Evaluation of a novel media Sucrose Activated Carbon for removal of methylene blue, nitrate and phosphate from solution and comparison with Granular Activated Carbon.

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by

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Abstract

The adsorptive capacity of a novel green media Sucrose Activated Carbon (SAC) was compared with the more traditional Granular Activated Carbon (GAC) used for water treatment which has certain disadvantages including high price, is coal based and has adverse affects on performance by variations in pH, temperature and flow rate. SAC is obtained from the hydrothermal carbonization of sucrose followed by pyrolysis at 900°C. Preliminary tests indicate Iodine number for SAC is 1150 mg/g which is comparable to GAC in the range of 500-1200 mg/g. Scanning electron microscopic (SEM) images of SAC show spherical particles with average particle size in the range of 2-9 μm with smooth external surface. SAC also shows good adsorptive capacity for methylene blue, nitrate, and phosphate with adsorption capacities, 196 mg/g, 1.07 (mg/g(L/mg)^{1/n}) and 1.71 mg/g, respectively. Thus, based on the initial studies, this media has potential to be a sustainable substitute for GAC and can further be tested for its economic value and column-based performance on pilot scale.

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List of Acronyms

ATP	Adenosine Tri Phosphate
BET	Brunauer Emmett Teller
CANMET	Canada Centre for Mineral and Energy Technology
C:N:P	Carbon:Nitrogen:Phosphorus
CFU	Colony Forming Unit
DBP	Disinfection Byproducts
EBCT	Empty Bed Contact Time
GAC	Granular Activated Carbon
HACH	Manufacturing industry
HPC	Heterotrophic Plate Count
MSE	Mean Square Error
PAH	Polycyclic aromatic hydrocarbons
PBS	Phosphate buffered saline
PCB	Polychlorinated biphenyls
SAC	Sucrose Activated Carbon
SEM	Scanning Electron Microscopy
TCT	Total Coliform Test
TNT	Test `N Tube
TOC	Total Organic Carbon

Chapter 1- Introduction

1.1 Problem statement

The influent surface water into water treatment plants are treated by several technologies including chemical treatment, sedimentation, filtration, adsorption, biofiltration and ion exchange. Adsorption is one of the most popular technologies used in water treatment plants. Adsorption involves removal of contaminants from the solution by adsorption onto the surface of the adsorbent. Its simplicity in design, low initial cost, ease of operation, insensitivity to toxic substances distinguishes it as a water treatment technology (Garg et al., 2004). Successful application of adsorption technique depends on the development of an efficient adsorbent (Wang and Peng, 2010).

A variety of media have been studied to be used as an adsorptive media including sand, anthracite, zeolite, peat, ceramic, resins and activated carbon. Granular activated carbon (GAC) is most commonly used because of its excellent adsorption capacity, high surface area and porous structure. However certain factors such as high cost of production, requirement for pre-treatment of influent to prevent clogging and regeneration processes involving the production of small quantities of additional effluent have been found to be the disadvantages of using GAC. Research has been directed towards finding low cost materials, preferably from natural, agricultural and industrial waste sources, with high efficiencies for removing different contaminants, so that they can be used as a substitute for GAC (Garg et al., 2004; El-Wakil et al., 2015; Pathania et al., 2017).

One major disadvantage of commercially available activated carbon is the fact that majority of the GAC is produced from coal that is fossil fuels. Sustainability, being the need of the hour and zero waste strategy as one of the primary focus' in sustainability, a lot of research is being focussed on

developing adsorptive media from renewable sources. These include industrial, household and agricultural wastes, thereby reducing waste disposal problems while generating renewable sources for adsorbent production. Intense research has been conducted to develop activated carbon from renewable sources that have high adsorptive capacity and versatility for treatment of a wide range of contaminants. Several activated carbons developed from renewable sources have been reported by Rafatullah et al., 2010. Some examples have been shown in Table 1.1. However, most of the green activated carbons require chemical modifications to increase the adsorptive capacity for different types of adsorbate. This adds to the cost of developing activated carbon. Regeneration of activated carbon also becomes difficult and, in some cases, this method also affects solute recovery. Therefore, there is an ongoing search to develop green adsorbents from renewable sources and to test their ability without requiring any surface modifications.

Table 1.1: Activated carbon adsorbent examples with their advantages and disadvantages

Adsorbent	Advantages	Disadvantages	References
<i>Salsola vermiculata</i> (perennial shrub plant) activated carbon	Green adsorbent, High adsorption capacity for methylene blue dye	Chemical activation, regeneration	(Bestani et al., 2008)
Cotton stalk activated carbon	Green adsorbent, High adsorption capacity for methylene blue	Chemical activation, regeneration	(Deng et al., 2009)
Hazelnut shell activated carbon	Green adsorbent	Low adsorption capacity	(Aygün et al., 2003)
Coconut granular activated carbon	Green adsorbent	Low adsorption capacity, chemical activation	(Liu et al., 2018)
Walnut shell activated carbon	Green adsorbent	Low adsorption capacity requires surface modification	(Alighardashi and Shahali, 2016)

A novel adsorbent is generally characterized in terms of physical properties such as attrition, ash content, BET surface area and particle size. Model compounds such as methylene blue and iodine molecule define media in terms of adsorptive capacity and define the physical structure of activated carbons based on the dimensions of the adsorbate molecules and how they accumulate within the pores, intraparticle space and over the surface of adsorbents (Cleiton et al., 2011). PCS Biofuels, Trusense Engineering along with Carleton University thus have worked on a novel media, Sucrose Activated Carbon (SAC) obtained from hydrothermal carbonization of organic material sucrose, at a temperature of 900°C, thus adding to the list of green activated carbons as obtained from renewable sources. This study represents the first step towards establishing SAC as an adsorbent. The aim of this experiment was to analyze the adsorption capacity of SAC and compare its properties to the commonly used media GAC.

1.2 Research objectives

In this study the adsorption capacity of novel media, SAC was investigated for removing various adsorbates from the solution. Phase 1 involved testing the adsorption capacity of media to adsorb contaminants like methylene blue and iodine from the solution, kinetic modelling to check the rate of adsorption for each adsorbate and to characterize the media in terms of surface area, particle size, attrition, ash content, moisture content and surface morphology based on SEM analysis. Phase 2 involved testing the novel media for removal of inorganic contaminants such as nitrate and phosphate and test the adsorption capacity for each adsorbate. This phase also involves a comparison of kinetic parameters for nitrate and phosphate removal by SAC versus GAC. Competitive analysis was also conducted to test the ability of SAC to remove contaminants in a multi component environment with several other competing ions in the solution mimicking surface water compositions.

Thus, the research objectives were as follows:

- To evaluate the possibility of using SAC as a new green adsorbent and test the physical characteristics of the media including specific surface area, average particle size, bulk density and surface morphology of the media.
- To test the adsorption capacity of the adsorbent to remove methylene blue dye and iodine from aqueous solution and study the rate of methylene blue removal through kinetic modelling.
- Test the adsorption capacity of the media to remove inorganic adsorbates, nitrate and phosphate from the solution and study the rate of adsorbate removal through kinetic modelling.
- To evaluate the effect of competing ions, present in the multi component solution, on the removal of specific inorganic adsorbates by SAC and GAC, mimicking a more real-life scenario.

1.3 Organization of thesis

The thesis is organized into 6 chapters. Chapter-1 involves an introduction into the need for development of green adsorbents and the main objectives of the study. Chapter-2 is the literature review giving a background information on the hypothesis behind the experimental process, setup, and the results. Chapter-3 gives information on the methodology adopted to test the objectives, experimental setup and standard protocols followed to complete the experiments. Chapter-4 and Chapter-5 are the results in the form of journal articles that are in the process of submission for publication. Finally, Chapter-6 is a summary of conclusions of all the tests conducted and suggestions for future work.

1.4 Articles Summary

1) Removal of Methylene Blue dye and Iodine molecule from water by adsorption using Sucrose Activated Carbon (SAC) (*Planned submission to Journal of Environmental Chemical Engineering*)

Authors: Saumya Suresh, Onita D. Basu, Sara Jamaliniya, Eustina Musvoto, Alexis Mackintosh

Author contributions:

- **Saumya Suresh:** Conducted the laboratory experiments as a part of a team with Sara Jamaliniya and Chamathka Varushawithana including adsorption, kinetic tests and characterization, compiled and analyzed all the data. Wrote the complete initial draft, implemented changes and edits as directed through Onita D. Basu.
- **Onita D. Basu:** Thesis supervisor. Drafted the experimental design. Provided guidance and feedback throughout the process of thesis completion. Provided edits and suggestions throughout the writing stage.
- **Sara Jamaliniya:** Conducted the laboratory experiments as a part of a team with Saumya Suresh and Chamathka Varushawithana. Assisted with analysis of the data. Assisted in writing the paper.
- **Eustina Musvoto:** Provided the adsorbent material in focus. Provided feedback on results and writing.
- **Alexis Mackintosh:** Provided the adsorbent material in focus. Assisted in overview of experimental design. Provided feedback on results and writing.

2) Investigation of a novel green adsorbent for nitrogen and phosphorous removal (*Planned submission to Separation and Purification Technology*)

Authors: Saumya Suresh, Sara Jamaliniya, Alexis Mackintosh, Eustina Musvoto, Onita D. Basu

Author contributions:

- ***Saumya Suresh:*** Conducted the laboratory experiments as a part of a team with Sara Jamaliniya and Chamathka Varushawithana including adsorption, kinetic tests and characterization, compiled and analyzed all the data. Wrote the complete initial draft, implemented changes and edits as directed through Onita D. Basu.
- ***Sara Jamaliniya:*** Conducted the laboratory experiments as a part of a team with Saumya Suresh and Chamathka Varushawithana. Assisted with analysis of the data. Assisted in writing the paper.
- ***Alexis Mackintosh:*** Provided the adsorbent material in focus. Assisted in overview of experimental design. Provided feedback on results and writing.
- ***Eustina Musvoto:*** Provided the adsorbent material in focus. Provided feedback on results and writing.
- ***Onita D. Basu:*** Thesis supervisor. Drafted the experimental design. Provided guidance and feedback throughout the process of thesis completion. Provided edits and suggestions throughout the writing stage.

2. Literature Review

This chapter seeks to provide an insight into the contaminants common in water streams for treatment, various water treatment technologies, adsorption process and adsorption and kinetic models used to study adsorption of contaminants onto adsorbents. It also introduces the readers to green adsorbents and sheds a note on recent green adsorbents reported in literature.

2.1 Adsorption in drinking water treatment

Biosorption, adsorption, coagulation, flocculation, ozonation, membrane filtration and liquid-liquid extraction have been employed to treat pollutants in source water as a part of water treatment technologies. (Pathania et al., 2017). Due to its simplicity, ease of operation and effectiveness, low initial cost, insensitivity to toxic substances and backwashing, adsorption is widely used water treatment process. Adsorption is the process of adhesion of gas, liquid or solid molecules from the solution onto a surface. It is a surface phenomenon and involves either physical or chemical interaction with the surface. Adsorption is a combination of two phases involved in process which include an adsorbent which is the surface onto which the contaminants get adsorbed and the adsorbate which are the pollutants present in the solution that get adsorbed onto the surface. Activated carbon, sand, peat, anthracite, and resins are some common examples of adsorbents used in water treatment. Successful application of adsorption depends on the efficiency of the adsorbent used (Wang and Peng, 2010). Adsorption can be physical or through chemical interaction. Physical adsorption process is due to van der Waal's forces between the adsorbate and the adsorbent whereas chemisorption involves chemical reaction between the adsorbate and the chemical groups on the surface of the adsorbent.

2.2 Adsorbates

The recent trend of rising industrial, agricultural activities increase in domestic wastes and their discharge into the water streams have lead to high contaminant content in water. Organic, inorganic nutrients, dyes, heavy metals, PCBs, PAH etc. are some common contaminants that are released along with industrial effluents from textile, pharmaceutical, paper, food and plastics industries. These contaminants when released into water streams promote algal bloom and enhance eutrophication. They can also lead to genetic mutations, are carcinogenic, esthetically unpleasant, lead to formation of DBP, cause odor and taste problems and are also known to be toxic to aquatic life forms (Sheing et al 2013). Removal of these contaminants from water has been extensively studied to establish a cost effective, efficient and easy operation on large scale in water treatment plants to bring water to the safety standards for drinking or release into water streams. Some adsorbates that have been studied in this thesis have been discussed below.

2.2.1 Dyes

Dyes are one such contaminant which are extensively studied as they hinder with light adsorption within water sources thus altering and disturbing aquatic ecosystem. They are esthetically unpleasant, carcinogenic and are proven to be toxic to some aquatic life forms. Congo red, brilliant blue, methylene blue, azo dyes are few examples of dyes released in effluents. Methylene blue is a commonly studied dye discharged from dyes, textile, plastics and food industries. Around 1-15% dyes are discharged from textile industries (Senthilkumaar et al., 2005; Hameed et al., 2007). Methylene blue is a cationic dye with the molecular formula $C_{16}H_{18}ClN_3S.XH_2O$, develops blue color in solution. It is amorphous in nature with molecular weight 320 g/mol, width 14.3 Å, depth 6.1 Å, thickness 4Å, molecular volume 241.9 cm³/mol and molecular diameter 0.8 nm. Methylene blue in excess amounts and with long term exposure can cause vomiting, nausea, hypertension,

anemia, eye burns, which may be responsible for permanent injury to the eyes of human and animals. Inhalation of methylene blue causes short periods of difficult breathing and if ingested could lead to burn sensation in the mouth with severe cases leading to burning sensation, nausea, vomiting and in extreme cases mental confusion and painful micturition. (Hameed et al 2007; Özer and Dursun, 2007). As a result, efficiency of methylene blue removal has been studied through different water treatment technologies and adsorption has shown successful application for dye removal. Methylene blue because of its molecular size and analogy to the mesopore and macropore sizes of activated carbon, strong adsorption onto solids and being model compound for removal of organic compounds and colored contaminants is used as a standard molecule to define adsorption capacity.

2.2.2 Iodine molecule

Iodine molecule is another commonly used adsorbate used to study adsorption process. The amount of iodine adsorbed in milligrams by 1 gram of carbon is called iodine number. Iodine number is indicative of the surface area contributed by the pores on the media larger than 1nm (Aygün et al., 2003). Iodine is a small molecule with a molar mass of 127 g mol^{-1} and an ionic radius of 0.22 nm therefore defines the ability of activated carbon to adsorb smaller particles. The dimensions of the iodine molecule help define physical structure and adsorptive capacity of adsorbents (Cleiton et al., 2011).

2.2.3 Inorganic nutrients

Inorganic nutrients such as nitrate, nitrite, phosphate, ammonia is another set of contaminants released in effluents from food, agricultural based industries, leachate from landfills, textile industries etc. These in water streams lead to eutrophication, which in turn leads to algal bloom hence, reduced dissolved oxygen content in water bodies. This results in loss of species and habitat.

It also leads to increase in turbidity and decrease in visibility. Therefore, there have been studies focussing around adsorption removal of these nutrients from water.

- **Nitrate:** It is one of the common anionic pollutants found in surface and ground water and elevated concentrations could lead to negative effects on the health of aquatic biota and human beings. Nitrate contamination in water sources have been found to be mostly due to excessive use of fertilizers in crops, livestock, sewage waste and septic tanks. In broad terms it is found in agricultural, municipal and industrial wastewaters (Moşneag et al., 2013; Nolan et al., 1997). Higher nitrate concentrations than standard levels permissible, that is more than recommended levels of 10 mg/L in drinking water can cause blue baby syndrome in infants. For discharge into water streams, the maximum recommended concentration of nitrate is 45 mg/L (Health Canada, 2013). Levels above this can lead to eutrophication in water body sources, increase chances of spreading several infectious diseases and potential formation of carcinogens that is nitrosamines (Cho et al., 2011; Kilpimaa et al., 2015; Manjunath and Kumar, 2018). It is recommended that nitrate to nitrite ratio should not exceed one in water sources (Alighardashi and Shahali; 2016). Some of the conventional methods used for nitrate removal from water include biological processes such as nitrification and denitrification, reverse osmosis, catalytic denitrification, ion exchange and chemical reduction and adsorption (Liu et al., 2018). Adsorption is found to be one of the most effective and inexpensive method for nitrate removal. Studies involving the use of various adsorbents to remove nitrate from solution have been reported. Most of the activated carbon studies reported in literature have low adsorption capacities for nitrate removal. Therefore, the activated carbons were modified by different methods

for example with ZnCl_2 , metal ions, cationic polymers and bio gasification to increase adsorption capacity. (Mizuta et al., 2004).

- **Phosphate:** Industrial wastes, discharge of sewage, agricultural runoff, urban runoff, septic tank leakage, effluent discharges from soak pits not treated properly and landfill leachates are the main sources of contamination of surface and ground water sources with phosphate. Every year around 1.3 million tons of phosphate is discharged into the water sources and systems throughout the world (Manjunath and Kumar, 2018). Phosphate is one of the important macronutrients for living organisms both in aquatic and terrestrial settings. It is one of the main factors leading to growth of aquatic micro and macro organisms hence leading to eutrophication in water bodies (Ragheb, 2013). When the concentration of phosphate exceeds 0.02 mg/L in water bodies it paves way for eutrophication which leads to loss of habitat, loss of species and makes water sources murky and turbid. Phosphate contamination in water sources is also responsible for over-fertilization and degradation of the ecosystem (Xiong et al, 2017). Phosphate can be removed from water sources and waste water via various physiochemical and biological methods. Chemical methods such as precipitation with alum, lime and iron salts have been tested for phosphate removal however, they are not cost effective and involves sludge handling issues. Biological methods have been studied but not found to be effective in bringing concentrations of phosphate in effluent to as low as 0.5 mg/L. Adsorption has been found to be comparatively more economical and useful in removal of phosphate. Studies have been conducted with various adsorbents such as blast furnace slag, dewatered alum sludge, red mud and fly ash. However, because of their low adsorption capacities several alternatives are being explored (Huang et al., 2009; Li et al., 2006; Yang et al., 2006; Johansson and Gustafsson, 2000).

2.3 Adsorbents

A good adsorbent provides large surface area, porous structure, large pore volumes and availability of abundant functional groups to adsorb wide range of adsorbates (Tran et al., 2016). GAC is the most preferred adsorbent in water and waste water treatment technologies because of its high adsorption capacities for diverse types of contaminants, high surface area and pore volume, ease of usage and maintenance. GAC is obtained from coal hence rely on fossil fuels for its production. According to a study the production rate of activated carbon was over 200,000 tonnes per annum and of this fraction 60% were coal- based carbons (Wilson, 1981) and this production currently has reached to levels of 1.7 million tons per annum over 36 years (Nowicki et al., 2015). A recent market research reported that the global activated carbon market was worth approximately USD 2.84 billion in 2017. The survey reported that China is the largest producer and exporter of activated carbon globally. This report shows that coal based activated carbon output in China reached 316 kilo tonnes in 2017 constituting 64% in national total output of activated carbon (Research and markets, 2018). This shows that a large fraction of commercial activated carbon, in the global market, is obtained from coal. Also, there are certain disadvantages to using GAC which include requirement for pre-treated sludge to avoid clogging, highly affected by variations in pH, temperature and flow rate. This presents the need to explore alternative media that can replace activated carbon obtained from coal sources with activated carbon obtained from by-products or from waste sources from large scale industrial operations. This will in theory reduce the cost of activated carbon as the source material is waste and increase the efficiency of effluent recovery. Coal based activated carbon are not sustainable hence, renewable sources need to be explored (Tan et al., 2008). Thus, research has been ongoing for development of activated carbon from sustainable sources such as coconut husk, agricultural waste, apricot, hazelnut, rice husk, corncob,

fir wood, wood chips, vetiver roots, oil palm shell, vermiculata plant, bamboo dust, bio-plant, wheat bran and peach stones (Rafatullah et al., 2010; Carney et al., 2013). Their abundance and recycling from waste make them efficient sources and provide potential for locally available sources to be used as activated carbon raw material.

2.4 Adsorption isotherm studies

The adsorption capacity of an adsorbent for an adsorbate is dependent on three main properties revolving around media and adsorbate which includes:

- the concentration of the adsorbate in the liquid phase,
- the concentration of the adsorbate in the solid phase and
- the temperature of the system.

With the temperature kept constant, the concentration variation within liquid and solid phases generate an adsorption isotherm. Freundlich and Langmuir isotherms are used commonly used equations for studying adsorptive capacity of many different adsorbents for a given adsorbate (Belhachemi and Addoun, 2011)

2.4.1 Equilibrium studies

To define adsorption isotherms, it is important to know the equilibrium time therefore the equilibrium concentration for any adsorbate for a given adsorbent. The time at which the amount of adsorbate adsorbed and desorbed is equivalent is considered equilibrium time. For adsorbents with macro and micro pore structures the adsorption of adsorbates like dye molecules, inorganic nutrients initially must overcome the boundary layer effect and then it must diffuse from the boundary layer film onto the adsorbent followed by diffusion into the porous structure of the adsorbent. Thus, the time profile of the adsorbate uptake will be a single, smooth and continuous

curve leading to saturation. This point where saturation is achieved will be considered equilibrium time and concentration as equilibrium concentration. Hence for adsorption studies the reading is taken at equilibrium time which is different for different adsorbate-adsorbent combinations.

2.4.2 Freundlich isotherm model

Freundlich isotherm model describes non-ideal, reversible adsorption of contaminants on the adsorbent which is not restricted by formation of monolayer. This model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and energy sites over heterogenous surface. Freundlich model is widely used to study heterogenous systems which mostly involves activated carbons and molecular sieves for adsorption of highly reactive species (Foo and Hameed, 2010).

Freundlich model is described by the following equation:

$$q_e = k \cdot C_e^{\frac{1}{n}} \quad (2.1)$$

Where q_e is the amount of adsorbate adsorbed per gram of the media, C_e is the equilibrium concentration of the solute, k and n are Freundlich constants and represent adsorption capacity and intensity of the system, respectively. $1/n$ is an indicator for the favourability of the adsorbent/adsorbate systems.

2.4.3 Langmuir isotherm model

Langmuir model describes adsorption of the adsorbate on the adsorbent as a monolayer that is the adsorbed layer is one molecule in thickness. This model describes that adsorption can occur only at finite number of definite localized sites, that are identical and equivalent. The model assumes

the adsorbent to be structurally homogenous where all sorption sites are identical and energetically equivalent (Foo and Hameed, 2010; Chan et al., 2012).

The Langmuir model is described by following equation:

$$q_e = \frac{q_m \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (2.2)$$

where q_e (mg/g) is the solid phase equilibrium concentration, q_m (mg/g) is Langmuir maximum monolayer adsorptive capacity, C_e (mg/L) is the liquid phase equilibrium concentration and b (L/mg) is the Langmuir equilibrium constant which is related to the energy of adsorption or in other terms affinity of the binding sites.

Langmuir isotherm can be linearized in four different forms. Simple linear regression will result in different parameter estimates. The different forms are presented in Table 2.1. The transformation of Langmuir equation to different linear forms results in the alteration of the error structures in diverse ways and hence results obtained from each form will be different (Yadav and Singh, 2017). The Langmuir-1 form gives best fit for the adsorption data because of the minimal deviations from the fitted equation resulting in best error distribution (Parimal et al., 2010).

Table 2.1: Isotherms and their linear forms

Isotherm	Linear form	Plot
Freundlich	$\log q_e = \log k + \frac{1}{n} * \log C_e$	$\log q_e$ vs $\log C_e$
Langmuir-1	$\frac{C_e}{q_e} = \frac{1}{q_m} * C_e + \frac{1}{b q_m}$	$1/q_e$ vs $1/C_e$
Langmuir-2	$\frac{1}{q_e} = \left(\frac{1}{b q_m} \right) * \frac{1}{C_e} + \frac{1}{q_m}$	$1/q_e$ vs $1/C_e$
Langmuir-3	$q_e = q_m - \left(\frac{1}{b} \right) * \left(\frac{q_e}{C_e} \right)$	q_e vs q_e/C_e
Langmuir-4	$\frac{q_e}{C_e} = b q_m - b q_e$	q_e/C_e vs q_e

2.5 Kinetic models

Kinetic performance of the adsorbent is also important to analyze its potential to be used for pilot application. The solute uptake rate, which determines the residence time required to complete the adsorption reaction is determined from kinetic analysis. Kinetic study is also a base to determine performance of flow through systems (Qiu et al., 2009). Kinetic studies assess the rates of chemical processes and the factors that influence them in the attainment of equilibrium in a reasonable amount of time and helps in estimation of adsorption capacity of the adsorbent (Aly et al., 2014).

2.5.1 Pseudo first order model

The kinetic model, pseudo first order is described by the Lagergren first order rate equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t$$

where k_l (min) is the pseudo first order adsorption rate constant and q_e and q_t are the (2.3)

values of the mass adsorbed per unit mass of the adsorbent at equilibrium and at time

t , respectively. The plot of $\log(q_e - q_t)$ versus t for the data gives a straight line from which the values of k_l and q_e from the slope and intercept are determined, respectively. The equation is called pseudo first order because of the following reasons:

- i. The parameter $k_l(q_e - q_t)$ does not represent the number of available sites.
- ii. The parameter $\log(q_t)$ is an adjustable parameter and is often found not equal to the intercept of a plot of $\log(q_e - q_t)$ against t , whereas in a true first order $\log(q_e)$ should be equal to the intercept of a plot of $\log(q_e - q_t)$ against t .

Pseudo first order equation of Lagergren does not fit well for the entire range of contact time as is shown in the literature and is generally applicable over the initial 20 to 30 minutes of the sorption process. In this model q_e is treated as an adjustable parameter to be determined by trial and error or by extrapolating the data to $t = \infty$. So, trial and error are applied in determining equilibrium sorption capacity, q_e in order to analyze pseudo first order kinetics (Ho and McKay, 1998).

2.5.2 Pseudo second order model

The linearized Lagergren second order kinetic equation represents pseudo second order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} * t \quad (2.4)$$

where q_e is the amount of adsorbate adsorbed per unit mass of sorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed (mg/g) at contact time t and k_2 is the pseudo second order rate constant (g/mg min). The linear plot of t/q_t versus t gives values of q_e and k_2 which can be determined from the slope and the intercept, respectively. The value of k_2 depends on the operating

conditions such as initial pH, solution concentration, temperature and agitation rate. Equation 2.4 does not have the disadvantage of assigning effective q_e . The main assumptions for this model is that pseudo second order model follows second order rate and the rate limiting step maybe chemisorption which involves valency forces through sharing or exchange of electrons between the adsorbent surface and the adsorbate (Aly et al., 2014).

2.5.3 Intraparticle diffusion model

The data was also analyzed using intra particle diffusion model to confirm whether rate limiting step is intraparticle diffusion or chemisorption of methylene blue across the adsorbent (Aly et al., 2014):

$$q_t = k_d t^{\frac{1}{2}} + C \quad (2.5)$$

where k_d is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$) and C is a constant that describes the thickness of boundary layer (mg/g) (Cabal et al., 2009). According to intraparticle model if the plot of q_t versus $t^{1/2}$ is a straight line passing through origin, then the adsorption process is controlled by the intraparticle diffusion. However, if the data exhibits multilinear plots then the adsorption process is influenced by two or more steps (Karthikeyan et al., 2010). In the multilinear plots the initial curved section represents external surface adsorption, the second stage reflects gradual adsorption into the intraparticle space as the rate controlling step. The last stage is equilibrium stage in which the intraparticle diffusion starts to slow down and levels out (Ofomaja and Naidoo, 2011; Deniz, 2013; Caccin et al., 2014).

2.6 Adsorbent characterization

2.6.1 Particle size

The particle size of the media is an important parameter for comparison as well as for defining surface characteristics such as surface area, pore volume and density. The particles of a media can be as small as unit micro scale to as large as 100 on the micro scale.

2.6.2 Brunauer-Emmett-Teller (BET) surface area

The BET method is the most widely used method for the determination of the area of adsorbents and uses BET equation given as follows:

$$1/(W \left(\left(\frac{P}{P_0} \right) - 1 \right)) = \frac{1}{W_m C} + \frac{C - 1}{W_m C \left(\frac{P}{P_0} \right)} \quad (2.6)$$

where W is the weight of gas adsorbed at a relative pressure, P/P_0 and W_m is the weight of adsorbate constituting a monolayer of surface coverage. The term C is the BET constant related to the energy of adsorption in the first adsorbed layer and is an indication of the magnitude of the adsorbent/adsorbate interactions. The BET isotherm is a linear plot of $1/(W(P/P_0)-1)$ versus P/P_0 which for most solids is obtained using nitrogen (N_2) as the adsorbate (Lu and Sorial, 2004; Li and Kumar, 2016). This model utilizes gases that do not react with the adsorbent surface but allows for adsorption of gas molecules on the surface that gives an estimate of the pore and surface volume (Fierro et al., 2008; Yang et al., 2017).

2.6.3 Bulk density

Bulk density is defined as the mass of a material under specified conditions of a unit volume of a solid sorbent including its pore volume and inter-particle voids (Alslaibi et al., 2013). Bulk density is an important parameter for designing adsorbent-based water treatment systems in operational terms.

2.6.4 Attrition

Attrition is the process of gradually reducing the effectiveness of a material through sustained attack or pressure. Lower attrition rates are suggestive of longer operating life for a material (Musterman and Boero, 1995).

2.6.5 Ash content

The ash content of the activated carbon influences the properties of adsorbents that are activated carbon based. The ash content depends on the carbonization process and increase in the ash content reduces surface area. This parameter is an indicator of purity of activated carbon in terms of presence of inorganic contaminants such as silicates, metal ions etc. (Kalderis et al., 2008; ASTM D2866-94, 2018)

Chapter 3- Materials and Methods

This chapter provides a description of the methods that were used to test the water quality parameters hence, the various adsorbate removal from the solution all of which were conducted as batch tests. In addition, it also provides information on the methods used to study media characteristics.

3.1 Adsorption setup

The adsorption tests were carried out in 125 ml Erlenmeyer flasks. The media mass was weighed and added to the flasks containing 125 ml of each of the adsorbate solutions prepared from stock solutions. The flasks were set on shaker at 50 rpm. The solution was analysed for residual adsorbate concentration over a span of days to find equilibrium time. Once equilibrium time was established, the samples were taken from each flask at equilibrium time and analysed in UV-Visible spectrophotometer for adsorption studies. This involved addition of required chemicals depending on the type of adsorbate to determine equilibrium concentration. pH adjustment was done using 1N HCl or 1N NaOH solution. The following Table 3.1 gives initial concentration of each adsorbate in the solution, pH conditions for the solution and the temperature at which the experiments were conducted. For methylene blue adsorption studies the pH of the solution was maintained by adding 0.1N HCl or 0.1N NaOH. For nitrate and phosphate studies the pH of the solution was favorable for adsorption of each adsorbate as observed in literature (Kilpimaa et al., 2015). The experiments were conducted at a fixed pH range which was monitored throughout the study. The temperature conditions were same as room temperature. All studies were conducted at fixed temperature range.

Table 3.1: Initial adsorbate concentration

Adsorbate	Initial Concentration (mg/L)	pH of solution	Temperature in °C
Methylene blue	5	7-8	21±3
Nitrate (NO ₃ ⁻ -N)	2	5-6	21±3
Phosphate (PO ₄ ³⁻ -P)	2	5-6	21±3

3.1.1. Setup for Phase 1

The solutions were prepared in 125 ml Erlenmeyer flasks and sealed with rubber corks. All the solutions were prepared in standard flasks. The flasks were then fixed onto the shaker set on 50 rpm. The tests for methylene blue equilibrium time determination and adsorption studies were carried out in flasks covered with aluminium foil to prevent light degradation of the adsorbate methylene blue. The experiments were conducted as duplicates under the same experimental setup to see the reproducibility of data and to account for error involved in study. For Iodine adsorption analysis the standardization of solutions was carried out in a titration setup with the burette clamped to a support and conical flask with the indicator at the base of the burette in the fume hood. The adsorption of iodine was carried out in setup with a funnel mounted on a conical flask. The filtrate for residual iodine analysis was collected in a conical flask.

Figure 3.1. Setup for adsorption phase

3.1.2 Setup for Phase 2

The solutions were prepared in 125 ml Erlenmeyer flasks and sealed with rubber corks. All the solutions were prepared in standard flasks. The flasks were then fixed onto the shaker set on 50 rpm. The experiments were conducted as duplicates in the same experimental setup to observe the reproducibility of the data and reduce error involved in the study.

3.2 Analytical Methods

A summary of the parameters analyzed has been provided in Table 3.2. The table includes parameters analyzed in both adsorption phases, the instrument used, and the analysis test kit/method used for each parameter.

Table 3.2: Test parameter kit

Test parameters	Experimental Phase	Testing kit	Testing instrument
Methylene Blue	Adsorption	UV absorption	UV-Visible spectrophotometer
Nitrate	Adsorption	Nitrate TNTPlus HACH method	UV-Visible spectrophotometer
Phosphate	Adsorption	Phosphate TNT 843 HACH method	UV-Visible spectrophotometer
pH	Adsorption	pH probe	pH meter

3.2.1 Glassware and Sample Storage

All the flasks and cuvettes used for adsorption phase were washed with ethanol solution and rinsed with milliQ water. All the glassware used for biological studies were placed in 10% HCl solution overnight. Following this the glassware were rinsed thoroughly with milliQ water, wrapped in aluminium foil and autoclaved for 30 minutes at 400°C.

3.2.2 Solution preparation

All solutions were prepared in milliQ water. All stock solutions were prepared in 100 ml standard volumetric flasks. Methylene blue stock solution was prepared and covered in foil and left on magnetic stirrer overnight. All other stock solutions were prepared freshly in the laboratory.

3.2.3 Adsorbents

SAC used in the experiments was developed by PCS Biofuels and Trusense Engineering. The ownership of intellectual property rights for manufacturing process by PCS Biofuels and Trusense Engineering, restricts from mentioning the procedure involved in developing SAC. SAC can be described as a powdered material with particle size range within 2-10 μm and bulk density of 0.40 g/cm^3 . The GAC used in this study is from Acros Organics, NORIT® GAC. It is obtained from bituminous coal, is within particle size range 420-840 μm and bulk density of 0.50 g/cm^3 .

3.2.4 Ultraviolet- Visible Absorbance

Samples were analyzed in UV-Visible spectrophotometer at specific wavelength and were measured in accordance with Standard Methods 5910B (APHA, 2012). Samples were placed in a quartz cuvette (1 cm in length) and UVA value at specific wavelength was then recorded using a UV visible Spectrophotometer (Spectronic Unicam).

3.2.5 Methylene Blue

The samples for testing methylene blue were taken into the quartz cuvette and placed in the spectrophotometer. The absorbance was read at 650 nm. Duplicate analysis was done for each round of sampling to account for the human error involved in sampling and measurement. It evaluates the variance in measurement. The standard deviation involved in calculation of methylene blue concentration was determined to see how far the concentration deviates from the theoretical concentration. This also gives an indication of accuracy of sample preparation and analysis. The deviation also gives an idea of the scope of error involved in experiments and hence the conclusive results. In preliminary tests, using methylene blue standard, the standard deviation involved in sampling and analysis of absorbance values was found to be ± 0.06 mg/L methylene blue. The adsorption phase involved three sets of experiments.

3.2.5.1 Calibration

Calibration experiments involved preparation of five different known concentrations of methylene blue solution in the range of 0-5 mg/L. Then the samples were read for absorbance in the spectrophotometer. This data was used to generate standard calibration curve by plotting the known concentrations of methylene blue solutions against absorbance values. The equation obtained for the standard curve is used to determine unknown methylene blue concentration in the solution based on the absorbance values read in the spectrophotometer. The calibration curves are reported in Appendix A.

3.2.5.2 Equilibrium time

The second set of experiments involved finding the equilibrium time for adsorption of methylene blue onto the two media. The time at which no more adsorbate gets adsorbed onto the media is

called equilibrium time. At equilibrium time, no more adsorption of adsorbate occurs and the concentration of the adsorbate in the solution becomes steady. The concentration of methylene blue reaches equilibrium when the curve of q_t (amount of adsorbate adsorbed per gram of media) vs time reaches a steady phase as shown in Appendix A.A.2.

3.2.5.3 Adsorption isotherm study

The third set of experiments involve finding adsorption capacity of the two media for methylene blue by finding residual concentration of methylene blue at equilibrium time for ten different weight sets and fitting the data to adsorption isotherms. The residual concentration of adsorbate at different time was also analyzed by fitting the data to kinetic models.

3.2.6 Nitrate

The samples for testing nitrate nitrogen were taken into the TNT 835 vials and tested by Dimethylphenol Method (#10206). After a reaction period of 15 minutes the sample was added to the quartz cuvette and placed in the spectrophotometer. The absorbance was read at 345 nm. Duplicate analysis was done for each round of sampling to account for the human error involved in sampling and measurement. It evaluates the variance in measurement. The standard deviation involved in calculation of nitrate concentration was determined to see how far the concentration deviates from the theoretical concentration. This also gives an indication of accuracy of sample preparation and analysis. The deviation also gives an idea of the scope of error involved in experiments and hence the conclusive results. In preliminary tests, using nitrate standard solution, the standard deviation involved in sampling and analysis of absorbance values was found to be ± 0.32 mg/L nitrate. The adsorption phase involved three sets of experiments.

3.2.6.1 Calibration

Calibration experiments involved preparation of five different known concentrations of nitrate solution in the range of 0-2 mg/L. Then the samples were read for absorbance in the spectrophotometer. This data was used to generate standard calibration curve by plotting the known concentrations of nitrate solutions against absorbance values. The equation obtained for the standard curve is used to determine unknown nitrate concentration in the solution based on the absorbance values read in the spectrophotometer. The calibration curves are reported in Appendix A.

3.2.6.2 Equilibrium time

The second set of experiments involved finding the equilibrium time for adsorption of nitrate onto the two media. The time at which no more adsorbate gets adsorbed onto the media is called equilibrium time. At equilibrium time, no more adsorption of adsorbate occurs and the concentration of the adsorbate in the solution becomes steady. The concentration of nitrate reaches equilibrium when the curve of q_t (amount of adsorbate adsorbed per gram of media) vs time reaches a steady phase as shown in Appendix A.A.2.

3.2.6.3 Adsorption isotherm study

The third set of experiments involve finding adsorption capacity of the two media for nitrate by finding residual concentration of nitrate at equilibrium time for ten different weight sets and fitting the data to adsorption isotherms. The residual concentration of adsorbate at different time was also analyzed by fitting the data to kinetic models.

3.2.7 Phosphate

The samples for testing phosphate were taken into the TNT 843 vials and tested by Ascorbic Acid Method (#10209). The vials were heated for 1 hour at 100°C following which they were cooled to room temperature. After a reaction period of 10 minutes the samples were added to the quartz cuvette and placed in the spectrophotometer. The absorbance was read at 880 nm. Duplicate analysis was done for each round of sampling to account for the human error involved in sampling and measurement. It evaluates the variance in measurement. The standard deviation involved in calculation of phosphate concentration was determined to see how far the concentration deviates from the theoretical concentration. This also gives an indication of accuracy of sample preparation and analysis. The deviation also gives an idea of the scope of error involved in experiments and hence the conclusive results. In preliminary tests, using phosphate standard solution, the standard deviation involved in sampling and analysis of absorbance values was found to be ± 0.14 mg/L phosphate. The adsorption phase involves three sets of experiments.

3.2.7.1 Calibration

Calibration experiments involved preparation of five different known concentrations of phosphate solution in the range of 0-2 mg/L. Then the samples were read for absorbance in the spectrophotometer. This data was used to generate standard calibration curve by plotting the known concentrations of phosphate solutions against absorbance values. The equation obtained for the standard curve is used to determine unknown phosphate concentration in the solution based on the absorbance values read in the spectrophotometer. The calibration curves are reported in Appendix A.

3.2.7.2 Equilibrium time

The second set of experiments involved finding the equilibrium time for adsorption of phosphate onto the two media. The time at which no more adsorbate gets adsorbed onto the media is called equilibrium time. At equilibrium time, no more adsorption of adsorbate occurs and the concentration of the adsorbate in the solution becomes steady. The concentration of phosphate reaches equilibrium when the curve of q_t (amount of adsorbate adsorbed per gram of media) vs time reaches a steady phase as shown in Appendix A.A.2.

3.2.5.3 Adsorption isotherm study

The third set of experiments involve finding adsorption capacity of the two media for phosphate by finding residual concentration of phosphate at equilibrium time for ten different weight sets and fitting the data to adsorption isotherms. The residual concentration of adsorbate at different time was also analyzed by fitting the data to kinetic models.

3.2.8 Iodine Test

The three-different weighed sample of the two media were transferred to a clean, dry 250 ml Erlenmeyer flask equipped with a ground stopper. 5 wt % hydrochloric acid solution was added to each flask containing media and then it was closed and swirled gently until the carbon was completely wetted. Loosening the stoppers to vent the flasks, they were then placed on a hot plate in a fume hood and brought boil for 30 ± 2 seconds to remove any sulfur which may interfere with the test results. The flasks were removed from the hot plate and cooled to room temperature. Using a glass pipette 100 mL of 0.100 *N* iodine solution was added into each flask. Standardization of the iodine solution was done just prior to use. The flasks were corked immediately and shaken vigorously for 30 ± 1 s. Each mixture was filtered by gravity through one sheet of folded filter paper

(Whatman No. 2V or equivalent) into a beaker. Each filtrate was mixed and pipetted 50.0 mL of each filtrate into a clean 250 ml Erlenmeyer flask. Titrated each filtrate with standardized 0.100 *N* sodium thiosulfate solution until the solution was a pale yellow. 2 mL of the starch indicator solution was added to continue the titration with sodium thiosulfate until one drop produced a colorless solution that is the end point. The volume of sodium thiosulfate used was recorded. Two calculations are required for each carbon dosage, as *X/M* that is the amount of iodine adsorbed per gram of the media and *C* is the normality of the residual filtrate.

To calculate the value of *X/M*, first derive the following values:

$$A = (N_2) (12693.0) \quad (3.1)$$

where:

*N*₂ = iodine, *N*

$$B = (N_I) (126.93) \quad (3.2)$$

where:

*N*_I = sodium thiosulfate, *N*

$$DF = (1 + H)/F \quad (3.3)$$

where:

DF = dilution factor,

I = iodine, mL

H = 5 % hydrochloric acid used, mL, and

F = filtrate, mL.

Using the values obtained from above equations, calculate the value of X/M as follows:

$$X/M = [A - (DF)(B)(S)]/M \quad (3.4)$$

where:

X/M = iodine absorbed per gram of carbon, mg/g,

S = sodium thiosulfate, mL, and

M = carbon used, g.

Calculate the value of C as follows:

$$C = (N_1 \cdot S)/F \quad (3.5)$$

where:

C = residual filtrate, N ,

N_1 = sodium thiosulfate, N , and

F = filtrate, mL.

The X/M values were then plotted against the three C values to obtain three-point isotherm on a logarithmic graph. The X/M value at 0.02 N C was determined as the Iodine number.

3.2.9 Competitive adsorption study

The competitive adsorption studies were carried out by subjecting SAC and GAC to multi component solutions with the composition mentioned in Table 3.3 and the residual equilibrium concentration was determined for both the systems. The removal percentage of each adsorbate that is nitrate and phosphate, by both the media in the two solutions were analyzed and compared.

Table 3.3: Composition of multi component solutions

Solution	Components	Source chemicals
Single component	Nitrate	Potassium nitrate
Single component	Phosphate	Potassium dihydrogen phosphate
Two components (N: P ratio: 1:1) Solution-I	Nitrate	Sodium nitrate
	Phosphate	Potassium dihydrogen phosphate
Synthetic raw water (C: N: P ratio: 25:5:1) Solution-II	Carbon	Glyoxal, formic acid and acetic acid
	Nitrate	Ammonium sulphate, Sodium nitrate
	Phosphate	Potassium dihydrogen phosphate
	Alkalinity	Sodium bicarbonate

3.2.10 Characterization

For specific surface area analysis that is BET surface area, the sample of media was submitted to CANMET. The surface area was analyzed based on adsorption of nitrogen gas on the surface of the media at 77.3 K. For attrition percentage, ash content and bulk density method by Toles et al., 2000 and ASTM methods ASTM D2866-94 and ASTM D2854-96, respectively were followed.

3.2.10.1 Attrition percentage

Approximately 1 g (initial weight) of both media, SAC and GAC were placed in 100 ml of 0.07M sodium acetate $\pm$ 0.03M acetic acid buffer, pH 4.8. The mixture was stirred at 500 rpm for 24 hours at room temperature. The mixture was then placed on a 50-mesh sieve and washed with distilled water. The carbon content that did not pass through the sieve was transferred to pre-weighed aluminium weighing pan. The samples were heated to 105°C for 2 hours, cooled and a final weight was measured. The percentage attrition is given by following equation:

$$\%attrition = \left(\frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \right) * 100 \quad (3.6)$$

3.2.10.2 Ash content

For ash content measurement first, the crucible was heated in the muffle furnace at $650 \pm 25^\circ\text{C}$ for 1 hour. The crucible was then placed in a desiccator to cool to room temperature and the weight was measured to the nearest 0.1 mg. An adequate amount of the media (60.5 mg) was dried and weighed at $150 \pm 5^\circ\text{C}$ for 3 hours. The dried activated carbon was weighed to a nearest of 0.1 mg into the ignited crucible and the crucible was then placed in the furnace at $650 \pm 25^\circ\text{C}$ for 3-16 hours. Once ashing was completed the sample was placed in a desiccator to cool and air was admitted slowly to avoid loss of ash. The cooled material was weighed to the nearest 0.1 mg. Ash content is determined based on following equation:

$$\text{ash \%} = \left[\frac{D - B}{C - B} \right] * 100 \quad (3.7)$$

Where D is weight of crucible plus ashed sample (g), B is weight of crucible (g) and C weight of crucible was original sample (g).

3.2.10.3 Bulk density

A funnel was suspended over a measuring cylinder of known weight and volume. The funnel was filled with the media sample and allowed to flow freely into the measuring cylinder. The excess material on top of the measuring cylinder was scrapped off with a straight edge. The media and the cylinder were then weighed, and the weight/ volume was determined.

3.2.11 pH

pH was monitored using a pH probe (Thermo Scientific ORION 087003).

3.2.12 SEM analysis

The media samples of both SAC and GAC were analysed by scanning electron microscope in the Nanotech imaging facility, Carleton University to study surface morphology of the media and particle structure.

3.2.13 Average particle size analysis

The SEM image of media was analyzed in ImageJ and OriginPro software to determine average particle size.

3.2.14 Data Analysis

Analysis of data to fit linear isotherm was done in Microsoft Excel. Average, maximum, minimum and standard deviations of sample range were determined. All image analysis was done using ImageJ software.

Chapter 4- Results

Removal of Methylene Blue dye and Iodine molecule from water by adsorption using Sucrose Activated Carbon (SAC)

Chapter 4 will be submitted as a journal article. As such, this chapter has been presented in the format of a journal article with planned submission to the *Journal of Environmental Chemical Engineering*. This paper will be published by co-authors Saumya Suresh (student), Dr. Onita Basu (supervisor), Sara Jamaliniya (graduate), Eustina Musvoto (Trusense Engineering) and Alexis Mackintosh (PCS Technologies Inc.). Saumya Suresh was primarily responsible for data collection, analysis and writing of this chapter.

Abstract

The adsorptive capacity of a novel green Sucrose Activated Carbon (SAC) media was compared with the more traditional bituminous coal based Granular Activated Carbon (GAC). SAC is obtained from the hydrothermal carbonization of sucrose followed by pyrolysis at 900°C. The methylene blue adsorption data for SAC and GAC were investigated with Langmuir and Freundlich isotherms. The Langmuir isotherm demonstrated best fit for the adsorption of methylene blue on both media types with comparable adsorption values of 196 mg/g for SAC and 200 mg/g for GAC. Iodine adsorption capacity of SAC was found to be 1,038 mg/g and was further analyzed for Brunauer-Emmett-Teller surface area for physical characterization. Kinetic studies were conducted showing that methylene blue adsorption on the SAC media follows pseudo second order model. The value of kinetic rate constant k for SAC and GAC were found to be comparable at 0.005 (g/mg min) and 0.004 (g/mg min), respectively. Based on its adsorptive capacity SAC proves to be a competitive green alternative for GAC.

Keywords: Adsorption; activated carbon; methylene blue; iodine number; green adsorbent

4.1 Introduction

Industrial effluents discharged from textile, food, leather, cosmetics, dye and paper industries raise aesthetic and toxicological concerns when released into water streams without adequate treatment. For instance, industrial effluents may contain colored dyes which reduce sunlight penetration and hinder aquatic photosynthesis in the receiving water bodies. This in turn leads to loss of species and consequently loss of habitat resulting from murky water with less visibility and high turbidity. Colored and turbid water streams are aesthetically unpleasant, and dyes such as methylene blue, azo dyes, brilliant blue, congo red etc. are found to be toxic to various aquatic organisms. Thus, extensive research to determine efficient technologies to remove dyes from effluent streams is critical (Garg et al., 2004). Methylene blue is one such cationic dye used in textile, pharmaceutical, food, paper and plastics industries, which is difficult to degrade in the natural environment. Long term exposure to methylene blue can cause nausea, vomiting, anemia and hypertension hence removal of methylene blue from water has been extensively studied (Foo et al., 2012; Hameed et al., 2009).

Water and waste water treatment technologies such as biosorption, adsorption, coagulation, flocculation, ozonation, membrane filtration and liquid-liquid extraction have been used to treat the various pollutants that contaminate water (Pathania et al., 2017). Adsorption is one of the most commonly used technologies to treat water because of its simplicity and effectiveness in the treatment process. Adsorption involves binding and removing of contaminants from the solution. Adsorption efficiency depends on the type of adsorbent employed for the treatment. Various kinds of adsorbents are used in water treatment plants including granular and powdered activated carbon, zeolites, and ion exchange resins; with coal based activated carbon dominating the market.

Several parameters are used to define the capacity of a given adsorbent to remove specific contaminants. Methylene blue number is a common parameter used to determine adsorption capacity of various media as it represents the mesopore and macropore capacity of adsorbents. Further, it is considered as a model compound for removal of organic compounds and colored contaminants from aqueous solutions because of its strong adsorption onto solids and is thus used as a standard for describing a new media (Hameed et al., 2007; Raposo et al., 2009). Iodine adsorption capacity is another typical parameter used to characterize adsorbents for a given media sample. The iodine molecule is an indicator of surface area contributed by pores on activated carbon media larger than 1 nm (Aygün et al., 2003). The amount of iodine absorbed in milligrams by 1 gram of carbon is called the iodine number. Iodine as a molecule is relatively small with a molar mass of 127 g/mol and an ionic radius of 0.22 nm. Thus, it defines the capacity of activated carbon to adsorb smaller particles. The adsorbate molecules, methylene blue and iodine together characterize the media in terms of adsorptive capacity and define the physical structure of activated carbons based on the dimensions of the adsorbate molecules and how they accumulate within the pores, intra particle space and over the surface of adsorbents (Cleiton et al., 2011).

Granular activated carbon (GAC) is one of the favored choices because of its high adsorption capacity for various type of contaminants, high surface area and pore volume, ease of usage and maintenance. However, commercially used GAC is expensive to buy and regenerate and has certain disadvantages such as high corrosiveness when wet as well as the requirement for pre-treated influent to avoid clogging. In addition, GAC efficacy is also highly affected by variations in pH, temperature and flowrate. The source of most GAC is coal. The production rate for activated carbons approx. 200,000 tonnes per annum in 1981 with 60 % of GAC from coal-based carbons (Wilson, 1981). This production rate currently has increased to levels of 1.7 million tons per annum

over 36 years (Nowicki et al., 2015). Continued coal production at these high rates is not sustainable, hence adsorbents obtained from waste sources are pivotal in adsorption research. A diverse range of source materials have been explored in literature for activated carbon (for example: sawdust, coconut shell, prawn shell, mango seed kernel, wood chips, wheat straws, lemon peel, orange peel, tree barks etc.) paving a pathway for practical application of green adsorbents. Transition to these sources of materials offers several advantages including low cost, improved efficiency, adsorbent regeneration and reduction of waste disposal issues as they are converted to commercially valuable activated carbon (El-Wakil et al., 2015; Namasivavam and Kavitha, 2002).

Sucrose is a disaccharide formed by two units of monosaccharides glucose and fructose which are joined by glycosidic linkage. Sucrose as a source can be obtained from household as well as agro and food based industrial wastes. It is also abundantly found in plants as a source of storage energy. A new green alternative being explored in this study is Sucrose Activated Carbon (SAC) which is obtained by hydrothermal carbonization of organic material, sucrose followed by activation by pyrolysis at 900°C. The SAC is compared to traditional GAC with respect to adsorption isotherm and kinetic models to determine if the SAC is competitive to GAC with respect to adsorption ability. SAC source being sucrose can be extracted from various renewable agricultural sources and thus this adsorbent may be more economical and be produced from a sustainable carbon source. Therefore, the main objectives of this study are to evaluate the possibility of using sucrose to develop a new green, low cost adsorbent and study its application to remove methylene blue dye and iodine from aqueous solution.

4.2 Experimental

4.2.1 Methods

4.2.1.1 Characterization

The characterization of the SAC media was performed by N₂ adsorption test to determine BET specific surface area at CANMET, Canada. Particle size analysis was carried out using ImageJ™ from the SEM images of the media (Fig. 4.1a and 4.2a). The attrition percentage was determined by suspending approximately 1 g of the adsorbent in 100 ml of 0.07M sodium acetate-0.03M acetic acid buffer. The mixture was left on a stirrer for 24 hours. This mixture was then washed with distilled water on 50 mesh sieve and the carbon that did not pass through the sieve was transferred to an aluminium pan and heated to 105°C for 2 hours, allowed to cool and the final weight was noted. The attrition percentage is the weight difference of the adsorbent before and after the treatment (Toles et al., 2000). Bulk densities were analyzed by weight difference where in a funnel was suspended over a measuring cylinder of known weight and volume and filled with the adsorbent. The adsorbent was allowed to fall freely from the funnel into the cylinder and excess material on top was scrapped off with a straight edge. The adsorbent and the cylinder were then weighed, and the weight/ volume was determined (Alslaibil et al., 2013; ASTM D2854-96), respectively. Table 4.1 presents the properties of SAC.

4.2.1.2 Adsorption studies

Adsorption experiments were carried out by agitating different masses of SAC and GAC suspended in 5 mg/L solution of methylene blue dye in Erlenmeyer flasks at 50 rpm, 21 ± 3°C in a rotary shaker (New Brunswick Excella E-1 Open Air Shaker). Dye concentration was investigated using UV-Visible spectrophotometer (Spectronic Unicam) by measuring the absorbance at 650

nm. pH was measured using pH meter (Thermo Scientific ORION 087003). The pH of the solution was maintained in the 7-8 range by addition of sodium hydroxide and/ or hydrochloric acid solution. The sample was withdrawn from the flasks at pre-determined equilibrium time of 100 hours. The equilibrium time was determined by subjecting SAC and GAC to methylene blue solution in the same setup as adsorption studies and determining the residual concentration at specific time intervals until there was no more adsorption observed in the system. The absorbance of the solution subjected to different masses of both media were then measured. All analysis was conducted as duplicates. In preliminary tests, using methylene blue standard, the standard deviation involved in sampling and analysis of absorbance values was found to be ± 0.06 mg/L methylene blue. Langmuir and Freundlich isotherms were employed for the data obtained to study the adsorption capacity of the two media. Scanning electron microscopic (SEM) images of the media samples were taken before and after adsorption of methylene blue for visual depiction of adsorption. Iodine adsorption studies were carried out according to ASTM D 4607-94, 2006. Three sets of masses of the two media samples were taken and mixed with 100 ml of 0.100 ± 0.001 N standard iodine solution, after 30 seconds of equilibrium time the solution was filtered, and 50 ml of filtrate was used to determine residual iodine concentration by titration with standard sodium thiosulfate with starch as the indicator.

4.2.1.3 Kinetic studies

Kinetic studies were carried out by subjecting SAC and GAC to 5 mg/L methylene blue dye solution in Erlenmeyer flasks agitated on rotary shaker (New Brunswick Excella E-1 Open Air Shaker) at 50 rpm, $21 \pm 5^\circ\text{C}$. Solution samples were withdrawn at different time intervals and the absorbance was measured using UV-Visible spectrophotometer (Spectronic Unicam) to determine

residual methylene blue concentration. The amount of adsorption at time t , q_t (mg/g) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (4.1)$$

where C_0 and C_t (mg/L) are the liquid phase concentrations of methylene blue at initial and any time t , respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g).

4.2.1.4 Statistical analysis

The model parameters were analyzed using linear regression using Excel 2010 program. In addition, the mean square error (MSE) test method was used to evaluate best fit of the adsorption isotherm model to the experimental data using equation 4.2.

$$MSE = \ln \Sigma i = \ln(q_{ecal} - q_e)^2 \quad (4.2)$$

Where n is the number of data points, q_{ecal} is the calculation from the models and q_e is the observation from experiments. The smaller function values point out best fitting curve (Deniz, 2013).

4.2.2 Material

SAC was obtained by hydrothermal carbonization of sucrose followed by pyrolysis at 900 °C in a muffled furnace. GAC (NORIT® GAC 1240) was obtained from Acros Organics. The carbonized material and GAC were used for adsorption studies.

4.3 Results and discussion

4.3.1 Characterization

The BET surface area based on N₂ adsorption and average particle size of the SAC were found to be 466±7 m²/g and 2.96-9.68 µm, respectively, compared to 735 m²/g and 420-840 µm surface area and average particle size range for GAC, respectively. The physical properties of the SAC and GAC are presented in Table 4.1. The SEM images of SAC (Fig. 4.1a and 4.1b), show that the media has smaller spherical particles with smooth surfaces whereas GAC (Fig. 4.2a and 4.2b), has larger particles with more porous and rough surfaces. SAC has lower bulk density compared to GAC indicating that at lower masses of the adsorbent, the surface area available per volume of liquid for adsorption is less. The lower attrition of SAC is suggestive of a longer operating life which is an important physical property in the study of activated carbon as they encounter intraparticle abrasion due to different natures of their applications, also supports the lower bulk density of SAC as higher density supports particle inertia but the mobility of particles of the media will be restricted which is a dominant factor in attrition (Amblard et al., 2015; Toles et al., 2000; Musterman and Boero, 1995).

4.3.2 Adsorption isotherms

Adsorption isotherms determine the adsorption capacity of an adsorbent for the given adsorbate. The parameters obtained by fitting the data to the adsorption isotherms can be utilized to optimize the media for practical use and design purposes (Tan et al., 2008). Successful application of adsorption depends on employment of an efficient adsorbent. Adsorption can be either chemical or physical. Chemical adsorption involves reaction between the adsorbent and the adsorbed solute where as physical adsorption is due to van der Waal's forces. Adsorption occurs when the molecular forces of attraction between the solute and the adsorbent overcomes the forces of attraction between the solute and the solution. The total surface area for adsorption of solutes involves external surface area of particles as well as the surface area of the pores and in case of

activated carbon porous surface area provides more adsorption surface. Thus, adsorption efficiency of the adsorbents was investigated through adsorption isotherm studies. Adsorption isotherm studies were carried out using two typical models; Freundlich and Langmuir isotherm.

Freundlich isotherm was applied to the experimental data for adsorption of methylene blue on SAC and GAC:

$$\log(q_e) = \log k_f + \left(\frac{1}{n}\right) \log C_e \quad (4.3)$$

where q_e is the amount of dye adsorbed per mass of the adsorbent used (mg/g) at equilibrium, C_e is the equilibrium concentration of dye in solution (mg/L), k_f and n are constants representing the adsorption capacity and intensity of adsorption. The Freundlich model assumes heterogeneity of adsorption sites and suggests the possibility of multilayer adsorption with non-uniform distribution of adsorption site energies (Foo et al., 2010). The plot of $\log q_e$ versus $\log C_e$ gives a straight line and the k_f and n values were calculated from the intercept and slope of the plots (Fig. 4.3a), respectively. These values for SAC and GAC and are presented in Table 4.2.

The Langmuir isotherm model represented by the following equations was also applied to the adsorption of methylene blue on SAC and GAC. Three different linearization forms of Langmuir isotherm were studied including Langmuir-1, Langmuir-2 and Langmuir-3 represented by equations 3,4 and 5, respectively:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (4.4)$$

$$\frac{1}{q_e} = \left(\frac{1}{bQ_0}\right) * \frac{1}{C_e} + \frac{1}{Q_0} \quad (4.5)$$

$$\frac{q_e}{C_e} = bQ_0 - bq_e \quad (4.6)$$

where C_e is the concentration of methylene blue solution (mg/L) at equilibrium. The constant Q_o signifies the adsorption capacity (mg/g) and b is related to the energy of adsorption (mg^{-1}). The data was plotted to three different linearization forms of Langmuir isotherms to compare the linear plots. Langmuir-1 gives best fit because of minimal deviations from the fitted equation resulting in the best error distribution (Ho, 2006). The values of Q_o and b for SAC and GAC were calculated from the slope and the intercept, respectively of the linear plots and presented in Table 4.2. A comparison was made between the different isotherms. The correlation coefficients for the Langmuir-1 model ($R^2 = 0.931$ and 0.950) were found to be closer to unity than the Freundlich model ($R^2 = 0.927$ and 0.949) for SAC and GAC, respectively. MSE analysis was done to find the error involved in fitting of experimental data to the isotherm models. It was found to be lower for Langmuir-1 (9.01 and 8.03) and higher for Freundlich model (12.1 and 11.4) for SAC and GAC, respectively. Therefore, based on coefficient of regression and MSE, Langmuir-1 model shows better fit for adsorption of methylene blue on SAC and GAC, respectively. The linear plot of data for Langmuir-1 isotherm (Fig. 4.3b) suggests that the adsorption of methylene blue on SAC and GAC is monolayer adsorption and reflects on the homogenous nature of the two media (Song et al., 2013). The Q_o values for SAC and GAC are 196 mg/g and 200 mg/g which indicates that the SAC has comparatively similar adsorption capacity for methylene blue dye as that of GAC. The value of the slope $1/n$ between 0 to 1 indicates favorable adsorption of the adsorbate on the media. The closer the value to 0 indicates more heterogenous the adsorption is on activated carbon. As observed from Table 4.2. $1/n$ for SAC is 0.88 and for GAC is 0.85, which indicates favorable adsorption and supports homogenous adsorption for methylene blue on both SAC and GAC supporting Langmuir-1 adsorption. The BET surface area calculated in section 4.3.1 for SAC and GAC as well as the adsorption capacity of each adsorbent from adsorption studies when

investigated together gives the adsorption capacity of each media for methylene blue per surface area. Therefore, adsorption capacity per surface area for SAC was found to be 0.42 mg/m^2 and for GAC was found to be 0.27 mg/m^2 . These values show that SAC has higher adsorption capacity per area compared to GAC.

The Iodine number for SAC was found to be slightly higher than GAC as presented in Table 4.2. This indicates SAC is more microporous compared to GAC which has a high macroporous structure. This finding is also supported by the BET specific surface area as the available surface for adsorption of methylene blue per gram of media for GAC is higher than SAC (see Table 4.1) because of larger size particles and exposed porous surface as opposed to smaller particles providing less external surface per gram for adsorption in the case of SAC. The adsorption of Iodine in aqueous phase is more surface adsorption oriented because of hindrance of pore filling by potassium iodide (KI) in the solution which further supports higher iodine adsorption per gram of adsorbent for SAC as compared to GAC (Juhola, 1975). This supports the higher iodine number for SAC as it has more exposed surface area as opposed to a more porous surface for GAC (Fig. 4.4).

Table 4.2. reports comparison of the Langmuir, Freundlich parameters and Iodine number for different green adsorbents investigated in literature. The adsorption capacity of methylene blue on vetiver activated carbon, cotton stalk activated carbon and PBCF activated carbon is high with lower values of iodine number than SAC (Table 4.2) indicating that these media have more mesopores than SAC and GAC. Vetiver activated carbon has low pH due to phosphoric acid activation (Altenor et al., 2009) and PBCF activated carbon has high surface negative charge due to low pH (Abdelkarim et al., 2017) which increases fixation of positively charged methylene blue on the surface of both media. Cotton stalk activated carbon prepared with ZnCl_2 impregnation and

microwave radiation produces mesopores which results in high adsorption (Deng et al., 2009) as compared to SAC which has less porous structure and more micropores as discussed above. *S.vermiculata* activated carbon at low pH and high iodine number has similar adsorption capacity for methylene blue as that of SAC (Bestani et al., 2008). The presence of less acidic groups on the hazelnut and apricot activated carbon and lower iodine number compared to SAC and other green adsorbents as indicated in Table 4.2 supports the lower adsorption capacity for methylene blue on hazelnut and apricot activated carbon (Aygün et al., 2003).

Figure 4.1. (a) SEM image of SAC media and (b) SEM image of SAC with adsorbed methylene blue

Figure 4.2. (a) SEM image of GAC media and (b) SEM image of GAC with adsorbed methylene blue

Table 4.1. Physical properties of SAC and GAC

Properties	SAC	GAC
Particle size (μm)	2.96-9.68 ¹	420-840 ²
Surface area (BET N ₂) (m ² /g)	466±7 ¹	735 ²
Bulk density (g/cm ³)	0.40 ¹	0.51 ¹
Ash content (%)	0.1 ¹	12 ²
pH of adsorbent	5.96 ¹	5.79 ¹
Moisture content (%)	1.9 ¹	2 ²
Attrition (%)	0.04 ¹	1.94 ¹

1: Experimentally determined

2: Manufacturer provided

Table 4.2: Langmuir and Freundlich parameters and Iodine number comparison for different green activated carbon adsorbents with experimentally obtained results

Media	Langmuir		Freundlich		Iodine number (mg/g)	References
	Q_0 (mg/g)	b (L/mg)	1/n	k (mg/g(L/mg) ^{1/n})		
GAC	200	0.039	0.85	8.39	1,038/1,020	Experimental/MSDS
SAC	196	0.023	0.88	4.92	1,191	Experimental
Vetiver roots activated carbon-H ₂ O*	375	0.683	0.11	216	508	(Altenor et al., 2009)
Cotton stalk activated carbon	315.4	0.060	0.14	116.9	972.9	(Deng et al., 2009)
PBCF**	222.2	0.034	0.81	2.21	436	(Abdelkarim et al., 2017)
Salsola vermiculata (perennial shrub plant) activated carbon	130	0.77	N/A	N/A	1,178	(Bestani et al., 2008)
Hazelnut shell activated carbon	8.82	0.058	0.23	3.31	965	(Aygün et al., 2003)
Apricot activated carbon	4.11	0.83	0.52	0.43	754	(Aygün et al., 2003)

*activated carbon prepared by physical activation using steam.

**prickly bark of cactus fruit, biosorbent.

Figure 4.3. Adsorption of methylene blue on SAC (○) and GAC (▲) with: (a) Freundlich, (b) Langmuir 1, (c) Langmuir 2 and (d) Langmuir 3 plot

Figure 4.4. SAC and GAC iodine adsorption isotherm

SEM images of SAC and GAC were taken before and after adsorption of methylene blue on the media. Fig. 4.1a shows SAC as having smooth surface with spherical particles with smaller particle diameter (Table 4.1) and Fig. 4.1b represents a layer covering the SAC media particles representative of the methylene blue surface adsorption on SAC. The image supports the homogenous surface adsorption of methylene blue on the surface of SAC supporting assumptions of Langmuir fit of data. Fig. 4.2a represents porous and rough surface of GAC with larger size particles compared to SAC and Fig. 4.2b shows white layer on media indicative of methylene blue adsorption also supporting the theory of monolayer adsorption of methylene blue on GAC.

4.3.3 Kinetic studies

The initial kinetic studies for adsorption of methylene blue on SAC and GAC were carried out for different adsorbent dosages 0.04, 0.08, 0.2 and 0.4 g/L to observe the range over which kinetic studies are feasible and not limited by the lower dosage of the adsorbent. It was observed that at lower dosages the removal of methylene blue dye by the adsorbents was low and the difference in the q_e values, obtained from kinetic studies of methylene blue varied highly with the experimental q_{exp} values, obtained from adsorption studies as compared to higher dosages of the adsorbents (Fig. 4.5a and 4.5b). This suggests kinetic studies should be conducted over a range of adsorbent dosages to establish the lowest adsorbent dosage over which the error involved in the kinetic study is less and the kinetic model provides accurate adsorption capacity for the adsorbent. The data obtained in this study highlights the difference in accuracy of the data obtained as the dosage of adsorbent is changed (Table 4.3). Thus, this procedure can be utilized for designing experiments providing lowest limits for dosage of adsorbent up to which the data obtained would be accurate for comparison and analysis. It can be observed from the study that at lower dosages the available surface for methylene blue adsorption is less for both SAC and GAC (Fig. 4.5). Methylene blue

adsorption involves chemical interaction of the dye with the adsorbent surface and in aqueous solution there are competing ions trying to bond with the adsorbent surface. As a result, at lower dosages of the adsorbent there is higher difference observed between the q_e and q_{exp} values of SAC and GAC as lesser surface of adsorbent is available for adsorption of methylene blue. However, as the dosages increase the removal capacity almost approaches 90 % and above and there is less difference between q_e and q_{exp} values. Therefore, determining the range over which adsorption and kinetic studies are feasible using this procedure can be helpful in optimizing the adsorption process at pilot scale. This study also supports the experimental observation that SAC has a higher adsorption capacity and removal percentage for methylene blue than GAC at higher adsorbent dosage. Efficiency of GAC is better than SAC at lower masses supported by its porous structure which allows for adsorption of methylene blue onto the porous surface and the external surface at lower masses. This can be observed from Fig. 4.5a and 4.5b, at lower dosage of 0.04 g/L, GAC gives higher removal percentage of 51% and SAC has a removal percentage of 21% for methylene blue because at lower dosages GAC has pores available for methylene blue adsorption alongside the external surface where as when the dosage is increased, for example at the highest dosage of 0.4 g/L, SAC has removal percentage of 97% where as GAC has a removal percentage of 90% for methylene blue from the solution. This is because of increase in available external surface area for adsorption of methylene blue on SAC as the mass of SAC is increased as compared to GAC where adsorption is affected by film diffusion and pore filling which reduces the porous surface available for adsorption. Based on the initial kinetic studies, the dosage of 0.2 g/L was selected for kinetic modelling of methylene blue adsorption on SAC and GAC.

Figure 4.5. Dosage limit for kinetic studies of methylene blue adsorption on (a) SAC and (b) GAC

Table 4.3: Error % for deviation of q_e from kinetic studies, from experimental q_{exp} values from adsorption studies for methylene blue

Dosage of adsorbent (g/L)	Error % SAC	Error % GAC
0.04	47 %	69 %
0.08	51 %	48 %
0.2	0.2 %	5.6 %
0.4	6.5 %	17 %

To study the kinetics of methylene blue adsorption on SAC and GAC, three kinetic models, pseudo first order, pseudo second order and intraparticle diffusion models have been used.

Pseudo first order model expressed by Lagergren equation following the first order rate equation is given by:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (4.6)$$

where q_e and q_t (mg/g) are the amount of dye adsorbed on sorbent at equilibrium and time t and k_1 is the first order rate constant (min^{-1}). The Lagergren first order equation is defined as pseudo first order (Ho and McKay, 1998). The plot of $\log(q_e - q_t)$ versus t for the data gives a straight line from which the values of k_1 and q_e from the slope and intercept are determined, respectively.

Pseudo second order model is expressed by second order rate equation to analyze kinetics of methylene blue adsorption:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4.7)$$

where q_e is the amount of adsorbate adsorbed per unit mass of sorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed (mg/g) at contact time t and k_2 is the pseudo second order rate constant (g/mg min). The linear plot of t/q_t versus t gives values of q_e and k_2 which can be determined from the slope and the intercept, respectively.

The data was also analyzed using intra particle diffusion model to confirm whether rate limiting step is intraparticle diffusion or chemisorption of methylene blue across the adsorbent (Aly et al., 2014):

$$q_t = k_d t^{\frac{1}{2}} + C \quad (4.8)$$

where k_d is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$) and C is a constant that describes the thickness of boundary layer (mg/g).

The adsorption data for methylene blue on SAC and GAC were applied to all three models and the results are presented in Table 4.4. Based on regression of coefficient and the correlation of experimental q_{exp} obtained from adsorption studies with the q_e from kinetic studies, as shown in Table 4.4, the data fits pseudo second order kinetics better compared to pseudo first order and intraparticle model. This suggests that the rate limiting step in the process is chemisorption of the dye molecule on activated carbon which involves the effect of valence forces through sharing or exchange of electrons. Methylene blue dye being cationic has high affinity for negative surfaces such as that of SAC and GAC observed at lower pH values due to deprotonated acidic groups. This contributes to chemisorption of methylene blue in addition to physical adsorption on the surface of the activated carbon (Aygün et al., 2003). Based on k_2 values of SAC and GAC from pseudo second order as presented in Table 4.4, SAC has similar second order rates for methylene blue removal from the solution as that of GAC for the given concentration. Preliminary tests were conducted at 0.4 g/L dosage of SAC and GAC show that methylene blue adsorption reaches equilibrium at 100 hours of contact time. Therefore, equilibrium time for methylene blue adsorption on SAC was found to be 100 hours which is the same as GAC. The intraparticle diffusion model gave curvilinear line as opposed to a straight line supporting the results from adsorption isotherm plot stating sorption mechanism of methylene blue on both SAC and GAC is controlled by more than one mechanism and involves initial surface diffusion followed by intraparticle diffusion. This involves adsorption of methylene blue on the surface in the case of SAC and adsorption of methylene blue on the surface as well as within the pores in the case of

GAC hence, there is a difference observed in the layer thickness formed over both adsorbents. As can be seen from Fig. 4.6c the line does not pass through the origin which indicates that intraparticle diffusion is not the rate limiting step and the layer thickness was found to be 15.17 mg/g and 13.18 mg/g for SAC and GAC, respectively based on intercept of the plot representing boundary layer effect. Therefore, it can be concluded that the mechanism of methylene blue adsorption on SAC and GAC proceeds through fast second order adsorption of the dye followed by slow diffusion into the intraparticle space in the case of SAC and into the interior pores in the case of GAC. Similar mechanisms have been suggested by various dye adsorption experiments in literature (Bhattacharyya and Sarma, 2003).

Figure 4.6. (a) Pseudo first order kinetics, (b) Pseudo second order kinetics and (c) Intraparticle diffusion model for adsorption of methylene blue on SAC and GAC

Table 4.4. Kinetic parameters for adsorption of Methylene blue on SAC and GAC

Adsorbent	q_{exp} (mg/g)	Pseudo first order			Pseudo second order			Intraparticle diffusion		
		q_e (mg/g)	k_1 (hr ⁻¹)	R^2	q_e (mg/g)	k_2 (g/mg hr)	R^2	q_e (mg/g)	k_d (mg/g min ^{1/2})	R^2
SAC	27.4	14.04	0.0276	0.84	27.47	0.005	0.99	15.17	2×10^{-5}	0.58
GAC	25.1	15.36	0.0276	0.73	26.59	0.0048	0.99	13.18	4×10^{-5}	0.52

4.4 Conclusion

This research demonstrated that a novel green activated carbon SAC, can be developed to exhibit comparable properties to a more typical coal based GAC. Methylene blue was efficiently removed from solution at over 97%. The adsorption followed Langmuir isotherm and the kinetic data follows pseudo second order kinetics indicating that homogenous monolayer adsorption of methylene blue occurs on the surface of SAC and chemical adsorption is the rate limiting step. The

methylene blue number for SAC was found to be 196 mg/g which is competitively comparable to 200 mg/g for GAC used in the study. The pseudo second order rate constant for SAC is also comparable with GAC at 0.005 g/mg hr and 0.0048 g/mg hr. The study also investigates the range of adsorbent dosage over which the adsorption and kinetic studies are feasible suggesting that the higher the dosage of the adsorbent the more accurate is the adsorption and kinetic model parameter predictions. Consequently, SAC has potential to be used as a green adsorbent substitute for coal based GAC. It's potential to be used for treatment of different organic and inorganic matter could be suggestive future work.

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Chapter-5 Results

Investigation of a novel green adsorbent for nitrogen and phosphorous removal

Chapter 5 will be submitted as a journal article. As such, this chapter has been presented in the format of a journal article with planned submission to the journal *Separation and Purification*. This paper will be published by co-authors Saumya Suresh (student), Sara Jamaliniya (graduate), Alexis Mackintosh (PCS Technologies Inc.), Eustina Musvoto (Trusense Engineering) and Dr. Onita Basu (supervisor). Saumya Suresh was primarily responsible for data collection, analysis and writing of this chapter.

Abstract

The adsorption capacity of a sucrose activated carbon (SAC) was used to study single solute and competitive nitrate and phosphate removal from solution in a series of batch tests. The capacity and compared with the ability of traditional bituminous coal based Granular Activated Carbon (GAC). Nitrate and phosphate adsorption data were fitted to Langmuir and Freundlich isotherm models. Nitrate adsorption on SAC and GAC fit to Freundlich model with an adsorption capacity of $1.07 \text{ (mg/g(L/mg)}^{1/n})$ and $1.22 \text{ (mg/g(L/mg)}^{1/n})$ respectively. Phosphate adsorption on Sucrose Activated Carbon (SAC) and GAC demonstrated a best fit with the Langmuir model with an adsorption capacity of 1.71 m/g and 2.07 mg/g, respectively. The kinetics data show that adsorption of nitrate and phosphate follow pseudo second order kinetics with rate constant values 0.061 and 0.063 g/mg hr, respectively. Competitive studies between nitrate and phosphate in a multi component solution mimicking surface water was also investigated with preferential nitrate removal with GAC adsorbent system and preferential phosphate removal in SAC adsorbent

system. SAC proves to be competitively equivalent to GAC in removal of inorganic contaminants and may represent a green alternative to coal based activated carbon.

Keywords: Green adsorbent; nitrate; phosphate; adsorption; kinetics

5.1 Introduction

Inorganic nutrients in effluent waters from industrial or municipal effluents commonly include phosphates, nitrate, nitrite, ammonia and potentially heavy metals which contaminate surrounding water streams. Municipal wastewater in general has high phosphate and nitrate content which needs to be treated before discharge. Phosphate and nitrate are known to be the main causes for eutrophication of water bodies. High phosphate and nitrogen levels in water bodies lead to algal bloom in water which in turn leads to loss of species, loss of habitat, increased turbidity and reduced visibility of water. When the concentration of phosphate increases over 0.02 mg/L in the industrial discharge it is considered as a trigger for algal bloom (Kilpimaa et al., 2015; Huang et al., 2009). Exposure to elevated levels of nitrate in water; (> 45 mg/L) is hazardous to health mainly causing a condition called methemoglobinemia and increases the chances of stomach cancer, colorectal cancer and non-Hodgkin's Lymphoma in adults (Esmaeili et al., 2014). Phosphate and nitrate removal can be accomplished via various physical, chemical and biological process including reverse osmosis, adsorption, ion exchange, electro-coagulation, catalytic denitrification, chemical precipitation, microbial phosphorus uptake and biological denitrification (de-Bashan and Bashan, 2004). Adsorption is one popular option due to ease of implementation and capacity to treat a broad range of concentrations of nitrate and phosphate in water.

Adsorption efficiency depends on the adsorbent used for the given adsorbate. GAC is one of the most commonly used adsorbent because of its high adsorption capacity, ease of operation and

maintenance, high surface area and pore volume. However, there are several factors such as excessive cost, corrosiveness in wet state and the fact that GAC is obtained from fossil fuels such as bituminous coal leading to high energy requirements. Zero waste strategies are an important concept in sustainable development, utilizing the waste generated is being focussed on to reduce waste disposal hence there has been investigation into exploring alternative sources for activated carbon specifically from waste sources. Activated carbons obtained from various renewable sources and modified with different chemicals such as surfactants, cationic polymers, ZnCl_2 or chemical processes such as bio gasification have been studied for nitrate removal in literature (Liu et al., 2018; Kilpimaa et al., 2015; Cho et al., 2011; Ahn et al., 2010). Phosphate removal by adsorbents such as blast furnace slag, dewatered alum sludge and fly ash have also been investigated (Namasivayam and Prathap, 2005). The adsorption capacities of some of these adsorbents are low such as 11.2 mg N/g, 3.5 mg P/g, 0.65 mg P/g for bio gasification based activated carbon, dewatered alum sludge and blast furnace slag, respectively. The adsorption capabilities of the above-mentioned adsorbents are reported to be unstable because of the affect of competing ions in the solution and adsorbent surface availability, removal of nitrate and phosphate using these adsorbents have not been applied for practical use (Huang et al., 2009). Production of inexpensive adsorbent material by waste utilization has been focussed upon in the last decade because of the rising need for sustainable solutions. Activated carbon is preferred in water treatment because of its high adsorption capacity and efficient removal of various contaminants. Thus, research has been ongoing for development of activated carbon from sustainable sources such as coconut husk, agricultural waste, apricot, hazelnut, rice husk, corncob, fir wood, vetiver roots, oil palm shell, vermiculata plant, bamboo dust, bio-plant, wheat bran and peach stones (Rafatullah et al., 2010). Their abundance and recycling from waste make them efficient sources

and provide potential for locally sources activated carbon raw material. One potential renewable carbon source that requires further research is sucrose. Sucrose can be obtained from household, agricultural and food based industrial wastes. Sucrose is a disaccharide formed by two units of monosaccharides glucose and fructose which are joined by glycosidic linkage. It is also abundantly found in plants as a source of storage energy.

Therefore, the main objective of this study is to evaluate the possibility of using sucrose to develop a new green, low cost adsorbent and study its application to remove nitrate and phosphate from aqueous solution. Sucrose Activated Carbon (SAC) obtained by hydrothermal carbonization of organic material sucrose followed by pyrolysis activation at 900°C was analyzed for its capacity to remove nitrate and phosphate from the solution. Currently most research work on nitrate and phosphate removal has been focussed on single contaminant removal from water for example removal of nitrate by ZnCl₂ modified activated carbon, cationic polymer modified GAC (Liu et al., 2018; Cho et al., 2011) and removal of phosphate by skin split waste, slag and fly ash, hydroxyl iron lanthanum doped activated carbon, limestone and GAC are some of the recent works (Liu et al., 2013; Ragheb, 2013; Hussain et al., 2011; Huang et al., 2009). However, in practise these contaminants will be present together along with several other competing contaminants in water. Therefore, multi component water studies will aid in an improved understanding of phosphate and nitrate removal in the environment. Thus, this research includes multicomponent analysis in two types of water systems while simultaneously investigating a new green activated carbon source. Adsorption isotherm and kinetic models were investigated to evaluate experimental data.

5.2 Experimental

5.2.1 Adsorbents

SAC with a surface area of 466 m²/g and particle size range of 2.96-9.68 µm was obtained by hydrothermal carbonization of sucrose by pyrolysis at 900 °C. GAC (NORIT® GAC 1240) with surface area 735 m²/g and particle size range of 420-840 µm was obtained from Acros Organics. The carbonized material and GAC were used for adsorption and kinetic studies.

5.2.2 Adsorbates

Nitrate stock solution was prepared by dissolving potassium nitrate (Sigma-Aldrich) in milli-Q water (Biolab). Phosphate stock solution was prepared by dissolving potassium dihydrogen phosphate (Sigma-Aldrich) in milli-Q water (Biolab). Two components solution was prepared by dissolving sodium nitrate (Sigma-Aldrich) and sodium hydrogen phosphate (Fisher-Scientific) in milli-Q water. Synthetic raw water mimicking surface water was prepared by dissolving sodium nitrate (Sigma-Aldrich), sodium hydrogen phosphate (Sigma-Aldrich), glyoxal (Sigma-Aldrich), acetic acid (Sigma-Aldrich), formic acid (Sigma-Aldrich) and sodium bicarbonate (Arm and Hammer) in milli-Q water. Sodium hydroxide and/ or hydrochloric acid were used to maintain the pH.

5.2.3 Batch adsorption experiments

Adsorption experiments were carried out by agitating different masses of SAC and GAC suspended in 2 mg/L solution of potassium nitrate for nitrate adsorption studies and 2 mg/L solution of potassium dihydrogen phosphate for phosphate adsorption studies in Erlenmeyer flasks at 50 rpm, 21±3°C in a rotary shaker (New Brunswick Excella E-1 Open Air Shaker). The concentration of nitrate and phosphate in solution was investigated using UV-Visible spectrophotometer (Spectronic Unicam) by measuring the absorbance at 345 nm and 660 nm respectively. pH was measured using pH meter (Thermo Scientific ORION 087003). The samples

were withdrawn at pre-determined equilibrium time of 80 hours for both adsorbates. The absorbance of the solutions in contact with both media were then measured to determine residual concentration. All analysis was conducted as duplicates. In preliminary tests, using nitrate and phosphate standard, the standard deviation involved in sampling and analysis of absorbance values was found to be ± 0.32 mg/L nitrate and ± 0.14 mg/L phosphate, respectively. Langmuir and Freundlich isotherms were then employed for the data obtained to study the adsorption capacity of the two media for each adsorbate. The competitive adsorption studies were carried out by subjecting SAC and GAC to multi component solutions with the composition mentioned in Table 5.1 and the residual equilibrium concentration was determined for both the systems.

Table 5.1: Composition of multi component solutions

Solution	Components	Source chemicals
Single component	Nitrate	Potassium nitrate
Single component	Phosphate	Potassium dihydrogen phosphate
Two components (N: P ratio: 1:1) Solution-I	Nitrate	Potassium nitrate
	Phosphate	Potassium dihydrogen phosphate
Synthetic raw water (C: N: P ratio: 25:5:1) Solution-II	Carbon	Glyoxal, formic acid and acetic acid
	Nitrogen	Ammonium sulphate
	Phosphorus	Potassium dihydrogen phosphate
	Alkalinity	Sodium bicarbonate

5.2.4 Batch kinetic studies

Kinetic studies were carried out by subjecting SAC and GAC media to test solutions in Erlenmeyer flasks agitated on rotary shaker (New Brunswick Excella E-1 Open Air Shaker) at 50 rpm, $21 \pm 3^\circ\text{C}$.

Solution samples were withdrawn at various time intervals and the absorbance was measured using UV-Visible spectrophotometer (Sectronic Unicam) to determine residual nitrate and phosphate concentrations. The amount of adsorption at time t , q_t (mg/g) was calculated by:

$$q_t = \frac{(C_o - C_t) * V}{W} \quad (5.1)$$

Where C_o and C_t (mg/L) are the liquid phase concentrations of nitrate and phosphate at initial and predetermined times t , respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

5.2.5 Statistical analysis

The model parameters were analyzed using linear regression using Excel 2010 program. In addition, the mean square error (MSE) test method was used to evaluate best fit of the adsorption isotherm model to the experimental data using equation 4.2.

$$MSE = \ln \Sigma i = \ln(q_{ecal} - q_e)^2 \quad (5.2)$$

Where n is the number of data points, q_{ecal} is the calculation from the models and q_e is the observation from experiments. The smaller function values point out best fitting curve (Deniz, 2013).

5.3. Results and Discussion

5.3.1 Adsorption studies

Adsorption isotherm studies were conducted to determine the maximum adsorption capacities of SAC and GAC for nitrate and phosphate adsorbates to assess for side-by-side comparisons of a

novel green activated carbon produced in this research that is SAC to GAC. The most commonly studied adsorption models, Freundlich and Langmuir, were analyzed in this study.

Freundlich isotherm was applied to adsorption data for nitrate and phosphate adsorption on SAC and GAC:

$$\log(q_e) = \log k_f + \left(\frac{1}{n}\right) \log C_e \quad (5.3)$$

where q_e is the amount of adsorbate adsorbed per mass of the adsorbent used (mg/g), C_e is the equilibrium concentration of the adsorbate in solution (mg/L), k_f and n are constants representing the adsorption capacity and intensity of adsorption. Freundlich is an empirical model which suggests heterogeneity of adsorption sites attributed to non-uniform distribution of energy sites for adsorption and that adsorption is not limited to single layer formation on the adsorbent (Foo et al., 2010). The plot of $\log q_e$ versus $\log C_e$ gives a straight line and the k_f and n parameters were calculated from the intercept and slope of the plots, respectively for SAC and GAC (see Table 5.2).

The Langmuir isotherm model represented by the following equations was also applied to the adsorption of nitrate and phosphate on SAC and GAC. Three different linearization forms of Langmuir isotherm were studied including Langmuir-1, Langmuir-2 and Langmuir-3 represented by equations 3,4 and 5, respectively:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (5.4)$$

$$\frac{1}{q_e} = \left(\frac{1}{bQ_0}\right) * \frac{1}{C_e} + \frac{1}{Q_0} \quad (5.5)$$

$$\frac{q_e}{C_e} = bQ_0 - bq_e \quad (5.6)$$

where C_e is the concentration of adsorbate in solution (mg/L) at equilibrium. The constant Q_o signifies the adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). The data was plotted to three different forms of Langmuir isotherms to obtain linear plots as simple linear regression of each form of Langmuir isotherm result in different parameter estimates thus applicability of each form varies (Ho, 2006). The values of Q_o and b for SAC and GAC were calculated from the slope and the intercept, respectively of the linear plots (Fig.5.1) and presented in Table 5.2. Comparisons were made between the different isotherms for adsorption of nitrate and phosphate. The correlation coefficients for Freundlich model ($R^2 = 0.942$ and 0.941) (Fig. 5.1a) were compared with Langmuir-1 model ($R^2 = 0.917$ and 0.941) (Fig. 5.1b) for adsorption of nitrate on SAC and GAC, respectively. MSE analysis to determine error involved in fitting this data to isotherm models were found to be Freundlich (14.2 and 13.9) and Langmuir-1 (16.7 and 16.4) for SAC and GAC, respectively. This suggests that nitrate adsorption on activated carbon is variable and heterogenous and not restricted to monolayer adsorption. The values obtained for $1/n$ are 0.87 and 0.76 for SAC and GAC, respectively indicating that nitrate is favorably adsorbed onto both the adsorbent surfaces under study as they are in the range $0 < 1/n < 1$. The adsorption capacities for nitrate adsorption on SAC and GAC are 1.16 and 1.22 (mg/g(L/mg)^{1/n}) respectively. In the adsorption study, it was observed that SAC provides 55% nitrate removal from the solution at the highest dosage of the adsorbent used in the adsorption study as compared to GAC which provides 52% removal of nitrate. Therefore, SAC is competitively efficient to GAC in adsorption of nitrate from solution.

The adsorption capacity of SAC for nitrate obtained in this study correlates with the values obtained in literature for adsorption capacity of nitrate by other green adsorbents. Mizuta et al.,

2004 reported 1.25 mg/g adsorption capacity for nitrate by bamboo powder charcoal, coconut activated carbon reports adsorption capacity of 1.7 mg/g for nitrate (Bhatnagar and Sillanpää, 2011) which is contributed by increase in pore volume due to increase in carbonization temperature however, SAC reports similar adsorption capacity because of the external surface available for nitrate adsorption.

The correlation coefficients for Freundlich model ($R^2=0.454$ and 0.566) (Fig. 5.2a) for adsorption of phosphate on SAC and GAC, respectively were found to be lower compared to Langmuir-2 model ($R^2=0.944$ and 0.930) (Fig. 5.2c) and hence Langmuir-2 isotherm shows better fit for adsorption of phosphate compared to Freundlich model. This was also supported by MSE analysis which gives lowest error value for Langmuir-2 (2.33 and 2.16) as compared to Freundlich model (9.82 and 8.77) for SAC and GAC, respectively. This represents monolayer adsorption of phosphate onto homogenous adsorption sites on both SAC and GAC. The low pH condition of the adsorbent surface for the study that is at pH 4, further support adsorption of phosphate ions on acidic media as negatively charged phosphate groups will be attracted to the acidic media surface with protonated OH^- ions. In the adsorption study, it was observed that SAC provides 74% phosphate removal from the solution at the highest dosage of the adsorbent used in the adsorption study as compared to GAC which provides 82% removal of nitrate. The q_e values for SAC and GAC are 1.71 mg/g and 2.07 mg/g which indicates that SAC has lower adsorption capacity for phosphate than that of GAC.

Multi component adsorbent studies were also conducted in two different solution systems, solution-I and solution-II (Table 5.1). Nitrate and phosphate removal in single component solution by SAC and GAC show high removal of these contaminants with removal percentages of 50% and above. However, the removal percentage for these contaminants drop when they are present in a

solution with other contaminants which reflect on more realistic scenarios in water treatment. The nitrate removal drops to 40% from 55% by SAC when present in solution-I and to 33% when present in solution-II. Similarly, phosphate removal dropped from 74% by SAC in single component solution to 41% in solution-I and to 36% in solution-II system. Solution-I with just the nitrate and phosphate sources in milli-Q water show higher phosphate removal by SAC and higher nitrate removal by GAC (Table 5.3). Thus, it appears as though nitrate adsorption is preferable with more porous media GAC while phosphate has a preferential surface monolayer adsorption. The same observations for phosphate removal and nitrate removal occur with solution-II. Reduction in nitrate removal percentages of 6% by SAC and 15% by GAC was observed in multi component solution-II (Fig. 5.3c) as compared to just the adsorbates adsorption from solution-I (Fig. 5.3a). Similarly, phosphate removal percentages of 5% by SAC and 8% by GAC was observed in solution-II (Fig. 5.3d) as compared to solution-I (Fig. 5.3b) therefore, suggesting that the adsorption of nitrate and phosphate is depressed by other competing components in the solution creating an antagonistic effect (Manjunath and Kumar, 2018). The adsorption capacity was also determined in terms of per area which shows SAC is comparatively better than GAC in nitrate and phosphate removal for the given initial concentration of nitrate and phosphate and for given mass of both media per area. SAC has an adsorption capacity per area of $2.5\text{E-}03 \text{ mg/m}^2$ as compared to GAC which has a capacity of $1.6\text{E-}03 \text{ mg/m}^2$ for nitrate removal. In terms of phosphate removal, SAC has an adsorption capacity of $3.6\text{E-}03 \text{ mg/m}^2$ as compared to $2.8\text{E-}03 \text{ mg/m}^2$ of GAC. This suggests the capability of SAC to be used in water treatment for as a green substitute.

Table 5.2: Freundlich and Langmuir parameters for adsorption of nitrate and phosphate on SAC and GAC from single solute experiments

Adsorption Isotherm	Parameters	Unit	Nitrate		Phosphate	
			SAC	GAC	SAC	GAC
Freundlich	K	$(\text{mg/g(L/mg)}^{1/n})$	1.16	1.22	1.35	1.73
	$1/n$		0.87	0.76	0.16	0.18
	R^2		0.942	0.941	0.454	0.566
Langmuir 1	Q	mg/g	0.17	6.38	1.52	1.95
	b	L/mg	8.05	0.23	8.20	7.76
	R^2		0.917	0.941	0.350	0.521
Langmuir 2	Q	mg/g	11.3	5.80	1.71	2.07
	b	L/mg	0.11	0.26	3.82	5.45
	R^2		0.220	0.644	0.944	0.930
Langmuir 3	Q	mg/g	16.2	7.27	2.12	0.64
	b	L/mg	0.07	0.20	1.89	2.32
	R^2		0.088	0.388	0.167	0.437

Table 5.3: Competitive adsorption study parameters for SAC and GAC

Solution	Media	Nitrate		Phosphate	
		Removal %	Equilibrium time (hours)	Removal %	Equilibrium time (hours)
Solution-I	SAC	39.7	105	40.8	220
	GAC	51.5	105	42.2	105
Solution-II	SAC	33.0	220	35.8	200
	GAC	36.8	200	34.3	220

Figure 5.1. Adsorption of nitrate on SAC (Δ) and GAC ($\bullet$) with: (a) Freundlich, (b) Langmuir 1, (c) Langmuir 2 and (d) Langmuir 3 plot

Figure 5.2. Adsorption of phosphate on SAC (Δ) and GAC ($\bullet$) with: (a) Freundlich, (b) Langmuir 1, (c) Langmuir 2 and (d) Langmuir 3 plot

Figure 5.3. (a) Nitrate (b) Phosphate removal in Solution I, (c) Nitrate (d) Phosphate removal in Solution II in competitive adsorption studies

5.3.2 Kinetic Studies

To study the kinetics of nitrate and phosphate adsorption on SAC and GAC, three kinetic models, pseudo first order, pseudo second order and intraparticle diffusion models have been used.

Pseudo first order model expressed by Lagergren equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (5.6)$$

where q_e and q_t (mg/g) are the amount of adsorbates adsorbed on sorbent at equilibrium and time t and k_1 is the first order rate constant (min^{-1}). The plot of $\log(q_e - q_t)$ versus t for the data gives linear relationship which was used to find the values of k_1 and q_e from the slope and intercept respectively.

Pseudo second order model is expressed by following equation to analyze second order kinetics of nitrate and phosphate adsorption on SAC and GAC:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5.7)$$

where q_e is the amount of adsorbate adsorbed per unit mass of sorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed (mg/g) at contact time t and k_2 is the pseudo second order rate constant (g/mg min). The linear plot of t/q_t versus t gives values of q_e and k_2 which can be determined from the slope and the intercept respectively.

The data was analyzed using intra particle diffusion model to confirm rate limiting step and diffusion of nitrate and phosphate across the adsorbent:

$$q_t = k_d t^{\frac{1}{2}} + C \quad (5.8)$$

where k_d is the intraparticle diffusion rate constant (mg/g min^{1/2}) and C describes the thickness of boundary layer (mg/g).

The kinetic studies for adsorption of nitrate and phosphate on SAC and GAC were carried out for different adsorbent dosages 0.24, 0.48, 0.64 and 0.96 g/L to observe the range over which kinetic studies are feasible and not limited by masses. It was observed that at lower dosages of the media both SAC and GAC, the removal obtained for both nitrate and phosphate adsorbates was low and the difference between the q_e values obtained from kinetic studies and experimental q_{exp} values obtained from adsorption experiments were higher compared to higher dosages of both media (Fig. 5.4). This study gives the range for adsorbent dosages over which more accurate kinetic and adsorption experimental data can be obtained. As can be seen from this study, kinetic experiments can provide values for rate constants at different dosages of the adsorbent however the values will have error associated with them and this study provides a procedure to establish the lowest dosage of the adsorbent up to which kinetic parameters can be evaluated with more accuracy. Another factor this study demonstrates is the comparison of removal % of each contaminant by both SAC and GAC at the given dosage. At higher dosages there is higher nitrate removal and the ratio of q_e

and q_{exp} values is close to one (Fig. 5.4a and 5.4b) indicating towards the sensitivity of the study and its accuracy at higher adsorbent dosages of 0.96 g/L and above. Similarly, in case of phosphate studies, the ratio of q_e and q_{exp} values are close to one in case of higher adsorbent dosages of 0.96 g/L and gives higher phosphate removal by both media (Fig. 5.4c and 5.4d) thus the final kinetic studies were carried out at SAC and GAC dosages of 0.96 g/L.

The adsorption data obtained for removal of nitrate and phosphate by SAC and GAC over equilibrium time period was applied to all three kinetic models and the data obtained is presented in Table 5.4. For each adsorbate based on regression of coefficient analysis and based on lower degree of difference between the calculated and experimental q_e values, pseudo second order model showed better fit for both nitrate and phosphate removal by SAC and GAC compared to pseudo first order and intraparticle diffusion model. The coefficient of regression is closer to unity for pseudo second order model. Ho and McKay, 1998 reported that pseudo first order model shows good fit for experimental data only up to first 20-30 minutes of contact time. They reported that for pseudo first order model, the assumption $t = \infty$ has to be made to fit the experimental data over the entire range of contact time. This introduces error in the q_e value obtained from this kinetic model. Therefore, this study along with the coefficient of regression analysis, support better fit of pseudo second order model for nitrate and phosphate adsorption on both SAC and GAC. Pseudo second order model fit for both adsorbates indicate that rate limiting step in the process is chemisorption of nitrate and phosphate on activated carbons which involves valence exchange via sharing or exchange of electron (Aygün et al., 2003). This complies with adsorption study data which does not give very high adsorption capacity and complies with studies which show nitrate and phosphate adsorption depend more on surface chemistry than structural properties (Nunell et al., 2015). The pseudo second order rate constant k_2 for nitrate and phosphate removal as presented

in Table 5.4 are comparatively similar making SAC as fast as GAC in the adsorption process of both nitrate and phosphate. Preliminary tests were conducted at 0.96 g/L dosage of SAC and GAC which show that nitrate and phosphate adsorption on both the media reaches equilibrium at 80 hours of contact time. Therefore, equilibrium time for both nitrate and phosphate adsorption on SAC was found to be 80 hours, which is the same as GAC. Intraparticle diffusion plot for both nitrate and phosphate did not pass through origin and does not give a straight-line indicating rate limiting step in the process is not intraparticle diffusion (Fig. 5.5c and 5.6c). The adsorption of nitrate and phosphate involve initial instantaneous adsorption on the external surface of both SAC and GAC followed by diffusion into the spaces between particles and pores on both media this generates difference in layer thickness over both the adsorbents which is given by the intercept from intraparticle diffusion plot for SAC as 0.14 mg/g and for GAC as 0.60 mg/g for nitrate and 0.08 mg/g SAC and 0.43 mg/g GAC for phosphate adsorption. The kinetic studies conclude that adsorption of nitrate and phosphate on SAC and GAC follow initial pseudo second order adsorption on the surface transitioning to slow diffusion into intraparticle space in SAC and pores in GAC.

Table 5.4: Kinetic model parameters for adsorption of nitrate and phosphate on SAC and GAC

Kinetic Model	Parameters	Unit	Nitrate		Phosphate	
			SAC	GAC	SAC	GAC
Pseudo-first order	q_e	mg/g	1.00	1.21	1.19	1.42
	q_{cal}	mg/g	1.27	1.17	1.74	1.48
	k_1	hr ⁻¹	0.07	0.04	0.08	0.05
	R^2		0.964	0.937	0.820	0.547
Pseudo-second order	q_{cal}	mg/g	1.35	1.34	1.19	1.40
	k_2	g/mg hr	0.07	0.06	0.06	0.06
	R^2		0.976	0.949	0.948	0.960
Intraparticle diffusion	q_{cal}	mg/g	0.14	0.60	0.08	0.43
	K_d	g/mg min ^{1/2}	1.73E-02	0.02	0.01	3E-06
	R^2		0.876	0.651	0.933	0.730

Figure 5.4. (a) SAC (b) GAC adsorbent dosage for nitrate removal and (c) SAC (d) GAC adsorbent dosage for phosphate removal versus q_{exp}/q_e

Figure 5.5. Kinetic modelling for adsorption of nitrate on SAC and GAC with: (a) Pseudo first order kinetics, (b) Pseudo second order kinetics and (c) Intraparticle diffusion model

Figure 5.6. Kinetic modelling for adsorption of phosphate on SAC and GAC with: (a) Pseudo first order kinetics, (b) Pseudo second order kinetics and (c) Intraparticle diffusion model

5.4. Conclusion

The experimental results suggest that SAC can be used as a viable alternative for GAC in removal of phosphate and nitrate from water. The adsorption data for removal of nitrate by SAC fits Freundlich isotherm with an adsorption capacity of $1.16 \text{ (mg/g(L/mg)}^{1/n})$ and for phosphate removal it fits Langmuir-2 isotherm with an adsorption capacity 1.71 mg/g which are both competitively comparable to GAC. Competitive adsorption studies with multiple contaminants in water show reduction in amount of nitrate and phosphate removed from solution by SAC and GAC due to the effect of hindrance therefore, by optimizing the conditions based on effluent source, phosphate and nitrate removal can be achieved with higher percentage removal in practical environment. The investigation of different adsorbent dosages of SAC and GAC for phosphate and nitrate removal reveal that higher accuracy in adsorption studies can be obtained at higher adsorbent dosage of 0.96 g/L and above. Kinetic modelling show nitrate and phosphate removal fit pseudo second order with similar rate of adsorption for both the adsorbates on SAC and GAC thus reflecting on the potential of SAC to be used for water treatment. SAC source can be obtained from different waste sources generated everyday and with its comparable adsorption capacities to GAC has high prospective to be used in water treatment plants.

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6. Conclusions

Adsorption is a very efficient technology for treating various pollutants in water sources because of its simplicity in design, effectiveness, low cost of operation and maintenance and availability of wide range of adsorbents. Activated carbon obtained from coal sources is widely used as an adsorbent because of its structural properties such as high surface area, porous structure, large pore volume and ability to adsorb wide range of contaminants. However, the demand for activated carbon has increased significantly over the years and with sustainable development as an important factor there is a switch from using non-renewable to renewable sources. Also activated carbon obtained from coal sources are of prohibitive cost. Therefore, there has been research going on to develop activated carbon from green/renewable sources such as waste products and organic sources with comparable properties as coal-based carbons, thus, making the adsorbents cost effective and sustainable sources. One such activated carbon developed from sucrose; SAC, was characterized in terms of physical properties and tested for its adsorptive capacities for different contaminants. Sucrose is an organic compound found in plants, agricultural and food based industrial wastes thus making it a renewable source.

Phase 1 involved testing SAC for its removal capacity for model compound, dye molecule methylene blue and iodine molecule which defines the media in terms of pores and external surface area. This phase also involved characterizing the activated carbon in terms of BET surface area, attrition, ash content, moisture content, particle size and surface morphology. Following this in Phase 2, the media was tested for removing common inorganic compounds such as nitrate and phosphate molecules from water. SAC was also tested in a competitive environment for removal of nitrate and phosphate from a binary solution having both adsorbates and a synthetic solution

having several other competing molecules to study the adsorptive capacity of the media in more real-life scenarios and compare its ability to GAC in similar conditions.

6.1 Phase 1 conclusions

Methylene blue and iodine studies

Phase 1 demonstrated that the novel green activated carbon SAC, can be developed to exhibit comparable properties to a more typical coal based GAC. SAC was studied to characterize the media in terms of its physical properties. SAC has a BET specific surface area of $466 \text{ m}^2/\text{g}$ and average particle size in the range of $2.96 - 9.68 \text{ }\mu\text{m}$ with an ash and moisture content of 0.1% and 1.9% , respectively. SAC has an attrition percentage of 0.04% . Low ash content and low attrition is suggestive of high surface area and longer operational life. SEM image of SAC shows SAC having small spherical particles with smooth surface as opposed to more porous and rough surface of GAC with larger particle sizes. SAC has bulk density of 0.40 g/cm^3 which supports the higher adsorption capacities of SAC for methylene blue at higher masses of the media. Methylene blue was efficiently removed from solution at over 97% by SAC. The adsorption of methylene blue followed Langmuir-1 isotherm on both SAC and GAC and the kinetic data follows pseudo second order kinetics indicating that homogenous monolayer adsorption of methylene blue occurs on the surface of SAC and GAC and chemical adsorption is the rate limiting step. The methylene blue number for SAC was found to be 196 mg/g which is competitively comparable to 200 mg/g for GAC used in the study. The pseudo second order rate constant for SAC is also comparable with GAC at 0.005 g/mg hr and 0.0048 g/mg hr . The study also investigates the range of adsorbent dosage over which the adsorption and kinetic studies are feasible suggesting that the higher the dosage of the adsorbent the more accurate is the adsorption and kinetic model parameter predictions. Iodine adsorption studies show SAC has an iodine number of 1191 mg/g which was

found to be slightly higher than GAC with an iodine number of 1038 mg/g as presented. This indicates SAC is more microporous compared to GAC which has a high macroporous structure. Consequently, SAC has potential to be used as a green adsorbent substitute for coal based GAC.

6.2 Phase 2 conclusions

Nitrate and phosphate adsorption studies

Phase 2 involved studying removal of inorganic nutrients such as nitrate and phosphate. The study shows SAC can be used as a viable alternative for GAC in removal of phosphate and nitrate from water. The adsorption data for removal of nitrate by SAC fits Freundlich isotherm with an adsorption capacity of $1.16 \text{ (mg/g(L/mg)}^{1/n})$ and for phosphate removal it fits Langmuir-2 isotherm with an adsorption capacity 1.71 mg/g which are both competitively comparable to GAC. Competitive adsorption studies with multiple contaminants in water show reduction in amount of nitrate and phosphate removed from solution by SAC and GAC due to the effect of hindrance therefore, by optimizing the conditions based on effluent source, phosphate and nitrate removal can be achieved with higher percentage removal in practical environment. The investigation of different adsorbent dosages of SAC and GAC for phosphate and nitrate removal reveal that higher accuracy in adsorption studies can be obtained at higher adsorbent dosage of 0.96 g/L and above. Kinetic modelling shows that nitrate and phosphate removal fit pseudo second order with a similar rate of adsorption for both the adsorbates on SAC and GAC thus reflecting on the potential of SAC to be used for water treatment. SAC source can be obtained from different waste sources generated everyday and with its comparable adsorption capacities to GAC has high prospective to be used in water treatment plants.

6.3 Limitations of the study

This project involved establishing SAC as an adsorbent in terms of its adsorption capacity for model compound, methylene blue and inorganic contaminants, nitrate and phosphate. However, within the scope of this study, the feasibility of using SAC as a low-cost substitute for commercial GAC could not be established. Furthermore, SAC being fine powder would create problems in terms of regeneration. It would also require filters prior to effluent stream to prevent washing away of media with the effluent. The effect of varying operating conditions on the performance of SAC must also be monitored for more successful application of SAC as an adsorbent. Therefore, the following future work must be considered.

6.4 Future work

From the results obtained from all the phases and limitations of this study, following can be established as the future work:

- To test the ability of SAC in a column as an adsorption unit and study the effect of flow rate, EBCT, pH, temperature, pressure on removal of various contaminants by SAC. Thus, extrapolate from batch tests to column tests on pilot scale.
- To compare the adsorption capacity of SAC for various contaminants with activated carbon in the particle size range similar to SAC, therefore comparing with Powdered Activated Carbon (PAC).
- To conduct an economic model study, to see how cost effective it is to utilize SAC as an adsorptive media as compared to GAC. This involves taking into consideration the source of SAC, manufacturing process etc.

- To test for formation of by-products, due to the nature of SAC being an organic compound based activated carbon.
- Future studies also involve testing the biofiltration capacity of SAC. To establish a baseline removal for water quality parameters by adsorption on SAC followed by testing the removal of same parameters at similar conditions by SAC with microbial growth on it.

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Appendix A- Calibration, equilibrium studies and error evaluation of adsorption tests.

A.A.1 Calibration curves

Calibration curves for methylene blue, nitrate and phosphate were developed. This involved preparation of five different concentrations of standard solution and evaluation of the absorbance for each concentration for each adsorbate. The absorbance was then plotted with concentration to obtain standard linear plot with regression of 0.95 and above. The equation obtained from this plot is used to determine concentration of each adsorbate in equilibrium, adsorption and kinetic experiments.

Figure A.A.1. Calibration curves for (a) methylene blue, (b) nitrate and (c) phosphate

A.A.2 Equilibrium studies

Equilibrium studies involved subjecting the adsorbent media to adsorbate solution and to determine time at which the adsorbate reaches equilibrium. At this point no more adsorption of the solute on the media takes place.

Figure A.A.2. Equilibrium time studies for methylene blue adsorption on (a) SAC and (b) GAC

Figure A.A.3. Equilibrium time studies for adsorption of nitrate on (a) SAC and (b) GAC

Figure A.A.4. Equilibrium time studies for adsorption of phosphate on (a) SAC and (b) GAC

Standard solutions of methylene blue (5 mg/L), nitrate (2 mg/L) and phosphate (2 mg/L) were prepared and analyzed in spectrophotometer. This gives the standard deviation that occurs while sampling and measurement of each solution concentration as given in Table A.A.1.

Table A.A.1: Standard deviation of concentration of each solute from standard concentration value

Adsorbate	Standard deviation
Methylene blue	± 0.06 mg/L
Nitrate	± 0.32 mg/L
Phosphate	± 0.14 mg/L

Appendix B- Langmuir linear forms derivations

Non-linear form of Langmuir isotherm equation is as follows:

$$q_e = \frac{q_m \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (\text{A.B.1})$$

Linearized form of Langmuir equation is derived from equation A.B.1

Rearrange the equation A.B.1 and divide by $q_m q_e$

$$\frac{q_e}{q_e * q_m} + b * \frac{C_e * q_e}{q_e * q_m} = q_m * b * \frac{C_e}{q_e * q_m}$$

Rearranging the equation, we get **Langmuir-1** model:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (\text{A.B.2})$$

Divide equation A.B.2 by C_e

$$\frac{C_e}{q_e * C_e} = \frac{C_e}{q_m * C_e} + \frac{1}{b q_m * C_e}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m} * \left(\frac{1}{C_e}\right) \quad (\text{A.B.3})$$

This gives **Langmuir 2** model.

Now multiply equation A.B.2 by $q_e q_m / C_e$

$$\frac{C_e}{q_e} * \left(q_e * \frac{q_m}{C_e}\right) = \frac{C_e}{q_m} * \left(q_e * \frac{q_m}{C_e}\right) + \frac{1}{b q_m} * \left(q_e * \frac{q_m}{C_e}\right)$$

$$q_m = q_e + \frac{q_e}{bC_e}$$

Rearranging the equation,

$$q_e = q_m - \frac{q_e}{bC_e} \quad (\text{A.B.4})$$

This gives **Langmuir-3** model.

Now multiply equation A.B.2 $q_e q_m b/C_e$

$$\frac{C_e}{q_e} * \left(q_e * q_m * \frac{b}{C_e} \right) = \frac{C_e}{q_m} * \left(q_e * q_m * \frac{b}{C_e} \right) + \frac{1}{bq_m} * \left(q_e * q_m * \frac{b}{C_e} \right)$$

$$q_m * b = q_e * b + \frac{q_e}{C_e}$$

Rearranging the equation,

$$\frac{q_e}{C_e} = q_m * b - q_e * b \quad (\text{A.B.5})$$

This gives **Langmuir-4** model.

Appendix C- Biological growth studies

Introduction

A.C.1 Biological studies

Adsorbents are also studied with biological growth on them forming biofilm layer and thus forming biofiltration unit. Such a setup provides the benefit of initial adsorption of the contaminant on the adsorbent followed by degradation by the microbial growth on the media. In a biofilter, the contaminant is moved through column packed with the adsorbent and the biofilm, the microorganisms degrade the compounds into mineral end products and new cell materials (Aizpuru et al., 2003). The packing media in a biofilter column is a key factor influencing biofilm growth. The traditional media used has the disadvantages such as compaction, acid degradation and frequent regeneration. Therefore, several new adsorbents are being tested to be used as biofilter media, GAC being one of them (Liang et al., 2006; Sharma et al., 2018). Apart from the media, the characteristics of the influent, temperature, pH and the contaminant composition also affect the biofiltration efficiency (Liu et al., 2001; Emelko et al., 2006).

Appendix D- Biological growth studies methodology

Biological growth studies were also conducted with SAC, fresh GAC and exhausted GAC to see the feasibility of using each media to support biological growth and test water quality parameters removal by the media and biological growth unit.

A.D.1 Biological studies setup

The experiments were conducted as batch tests in 500ml Erlenmeyer flasks where in 500ml of synthetic raw water solution was added with three different weight sets of SAC, fresh GAC and exhausted GAC. The setup was inoculated with backwash water from the biofiltration column in Environmental laboratory, Carleton University as the source of biological growth. The composition of the synthetic raw water is given in Table A.D.1 below.

Table A.D.1: Synthetic raw water composition

Parameter	Conc. mg/L
Ammonia	2.37±0.07
Nitrate	11.94±0.41
Nitrite	0.02±0.0007
Phosphate	1.309±0.09
Total Organic Carbon	10.5±0.20

The C:N:P ratio maintained in the raw water was 25:5:1. The initial pH of the solution was within the range of 6.3-7.5 and the raw water had an initial alkalinity value of 20.84±0.25 mg/L CaCO₃. For each media three different weight sets were studied in a duplicate set of analysis involving 2.5, 3 and 4.5 grams of each media. The raw water was exposed to the different media in the

Erlenmeyer flasks which were then inoculated with backwash water from the biofilter columns in the Environmental laboratory which was initially tested for source of microorganisms through Heterotrophic Plate Count (HPC) and Total Coliform Test (TCT) and shows the following values in Table A.D.2 indicating presence of microbes in the backwash water.

Table A.D.2: Backwash water as source of inoculum

Test	Colony Forming Unit (CFU/ml)
HPC	1080
TCT	132

The following figure shows the batch setup with 500ml Erlenmeyer flasks having 500ml of synthetic raw water and the three-different media with the inoculum.

Figure A.D.1. Biological studies batch tests setup

A.D.1.1 Setup for biological studies

The batch tests were setup by preparing synthetic raw water by addition of Glyoxal, formic acid and acetic acid as carbon source, ammonium sulphate as nitrogen source and potassium dihydrogen phosphate as potassium source. Sodium bicarbonate was added to reflect initial alkalinity and 1N NaOH or 1N HCl was used to adjust initial pH. The backwash water from the biofiltration column was collected and serially diluted using Phosphate buffered saline (PBS) solution and 10^{-2} dilution sample was taken as the inoculum and added to the flasks with the synthetic raw water. Prior to addition of the inoculum it was tested for presence of microbial content via HPC and TCT tests. The media were weighed and then added to the flasks which were then fixed on a shaker set to 100 rpm. The initial values of the synthetic raw water that is the test quality parameters were evaluated prior to media addition which include initial ammonia, nitrate, nitrite, phosphate, alkalinity, pH and Total organic content.

A.D.2 Analytical Methods

A summary of the parameters analyzed has been provided in Table A.D.3. The table includes parameters analyzed in biological study phase, the instrument used, and the analysis test kit/method used for each parameter.

A.D.2.1 Total Organic Carbon

TOC was measured in accordance with the Persulfate Ultraviolet Oxidation Method in Standard Methods 5310C (APHA, 2012).

A.D.2.2 Ammonia nitrogen

The Salicylate method (#10023) was used to analyze ammonia nitrogen with HACH DR2800 spectrophotometer. This method can detect 0.02 to 2.50 mg/L $\text{NH}_3\text{-N}$. The samples for analysis were taken using a micropipette from the batch flasks into glass vials which were washed prior to analysis as per the procedure described in Section 3.2.1. 2 ml of sample was taken and added to HACH kit vial followed by addition of ammonium salicylate and ammonium cyanurate. This mixture was left for 20 minutes for reaction following which it was analysed for absorbance in the spectrophotometer at a wavelength of 660 nm.

A.D.2.3 Nitrate nitrogen

Nitrate nitrogen was analyzed using Cadmium reduction method (#8171) in DR2800 spectrophotometer. This method can detect 0.1 to 10.0 mg/L $\text{NO}_3^-\text{-N}$ in the solution. The samples for analysis were taken using a micropipette from the batch flasks into glass vials which were washed prior to analysis as per the procedure described in Section 3.2.1. 10 ml of sample was taken for analysis to which powder pillows were added and after reaction were analyzed for absorbance at a wavelength of 400 nm.

A.D.2.4 Nitrite nitrogen

Nitrate nitrogen was analyzed using USEPA Diazotization method (#8507) in DR2800 spectrophotometer. This method can detect 0.002 to 0.300 mg/L $\text{NO}_2^-\text{-N}$ in the solution. The samples for analysis were taken using a micropipette from the batch flasks into glass vials which were washed prior to analysis as per the procedure described in Section 3.2.1. 10 ml of sample was taken for analysis to which powder pillows were added and after reaction were analyzed for absorbance at a wavelength of 880 nm.

A.D.2.5 Phosphorus

Phosphorus was analyzed using USEPA PhosVer3 method (#8048) in DR2800 spectrophotometer. This method can detect 0.06 to 5.00 mg/L PO_4^{3-} in the solution. The samples for analysis were taken using a micropipette from the batch flasks into glass vials which were washed prior to analysis as per the procedure described in Section 3.2.1. 10 ml of sample was taken for analysis to which powder pillows were added and after reaction were analyzed for absorbance at a wavelength of 660 nm.

A.D.2.6 Alkalinity

Alkalinity of the solution was determined by Colorimetric method (#10239). 2 ml of sample was added to testing vials and after 5 minutes of reaction time the mixture was tested in DR2800 spectrophotometer.

A.D.2.7 Inoculum test (Backwash water testing)

The inoculum of microbial source that is backwash water from biofilter column was tested for presence of microorganism by Total Coliform test and Heterotrophic Plate Count.

A.D.2.7.1 Total Coliform Test

Backwash water was collected and diluted in PBS solution. The mEndo agar medium was used as nutrient medium and poured into the petri dishes. Flamed the forceps and removed the membrane from the sterile package. Placed the membrane filter into the funnel assembly. Flamed the pouring lip of the sample container and poured the sample into the funnel. Dispensed the diluted backwash water into the sterile petri dish, evenly saturating the absorbent pad. The sample was vacuum filtered. Flamed the forceps and removed the membrane filter from the funnel. The membrane

filter was placed into the prepared petri dish. The plates were incubated for 24 hours at 35°C. The colonies were counted, and CFU/ml was reported.

A.D.2.7.2 Heterotrophic Plate count

The backwash water was serially diluted in PBS solution following which it was spread plated onto R2A agar and incubated at 25°C for 24 hours. Viable counts were enumerated on R2A agar.

A.D.2.8 pH

pH was monitored using a pH probe (Thermo Scientific ORION 087003).

A.D.2.9 Biological Assay

The microbial assay to determine biofilm growth and compare for two media were done using TCT, HPC and EPS tests.

A.D.2.10 Total Coliform Test

This test was performed as described in Section A.D.2.7.1 with the difference of the initial sample for testing which here is the solution from batch flask.

A.D.2.11 Heterotrophic Plate Count

This test was performed as described in Section A.D.2.7.2 with the difference of the initial sample for testing which here is the solution from batch flask.

A.D.2.12 Extra Cellular Polymeric Test

For extraction 2g of both media were taken separately with 0.5 g of CER. (Dowex marathon CNa) to which 10 ml of extraction buffer was added and centrifuged at 3.6 rpm for 20 minutes. The extract was then filtered through 0.45 µm filter. The filtrate was then taken to test for

polysaccharides and protein. For polysaccharides test 2.5g of glucose anhydride was added 50 ml milliQ water (solution 1, 50mg/ml standard) following which 1 ml of sol.1 was added to 50 ml of milliQ water (1mg/ml washing standard). 200 μ l glucose working standard was added to 9800 μ l milliQ water (solution 3, 100 μ g/ml). The 2 ml from solution 3 was taken and 1ml was added to 1 vial (first vial-100 μ g/ml) and then to the remaining 1 ml added 1 ml milliQ water and from this 2ml added 1 ml to next vial (second 50 μ g/ml) and kept going till you get 1.56 μ g/ml and blank was 1ml milliQ water. Following this added 1ml of 5% phenol to all vials and vortexed it. Added 5 ml of 98% H₂SO₄ in fume hood. Incubated the samples for 10 min (in dark) and vortexed for 1 minute and incubated in dark for 30 minutes again and finally read absorbance at 492 nm. For protein part of the test hot waterbath was set up in the fume hood and heated to 60°C. Pierce™ BCA working reagent was prepared by adding 50 parts reagent A to 1-part reagent B. (Working Solutions (1 mg/mL): Added 100 μ L of the BCA standard to 900 μ L of milliQ). For analysis added 400 μ L of working solution to 3600 μ L of milliQ to prepare 100 μ g/mL standard and then transferred 150 μ L of the 100 μ g/mL standard to a microcentrifuge tube. Following this added 75 μ L of each concentration of the BCA standards into the next lower concentration in microcentrifuge tubes (filled with 75 μ L of milliQ) to prepare the serial dilution standards. Then added 75 μ L of sample into microcentrifuge tubes (duplicates for each sample). Added 75 μ L of milliQ water into a microcentrifuge tube for the blank. In the fume hood, added 1.5 μ L of Peirce™ BCA working reagent to the blank, the BSA serial dilution, and the samples and incubated in water bath at 60°C for 30 min. After the samples were cooled to room temperature and the absorbance was measured at 562 nm with the spectrophotometer (UV-Visible Spectrophotometer).

A.D.2.13 SEM Analysis

The samples of media with biological growth on them were transferred to an aluminium boat and left for 24 hours for air dry. The sample was then submitted for scanning electron microscopy analysis to Nanotech Imaging Laboratory, Carleton University.

Table A.D.3: Test parameter kit

Test parameters	Experimental Phase	Testing kit	Testing instrument
Ammonia	Biological studies	TNT, AmVer Salicylate HACH method	HACH DR2800 spectrophotometer
Nitrate	Biological studies	NitraVer 5 Nitrate powder pillows HACH method	HACH DR2800 spectrophotometer
Nitrite	Biological studies	NitriVer 3 Nitrite powder pillows HACH method	HACH DR2800 spectrophotometer
Phosphate	Biological studies	Phosphate TNT HACH method	HACH DR2800 spectrophotometer
Alkalinity	Biological studies	Alkalinity TNTPlus HACH method	HACH DR2800 spectrophotometer
pH	Biological studies	pH probe	pH meter
TOC	Biological studies	Persulfate Ultraviolet Oxidation Method	SHIMADZU TOC- VCPH/ CPN total organic carbon analyzer

Appendix-E Biological growth measure

Biological Assay Analysis

Biomass growth on media as biofilm was analysed by various biological parameters such as Extracellular polymeric substances, Total Coliform test and Heterotrophic Plate Count.

Extracellular Polymeric Substances (EPS test)

Extracellular Polymeric Substances test was conducted which determines the concentration of polysaccharides and protein secreted by microorganisms which gives structural and functional integrity to biofilms. This parameter is a useful indicator of biomass. Following is the summary of EPS analysis for the biofiltration batch tests.

Table A.E.1: EPS concentration for biofilm growth on different media

Sample	(Polysaccharide) EPS ng/mg of media	(Protein) EPS ng/mg of media
Fresh GAC (2.5 g)	1.43	2.60
Fresh GAC (3 g)	6.18	2.73
Exhausted GAC (2.5 g)	7.41	2.52
Exhausted GAC (3 g)	5.12	2.63
Exhausted GAC (4.5 g)	12.5	8.74
SAC (2.5 g)	10.4	5.44
SAC (3 g)	24.1	8.47
SAC (4.5 g)	17.2	5.96

SAC has higher EPS content compared to exhausted GAC which has more EPS content compared to fresh GAC which is an indication of biomass content within the media, this could be because Exhausted GAC already has nutrients which allow microorganisms to develop and SAC might provide better adhesion for microorganisms to develop resulting in higher EPS content.

Total Coliform Test

Total Coliform test was conducted which indicates the presence of different species and genus of Gram negative, rod shaped bacteria some of which may be responsible for development of biofilm. Following is the count of bacterial colonies developed on each media in terms of Colony Forming Units.

Table A.E.2: Total Coliform Count for biomass growth on different media

Sample	Colony Count (CFU)
Fresh GAC (2.5 g)	53200
Fresh GAC (3 g)	TNTC
Exhausted GAC (2.5 g)	12000
Exhausted GAC (3 g)	206500
Exhausted GAC (4.5 g)	28000
SAC (2.5 g)	TNTC
SAC (3 g)	25000
SAC (4.5 g)	2094000

The development of colonies on mEndo agar media after inoculation of sample from the batch biological growth study flasks indicate presence of microorganisms in the setup and hence biological growth on the media.

Heterotrophic Plate Count

Heterotrophic Plate count was measured which indicates the presence of different heterotrophic population of microorganisms some of which may be responsible for development of biofilm. Following is the count of bacterial colonies developed on each media in terms of Colony Forming Units.

Table A.E.3: Heterotrophic Plate count indicating biomass growth on the media

Sample	Colony Count (CFU)
Fresh GAC (2.5 g)	115600
Fresh GAC (3 g)	127800
Exhausted GAC (2.5 g)	509000
Exhausted GAC (3 g)	37200
Exhausted GAC (4.5 g)	397000
SAC (2.5 g)	TNTC
SAC (3 g)	535000
SAC (4.5 g)	2926000

The development of colonies on R2A agar media after inoculation of sample from the batch biofilter flasks indicate presence of microorganisms in the setup and hence biological growth on the media.

Appendix-F Water quality parameter removal

Table A.F.1: Water quality parameter removal percentage by SAC, fresh GAC and exhausted GAC

Water quality parameter	SAC			Fresh GAC			Exhausted GAC		
	2.5 g	3 g	4.5 g	2.5 g	3g	4.5 g	2.5 g	3 g	4.5 g
Nitrate	77%	82%	86%	81%	83%	85%	49%	67%	45%
Nitrite	13%	11%	21%	31%	19%	25%	25%	17%	12%
Ammonia	77%	80%	92%	70%	70%	92%	70%	64%	72%
Phosphate	79%	87%	93%	77%	83%	92%	58%	77%	80%
TOC	88%	92%	98%	91%	94%	96%	75%	78%	86%

The above table presents removal of the various water quality parameters from solution by SAC, fresh GAC and exhausted GAC over a span of 14 days. The removal was substantial however, it could not be concluded from the study if the removal was as a result of biological growth along with adsorption or just by the process of adsorption.

Appendix-G Ammonia adsorption

Ammonia adsorption by the biological study setup. The two media SAC and GAC were subjected to synthetic raw water and the solution was inoculated with microbial source to initiate biological growth. The removal of ammonia over a certain period was monitored and compared and is shown in Table A.G.1.

Table A.G.1: Ammonia removal by various media

	Removal %					
Water quality parameter	SAC		Fresh GAC		Exhausted GAC	
	2.5g	3g	2.5g	3g	2.5g	3g
Ammonia	77%	78%	69%	70%	69%	64%

Even with biological growth which involves removal by adsorption and biological degradation the removal percentage over span of 3 weeks was in the range of 69-78%.

Figure A.G.1. Ammonia removal by biofilter

Adsorption phase

The preliminary tests were conducted to study adsorption of ammonia on GAC and SAC by exposing the media to solution with initial ammonia concentration of 2mg/L.

Figure A.G.2. Ammonia equilibrium study on GAC in two trials

Figure A.G.3. Ammonia equilibrium study on SAC in two trials

Table A.G.2: Percentage removal over a span of 5 days (Trial 1)

	GAC		SAC	
	1	2	1	2
Equilibrium Time	-	-	-	-
Removal Percentage	7.48	77.1	6.48	1.30

The above tests show no particular trend for ammonia adsorption and the duplicate results were very different from each other so no indicative results about equilibrium time could be drawn from the above tests. Also, the removal rate is very slow and low for ammonia adsorption for both the media between 1-10%.

Equilibrium trial 2

Figure A.G.4. Ammonia equilibrium study on GAC

Figure A.G.5. Ammonia equilibrium study on SAC

Table A.G.3: Percentage removal over span of 5 days (Trial 2)

	GAC		SAC	
	1	2	1	2
Equilibrium Time	-	-	-	-
Removal Percentage	9.40	7.83	14.0	8.39

Table A.G.4: pH of media

Media	pH
SAC	5.91
GAC	5.06

In general, below pH 7, virtually all the ammonia will be soluble ammonia ions. Above pH 12, virtually all the ammonia will be present as a dissolved gas. The range between 7 and 12, both

ammonium ions and dissolved gas exist together. Percentage of dissolved gas increases with temperature and pH. Where temperature and pH favor removal of ammonia from solution.

Even with pH adjustment the pH of solution keeps changing due to low pH of the media making it difficult to maintain pH range of 6.5-9. Since the pH of media is lower than 7 it is difficult to have ammonia in solution thus leading to difficulty in correctly studying ammonia adsorption.

The two media do not provide adequate adsorption of ammonia from the solution because of high sensitivity of ammonia concentration in solution to pH.

Appendix-H SEM images

Figure A.H.1. SEM images of SAC with biological growth on it

Figure A.H.2. SEM images of GAC with biological growth on it

Figure A.H.3. SEM images for biological growth on exhausted GAC

SEM images show biological growth in batch tests setup on all three media tested that is SAC, GAC and exhausted GAC. However, conclusive results could not be established if the removal capacity for each water quality parameter was by the microbial growth or just adsorption.