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Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment

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ABSTRACT

Chemical oxygen demand (COD) and ammoniacal nitrogen have always been the crucially problematic parameters in landfill leachate treatment. This study was conducted to investigate the adsorption properties of ammoniacal nitrogen and COD in semi-aerobic leachate from the Pulau Burung landfill site on zeolite, activated carbon and a new composite media in terms of adsorption isotherm and kinetic. The results show that all adsorbents fitted well with both Langmuir and Freundlich isotherms (R^2>0.9) for ammonia adsorption. A comparison study indicated that the adsorption capacity of composite adsorbent towards ammoniacal nitrogen was higher than zeolite and activated carbon and comparable to activated carbon for COD. Findings from a kinetic study indicated that the adsorption of ammonia on new composite adsorbent and zeolite follow almost all kinetic models such as pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion model, although pseudo-second-order was the most dominant. COD adsorption fitted well with the pseudo-second-order kinetic model, while activated carbon obeys the pseudo-first-order and intra-particle models.

1. Introduction

Organic contaminant and ammoniacal nitrogen are two of the problematic parameters in landfill leachate treatment. Biological treatment of landfill leachates have been shown to be very effective in removing organic matter in early stages [1] when the BOD/COD ratio of the leachate is high. This ratio decreases with the age of the landfill [2] and the process is less effective with time [3] due to the presence of refractory organic matter. A high concentration of ammoniacal nitrogen is also known to inhibit the biological degradation by the micro organism [4,5]. Young landfill leachates are usually treated more easily as compared to the old ones [6]. As a landfill stabilizes with the passage of time, the biodegradable organic content of the leachate tends to decrease, and consequently, the effectiveness of the biological process decreases and physico-chemical processes may become one of the appropriate options. The common features of stabilized leachate are high strengths of ammoniacal nitrogen (3000–5000 mg/L) and moderately high strengths of COD (5000–20,000 mg/L), as well as a low ratio of BOD/COD (less than 0.1) [7].

One of the physico-chemical processes is adsorption using either activated carbon or other adsorbents such as zeolite, activated alumina or low cost adsorbents such as limestone, rice husk ash and peat. Activated carbon provides an attachment surface for micro-organisms to bioregenerate the activated carbon [8]. Combinations of organic and inorganic pollutants that exist in landfill leachate need adsorbents which have the ability to remove a variety of pollutants including organic and inorganic species. It is well known that activated carbons are the most effective adsorbents for the removal of organic pollutants from the aqueous or gaseous phase. Therefore, this type of adsorbent is widely applied as a commercial adsorbent in the purification of water and air [9,10]. Zeolite is widely used as a natural ion exchanger to remove ammonia and other inorganic pollutants from leachate or other wastewater.

However, general activated carbon does not have enough adsorption capacity for ammonia because it usually possesses a non-polar surface due to manufacturing conditions at high temperatures, which is a disadvantage for some applications because of poor interaction with some polar adsorbates [11]. This is the reason that much research has been focused on modifying the AC surfaces or to produce composite adsorbent that have the ability to interact with either polar or non-polar adsorbates.

Gao and co-workers found new composite materials of zeolite–carbon (Z–C), which combines the excellent properties of zeolites and carbon [12]. 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 [13]. On the other hand, the surface of carbon is hydrophobic with pore sizes in the nanometer

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range or above which makes it more suitable for the adsorption of organic substances [14].

A new composite adsorbent media was produced previously by combining activated carbon, zeolite and low cost materials such as limestone, rice husk carbon waste and ordinary Portland cement. The latest was used as a binder [15]. The purpose of this study is to compare the adsorption properties of new composite adsorbents, zeolite and activated carbon in terms of ammonia, COD, color and iron removal.

2. Materials and methods

2.1. Composite adsorbent preparation

The development of a new adsorbent using coconut shell activated carbon (surface area, 1240 m^2/g), zeolite (mordenite, $Na_8Al_8Si_{40}O_{96}$•24-H_20 with cation exchange capacity of 0.31 meq/g), limestone and rice husk carbon as composite materials was based on previously reported findings [15]. This adsorbent contains 45.94% zeolite, 15.31% limestone, 4.38% activated carbon and rice husk carbon respectively, and 30% of ordinary Portland cement (OPC) which was used as a binder. All the materials were ground to obtain particle sizes of less than 150 µm and then mixed together with OPC. About 60% (by weight) of water was added and the mixture paste was allowed to harden for 24 h and then submersed in water for three days for curing. This composite adsorbent was crushed and sieved to a working size of 1.18 mm–2.36 mm. The physico-chemical properties of the composite adsorbent are listed in Table 1.

2.2. Semi-aerobic landfill leachate

Leachate sample was collected from the Pulau Burung Landfill Site (PBLS) which is situated within Byram Forest Reserve at 5° 24′ N, 100° 24′ E in Penang, Malaysia. The total area of the landfill is 23.7 ha and it is equipped with a leachate collection pond but does not have other treatments. This site has a natural marine clay liner. PBLS has a semi-aerobic system and it is one of only three sites of its kind found in Malaysia. PBSL has been developed semi-aerobically into a Level II sanitary landfill by the establishment of a controlled tipping technique in 1991. It was upgraded to a Level III sanitary landfill by employing controlled tipping with leachate recirculation in 2001. This site receives 1500 t of solid waste daily [16].

Samples were collected from the active detention pond with a leachate age of less than 5 years. The sample was filled into a 30-L plastic container, transported to the laboratory and stored at 4 °C. Chemical analysis was performed for the following two days, according to Standard Methods for the Examination of Water & Wastewater [17]. All chemicals used for the analytical determinations were of analytical grade. The characteristics of the leachate from the semi-aerobic landfill site (Pulau Burung, Penang, Malaysia) are listed in Table 2 [18]. The leachate is considered stable because its pH exceeds 5 and the BOD_5–COD ratio is very small (<0.1) [19].

2.3. Batch adsorption experiments

To maximize removal by the adsorbent, batch experiments were conducted at ambient temperature using the optimum conditions of all pertinent factors, such as dose, pH, agitation speed, and contact time. Subsequent adsorption experiments were carried out with only optimized parameters. The optimum conditions for the adsorption batch study taken from the previous study are pH 7, 200 rpm of shaking speed and 105 min of contact time [15,18,20]. A similar pH range was reported for ammonia removal in other batch adsorption studies [21]. All of the ammonia present was expected to be in ionic form and available for ion exchange. Adsorption isotherm tests were also carried out in the reaction mixture consisting of 100 ml of leachate solution with varying adsorbent weight. Ammoniacal nitrogen and COD was determined using the Nesslerization method and closed reflux colorimetric method respectively [17].

Table 1
Physico-chemical characteristics of composite adsorption media.

Physico-chemical properties of composite media	
Specific gravity (g/cm^3)	2.80
BET Surface area (m^2/g)	60.94
Porosity (%)	55.76
Water absorption (%)	52.48
Methylene blue number (mg/g)	6.33
Iodine number (mg/g)	16.92
Cation exchange capacity, CEC (meq/g)	0.9204

Table 2
Semi-aerobic landfill leachate characteristics [18].

	Range	Average
pH	8.09–8.66	8.29
Suspended solids (mg/L)	124–190	165.57
Ammoniacal nitrogen (mg/L)	1010–2740	1890.95
COD (mg/L)	1478–3540	2338.29
BOD_5 (mg/L)	160–345	227.58
BOD_5/COD	0.06–0.15	0.09
Fe (mg/L)	2.94–7.30	5.41
Color (mg/L)	3773–5100	4527.36

3. Results and discussion

3.1. Adsorption equilibrium

Adsorption isotherms are essential for the description of how adsorbate concentration will interact with adsorbent media and are useful to optimize the use of media as adsorbents. Therefore, empirical equations (Langmuir and Freundlich isotherm model) are important for adsorption data interpretation and predications. Both Freundlich and Langmuir models were used for the evaluation of experimental results. The Langmuir model assumes only one solute molecule per site, and also assumes a fixed number of sites. The Langmuir isotherm relates q_e (mg of adsorbate adsorbed per gram of adsorbent media) and C_e (the equilibrium adsorbate concentration in solution) as shown in Eq. (1) as

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

where coefficient Q represents the maximum adsorption capacity in mg/g and b is the Langmuir constant in L/mg. The constants in the Langmuir isotherm can be determined by plotting $1/q_e$ versus $1/C_e$, where the equation can be rewritten in the linear form;

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QbC_e}. \tag{2}$$

Freundlich isotherm assumes that the uptakes of adsorbate occur on a heterogeneous surface by multilayer adsorption and the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The Freundlich equation is given as

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

where K_F is, roughly, 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 $1/n$.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$