

Adsorption of Ammonia on Municipal Solid Waste Incinerator Bottom Ash Under the Landfill Circumstance

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Abstract – The adsorption characteristics of ammonia on MSWI bottom ash were investigated. The effect of the variation of the landfill environmental parameters including pH, anions and organic matter on the adsorption process was discussed. Results showed that the adsorption could be well described by pseudo-second-order kinetics and Langmuir model, with a maximum adsorption capacity of 156.2 mg/g. The optimum adsorption of ammonia was observed when the pH was 6.0. High level of ion and organic matter could restrict the adsorption to a low level. The above results suggested that MSWI bottom ash could affect the migration of ammonia in the landfill, which is related to the variation of the landfill circumstance.

Key words: Adsorption, Ammonia, MSWI Bottom Ash, Landfill

1. Introduction

Incineration, due to the primary advantages of hygienic control, volume reduction, mass reduction and energy recovery, has become an attractive way for municipal solid waste (MSW) treatment in China [1]. Till 2013, there were a total 138 MSW incinerators (MSWI) in China, with a treatment capacity of 122,649 t/d [2]. Because of the incineration process, a large volume of MSWI bottom ash is produced [3]. Nowadays, MSWI bottom ash is either reused as a secondary construction material or disposed in landfills with MSW [4]. In many countries and areas, such as China, Japan and Taiwan, MSWI bottom ash is allowed to be disposed in the MSW landfill site [5-7]. Moreover, large amounts of MSWI bottom ash have been used as the liner, protection layer and leachate drainage layer instead of natural minerals (e.g., gravel, sand, till, and clay) [8-10].

MSWI bottom ash has high porosity and large surface area. It also contains several hydr (oxide) minerals (e.g., aluminum (hydr)-oxides, iron (hydr)-oxides) and layered double hydroxides (e.g., Friedel's salt), which have great adsorption ability [11-14]. Several researchers have used MSWI bottom ash as the adsorbent towards heavy metals, dyes, organic matter and sulfur compounds [15-18]. On the other hand, due to the lack of the nitrogen degradation pathway in the anaerobic system, nitrogen pollution is a long-term problem in landfills. According to our previous research, the level of ammonia in the leachate ranged from 159 to 2298 mg/L (see Fig. S1). A high level of ammonia released from the landfill can cause the eutrophication of waters. When MSWI bottom ash is disposed or reused in the landfill, the ammonia in the leach-

ate might be adsorbed by the bottom ash. Therefore, the migration and release of the ammonia can be changed. Several researches have investigated the environmental impact of the disposal or reuse of MSWI bottom ash in the landfill. However, to our knowledge to date, most of these researches focus on the metal pollution. Few studies have been done to investigate the effect of MSWI bottom ash on the migration of ammonia in the landfill.

In this work, the adsorption characteristics of ammonia on MSWI bottom ash were investigated by batch experiments. The kinetics and isotherms of the adsorption were investigated. The effects of the variation of environmental parameters, such as the pH and ion competition, on the adsorption were also examined. We aim to provide insights into the effect of MSWI bottom ash on the migration of ammonia when it was disposed or reused in the landfill.

2. Materials and Methods

2-1. MSWI bottom ash sampling

Bottom ash from MSWI incinerator was taken from the Green Energy MSWI plant in Zhejiang province, East China. The plant consists of three parallel incinerator stokers with an MSW treatment capacity of 650 t/d. The source MSW was collected from several residential areas of Hangzhou without any industrial solid waste. The operating temperature of the incinerators was 850-1,100 °C, and the residence time of waste in the incinerator was about 50 min. Bottom ash underwent water quenching and magnetic separation before it was sampled. The sampling period lasted for 5 days. Approximately 25 kg fresh bottom ash sample was taken daily from the plant. A total 125 kg bottom ash sample was obtained. Then, the bottom ash sample was mingled and homogenized. Subsequently, an approximate 25 kg of the MSWI bottom ash was oven-dried and ground into less than 154 µm by the grinder for bulk composition analysis and adsorption test.

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2-2. Characterization

The content of individual elements in the MSWI bottom ash sample was analyzed after it was digested according to the method of Yamasaki [19]. 0.5 g air dried sample was weighed into a Teflon beaker. 2.5 mL HNO₃ and 2.5 mL HClO₄ were added and heated on the hot plate at 150 °C for 2~3 h. After cooling, 2.5 mL HClO₄ and 5 mL HF were added and heated at 150 °C for 15 min, and then 5 mL HF was added until the residue became almost dry. The residue was dissolved in 5 mL HNO₃ and diluted to 100 mL. The elemental concentrations in the solution were determined by ICP-OES (Thermo Electron Corporation IRIS/AP, USA). The samples were digested and analyzed in triplicate. The ammonia content of MSWI bottom ash was also determined according to the Chinese standard HJ 634-2012. The mineralogy of the bottom ash samples was investigated by XRD (Rigaku D/max-r B, Japan).

2-3. Batch adsorption studies

Batch adsorption experiments were conducted and equilibrated by using a model KYC-1102 air-temperature-controlled shaker (Ningbo Jiangnan Instrument Factory, China) at 100 rpm. The solution was then continually flushed with N₂ to avoid contact with the atmosphere. Batch experiments were conducted in triplicate to ensure the accuracy of the obtained data.

According to our previous research, the level of ammonia in landfill leachate ranged from 159 to 2298 mg/L (see Fig. S1). Therefore, the initial concentration of ammonia used in this study was 2000 mg/L.

The adsorption kinetics process of ammonia on MSWI bottom ash was studied by adding 100 mL ammonia solution (2000 mg/L) and 2.0 g MSWI bottom ash to a 100 mL beaker for the contact time ranging from 5 to 250 min at 25 °C.

Isotherm studies were conducted with a constant MSWI bottom ash dosage (2.0 g) and 100 mL ammonia solution with the initial concentrations varying from 50 to 3000 mg/L. The mixture was equilibrated at 25 °C for 160 min.

The effect of pH on the adsorption was conducted at the range from 5.0 to 10.0, which corresponded to the variation of leachate pH [20]. 100 mL ammonia solution (2000 mg/L) and 2.0 g MSWI bottom ash were added and equilibrated at the desired temperature for 160 min.

The coexisting ions, such as Na⁺, Mg²⁺ and Fe³⁺, were imposed to explore their impacts on the adsorption. The concentration of Na⁺, Mg²⁺ and Fe³⁺ ranged from 500 to 3000 mg/L, 100 to 1000 mg/L and 100 to 1000 mg/L, respectively, which were set according to the previous literature report [21]. The mixture was equilibrated at 25 °C for 160 min.

Acetic acid and toluene were imposed to investigate the effect of organic matter on the adsorption, respectively. The concentration of the acetic acid ranged from 8000 to 40000 mg/L, which corresponded to the variation of COD in the leachate (see Fig. S2, 1.0 g acetic acid equal to 1.06 g COD). The concentration of the toluene ranged 1.0 to 12.0 mg/L, which was set according to the previous study [22]. The mixture was equilibrated at 25 °C for 160 min.

After the adsorption, the samples were centrifuged and the ammonia concentration in supernatant was determined immediately.

The amount of ammonia absorbed on MSWI bottom ash (q_t) and the removal percentage of nitrite ($\eta\%$) were calculated according to Eqs.

(1) and (2), respectively.

$$q_t = (C_0 - C_t) \times V/m \quad (1)$$

$$\eta\% = (C_0 - C_t) \times 100/C_0 \quad (2)$$

where C_0 and C_t are initial and instantaneous concentrations of ammonia (mg/L), respectively; V is the volume of the solution (L) and m is the mass of MSWI bottom ash.

3. Results and Discussion

3-1. Characterization of MSWI bottom ash

The bulk chemical composition of MSWI bottom ash is exhibited in Table 1. The result shows Si was the major element, which accounted for more than 20%. High levels were found for Ca, Al and Fe, whose content exceeded 20,000 mg/kg. Moreover, the content of Na, K and Mg was above 5,000 mg/L. As MSWI bottom ash was a high temperature product under the oxygen-enriched circumstance, CaO, Al₂O₃ and Fe₂O₃ might largely exist in it, which might be transformed into Ca(OH)₂, Al(OH)₃ and Fe(OH)₃ after the water quench treatment. And due to the complicated composition of MSWI bottom ash, the presence of some secondary minerals, such as the aluminosilicate and calcium aluminum compounds, was expected. Note that no ammonia was observed in MSWI bottom ash, as most of the nitrogen was transformed to the nitrogen oxides under the oxygen-enriched circumstance.

To further explore the mineral composition, the XRD pattern of

Table 1. Bulk chemical composition of the MSWI bottom ash sample

Element	Content (mg/kg dry ash)
Al	40,920±1,600
Si	223,600±4,657
Na	9,040±178
K	15,792±167
Mg	5,997±115
Ca	69,413±2,613
Fe	26,008±28
Mn	1,246±231

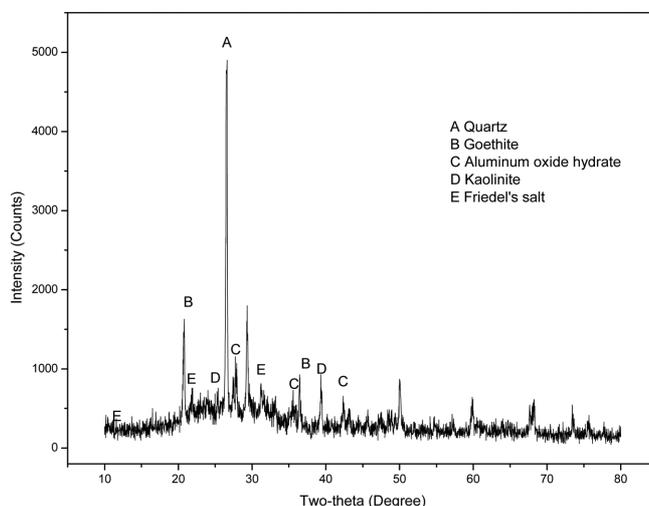


Fig. 1. XRD pattern of the MSWI bottom ash sample.

MSWI bottom ash was investigated (Fig. 1). The result confirmed the existence of quartz (SiO_2), goethite ($\text{FeO}(\text{OH})$) and aluminum oxide hydrate ($(\text{Al}_2\text{O}_3)_3\text{H}_2\text{O}$). Among the minerals, goethite and aluminum oxide hydrate were reported to have a certain adsorption capacity for various pollutants [23,24]. Kaolinite ($\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$) and Friedel's salt ($\text{Ca}_2\text{Al}(\text{OH})_6(\text{H}_2\text{O})_2$) were also observed. Kaolinite is a 1:1 phyllosilicate comprised of neutral layers containing an octahedral sheet of aluminum hydroxide bound to a tetrahedral sheet of silicon oxide through a plane of shared O atoms. It has a great adsorption capacity for ions [25]. Friedel's salt is a layer double hydroxide consisting of cationic brucite layers and interlayer anion. It is also reported to have great adsorption capacity due to its high specific area and ion exchange capacity [26]. The presence of these minerals suggested that MSWI bottom ash might have the adsorption capacity for the ammonium ion.

3-2. Adsorption of ammonia on MSWI bottom ash

3-2.1. Adsorption kinetics

The time-adsorption profile of the ammonia on MSWI bottom ash is shown in Fig. 2. The adsorption was rapid during the first 30 min, when 42.2% of the ammonia removal percentage was observed. Afterwards, the removal percentage showed a gradual increase. About 63.0% of the ammonia removal percentage was achieved at 100 min. The equilibrium was established after 160 min, when 65.6% of the removal percentage was reached.

Kinetic parameters are helpful for the prediction of adsorption rate, which gives important information for the efficiency of adsorption. To analyze the adsorption rate of the ammonia on MSWI bottom ash, three kinetic models including the Lagergren-first-order model (Eq. (3)), pseudo-second-order kinetic model (Eq. (4)) and intra-particle mass transfer diffusion model (Eq. (5)) were used to understand the dynamics of the adsorption process.

The Lagergren-first-order model is expressed as:

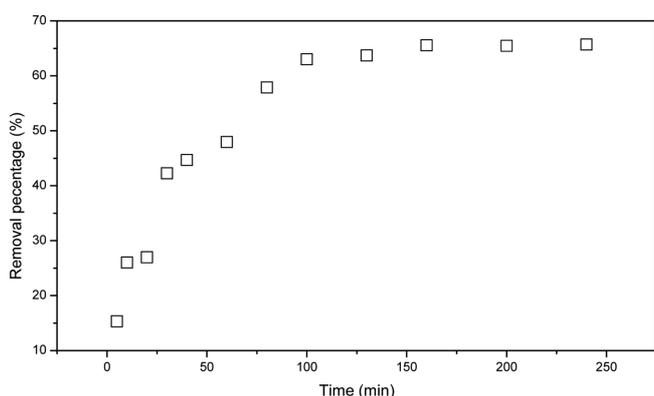


Fig. 2. Ammonia removal percentage as a function of shaking time (conditions: $V=100$ mL; ammonia concentration=2000 mg/L; MSWI bottom ash dosage=2.0 g; $T=298$ K).

Table 2. Kinetic parameters of ammonia adsorption on MSWI bottom ash

Lagergren-first-order			Pseudo-second-order			Intra particle diffusion		
q_e (mg/g)	k_1	R^2	q_e (mg/g)	$k_2 \times 10^4$	R^2	k_{id}	c	R^2
137.626	0.0311	0.925	146.627	2.929	0.994	7.710	35.852	0.861

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

where q_e and q_t are the amount of nitrite adsorbed (mg/g) on the adsorbents at the equilibrium and at time t , respectively; k_1 is the rate constant of adsorption (L/min). Values of k_1 are calculated from the plots of $\log(q_e - q_t)$ versus t .

The pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_2 is the rate constant of the pseudo-second-order adsorption (g/mg min). Values of k_2 are obtained from plotting (t/q_t) versus t .

The intra-particle mass transfer diffusion model is expressed as:

$$q_t = k_{id} t^{1/2} + c \quad (5)$$

where c is the intercept (mg/g) and k_{id} is the intra-particle diffusion rate constant (mg/g min^{1/2}), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$.

The kinetic parameters (k_1 , k_2 , k_{id} , q_e , c) and correlation coefficients (R^2) are summarized in Table 2. Compared with the Lagergren-first-order model and intra-particle mass transfer diffusion model, the value of the correlation coefficient (R^2) of the pseudo-second-order kinetic model was closer to 1.0, which shows that the pseudo-second-order kinetic model was more suitable to describe the adsorption process of the ammonia on MSWI bottom ash.

3-2-2. Adsorption isotherms

The adsorption isotherms provide a relationship between the solute concentration in the solution and the amount of ammonia adsorbed on the solid phase when the two phases are at equilibrium. The adsorption data were fitted by two common adsorption models: Langmuir and Freundlich [27-29]. The Langmuir (Eq. (6)) and Freundlich (Eq. (7)) models are represented by the following equations:

$$q_e = \frac{b q^0 C_e}{1 + b C_e} \quad (6)$$

$$q_e = K_F C_e^{1/n} \quad (7)$$

where C_e is the equilibrium concentration (mg/L); q^0 is the maximum amount of the ammonia ion per unit weight of MSWI bottom ash (mg/g); q_e is the amount adsorbed per unit mass of adsorbent, and b is the binding energy constant (L/mg). For the Freundlich model, n is the heterogeneity factor and K_F is the Freundlich constant (L/mg).

The results of the experimental data fitted to the equations and the parameters are shown in Fig. 3 and Table 3. The correlation coefficients (R^2) of Freundlich and Langmuir were 0.965 and 0.994, respectively. This result indicated the Langmuir model was more suitable to

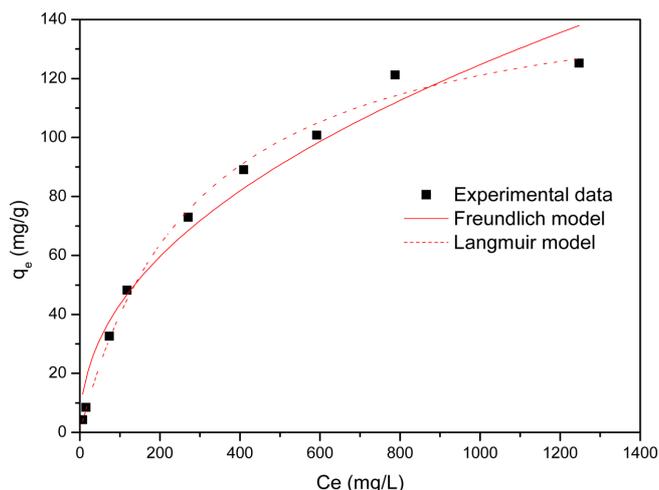


Fig. 3. Isotherm for adsorption of ammonia on MSWI bottom ash (conditions: $V=100$ mL; MSWI bottom ash dosage=2.0 g; $T=298$ K).

Table 3. Langmuir and Freundlich isotherm parameters and correlation coefficients for the adsorption of ammonia on MSWI bottom ash at 298 K

Freundlich model constants			Langmuir model constants		
K_F (L/mg)	n	R^2	q^0 (mg/g)	b (L/mg)	R^2
5.242	2.180	0.965	156.2	0.00344	0.994

describe the adsorption compared with the Freundlich model. According to the model result, the adsorption capacity of ammonia on MSWI bottom ash was 156.2 mg/g. The high adsorption capacity indicated that the migration of ammonia in the landfill could be alternated by MSWI bottom ash.

3-2-3. Effect of pH on the adsorption

As shown in Fig. 4, the adsorption of ammonia on MSWI bottom ash depended on the pH. The removal percentage shows a slight increase when the pH increased from 4.0 to 6.0. This might be because the increase of pH could decrease the concentration of H^+ , which could

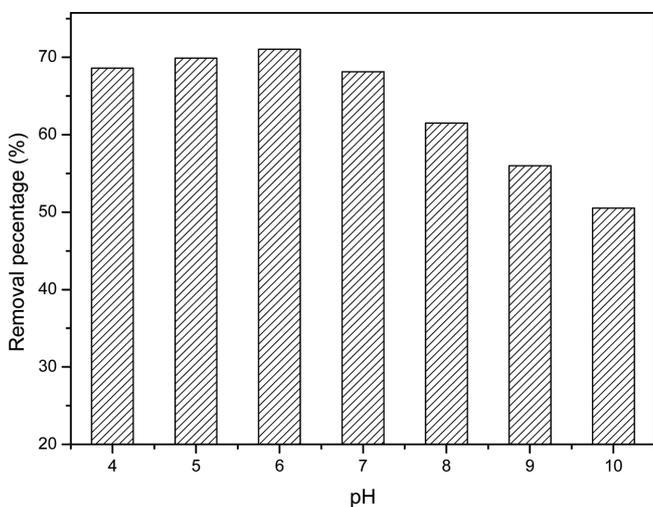


Fig. 4. Effect of pH on the ammonia adsorption on MSWI bottom ash.

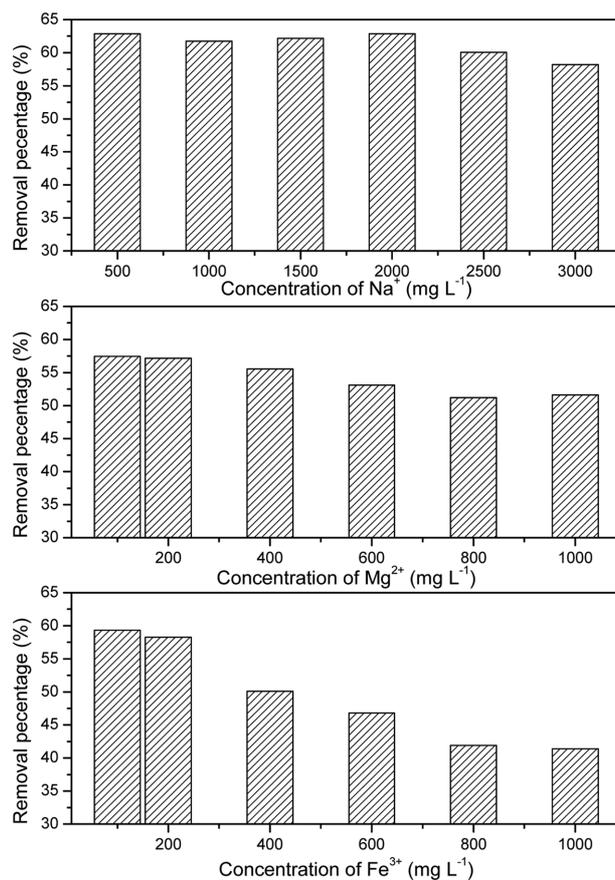


Fig. 5. Effect of Na^+ , Mg^{2+} and Fe^{3+} on the ammonia adsorption on MSWI bottom ash.

compete for the active adsorption sites with NH_4^+ . The removal percentage showed a reduction when the pH increased from 6.0 to 10.0. The further increase of pH might result in the precipitation of the metals in MSWI bottom ash, which might occupy the active adsorption sites and reduce the adsorption capacity of MSWI bottom ash.

3-2-4. Effect of coexisting anions on the adsorption

Landfill leachate contains various ions which may affect the adsorption process. In this study, the effect of Na^+ , Mg^{2+} and Fe^{3+} on the adsorption of ammonia on MSWI bottom ash was investigated. The result showed the presence of Na^+ , Mg^{2+} and Fe^{3+} could restrict the adsorption (Fig. 5). The presence of 3000 mg/L of Na^+ , 1000 mg/L of Mg^{2+} and 1000 mg/L of Fe^{3+} decreased the ammonia percentage removal from 65.6% to 58.2%, 51.6% and 41.4%, respectively.

3-2-5. Effect of the organic matter on the adsorption

Landfill leachate contains high level of organic matter. The high level of the organic matter might affect the ammonia adsorption on MSWI bottom ash. In this study, the acetic acid and toluene were selected to represent the polar and nonpolar organic matter, respectively [22]. Due to the increase of the acetic acid, the pH of the solution decreased from 10.7 to 6.8, which could increase the removal percentage of ammonia according to the result of the pH study. However, the removal percentage of ammonia decreased sharply from 65.6% to 10.9% when the con-

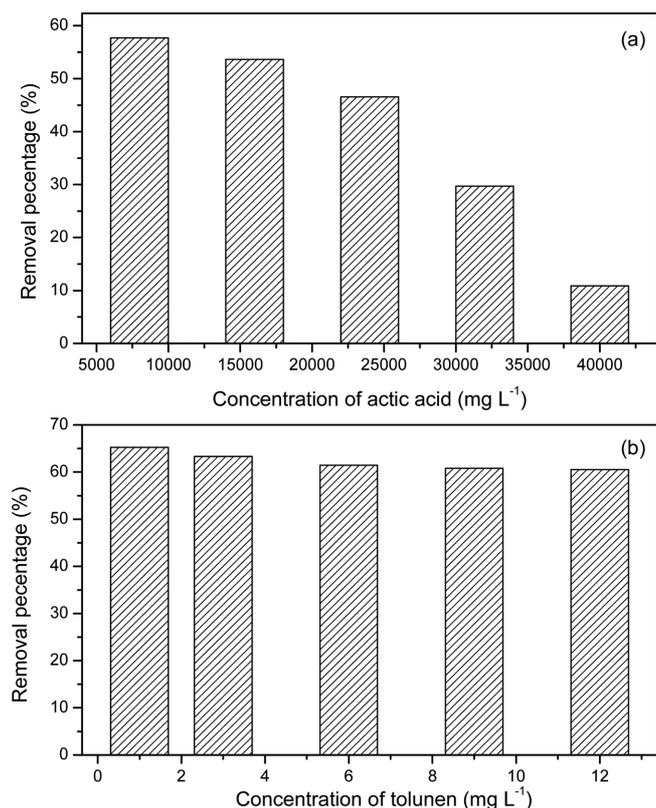


Fig. 6. Effect of acetic acid and toluene on the ammonia adsorption on MSWI bottom ash.

centration of the acetic acid increased to 40000 mg/L (Fig. 6(a)). This result shows the acetic acid in the leachate could restrict the adsorption of ammonia on MSWI bottom ash. Besides, the removal percentage decreased from 65.6% to 60.5% when the concentration of the toluene increased to 12.0 mg/L (Fig. 6(b)). This result suggested that the toluene in the leachate had a slighter effect on the adsorption compared with the acetic acid.

3-3. Effect of MSWI bottom ash on the migration of ammonia in the landfill

The adsorption study showed MSWI bottom ash had considerable adsorption capacity for the ammonia. The capacity of the ammonia on MSWI bottom ash was 156.2 mg/g. Therefore, the migration of the ammonia could be altered by MSWI bottom ash in the landfill. The adsorption was affected by the variation of pH, ion and organic matter level in the leachate. The high level of ion and organic matter was usually observed at the acidogenic stage of the landfill, due to the fermentation of the refuse. The fermentation also resulted in the low pH of the landfill. Such a condition could restrict the adsorption to a low level. Compared to the acidogenic stage, the level of the ion and organic matter was lower and the leachate pH was closer to neutral at the methane production stage and mature stage. This condition was beneficial for the adsorption of ammonia on MSWI bottom ash. Therefore, it seems the effect of MSWI bottom ash on the migration of ammonia in the landfill is greater at the methane production stage and mature stage than the acidogenic stage.

4. Conclusions

MSWI bottom ash has considerable adsorption capacity for ammonia. The observed adsorption capacity of ammonia on MSWI bottom ash was 156.2 mg/g. Therefore, the migration of the ammonia in the landfill could be affected by MSWI bottom ash. The adsorption process fit well to the pseudo-second-order kinetics and Langmuir model. The presence of Na⁺, Mg²⁺ and Fe³⁺ as well as organic matter could restrict the adsorption process. The variation of pH could also affect the adsorption process. According to the above results, the landfill circumstance at the methane production stage and mature stage was beneficial for adsorption. Thus, the migration of ammonia was more greatly affected at the methane production stage and mature stage than the acidogenic stage.

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