International Journal of Integrated Engineering: Special Issue 2018: Innovations in Civil Engineering, Vol. 10 No. 9 (2018) p. 6-10

DOI: https://doi.org/10.30880/ijie.2018.10.09.002

Utilization of Waste Paper Sludge as an Alternative Adsorbent for the Adsorption of Ammonia Nitrogen and COD in Stabilized Landfill Leachate

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Received 28 July 2018; accepted 19 November 2018, available online 31 December 2018

Abstract: Waste paper sludge (WPS) is produced by the paper industry during the wastewater treatment process of paper production. The disposal techniques of WPS pose a great concern for the environment. This study focuses on the evaluation of WPS as an alternative absorbent material to activated carbon (AC) for the removal of contaminants from stabilized landfill leachate. Ammonia nitrogen (NH_3-N) and chemical oxygen demand (COD) were identified as the two major contaminants in landfill leachate. Both AC and WPS were mixed together in different ratios. The optimum replacement for the absorbent was determined using the batch technique. The adsorption batch study was carried out under the optimum pH of 7, with a shaking speed of 200 rpm and a contact time of 120 minutes. The adsorption isotherms indicated that the Langmuir model was better fitted to the experimental data as it was found to have the highest regression values. The Langmuir adsorption capacities for COD and NH_3-N were 32.26 mg/g and 21.60 mg/g, respectively. The optimum replacements were initially at two different ratios of 2:2 and 3:1 based on the optimum removal of COD and NH_3-N, respectively. However, the final optimum replacement for the absorbents (AC: WPS) in this study was the ratio of 2:2 due to the higher removal of COD (85.9%) and NH_3-N (49.3%).

Keywords: Waste paper sludge, COD, NH_3-N, landfill leachate, adsorption

1. Introduction

Leachate is a very dark colour liquid that is produced from the percolation of rainwater and surface water runoff into solid waste layers by biological, chemical and physical decomposition processes. Water percolation occurs when the magnitude of gravitational forces exceeds the holding forces, where the higher moisture of water exceeds the absorption capacity of the solid waste layer [1]. Leachate flowing out through solid waste in landfills may contain large amounts of organic matter, ammonia nitrogen, heavy metals, chlorinated organic salts and inorganic salts which are toxic to living organisms and the ecosystem [2]. Therefore, in order to ensure that leachate is safe to be disposed into the environment without affecting the ecosystem, the pollutants found in leachate such as organic compounds, NH_3-N, heavy metals and other contaminants need to be treated and reduced to the minimum [3].

An important factor in determining the effectiveness of leachate treatment is the age of the landfill site. This is because leachate generated during the early stages of the landfill lifecycle is easily treated compared to mature leachate [4]. Biological processes are generally preferred for the treatment of leachate with high biodegradable value of BOD/COD ratio. However, these processes cannot effectively to treat mature leachate, which mainly contains recalcitrant matter and substances such as ammonia [5]. The biodegradation process and its organic content tend to decrease due to the high concentration of ammonia and a landfill stabilizes with the passage of time. With the decreased effectiveness of the biological process, a physicochemical process could be recommended as a more appropriate option for stabilizing landfill leachate [6].

Adsorption is one of the physicochemical processes which is widely employed for the removal of recalcitrant organic compounds from landfill leachate. Basically, adsorption is a mass transfer process in which a substance is transferred from a liquid phase to the surface of a solid and is later bound by physical and chemical interactions. Adsorption using either activated carbon (AC) or other adsorbents such as zeolite, activated alumina or low-cost adsorbents such as limestone, clay and peat has been investigated for the treatment of water, wastewater and leachate. Due to its inherent physical properties, large surface area, microporous structure adsorption capacity

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and surface reactivity, adsorption using AC has been receiving considerable attention recently for the removal of organic and inorganic pollutants from landfill leachate [7]. However, this material is expensive. Therefore, alternative materials are needed as an adsorbent for organic compounds as well as ion substances. The large amount of paper used produces a large amount of waste. About 50-60% of the waste is recycled.

During the manufacture of recycled paper, paper sludge is discharged as industrial waste [8]. In Malaysia, the amount of mill solid waste produced increased from 16,200 tons per day in 2001 to 19,100 tons in 2005, with an average of 0.8 kilogram *per capita* per day. The paper industrial sector in Malaysia produces about 30% of solid waste and this amount is increasing by about 4% annually [9]. The waste is also known as waste paper sludge (WPS). Its disposal through landfills or incineration incurs high cost and could harm the environment.

Besides disposing WPS in landfills, another option is to utilize WPS for other applications as it is an economically viable solution. WPS is generated by the paper industry and varies in composition from mill to mill. It is generally composed of organic fibers (cellulose, hemicellulose and/or lignin), inorganic fillers and coating materials such as kaolinite ($Al_2Si_2O_5(OH)_4$), limestone ($CaCO_3$) and talc ($Mg_3Si_4O_{10}(OH)_2$) [8]. WPS and other organic waste materials from the paper industry could be used as adsorbents due to their high carbon content and cellulose fiber proportion [10].

This study investigates the potential of WPS as an alternative adsorbent to activated carbon (AC) which has become costly due to high demand and limited resources. The aim is to develop an adsorbent material which is made up of the optimum mixture of WPS and AC. In order to achieve the main objective of this research, the optimum mixture for the above-mentioned adsorption materials should be determined based on the optimum removal of COD and NH_3-N from stabilized landfill leachate.

2. Materials and methods

2.1 Leachate sample

The study was conducted on leachate samples from the Simpang Renggam landfill site (SRLS) in Johor. This site is located at latitude 1^{o}53"41.64" North and longitude 103^{o}22"34.68" East in Kluang district, Johor state, Malaysia. The samples were collected and stored according to the Standard Methods for the Examination of Water and Wastewater [11]. Landfill leachate samples were placed into a 30-L polytetrafluoroethylene (PTFE) plastic container, transported to the laboratory and stored in a room at 4 °C prior to use to avoid degradation or changes to its characteristics. A chemical analysis was performed during the next two days [11]. All chemicals used for analytical determination were of analytical grade.

2.2 Adsorbent material preparation

Waste paper sludge (WPS) is a waste product from paper mills. It was obtained from a paper mill located in the east coast of Peninsular Malaysia. WPS and activated carbon (AC) were dried in an oven at 105 °C for 24 hours to expel moisture. The adsorbent materials were then ground to powder form using a ceramic ball mill. The ground adsorbents were sieved to obtain particle sizes ranging between 75–150 μm (passed through sieve No. 100 and retained on sieve No. 200).

2.3 Batch adsorption experiment

Batch adsorption was performed using 4 g of adsorbent and 100 mL of raw leachate or a media concentration of 40 g/L in a 250 ml conical flask. This amount of adsorbent was proposed by a previous researcher [12] and used in this study. The conventional adsorbent (AC) was partially replaced by the alternative adsorbent (WPS). To determine the optimum replacement, different amounts (by weight) and ratios of adsorbents have been examined by several researchers [6, 12] according to the physical characteristics of its density. Batch experiments were conducted at room temperature under the optimum pH of 7, with a shaking speed of 200 rpm and a contact time of 120 minutes [5]. Adsorption isotherm tests were also carried out on the reaction mixture consisting of 100 mL of leachate in varying concentrations. The optimum replacement was determined based on the removal of COD and NH_3-N from landfill leachate (as shown in Table 1).

Table 1 The amount of adsorbents, activated carbon (AC) : waste paper sludge (WPS), used

AC/g	0	0.5	1	1.5	2	2.5	3	3.5	4
WPS/g	4	3.5	3	2.5	2	1.5	1	0.5	0

2.4 Leachate analysis

The COD concentration was examined according to method 5220D (closed reflux, colorimetric method) while the concentration of NH_3-N was examined via the Nessler Method (Method: 8038) which required the use of a DR6000 spectrophotometer (HACH spectrophotometer) with a wavelength of 425nm. All these methods were performed according to the Standard Methods for the Examination of Water and Wastewater [11] and conducted in triplicate to obtain the average removal rate.

3. Results and Discussion

3.1 Characterization of leachate

Table 2 presents the initial characteristics of raw landfill leachate collected from SRLS. The results indicated that SRLS has very high NH_3-N ranging between 1555 mg/L to 2010 mg/L. The average values of BOD_5 and COD were 258.06 mg/L and 2739.06 mg/L respectively, and the ratio of BOD_5/COD of raw leachate was about 0.09. Old or stabilized leachate is usually high in pH (>7.5) and NH_3-N (>400 mg/L) but low in COD (<3000 mg/L) and BOD_5/COD (<0.1) [13].

Table 2 Characteristics of stabilized landfill leachate from Simpang Renggam landfill site (SRLS)

Parameter	Values		
	Minimum	Maximum	Average
pH	8.05	8.32	8.19
SS (mg/L)	143	213	177.22
Ammonia (mg/L)	1555	2010	1765.34
COD (mg/L)	2440	2990	2739.06
BOD_5 (mg/L)	156	379	258.06
BOD_5/COD (ratio)	0.06	0.13	0.09
Fe (mg/L)	6.45	8.94	7.19
Color (Pt-Co)	4061	4748	4548.72

3.2 Optimum mixture (AC:WPS)

The minimum percentage of AC that achieved the highest COD and NH_3-N removal was considered the optimum mixture for the adsorbent (AC:WPS). Fig. 3 showed that the optimum ratio was at 2:2 (50% AC and 50% WPS) with a COD removal of 85.9%. For maximum COD removal, this ratio is taken as the optimum replacement and approximately 50% of AC could be replaced with WPS. For NH_3-N removal, the optimum ratio was 3:1 (75% AC and 25% WPS) where a removal of 49.3% was achieved. For maximum NH_3-N removal, this ratio is taken as the optimum replacement and approximately 25% of AC could be replaced with WPS. Fig. 3 shows that increasing the amount of AC also increased the amount of COD removal as AC is known as the most effective adsorbent for the removal of organic substances [5].

The results indicated that there were two optimum ratios at 2:2 and 3:1 which result in the highest removal for COD and NH_3-N, respectively. However, the optimum mixture of the adsorbent (AC:WPS) was selected at a ratio of 2:2 due to the significant difference in terms of COD (85.9%) and NH_3-N (49.3%) removal. It was suitable for the adsorption of organic substances due to the hydrophobic surface of carbon with pore sizes within the nanometer range or above [14]. Thus, we can hypothesize that only hydrophobic interactions tend to drive organic sorption on the sludge surface. The hydrophobic adsorptive domains of the sludge surface are due to the organic matter present in WPS such as carbohydrates, lignin and tannins which are hydrophobic [15]. In addition, Likon *et al*. [16] reported that WPS has been widely used as an absorbing agent for the cleaning of water surfaces polluted by hydrophobic substances. On the other hand, in terms of NH_3-N removal, AC does not have enough adsorption capacity for ammonia due to its non-polar surfaces which contribute to poor interactions between some of the polar substances [17].

3.3 Adsorption isotherms

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface as in

$$q_e = \frac{QbC_e}{\left(1+bC_e\right)} \tag{1}$$

The Langmuir equation can be described by the linearized form as follows:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QbC_{e'}} \tag{2}$$

Where C_e (mg/L) represents the remaining concentration of adsorbate, while q_e (mg/g) is the amount of adsorption at equilibrium [18]. The maximum adsorption capacity Q (mg/g) and energy of adsorption b (L/mg) are the Langmuir constants, which were determined from the slope and intercept of the plot, respectively. The values are presented in Table 3 and the single-solute adsorption isotherm of NH_3-N and COD by the adsorbent is shown in Figs. 1(a) and 2(a), respectively.

The Freundlich isotherm is a special case for heterogeneous surface energy, in which the energy in the Langmuir equation varies as a function of surface coverage strictly due to variation of the sorption. The Freundlich equation is given as

$$q_e = K_F C_e^{1/n} \tag{3}$$

Where K_F represents an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. A linear form of the Freundlich expression will yield the constants K_f and $1/n$ as in

$$\log q_e = \log K_F + \frac{1}{n}\log C_{e'} \tag{4}$$

Values of K_F and $1/n$ can be determined from the intercept and slope of the linear plot of log q_e vs. log C_e. The values are presented in Table 3 and the Freundlich adsorption isotherms are shown in Figs. 1(b) and 2(b). The magnitude of the exponent $1/n$ gives an indication of the adorability of adsorption. Values of n>1 as shown in Table 3 represent favorable adsorption [19].

As a result, the experimental data for both NH_3-N and COD adsorption indicate that the Langmuir model is better fitted than the Freundlich model due to higher regression and adsorption capacity values as shown in Table 3. Therefore, this finding suggests that the adsorption is better represented by the monolayer coverage of NH_3-N and COD onto the adsorbent.

Table 3 Langmuir and Freundlich isotherm constants for the adsorption of NH_3-N and COD

Adsorbates	Langmuir			Freundlich		
	Q (mg/g)	b (L/mg)	R^2	K_F	n	R^2
Ammonia	21.60	1.21×10^{-3}	0.9876	0.056	1.300	0.9289
COD	32.26	4.25×10^{-3}	0.9901	0.187	1.171	0.9016

*Unit of K_F was $(mg/g)(mg/L)^n$.

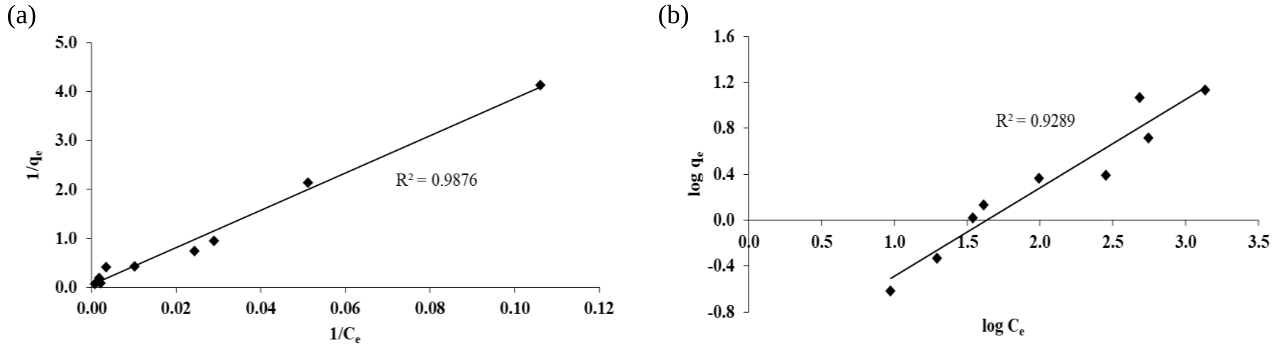

Fig. 1 Adsorption isotherm for ammonia at optimum replacement: (a) Langmuir and (b) Freundlich

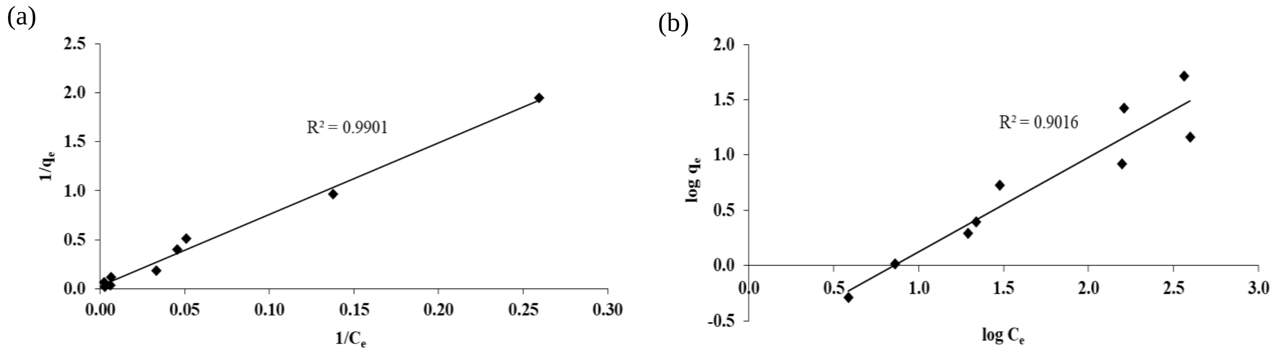

Fig. 2 Adsorption isotherm for COD at optimum replacement: (a) Langmuir and (b) Freundlich

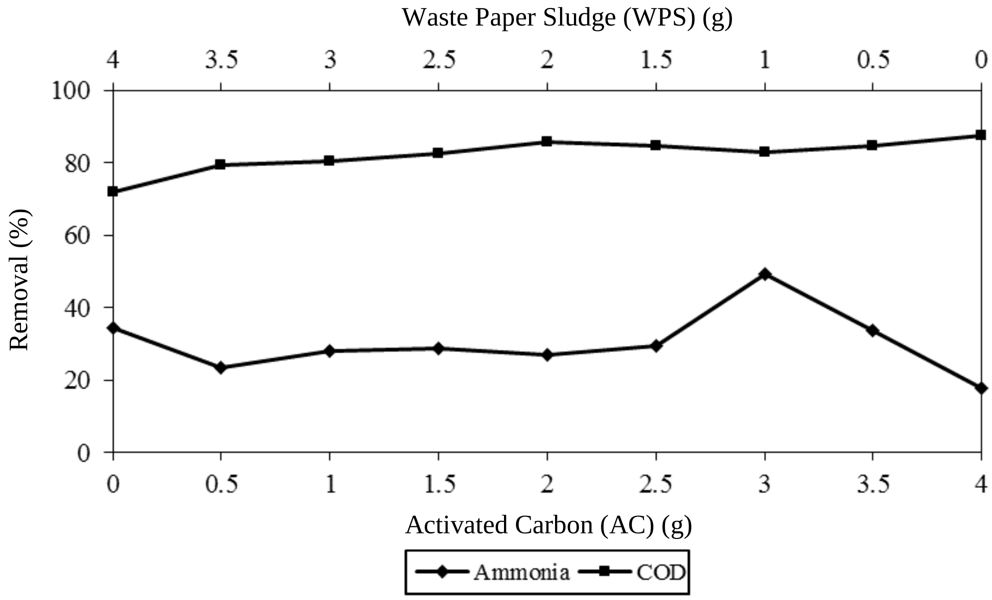

Fig. 3 The optimum mixture ratio between activated carbon (AC) and waste paper sludge (WPS) in a 4-g mixture based on the removal of COD and NH_3-N

4. Summary

To conclude, the final optimum replacement ratio of adsorbents (AC:WPS) in this study was 2:2 as it was more efficient with regards to the sorption of COD (85.9%) and NH_3-N (49.3%) than the 3:1 ratio. WPS performed moderately as an adsorbent material for NH_3-N removal. However, the application of this material has a number of advantages including lower costs and the reduction of solid waste disposals in landfills. The Langmuir and Freundlich isotherm studies proved that this adsorbent showed favourable results for both contaminants from landfill leachate. At the end of this study, it can be concluded that WPS showed potential as an effective adsorbent which may be able to replace conventional adsorbents such as AC. Furthermore, this material appears to be suitable for reducing environmental pollution caused by the presence of NH_3-N and COD in landfill leachate.

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