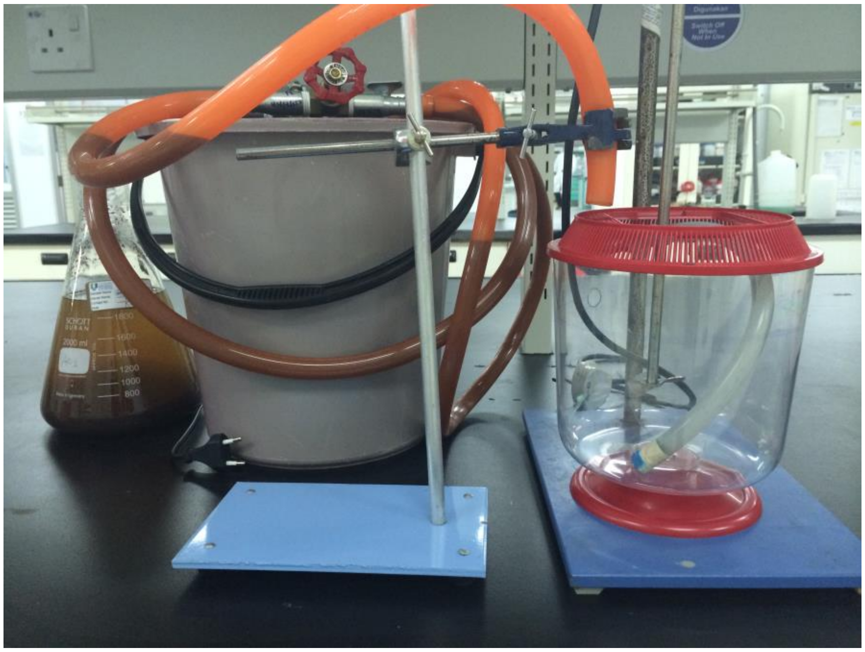

Figure 30: Rudimentarily constructed CSTR (not in operation)

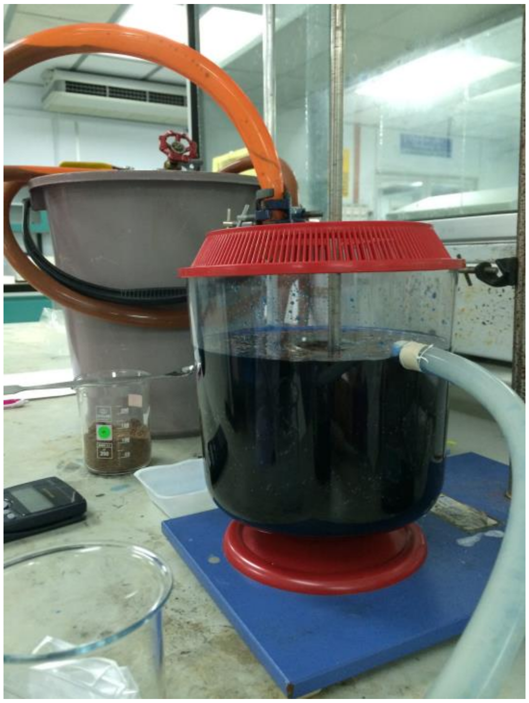

Figure 31: Rudimentarily constructed CSTR (Test in operation: Tao 120 minutes). Also visible is the beaker containing TW sample for adsorbent addition

Appendix A1: Documentations (Cont'd)

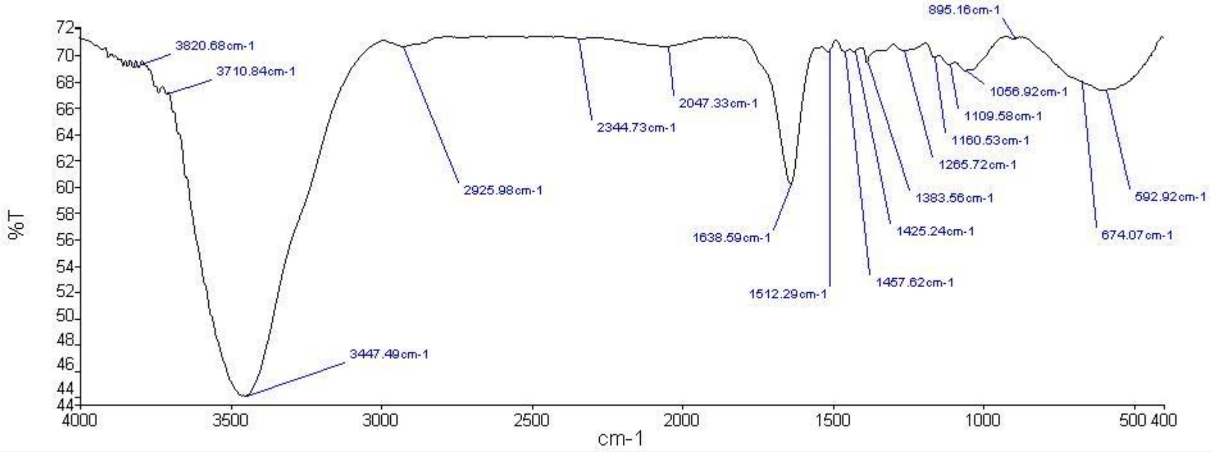

Figure 32: FT-IR Spectrum for TW with peaks shown

Figure 33: Perkin-Elmer Spectrum 100 FT-IR Spectrophotometer

Appendix A1: Documentations (Cont'd)

Figure 34: Rigaku MiniFlex II Desktop X-Ray Diffractometer

Appendix A2: Raw Data

Concentration (ppm)	**Absorbance (abs)**
1	0.203
2	0.404
4	0.803
6	1.161
8	1.51
10	1.91

Table 4: Calibration curve raw data

C_o (ppm)	**C_e (abs)**	**C_e (ppm)**	**W (g)**	**V (mL)**	**Q**
0	0	0	0	0	0
52.63	2.036	10.84	0.08	100	52.2375
73.46	0.435	21.55	0.0805	100	64.4845
111.09	1.141	58.88	0.0805	100	64.8571
115.17	1.228	63.84	0.0805	100	63.764
159.22	1.983	104.88	0.0816	100	66.5931

Table 5: Batch study raw data

C/Q (mg/g)	**C (mg/L)**
0.20751	10.84
0.33419	21.55
0.90784	58.88
1.00119	63.84
1.57494	104.99

Table 6: Langmuir isotherm plot data

Appendix A2: Raw Data (Cont'd)

Time (min)	C_e (abs)	C_e (ppm)	W (g)	V (L)	Q (mg/g)
0	1.398	75	0.0122	0.25	0
15	1.377	73.90	0.0122	0.25	22.44701
30	1.363	73.17	0.0122	0.25	37.41233
45	1.353	72.65	0.0122	0.25	48.10185
60	1.348	72.39	0.0122	0.25	53.44661
75	1.344	72.18	0.0122	0.25	57.72241
90	1.34	71.97	0.0122	0.25	61.99822
105	1.341	72.02	0.0122	0.25	60.92927
120	1.339	71.92	0.0122	0.25	63.06717

Table 7: Kinetic study data for 75 ppm

Time (min)	C_e (abs)	C_e (ppm)	W (g)	V (L)	Q (mg/g)
0	2.114	100	0.074	0.25	0
15	1.964333	95.48	0.074	0.25	15.27349
30	1.891333	91.67	0.074	0.25	28.13847
45	1.820333	87.96	0.074	0.25	40.65098
60	1.793	86.54	0.074	0.25	45.468
75	1.774	85.55	0.074	0.25	48.81642
90	1.767	85.19	0.074	0.25	50.05005
105	1.756	84.61	0.074	0.25	51.98861
120	1.75	84.30	0.074	0.25	53.046

Table 8: Kinetic study data for 100 ppm

Appendix A2: Raw Data (Cont'd)

Time (Min)	α	β	Y	Q_{exp}	Q_{calc}	Error (%)
0	6362.844	65.72532	0	0	0.00	0
15	6362.844	65.72532	1.034E-08	22.447	25.25	11.10
30	6362.844	65.72532	2.08714E-08	37.412	40.76	8.22
45	6362.844	65.72532	3.26614E-08	48.101	50.31	4.40
60	6362.844	65.72532	4.16592E-08	53.446	56.21	4.91
75	6362.844	65.72532	5.23257E-08	57.722	59.84	3.54
90	6362.844	65.72532	7.13809E-08	61.998	62.09	0.15
105	6362.844	65.72532	6.50917E-08	60.929	63.48	4.02
120	6362.844	65.72532	7.98125E-08	63.067	64.34	1.97

Table 9: Unified approach model data for 75 ppm

Time (Min)	α	β	Y	Q_{exp}	Q_{calc}	Error (%)
0	1282.699	66.21029	0	0	0.00	0
15	1282.699	66.21029	1.60391E-07	15.273	14.41	6.03
30	1282.699	66.21029	3.40416E-07	28.138	25.58	10.01
45	1282.699	66.21029	5.8936E-07	40.650	34.28	18.59
60	1282.699	66.21029	7.207E-07	45.468	41.08	10.68
75	1282.699	66.21029	8.31792E-07	48.816	46.41	5.18
90	1282.699	66.21029	8.78295E-07	50.050	50.60	1.08
105	1282.699	66.21029	9.5918E-07	51.988	53.89	3.52
120	1282.699	66.21029	1.00814E-06	53.046	56.48	1

Table 10: Unified approach model data for 100 ppm

Appendix A2: Raw Data (Cont'd)

Time (min)	Concentration (abs)	Concentration (ppm)	Theoretical Data (ppm)
0	1.917	100	100
15	1.634	85.23	77.88
30	1.184	61.76	60.65
45	0.985	51.38	47.24
60	0.79	41.21	36.79
75	0.536	27.96	28.65
90	0.373	19.45	22.31
105	0.194	10.11	17.38
120	0.179	9.33	13.53
135	0.113	5.89	10.54
150	0.057	2.97	8.21
165	0.035	1.82	6.39

Table 11: CSTR performance data (Residence time: 120 minutes)

Time (min	Concentration (abs)	Concentration (ppm)	Theoretical Data (ppm)
0	1.917	100	100
15	1.403	73.18	77.88
30	1.038	54.14	60.65
45	0.742	38.70	47.24
60	0.436	22.74	36.79
75	0.296	15.44	28.65
90	0.2	10.43	22.31
105	0.074	3.86	17.38
120	0.02	1.04	13.53

Table 12: CSTR performance data (Residence time: 60 minutes)

Appendix A2: Raw Data (Cont'd)

Time (min)	Concentration (abs)	Concentration (ppm)	Dose (g)	Adsorbent Dose
0	1.706	100	1	0.5 g/L
15	1.642	96.66145	0.25	
30	1.636	96.34846	0.25	
45	1.66	97.60042	0.25	
60	1.65	97.07877	0.25	
75	1.678	98.53938	1	1 g/L
90	1.582	93.53156	0.5	
105	1.566	92.69692	0.5	
120	1.543	91.49713	0.5	
135	1.539	91.28847	4	3 g/L
150	1.011	63.74544	1.5	
165	1.005	63.43245	1.5	
180	0.982	62.23266	1.5	
195	0.895	57.69431	2	4 g/L
210	0.647	44.75743	2	
225	0.624	43.55764	2	
240	0.617	43.19249	2	
255	0.609	42.77517	2	

Table 13: CSTR study raw data (Varied dosages, Residence time: 60 minutes)

W (g/L)	Concentration (ppm)	Concentration Difference (ppm)
0.5	98.53938445	1.460616
1	91.28847157	8.711528
3	57.69431403	42.30569
4	42.77516954	57.22483

Table 14: CSTR concentration difference vs. dosage data (Residence: 60 minutes)

Appendix A2: Raw Data (Cont'd)

Time (min)	Concentration (abs)	Concentration (ppm)	Dose (g)	Adsorbent Dose
0	1.917	100	1	0.5 g/L
15	1.852	96.60928534	0.25	
30	1.838	95.87897757	0.25	
45	1.852	96.60928534	0.25	
60	1.819	94.88784559	0.25	
75	1.824	95.1486698	1	1 g/L
90	1.74	90.76682316	0.5	
105	1.692	88.2629108	0.5	
120	1.679	87.58476787	0.5	
135	1.667	86.95878978	4	3 g/L
150	1.063	55.45122587	1.5	
165	1.009	52.63432447	1.5	
180	1.003	52.32133542	1.5	
195	0.996	51.95618153	2	4 g/L
210	0.794	41.41888367	2	
225	0.784	40.89723526	2	
240	0.753	39.2801252	2	
255	0.745	38.86280647	2	

Table 15: CSTR study raw data (Varied dosages, Residence time: 75 minutes)

W (g/L)	Concentration (ppm)	Concentration Difference (ppm)
0.5	94.88784559	5.112154408
1	87.58476787	12.41523213
3	52.32133542	47.67866458
4	38.86280647	61.13719353

Table 16: CSTR concentration difference vs. dosage data (Residence: 75 minutes)

Appendix A2: Raw Data (Cont'd)

Time (min)	Concentration (abs)	Concentration (ppm)	Dose (g)	Adsorbent Dose
0	1.917	100	1	0.5 g/L
15	1.847	96.34846114	0.125	
30	1.749	91.23630673	0.125	
45	1.684	87.84559207	0.125	
60	1.732	90.34950443	1	1 g/L
75	1.592	83.04642671	0.25	
90	1.665	86.85446009	0.25	
105	1.558	81.27282212	0.25	
120	1.553	81.01199791	2	2 g/L
135	1.363	71.10067814	0.375	
150	1.261	65.77986437	0.375	
165	1.221	63.69327074	0.375	
180	1.217	63.48461137	2	3 g/L
195	0.995	51.90401669	0.75	
210	0.864	45.07042254	0.75	
225	0.844	44.02712572	0.75	
240	0.846	44.1314554	0.75	
255	0.884	46.11371935	0.75	

Table 17: CSTR study raw data (Varied dosages, Residence time: 120 minutes)

W (g/L)	Concentration (ppm)	Concentration Difference (ppm)
0.5	90.34950443	9.650495566
1	81.01199791	18.98800209
2	63.48461137	36.51538863
3	46.11371935	53.88628065

Table 18: CSTR concentration difference vs. dosage data (Residence: 120 minutes)

Appendix A2: Raw Data (Cont'd)

u/V	1/η
-4.87123E-07	0
-2.56555E-07	0.5
-2.59862E-08	1
2.04582E-07	1.5
4.35151E-07	2
6.6572E-07	2.5
8.96288E-07	3
1.12686E-06	3.5
1.35743E-06	4
1.58799E-06	4.5
1.81856E-06	5
2.04913E-06	5.5

Table 19: CSTR model theoretical line data points

Residence Time (min)	u/V	1/η	η_{max}
120	1.25933E-06	3.787265	0.946654
75	1.3157E-06	4.451497	0.937339
60	1.58209E-06	4.759367	0.942729

Table 20: CSTR experimental data points for model fitting