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A Sustainable Adsorbent for Removal of Ammoniacal Nitrogen from Landfill Leachate: Isotherms Modelling

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Abstract. There is growing concern to determine an alternative adsorbent for remediating landfill leachate effluent with minimal environmental impact and operational cost. In this work, four low cost sustainable biocomposite materials such as limestone, peat, activated carbon and zeolite were employed as an adsorbent media in an adsorption batch study for the removal of ammoniacal nitrogen from landfill leachate. Isotherm adsorption models of Langmuir and Freundlich were utilized to analyze the adsorption data. The Langmuir isotherm model showed the best fit for experimental data with a maximum monolayer adsorption capacity of 26.18 mg/g which is indicated that the ammoniacal nitrogen adsorption took placed on the surface of biocomposite with monolayer formation of the adsorbate at a specific homogeneous site. The adsorption isotherm follows Langmuir's model (R^2 = 0.99) and Freundlich's model (R^2 = 0.98).

INTRODUCTION

Ammoniacal nitrogen is one of the most of the problematic parameters in landfill leachate treatment [1]. The selection of the treatment technology depending on the characteristics and composition of landfill leachate is varying, depending upon its age) can be classified into three types (young, intermediate, and old) listed in Table 1.

Generally, in early stages of landfill leachate treatment is clearly represented by biological treatment when the BOD/COD ratio of the leachate is high [2-3]. This is occurring due to the ratio decreases with the age of the landfill and the process is less effective with time due to the presence of refractory organic matter [4]. A high concentration of ammoniacal nitrogen is often referred to inhibit the biological degradation by the microorganism [5]. The young landfill leachates are usually treated more easily as compared to the old ones [6].

Several techniques have been employed in the removal of landfill leachate. These techniques include: membrane technology, coagulation, precipitation, ion-exchange and ozonation [2,7]. Among various leachate treatment approaches, the physico-chemical processes by using an adsorption is the most successful and cost effective for the stabilized landfill leachate. Adsorption can be performed either as batch adsorption or as a column adsorption analysis. Some research has been reported on develop low-cost composite materials to improve the surface of adsorbents that have the ability to interact with either polar or non-polar adsorbates [8]. Gao and co-workers [9] found new composite materials of zeolite–carbon (Z–C), which combines the excellent properties of zeolites and carbon. The surface of zeolite is hydrophilic with regular aligned molecular level pores and cationic exchange ability, which makes it a good adsorbent for metallic ions and catalysts [10]. Zeolite is widely used as a natural ion exchanger to remove ammonia and other inorganic pollutants from leachate or another wastewater [5].

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TABLE 1. The composition of leachate based on age [2].

Parameters	Young	Intermediate	Old
Age (years)	<5	5-10	>10
pH	<6.5	6.5-7.5	>7.5
COD (mg/L)	>10,000	4,000-10,000	<4,000
BOD_5/COD	>0.3	0.1-0.3	<0.1
Biodegrability	High	Medium	Low
NH_3-N (mg/L)	<400	-	>400
Organic composition	VFA (80%)	VFA (5–30%), humic and fulvic acid	Humic and fulvic acid
Heavy metals	Low-medium	Low	Low

The other adsorbents such as clay and zeolite [11], limestone [12], peat [13] and carbon-zeolite composite can be used as ammonia removal in wastewater. Furthermore, activated carbon is one of the most widely used as an alternative to biological and physico-chemical methods in wastewater treatment due to their good adsorptive ability [14]. The main advantage of activated carbon is that the unique and versatile adsorbents due to their extended surface area, micro-porous structure, high adsorption capacity and high degree of surface reactivity [15].

Development of a sustainable biocomposite adsorbent media based on combining zeolite, activated carbon and low-cost materials such as limestone, peat and ordinary Portland Cement in this work is a novel direction. Adsorption equilibrium experiments were used to investigate the adsorption behaviour of biocomposite adsorbent media. The adsorption isotherm modelling was studied by fitting the equilibrium data into different types of isotherm (Langmuir and Freundlich) models.

Materials and Method

Biocomposite Adsorbent Preparation and Influent

In this study, the fabrication of a new sustainable adsorbent was based on recent studies [12,13-15]. This adsorbent comprises 8.28% of zeolite, 13.43% of limestone, 16.67% of activated carbon, 13.33% peat and 40% of Ordinary Portland Cement (OPC). The OPC was mainly used as a binder. All the materials with particle sizes of less than 150 μm were ground and then mixed together with OPC. The water was added about 60% (by weight) and the mixture paste was allowed to harden for 24 h and then immersed in water for three days for curing. This biocomposite adsorbent was then crushed and sieved to a working size range of 2.36–3.55 mm. The physico-chemical properties of the biocomposite adsorbent are listed in Table 2.

TABLE 2. Physico-chemical characteristics of biocomposite adsorption.

Physico-chemical properties of bio-composite media	
Specific gravity (g/cm^3)	2.11
BET Surface area (m^2/g)	105.96
Porosity (%)	59.04
Water Absorption (%)	52.77
Methylene blue number (mg/g)	8.62
Iodine number (mg/g)	23.94
Cation exchange capacity, CEC (meq/g)	0.69

Leachate used in this study was obtained from Simpang Renggam Landfill Site (SRLS), previously described by the authors [16]. SRLS samples were collected in March 2014 until March 2016 and stored at 4°C prior to use [17]. All chemicals used for the analytical determinations were of analytical grade. The characteristics of the leachate from the SRLS are listed in Table 3. The leachate is considered stable because its pH exceeds 5 and the BOD_5:COD ratio is very small (<0.1) [2].

TABLE 3. Characteristic of raw leachate prior to treatment.

	Range	Average
pH	8.05-8.68	8.25
Suspended solids (mg/L)	131-213	161.45
Ammoniacal nitrogen (mg/L)	1530-2130	1836.48
COD (mg/L)	2440-2990	2752.25
BOD_5 (mg/L)	144-330	227.04
BOD_5/COD	0.05-0.12	0.08
Fe (mg/L)	4.12-8.94	6.32
Color (mg/L)	4061-4788	4500.09

Adsorption Isotherm

Adsorption isotherm was carried out using an experiment of dosage study that is by varying the amount of adsorbents. With the optimum conditions of pH 7, 200 rpm of agitation speed and 120 mins of contact time, 100 mL of adsorbates mixed with varying the dosages: 3, 5, 8, 12, 17, 23, 30, 38, 47, and 57 g at ambient temperature. The Langmuir and Freundlich models were used to analyze the experimental data for the adsorption isotherm [16]. The supposition of the Langmuir isotherm is based on sorption occurring at specific homogeneous sites of adsorbent heat (as adsorption for all sites is constant); however, the Freundlich isotherm is assumed to be a heterogeneous surface (multilayer adsorption) with a nonequal distribution of adsorption heat over the surface [18, 19].

The Langmuir and Freundlich equations with linear plotted can be written as shown below:

Langmuir model:

$$1/q_e = 1/q_m + [1/(K_L q_m C_e)] \tag{1}$$

Freundlich model

$$\log q_e = \log K_F + [1/n (\log C_e)] \tag{2}$$

Where q_e is the adsorption capacity at equilibrium on the adsorbent (mg/g) and C_e is the equilibrium concentration (mg/l); the other parameters are constants of different isotherms, which were determined based on the experimental data.

RESULTS AND DISCUSSIONS

Adsorption Isotherm Modelling

The results for single-solute adsorption isotherm of ammoniacal nitrogen by the biocomposite media is described in Figures 1 and 2, respectively. The parameters of these models with correlation coefficient R^2 were presented in Table 4 that is determined from the slope and intercept of the plot, respectively. The results show that the Langmuir and Freundlich models accurately describe the adsorption of ammoniacal nitrogen, with R^2 values larger than 0.98 for all models, but the Langmuir model coincides with the experimental data better than the Freundlich model with R^2 = 0.99. In addition, the *n* constant for the Freundlich isotherm measures exchange intensity or surface heterogeneity and also indicates the ease of adsorption when $n > 1$.

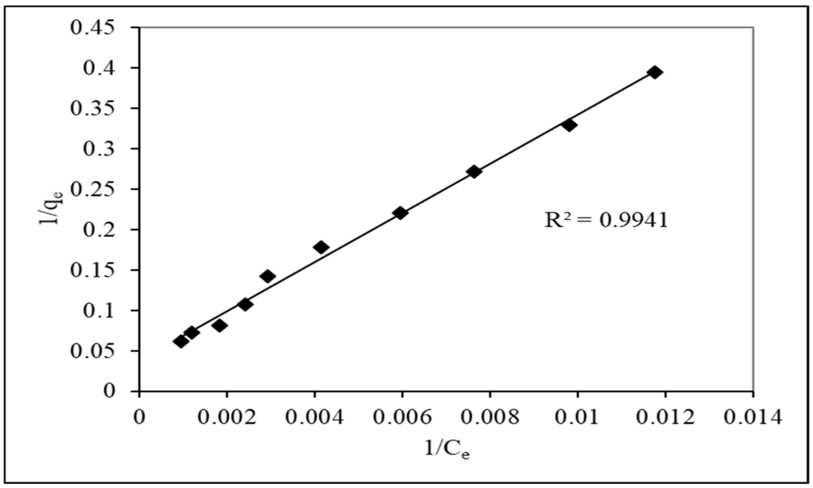

FIGURE 1. Fitting curve of Langmuir adsorption isotherm for ammoniacal nitrogen onto biocomposite media at optimum condition.

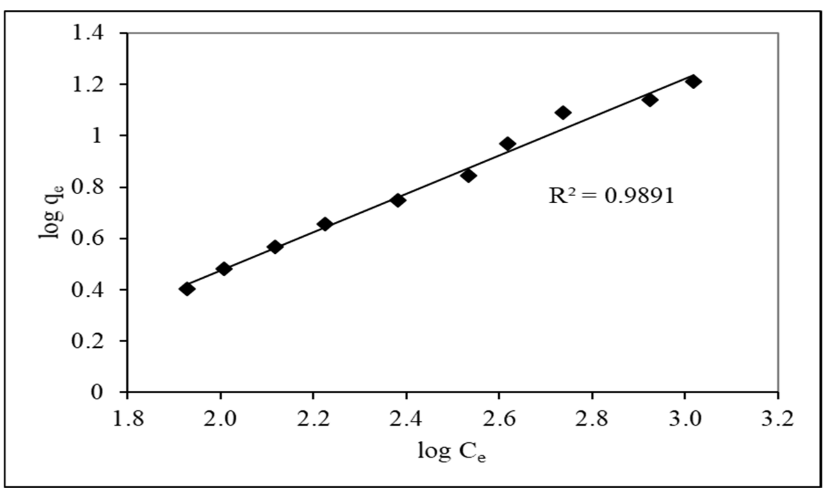

FIGURE 2. Fitting curve of Freundlich adsorption isotherm for ammoniacal nitrogen onto biocomposite media at optimum condition.

TABLE 4. Isothermal parameters for the Langmuir and Freundlich models of adsorbent ammoniacal nitrogen onto biocomposite media.

	Langmuir			Freundlich		
	K_L (L/mg)	q_m (mg/g)	R^2	K_f	n	R^2
Biocomposite media	1.26×10^{-3}	26.18	0.9941	0.0956	1.338	0.9891

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

The essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor or equilibrium parameter (R_L), as defined by [20];

$$R_L = 1/(1 + K_L C_o) \quad (3)$$

Where K_L is the Langmuir constant C_o is the initial concentration of adsorbate. The value of R_L indicates whether the type of Langmuir isotherm is irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavourable ($R_L > 1$). The value of $R_L = 0.3420$ was in range of $0 < R_L < 1$, indicating that the adsorption of ammoniacal nitrogen was favourable for this study.

The Langmuir model was better fitted to the experimental data than the Freundlich isotherm model for ammoniacal nitrogen adsorption as indicated by the higher R^2 values as shown in Table 3. This finding suggested that the adsorption conditions fit with the Langmuir model by the monolayer coverage of ammonia onto the biocomposite adsorbent.

CONCLUSIONS

The isotherm models were developed to determine the adsorption data of ammoniacal nitrogen onto biocomposite media. It was found that the isothermal data coincided with Langmuir's model, which achieved ($R^2 = 0.99$) and Freundlich's model ($R^2 = 0.98$). This mean that theoretically suggest that the ammoniacal nitrogen is removed by monolayer adsorption process. The present study shows that the biocomposite adsorbent media prepared from limestone, peat, activated carbon and zeolite has proved to be effective for the adsorptive uptake of ammoniacal nitrogen from stabilized leachate. Future work would attempt to involve the kinetic study mechanism.

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