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Study of an Activated Carbon System for the Treatment of Fermentation Wastewater from a Bioethanol Production Process

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Abstract: *The performance of activated carbon system for the treatment of wastewater from a bioethanol process was studied. Studies were performed using fermentation wastewater from bioethanol process containing salts and dissolved organics to determine the adsorption capacity of activated carbon to remove the dissolved organics. Continuous studies in a packed column containing sand and activated carbon resulted in the removal of dissolved organic compounds but the salts concentration was not significantly affected. Batch studies using the bottle point technique generated the specific adsorbate and equilibrium concentration data which fitted both the Langmuir and Freundlich isotherms with the former giving a better fit. The Freundlich capacity factor and the Freundlich intensity parameter were found to be 2.248 and 0.369, respectively. The Langmuir constant's a and b were found to be 58.82 and 0.0009, respectively. Using these parameters, a contacting system with multiple contacting beds in series is recommended due to the short bed life. Based on design calculations, for an effluent with a flow rate of 500 L/min with an empty bed contact time of 30 min allowed, 675 kg of activated carbon would be required to reduce the dissolved organic compound concentration by 74%.*

Keywords: *Fermentation wastewater, Activated carbon, adsorption isotherm, adsorption capacity*

1. Introduction

The use of fossil fuels is associated with two major problems: depletion and global warming. Fossil fuels reserves are finite and with the current consumption rate they face depletion in the near future. According to the International Panel on Climate Change comprising of a group of scientists formed by the United Nations (UN), excessive burning of fossil fuels produces carbon dioxide and other greenhouse gases in large amounts that are causing climate change (Parry et al., 2007). Many countries (especially the developed nations) are looking into ways of producing alternative energy that is renewable, sustainable and environmentally friendly. Ethanol has over the recent past stood out as one of the potential energy sources. Corn and sugar cane have been the main raw materials for ethanol production however this scenario might affect the food prices. According to United States Department of Agriculture (USDA), dependence on corn to meet ethanol production needs affects supplies and subsequently food and feed prices (Coyle, 2007).

Research is underway to use a microbe Sacharophagus degradan isolated from the Chesapeake Bay that is capable of degrading many organic matter with subsequent fermentation of sugars to ethanol at Zymetis Inc., College Park Maryland (Hutchenson, 2008). As the process is depicted in Figure 1 the wastewater produced in the process contains water, dissolved organics (primarily proteins), salts and small amount of suspended solids (trash).

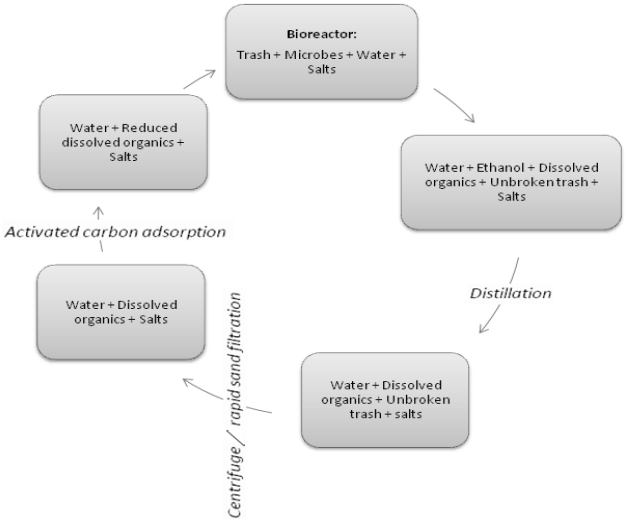

Figure 1. Bioethanol production process incorporating wastewater recycling

The total water used in bio refineries may be as high as 4 gallons of water per gallon of ethanol produced (Andy, 2007; NRC, 2008) and the effluent generated cannot be released to the environment without some form of treatment. To make the entire process more economically and environmentally friendly, the fermentation wastewater needs to be treated and recycled in the bioethanol production process. Suspended solids in the fermentation wastewater can be removed through centrifuge or using rapid sand filters. The resultant wastewater still contains dissolved organics (proteins, carbohydrates) and salts. There is therefore a need to develop a treatment process to recycle the wastewater back into the ethanol production process.

The objective of this study is to design a treatment system that will reduce the amount of dissolved organics but retain the salts which are necessary for microbial growth. This paper reports the studies on the adsorption capacity of activated carbon as a suitable medium for the treatment of fermentation wastewater from a bioethanol production process and the subsequent system for recycling the wastewater. Other methods that can be applied to remove or reduce dissolved organics in wastewater include reverse osmosis, slow sand filtration and activated sludge (Droste, 1997). Reverse osmosis would affect the salt concentration, slow sand filtration requires large land area and has low achievements in terms of dissolved organic removal (50% reduction) (Collins, 1998), and activated sludge process is associated with high operating costs and generation of solid waste that requires proper disposal. Apart from the problems associated with these methods, it would be difficult or impractical to study their performance in treating fermentation wastewater in the laboratory. These methods were therefore not suitable in this case.

2. Theory

Activated carbon as an adsorbent is often used to remove organic contaminants. It can be prepared from almost any carbonaceous material by heating it with or without addition of dehydrating chemicals in the absence of air. Activation is done to create a large surface area within the carbon which makes activated carbon ideal for adsorption. It occurs by passing mildly oxidative hot gases (carbon dioxide or steam) through the carbon at temperatures between 315°C and 925°C. This causes the formation of tiny fissures or pores (Clark and Lykins, 1989). Activated carbon can either be granular (Granular activated carbon-GAC) or powdered (Powdered activated carbon-PAC).

The amount of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and liquid phase characteristics such as pH and temperature (Droste, 1997; Chaudhary et al., 2003). Generally, the amount adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an adsorption isotherm which is the basic instrument for evaluating an adsorbent's use.

Adsorption isotherms describe the relation between the amount or concentration of adsorbate that accumulates on the adsorbent and the equilibrium concentration of dissolved adsorbate. Experiments must be conducted to gather adsorption data which is then analysed according to the following material-balance equation:

$$q_e = \frac{V(C_o - C_e)}{M}$$

where V is volume of the sample (L), C_o and C_e the initial and equilibrium concentration of the adsorbate in solution (mg/L), M is the mass of carbon in the bottle (g), and q_e is adsorbent phase concentration on the carbon after equilibrium (mg adsorbate/g adsorbent). The Freundlich and Langmuir isotherms are commonly used (Wei-chi et al., 2006: Naiya et al., 2008: Hernainz et al., 2008: Shahri et al., 2010). The adsorption data is plotted to fit a linearised form of the isotherms and the correlation coefficient of the straight-line plot determines the most appropriate isotherm form. The Freundlich isotherm is defined as:

$$\frac{x}{m} = K_f C_e^{1/n}$$

where *x/m* is the mass of adsorbate per unit mass of adsorbent (mg adsorbate/g carbon), K_f is Freundlich capacity factor (mg absorbate/g activated carbon)(L water/mg adsorbate)^n, and *1/n* is the Freundlich intensity parameter. The constants can be determined by plotting *Log (x/m)* versus *log* C_e where *1/n* is the slope of the line and K_f the y-intercept.

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e$$

The Langmuir isotherm is defined as:

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e}$$

where a and b are empirical constants with '*a*' representing the maximum monolayer adsorption capacity (mg adsorbate/g adsorbent). '*b*' has units of L/mg. The constants are also determined by plotting $C_e/(x/m)$ versus C_e where *1/a* is the slope of the line and *1/(ab)* the y-intercept.

$$\frac{C_e}{(x/m)} = \frac{1}{ab} + \frac{1}{a}C_e$$

In a continuous fixed bed column, solution containing the adsorbate is introduced from the top of the column containing fresh adsorbent and a dynamic condition starts to develop establishing a mass transfer zone or adsorption zone. This mass transfer zone is defined as the carbon bed depth required to reduce the contaminant concentration from the initial to the final level, at a given flow rate. As shown in Figure 2, the mass transfer zone moves through a carbon bed and

reaches its exit boundary, contamination begins to show in the effluent, a condition classified as "breakthrough" and the amount of material adsorbed is considered the breakthrough capacity. C_o, C_e and C_b are the initial, exhaustion concentration and breakthrough concentration respectively. V_b is the volume of water treated at breakthrough and V_e volume passed through an adsorption bed at exhaustion. The time taken to reach the breakthrough point is called the time to breakthrough. If the bed continues to be exposed to the adsorbate solution, the mass transfer zone will pass completely through the bed and the effluent contaminant level will equal the influent. At that point, saturation capacity is reached. The saturated capacity is that which is represented by the isotherm (Carbirol 1992).

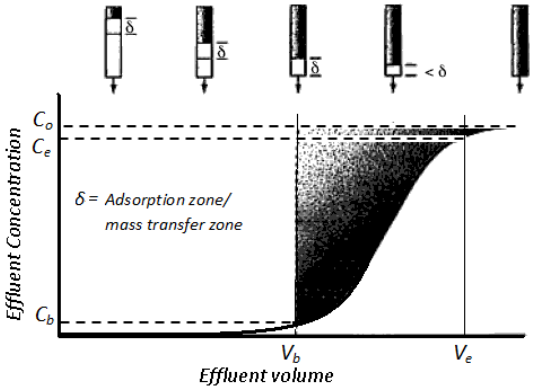

Figure 2. Breakthrough curve

3. Experimental Work

3.1 Continuous experiment

A continuous experiment was carried out in a packed column containing gravel, activated carbon and sand with depths of 50mm, 600mm and 80mm, respectively and filter at the bottom (see Figure 3).

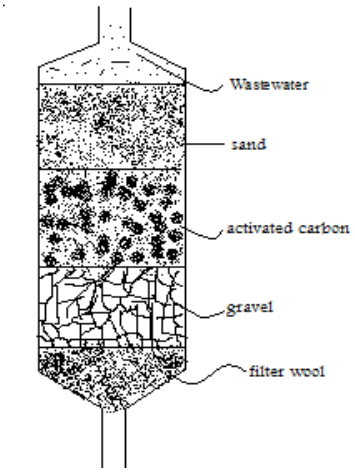

Figure 3. Packed column for continuous experiment

A sample of fermentation wastewater from a bioethanol production process from the degradation of trash by *S. degradan* microbe provided by Zymetis Inc., University of Maryland, College Park was used. The sample of wastewater was introduced at the top and allowed to filter through the packed column with a constant head of 20mm maintained above the sand. For every 100ml of filtrate collected, the time taken to collect was recorded throughout the entire filtration process. The absorbance at 280nm and 570nm of each 100ml of filtrate collected in different containers was measured using a Gensys 5 spectrophotometer. Electrical conductivity was measured for every 300ml of the filtrate collected using the conductivity meter. The recorded times for every 100ml of filtrate collected were used to calculate the filtration rate.

3.2 Batch experiment

In the batch experiment, fixed volumes (0.2 L) of the fermentation wastewater of known concentration were added to each of ten bottles containing different amounts of activated carbon. The bottles were incubated at room temperature for 7 days after which equilibrium concentrations in each of the bottles were then determined by measuring the absorbance at 280nm. Seven days provides adequate time for the organics to adsorb onto the activated carbon to the point of saturation (Collins 1998). The measured absorbance was converted into mass concentration using the following relationship (Stoscheck 1990).

Concentration (mg/ml)
= [Absorbance at 280 nm] / [path length (cm)]
Concentration (mg/L)
= [Absorbance at 280 nm] / [path length (cm)] x 10^3

This is a rough estimation of the concentration of unknown proteins or protein mixtures (dissolved organics). The path length is the light path through the cuvette which is equal to 1cm. The adsorption data was analysed using the mass-balance equation to obtain data that was used in the Langmuir and Freundlich isotherms.

4. Results and Discussions

Figure 4 shows the conductivity of the column effluent which was fairly constant over filtrate volume of 3600ml. Figure 5 shows the filtration rate profile. The filtration rate decreased from about 0.88mm^3/mm^2/sec to 0.58mm^3/mm^2/sec over 7000ml of filtration. The concentration of dissolved organic compounds was indirectly measured by measuring the absorbance at 280nm. Proteins in solution absorb ultraviolet light with absorbance maxima at 280 and 200 nm. Amino acids with aromatic rings are the primary reason for the absorbance peak at 280 nm (Stoscheck, 1990).

Figure 6 shows the absorbance at 280nm for the column effluent. The initial absorbance of the wastewater was 3.90 and that of the initial column effluent was 3.63. Over the next 2,600ml volume of effluent, the absorbance was fairly constant before increasing to 3.90. Similarly, the clarity of the column effluent was monitored by measuring the absorbance at 570nm. Figure 7 shows the absorbance at 570nm of the column filtrate. The absorbance of the initial wastewater was 0.295 while that of the initial column effluent was 0.250 and was fairly constant at this value for the first 2700ml of column effluent.

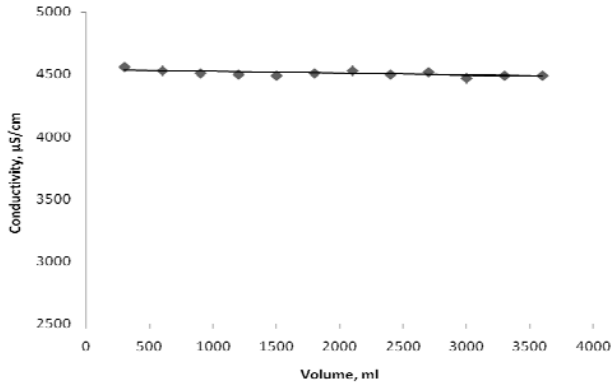

Figure 4. Conductivity vs. volume of filtrate

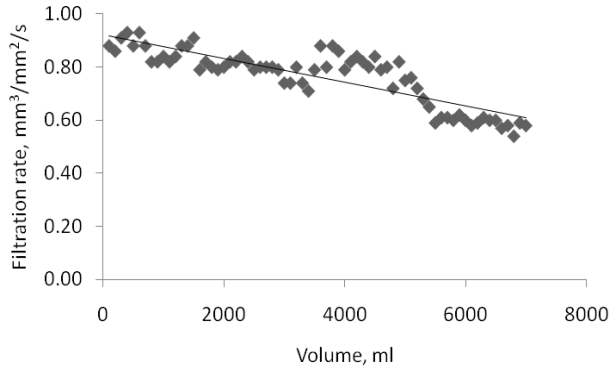

Figure 5. Filtration rate vs volume of filtrate

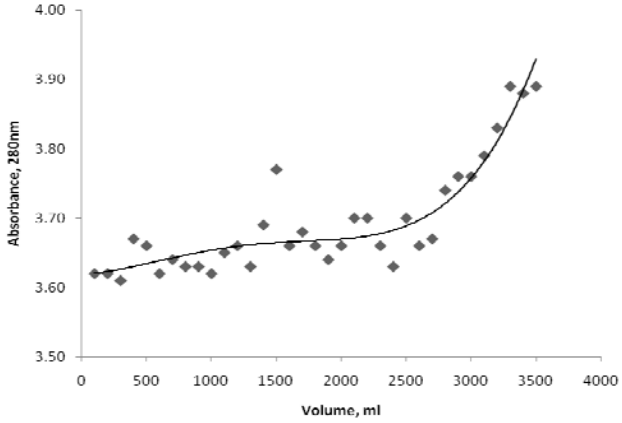

Figure 6. Absorbance at 280 nm vs. volume of filtrate

The mass concentrations were determined using the relationship for rough estimation of the concentration of unknown proteins or protein mixtures:

Concentration (mg/L)
= [Absorbance at 280 nm] / [path length (cm)] x 10^3

The results for the specific adsorbate q and the equilibrium concentration C_e were plotted to obtain the adsorption isotherm in Figure 8, and fitted to the linearised Freundlich and Langmuir isotherms in Figures 9 and 10, respectively. The Freundlich capacity factor K_f is given by the intercept when C_e = 1 and is equal to 2.248. The Freundlich intensity parameter *1/n* is given by the slope of the line = 0.369.

Thus, the Freundlich isotherm in this particular case is defined by:

$$q_e = \frac{x}{m} = 2.248 C_e^{0.369}$$

The value of empirical constants *1/ab* is given by the intercept when C_e = 0 and is equal to 18.985. The value of *1/a* is given by the slope of the line = 0.017

1/(ab) = 18.985; 1/a = 0.017; a = 58.82 mg/g

1/(ab) = (1/b)*(1/a) = 18.985

1/b = 18.985/(1/a) = 18.985/0.017 = 1116.76 ;

b = 0.0009 L/mg

58.82 mg/g represents the maximum adsorption capacity.

Thus the Langmuir isotherm in this particular case is defined by:

$$q_e = \frac{x}{m} = \frac{0.0527 C_e}{1 + 0.0009 C_e}$$

The packed column studies established that activated carbon was a suitable medium to remove dissolved organics and did not affect the amount of salts in the wastewater significantly as indicated by the absorbance values at 280 nm and electrical conductivity values, respectively. The electrical conductivity was an indicative measure of salts in the wastewater. The decrease in the filtration rate is an indication of clogging due to suspended solids getting trapped within the sand. Backwashing would therefore be necessary to remove the accumulated solids.

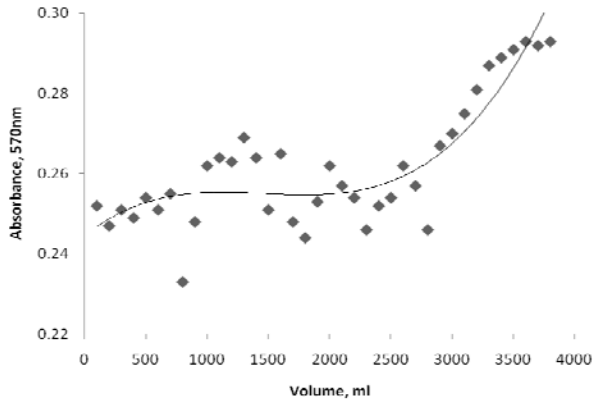

Figure 7. Absorbance at 570nm vs volume of filtrate

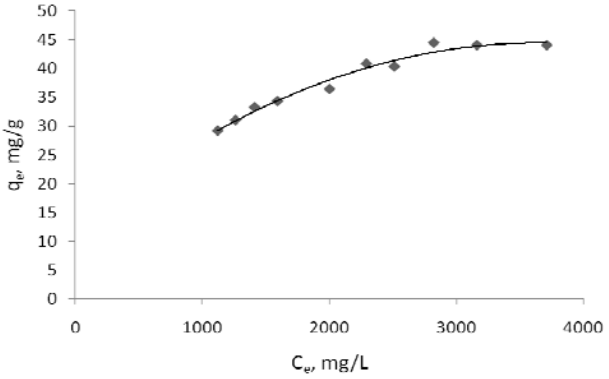

Figure 8. Adsorption isotherm

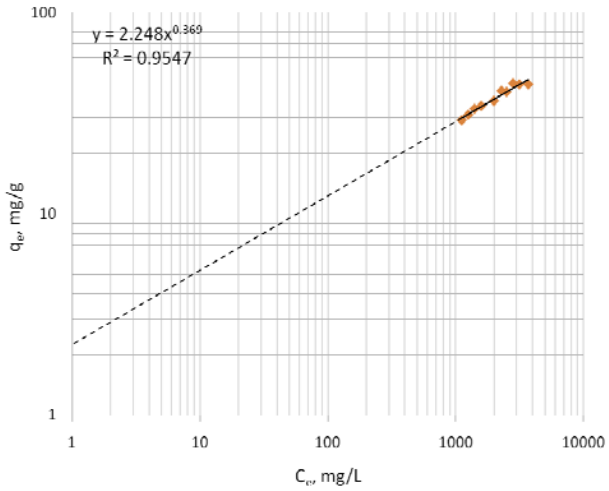

Figure 9. Linearised Freundlich Equation

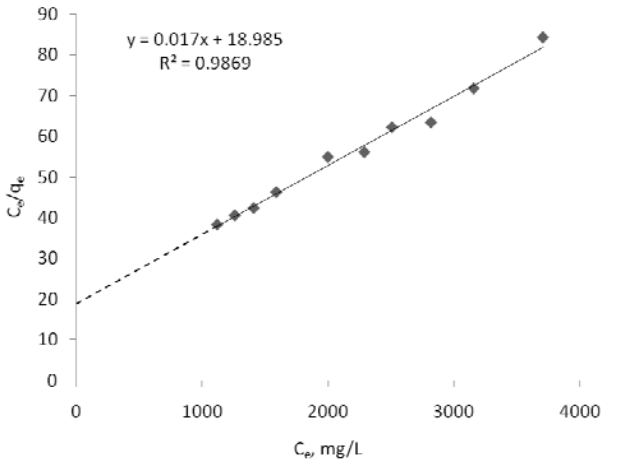

Figure 10. Linearised Langmuir Equation

The breakthrough volume, which is indicative of the useful period of activated carbon after which it should be replaced or regenerated, for this study was 2600ml. Figure 7 represents the clarity measure of the filtrate and after 2,700ml of filtration through the packed column, the filtrate becomes cloudy, an indication that the media needs to be regenerated.

In Figure 8, the vertical axis (q_e) represents the dissolved organic uptake per mass of activated carbon, the plateau observed means that there is a decrease of the active sites for adsorption indicating the maximum uptake capacity of the activated carbon for dissolved organics. The experimental data plotted on a log-log graph determines the Freundlich capacity factor and intensity parameter (K_f and *1/n*, respectively). In Figure 8, the linearised plot determines constants *a* and *b* for the Langmuir isotherm. Adsorption characteristics of activated carbon used in wastewater treatment are normally best described by the Freundlich isotherm (Tchobanoglous et al., 2002). Experimental data for activated carbon usually fits the Langmuir isotherm poorly. However, considering the correlation coefficient R^2 values in Figures 8 and 9 (0.9547 and 0.9869, respectively), the Langmuir isotherm was a better fit in this study. This could be attributed to the high organic concentration present in the wastewater. Langmuir isotherm accounts for surface-coverage in that when the fluid concentration is very high, a monolayer forms on the adsorbent surface.

5. Analysis

An analysis for an activated carbon contactor designed to treat wastewater similar to the sample used in the experiment is carried out below. As of 2006, different ethanol biorefineries in the US had capacities ranging 1-1,000 million gallons per year (mgy) (RFA, 2006). 97% of the plants had capacities ranging 1-100 mgy most of which were below 50 mgy. Considering a water consumption of up to 3 gallons water per 1 gallon ethanol produced, wastewater production is expected to be about 2 gallons per 1 gallon of ethanol. Therefore, a typical plant with an average production capacity of 35 mgy ethanol is expected to produce 70 mgy wastewater. This is about 504 L/min. For the purposes of analysis, 500 L/min will be used and a single bed will be considered. With the following information:

C_o = 3820 mg/L (experimental),
C_e = 1000 mg/L, GAC density
ρ_{GAC} = 450 g/L, *a* = 58.82 mg/g;
b = 0.0009 L/mg (experimental).

Carbon usage rate:

$$\frac{m_{GAC}}{V} = \frac{C_o - C_e}{q_e} = \frac{C_o - C_e}{\frac{abC_e}{1+bC_e}} = (C_o - C_e)\left(\frac{1+bC_e}{abC_e}\right)$$

$$= (3820 - 1000)mg/L\left(\frac{1 + 0.0009 * 1000 mg/L}{58.82 * 0.0009 * 1000 mg/L}\right)$$

= 101.2 g GAC/L

From typical design values for granular activated contactors (Sontheimer 1988; Nazaroff and Cohen 2001), if a bed volume of 15 m^3 is chosen (from the provided range 10-50 m^3), the empty bed contact time (EBCT) is given as:

$$EBCT = \frac{Volume}{Flowrate} = \frac{15000L}{500L/\min} = 30\min$$

The mass of carbon required for a 30 min EBCT:
Mass of GAC in bed $m_{GAC} = V_b \rho_{GAC}$ = EBCT * Q * ρ_{GAC};
where V_b is the volume of GAC in contactor

= 30 min * (500 L/min) * (450g/L)
= 6.75 x 10^6 g

The volume of wastewater treated using a 30 min. EBCT

= (mass of GAC for given EBCT) / GAC usage rate

$$= \frac{6.75*10^6 g}{101.2 gGAC/L} = 66700L$$

Bed life

= (volume of wastewater treated for given EBCT)/Q

$$= \frac{66700L}{500L/\min} = 133.4\min$$

To treat an effluent with a flow rate of 500 L/min (approximately 190,000 gal/d) and concentration of 3820 mg/L down to a concentration of 1000mg/l and with an empty bed contact time of 30 min allowed, 6.75 x 10^6 g of granular activated carbon is required. The total volume of effluent that will be treated will be 66,700 L (17,620 gal). However, the bed life which is approximately 2 hours is too short.

A schematic depicting the configuration of the process designed to remove dissolved organics from fermentation wastewater from a bioethanol plant is shown in Figure 11. At least two systems of sand filter units and activated carbon beds are set up in parallel to ensure continued operation while servicing the beds Activated carbon beds are further set up in series to take full advantage of the adsorption capacity difference between breakthrough and saturation.

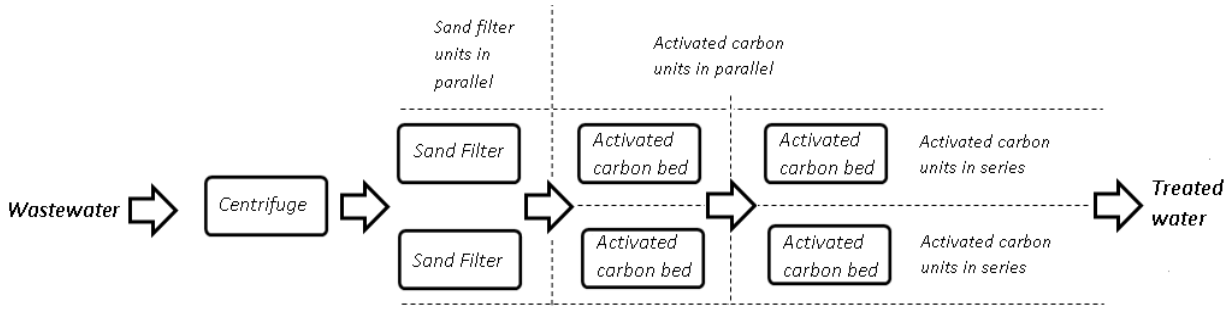

Figure 11. Organic removal process

6. Conclusions

The adsorption isotherms determined based on experimental data, show that activated carbon has the capacity to reduce dissolved organics in effluent from a bioethanol production process. The isotherms can be used to optimise activated carbon columns. Based on design calculations, for an effluent with a flow rate of 500 L/min with an empty bed contact time of 30 min allowed, 675kg of activated carbon would be required to reduce the dissolved organic compound concentration by 74%. To increase the bed life, greater carbon depth or beds in series are desired. This consequently increases the time after which the beds should be serviced. Multiple beds in series as mentioned earlier take full advantage of the adsorption capacity difference between breakthrough and saturation and thus can be used to increase this time. Increasing the volume of the beds will also increase the bed life. These findings and conclusion sets up a platform for further work to find systems and configurations that optimise the treatment efficiency.

Due to the large amounts of activated carbon that may be required to treat the fermentation wastewater (depending on the desired effluent concentration) it is necessary to incorporate carbon regeneration in order to save on the cost that would be incurred in replacing and disposing spent (saturated) carbon.

Acknowledgement

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