OPTIMISATION AND CHARACTERISATION OF BATCH ADSORPTION SYSTEM FOR ACETIC AND BUTYRIC ACIDS RECOVERY FROM LEACHATE BY ACTIVATED CARBON

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ABSTRACT

Municipal landfill sites generate a substantial amount of volatile fatty acids during acetogenesis of landfill decomposition. Valuable fatty acids such as acetic and butyric acids that presence in the leachate can be potentially recovered using adsorption method. With regard to that, adsorption equilibrium of acetic and butyric acids onto granular activated carbon were studied in landfill leachate. In batch system, a study on agitation speed, contact time, adsorbent dosage and pH have been investigated. After optimisation using one-factor-at-a-time, the selected levels of parameters were as follows: agitation speed (350 rpm), contact times (60 minutes), adsorbent dosage (200 g/L) and pH 2. Consequently, 59.1% removal of acetic and butyric acids was achieved. The results show that the adsorbent fitted well with both Langmuir (R^2=0.89) and Freundlich isotherms (R^2=0.93) for the fatty acids adsorption. Thus, activated carbon has the potential to be used as recovery method for the valuable acids from leachate but further study is required.

Keywords: Acetic acid, activated carbon, adsorption, butyric acid, leachate.

INTRODUCTION

Landfill leachate is a highly contaminated liquid that contain organic matter, inorganic matter, heavy metals and xenobiotic organic compounds due to percolation through solid waste dump. Leachate can be classified according to biological oxygen demand (BOD) to chemical oxygen demand (COD) ratio and generally indicates ages of leachate. Table 1 shows classification of leachate based on the age of the landfill [1]. The composition of leachate gradually changes through a process of microbial degradation that occurs under aerobic and anaerobic condition [2]. There are four phases involved in bacteria decomposition namely phase I to IV, which can be conveniently characterised by emitted gas composition and pH of leachate [3]. Phase I is an aerobic process while the following phases are vice versa.

Remarkably, the microbial decomposition of organic solid waste results in the formation of valuable organic compounds. Among the highest organic constituents presence in a municipal landfill leachate are acetic acid and butyric acid [4]. This is established by high BOD to COD ratio due to rapid hydrolysis of insoluble organic substances. The potentially recovered volatile fatty acids have many applications in various industry, namely textile, rubber, clinical, perfume and dye. Global market demand for acetic acid alone has recorded 13 million tons in 2015, which is expected to rise up to 18 million tons by 2020 [5]. While in the Asia-Pacific region, butyric acid market is one of the fastest growing markets across the world. Currently, Asia-Pacific is leading the global butyric acid market, and has contributed to 42.2% production in 2014.

Physico-chemical treatment such as adsorption by activated carbon has been effectively use to remove organic pollutants from leachate. Activated carbon particle has a porous framework with interlinked multi-size pores that impart good capacity for the adsorption of organic molecules. The surface chemistry of adsorbent such as point of zero charge, the chemical characteristics of adsorbate, such as polarity, ionic nature, functional groups and solubility and the properties of aqueos solution such as pH, concentration of adsorbate, the presence of other species determine the nature of bonding mechanisms and the strength of adsorption [6]. A study by Suescún-Mathieu et al. in 2014 has discovered that activated carbon from sugarcane bagasse can be utilised to recover carboxylic acid from aqueous solution. The researchers have accounted as high as 60% removal of acetic acid and 21% removal of butyric acid in individual adsorption study.

In this study, the adsorption properties of volatile fatty acids from leachate on granular activated carbon was investigated. The adsorption equilibrium was expressed by the Langmuir and Freundlich equation. These adsorption equations are extensively used because they are convenient to describe experimental results in a wide range of adsorbate concentrations [8]. Present paper is an attempt to remove valuable acetic and butyric acids from landfill leachate using granular activated carbon, thus opens up new opportunity in potential recovery process.

Table 1. Types of leachate according to landfill ages

Leachate type	Age	BOD/COD ratio
Old	>5 years	0-0.3
Medium	1-5 years	0.3-0.6
Young	3-12 months	0.6-1

METHODOLOGY

Adsorbent

An industrial grade activated carbon purchased from Century Chemicals Trading Sdn Bhd was used in this experiment. Certificate of analysis that describe the adsorbent characteristics was listed in table 2.

Table 2. Characteristics of the granular activated carbon

Parameter	Value
Loss on drying (%)	3.79
CTC (%)	52.4
Ignition residue (%)	1.2
Bulk density (gm/cc)	0.51
pH	9.82
Hardness (%)	98.2
8x30 mesh (%)	94.3

Landfill leachate

Leachate sample was collected from the Pulau Burung Landfill Site (PBLS) which is located within Byram Forest Reserve at 5º 24' N Latitude, 100º 24' E Longitude in Nibong Tebal, Penang. This site possess natural marine clay liner. It was first established in 1980s which covers an area of 62.4 ha but only 33 ha is currently operational with daily input of 2200 ton solid waste [9]. In 1991, the site was upgraded to Level II sanitary landfill with establishment of controlled tipping technique. A decade later, sanitary landfill Level III was developed by using controlled tipping technique with leachate recirculation [10]. This site was equipped with semi-aerobic system and is one of three sites available in Malaysia.

Samples were collected from the leachate collection pond. The leachate was filled into 20L plastic container, transported to laboratory and chilled at 4°C. Total of 200ml leachate was taken from the 20L sample for chemical analysis on the following day. All test were carried out according to Standard Methods for the Examination of Water and Wastewater (Standard Method) (APHA, 2005). The characteristics of leachate from the landfill are listed in Table 2.

Table 2. Characteristics of PBLS leachate

Parameters	Value (mg/L)
pH	7.92
BOD_5	6100
COD	11805
Total Kjeldahl Nitrogen	280
Phosphorus content	4.0
Total carbohydrate	97.11
Acetic acid	2274.3
Butyric acid	1213.721

Batch adsorption experiments

Batch experiments were conducted to maximise removal of acetic and butyric acids by activated carbon using the optimum condition of all relevant factors such as dosage, contact time, agitation speed, and pH. The experiment was carried out in 250ml Erlenmayer flask filled with 100ml leachate at ambient temperature (28°C). The optimum condition for the adsorption batch study was determined progressively by first varying dosage (100-200g/L), while other factors were fixed at specific level. Subsequent factor optimisation was performed by varying contact time (1-5h), agitation speed (200-400rpm) and pH (2-10). Initial pH of leachate was formed with addition of 5M sulphuric acid or 5M sodium hydroxide. The concentration of acetic and butyric acids were determined using the Standard Method. Finally, adsorption isotherm tests were carried out by varying the adsorbent dosage within extensive range of 50g/L to 500g/L.

RESULTS AND DISCUSSION

Effect of adsorbent dosage

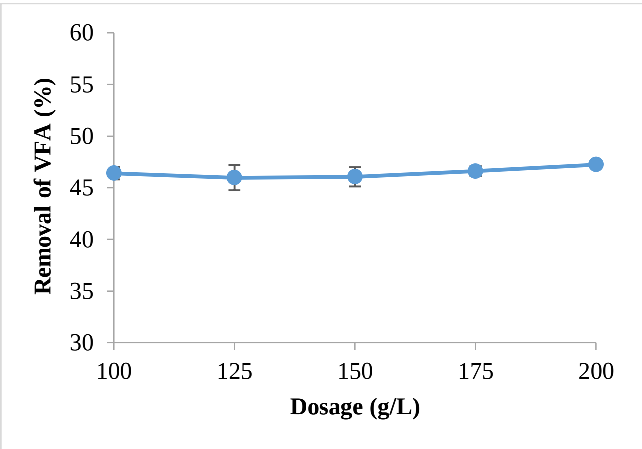

Figure 1. Effect of activated carbon dosage (g/L) on percent removal of VFA

In general, increasing amount of adsorbent will increase the adsorbent surface area and adsorption sites, hence increase the adsorption rate and efficiency [12]. In adsorbent dosage study, highest percent removal of VFA was recorded at 47.2%. However, there were no significant increase in percent removal of VFA when dosage was studied within range of 100g/L to 200 g/L. The dosage range could be perceived as the limiting factor in targeting higher percent removal. However, the dosage range was not intensified due to higher dosage will result in higher ratio of activated carbon to leachate, thus contributed to oversaturation and poor mixing during adsorption process.

Effect of contact time

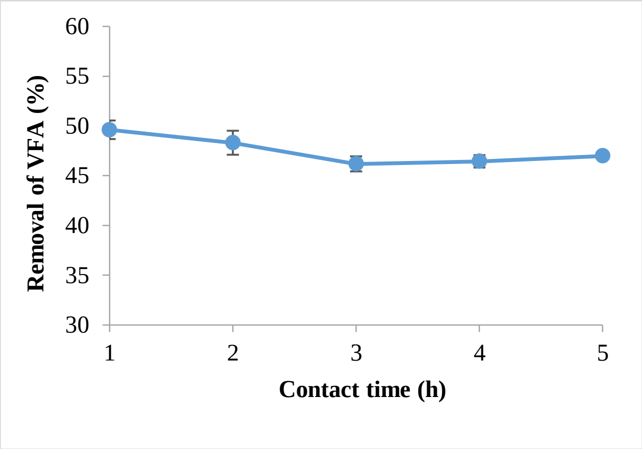

Figure 2. Effect of contact time (h) on percent removal of VFA

The effect of contact time on adsorption capacity by activated carbon was performed to achieve the adsorption equilibrium [12]. The equilibrium was achieved when equality of adsorption rate and desorption rate of adsorbate molecules have occurred. In this phenomenon, adsorption capacity will be at maximum and the determination of equilibrium time was essential to study adsorption isotherm. The result showed that equilibrium was attained at 1 hour contact time with 49.6% VFA removal. As the maximum adsorption capacity was achieved, increasing the contact time would only result in plateau or insignificant changes in adsorption efficiency.

Effect of agitation speed

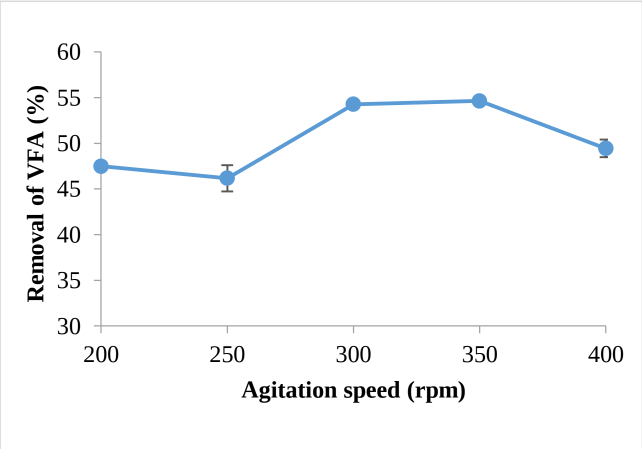

Figure 3. Effect of agitation speed (rpm) on percent removal of VFA

Maximum removal was achieved at 350 rpm with 54.6% VFA removal. In a liquid adsorption system, the transfer rate of adsorbate to adsorbent was influenced by film thickness surrounding the adsorbent particles, thus by increasing turbulence would increase the degree of mixing [12]. Nevertheless, further increasing the agitation speed in this experiment result in lowering percent removal of VFA may suggest that beyond 400rpm, film thickness has insignificant effect on the adsorption system.

Effect of initial pH

Maximum removal of VFA was recorded at pH 2 with 59.1% VFA removal. The pH value of leachate is an important factor for adsorption process. A study by [13], had discovered an increase in removal of 2,4-dichlorophenoxyacetic acid on lowering pH below 7.0. While another researcher [14] obtained maximum adsorption capacity for acetic acid in acidic solution but fell rapidly between pH 5 and 6. The result supported that recommendation of acidic solution at pH 6 and below for adsorption efficiency and higher percent removal of VFA.

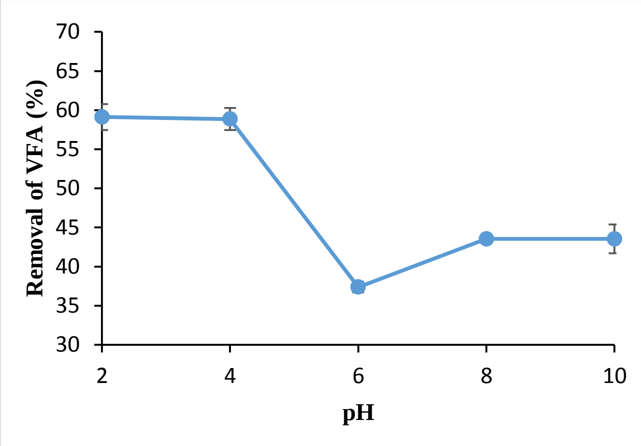

Figure 4. Effect of pH on percent removal of VFA

Adsorption equilibrium

In general, adsorption isotherms in aqueous solution relates the mass of solute adsorbed on the adsorbent surface to the concentration of adsorbate in the solution at a given temperature. Adsorption isotherms are important for describing the interaction of adsorbate concentration with adsorbent media. Therefore, two models, which are Langmuir and Freundlich isotherms, are essential and widely used for adsorption data analysis and predication. The Langmuir model proposes the adsorbent surface is homogenous and adsorption sites are equally distributed, adsorbed molecules do not interact with each other, all adsorption process occurs through the same mechanism and only monolayer of adsorbate is formed at maximum adsorption. The following assumptions can be represented by the equation:

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

A linear form can be derived from the equation, given as the following:

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

By plotting $1/q_e$ versus $1/C_e$, q_m and b of Langmuir constants can be resolved from the slope and intercept of the plot. They represents maximum adsorption capacity (mg/g) and energy of adsorption, respectively. C_e is remaining concentration of adsorbate in solution, while q_e is the adsorption capacity at equilibrium (mg/g).
Freundlich isotherm is empirical expression that shows the relationship between the remaining concentrations of adsorbate in a liquid (C_e) against the adsorption capacity at equilibrium (q_e). The isotherm assumes that the adsorption occur on a heterogeneous surface by multilayer formation and the adsorbate loading on adsorbent increases infinitely with an increase in adsorbate concentration until saturation point is reached. The Freundlich equation is given as:

$$q_e = K C_e^{\frac{1}{n}}$$

K is an indicator of the adsorption capacity and 1/n represent the adsorption affinity [15]. A linear form can be derived from the equation, given as the following:

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

By plotting $\log q_e$ versus $\log C_e$, value of K and 1/n can be determined from the intercept and slope of the linear plot. The values of $n<1$ for all parameters shown in table 3 suggest that adsorption is less favourable [16]. The adsorption equilibrium for total volatile acids on granular activated carbon is indicated in table 3.

Table 3. Total volatile fatty acids isotherm constant for granular activated carbon

Isotherm	Value
Langmuir	
R^2	0.9289
q_m (mg/g)	-0.706
b (L/g)	-1063.263
Freundlich	
R^2	0.8866
K	-8.0939
1/n	3.2527

CONCLUSION

Optimisation of factors viz dosage, time, agitation and pH were successfully performed. The identified level of optimisation were 200g/l adsorbent dosage, 1h contact time, 350rpm agitation speed and pH2. Granular activated carbon has the potential to adsorb volatile fatty acids, verified with highest removal of volatile fatty acids at 59.1%.

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