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RESEARCH ARTICLE

Factors affecting the adsorptive removal of bisphenol A in landfill leachate by high silica Y-type zeolite

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Abstract Although bisphenol A (BPA), a representative endocrine-disrupting compound, has been detected frequently in landfill leachate, effective technologies for BPA removal from landfill leachates are limited. We used high silica Y-type zeolite (HSZ-385) for the selective adsorption of BPA from landfill leachate, and factors affecting this adsorption are discussed. Higher removal efficiencies at pH 5.0–9.0 imply that neutral BPA is adsorbed more easily onto HSZ-385 than monomeric or divalent BPA anions. An increase in ionic strength and sodium acetate concentration did not affect BPA adsorption significantly, while the removal efficiency decreased slightly when more than 50 mgC/L of humic acid was added. HSZ-385 was applied to synthetic leachates that simulate the composition of landfill leachate at various degradation stages. In young acidic leachates that contain sodium acetate, the use of HSZ-385 for the adsorptive removal of BPA appears to be more effective than in old alkaline leachates, which contain large amounts of humic acid. In addition, 82 % BPA removal was achieved from young raw leachates using HSZ-385, which demonstrates that selective BPA removal from actual landfill leachate has been achieved.

Keywords Bisphenol A · High silica Y-type zeolite · Adsorption · Humic acid · Landfill leachate · Affecting factor

Introduction

Endocrine-disrupting compounds (EDCs) are a class of chemicals with xenobiotic and exogenous origins that mimic or inhibit the natural action of the endocrine system in various species (Chang et al. 2009; Basile et al. 2011). Generally, the primary source of EDC emission to the environment is expected to be from municipal wastewater (Fromme et al. 2002; Höhne and Püttmann 2008; Racz and Goel 2010), and numerous researchers have detected a wide range of EDCs in landfill leachates recently (Baun et al. 2004; Asakura et al. 2004; Öman and Junestedt 2008; Eggen et al. 2010). Municipal landfill leachates may represent a significant source for new and emerging pollutants (Eggen et al. 2010).

Landfill leachates generally contain high concentrations of organic matter, inorganic compounds (e.g., Ca^{2+}, Mg^{2+}, and Na^{+}), trace metals, and xenobiotic organic compounds (XOCs). Their constituents and concentrations vary according to the source and type of solid waste and operating conditions (Kjeldsen et al. 2002; Foo and Hameed 2009). The classification of landfill leachate is according to changes in composition. Young acetogenic landfill leachates are commonly characterized by large amounts of biodegradable organic matter, with major constituents being volatile fatty acids (VFAs), and pH values as low as 4.0. Old methanogenic landfill leachates are characterized by complex organic matter, mainly humic-like materials, and pH values greater than 7 (Foo and Hameed 2009).

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Various technologies, including biological (e.g., activated sludge process), chemical (e.g., advanced oxidation), and physical (e.g., adsorption and membrane filtration) processes, have been investigated to remove EDCs from contaminated drinking water, river water, and wastewater effluent (Johnson and Sumpter 2001; Liu et al. 2009b). However, minimal research has been conducted to determine the ability of these processes to remove target contaminants, particularly EDCs, from landfill leachates (Joseph et al. 2011). Adsorption has been applied extensively for water and wastewater treatment as this process has a low initial cost, is easy to operate, is unlikely to produce secondary harmful substances (Dong et al. 2010; Xu et al. 2012), and can be used to remove a wide variety of dissolved organic and inorganic contaminants. The removal of EDCs from landfill leachates presents a challenge because of the broad range of leachate characteristics, including differing pH levels, increased variation in type of dissolved organic matter (DOC), and increased amount of inorganic compounds (Joseph et al. 2011). Such factors that arise because of the landfill characteristics may affect EDC removal from landfill leachate significantly.

Bisphenol A (BPA), one of the representative EDCs, is used extensively as a monomer in the production of various polycarbonates, epoxy resins, and other plastics (Nam et al. 2010). BPA is detected frequently in raw leachate with its concentration varying significantly (Yasuhara et al. 1997; Yasuhara et al. 1999; Kjeldsen et al. 2002; Urase and Miyashita 2003; Asakura et al. 2004; Sakamoto et al. 2004; Sakamoto et al. 2006). As high as 17,200 μg/L BPA has been identified in a hazardous waste landfill site (Yamamoto et al. 2001). Furthermore, an investigation into the micropollutants in leachates from solid waste disposal sites in Thailand reported 5,200 and 9,200 μg/L BPA in samples from the deep and shallow leachate ponds, respectively (Urase et al. 2007). Therefore, there is an urgent need to develop an effective technology to remove BPA from landfill leachate.

Studies on the removal of BPA from water and wastewater have only been conducted using activated carbon (Bautista-Toledo et al. 2005; Liu et al. 2009a), carbon nanotubes (Pan et al. 2010a; Pan et al. 2010b), graphene (Xu et al. 2012), zeolites (Dong et al. 2010), membrane filtration (Wu et al. 2010), and photocatalytic degradation (Ohko et al. 2001). The removal of BPA from raw landfill leachate is seldom presented and the various contaminants in landfill leachate may complicate the issue (Joseph et al. 2011). Activated carbon is a common, well-established adsorbent and it has been used previously to treat landfill leachate (Foo and Hameed 2009). The advantages of using activated carbon are its large porous surface area, controlled pore structure, thermostability, and low acid/base reaction, which improve the removal of organic compounds from leachate samples (Foo and Hameed 2009). However, activated carbon is difficult to regenerate if large amounts of various pollutants are adsorbed. Furthermore, the mineral impurities or oxygen-containing functional groups in activated carbon may render it weakly hydrophilic (Tsai et al. 2006).

Zeolites are a crystalline alumina-silicate with a typical characteristic three-dimensional network containing channels and cavities. They have been used frequently as adsorbents to remove pollutants in water and in wastewater treatment (Shu et al. 1997; Chang et al. 2003; Ji et al. 2009; Braschi et al. 2010). Recently, hydrophobic and organophilic zeolites with high Si/Al ratio have been used extensively in adsorption-related applications (Chang et al. 2003; Braschi et al. 2010) or in TiO_2-zeolite composites (Fukahori et al. 2003a; Fukahori et al. 2003b; Ito et al. 2014; Fukahori and Fujiwara 2014). A study of BPA adsorption characteristics onto hydrophobic zeolite demonstrated the effects of initial BPA concentration, solution pH, and adsorbent dosage in aqueous solutions (Tsai et al. 2006), while the affecting factors originating from the complexity of raw landfill leachate have not been identified. It has been reported that high silica Y-type zeolite (HSZ-385) is effective for removing sulfonamide antibiotics in livestock urine containing various coexisting organics and ions (Fukahori et al. 2013). HSZ-385 can therefore potentially be applied in the removal of BPA from landfill leachates.

The main objectives of this study are (i) to identify factors affecting the adsorptive removal of BPA using high silica Y-type zeolite and (ii) to evaluate the applicability of high silica Y-type zeolite to remove BPA from landfill leachates.

Materials and methods

Materials and chemicals

High silica Y-type zeolite powder (HSZ-385; surface area 600 m^2/g; mean particle size, 4 μm; $SiO_2/Al_2O_3=100$) was provided by Tosoh Ltd. (Tokyo, Japan) and was used as adsorbent without further modification. A stock solution was prepared by adding 100 mg BPA (purity>99 %, Sigma-Aldrich, St. Louis, USA) into 100-mL Milli-Q water (Millipore, Bedford, MA, USA) and adjusting the solution pH to alkaline conditions to ensure that all the BPA powder was dissolved. The basic physicochemical properties of BPA are summarized in the supplementary material (Table S1). BPA is a hydrophobic compound with low solubility in water. Its pK_a ($pK_{a,1}=9.6$ and $pK_{a,2}=10.2$) indicates that the mole fraction of neutral and monomeric or divalent BPA varies according to the environmental pH as shown in the supplementary material (Fig. S1).

Humic acid (HA) (purity>98 %, Sigma-Aldrich, St. Louis, USA) was selected to represent the hardly biodegradable organic compounds in landfill leachate produced in the methanogenic phase. HA stock solution was prepared by adding 1 g of dry HA powder to 1 L of Milli-Q water with stirring overnight. The solution was filtered through 0.45-μm membrane filters (Toyo Roshi Kaisha Ltd., Tokyo, Japan) to remove undissolved materials. The HA concentration was determined by DOC measurement of the filtrate. A volume of 100 mg/L of HA solution had a DOC of 23.5 mgC/L. Sodium acetate (purity>98.5 %, Nacalai Tesque Inc., Kyoto, Japan) was used to represent the typical DOC in landfill leachate produced in the acetogenic phase.

The formic acid and acetonitrile as the mobile solvents in BPA analysis were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). All other chemicals were of analytical grade and were purchased from Nacalai Tesque Inc. (Kyoto, Japan).

Landfill leachate

Synthetic landfill leachate

To examine the adsorptive removal performance of BPA from landfill leachate, serial solutions of synthetic landfill leachates were prepared. First, two sets of leachate were produced to represent the degradation stages in the acetogenic and methanogenic phases, respectively. The synthetic leachate compositions in this study were based on literature information (Kjeldsen et al. 2002; Renou et al. 2008). The synthesized "young" leachates (type A) simulate the composition of leachate in the acetogenic phase, while the synthesized "old" leachates (type E being the oldest synthetic leachate) represent the composition during the methanogenic phase. Sodium acetate was used to represent the typical DOC in the acetogenic phase, and a pH level of as low as 5.0 was obtained by addition of 0.1 or 1 mol/L HCl. HA was used to represent the organic compounds produced in the methanogenic phase, and an alkaline pH of 9.0 was obtained using 0.1 or 1 mol/L NaOH.

Inorganic concentrations (e.g., Ca^{2+} and Mg^{2+}) can decrease over the life of landfill treatment. $CaCl_2$ and $MgSO_4$ were used as sources of Ca^{2+} and Mg^{2+}, respectively. No heavy metals were used in this study, and the XOCs are represented by BPA only. The initial BPA concentration of 10 mg/L in this study agrees with the reported levels in seepage and leakage water samples from a sanitary landfill of up to 25,000 and 4,200 μg/L, respectively (Schwarzbauer et al. 2002). To account for changes in landfill leachate over the degradation stage of the waste, the youngest (type A) and oldest (type E) leachates were mixed in different ratios, and the resultant mixtures were labeled types B–D. Detailed characteristics of this series of synthetic leachates are shown in Table 1.

Table 1 Composition of various synthetic leachates

Parameters	Synthetic leachate type				
	A	B	C	D	E
Young/Old [Y:O][a]	100:0	75:25	50:50	25:75	0:100
pH (−)[b]	5.0	5.2	5.6	8.5	9.0
DOC (mgC/L)[c]	2,500	2,075	1,350	775	200
NH_4^+-N (mg/L)[c]	250	438	625	813	1,000
Ca^{2+} (mg/L)[c]	1,200	915	630	345	60
Mg^{2+} (mg/L)[c]	470	398	325	253	180
K^+ (mg/L)[c]	50	338	625	913	1,200
BPA (mg/L)[d]	10				

[a] Young and old leachates were mixed in different ratios and mixtures were labeled types A–E. Type A represents the youngest leachate, while type E corresponds to the oldest leachate

[b] pH values in type A and type E were adjusted with 0.1 or 1 mol/L HCl and NaOH, respectively. Other pH values were measured in the mixture using a portable pH meter (D-51, Horiba, Tokyo, Japan)

[c] Values calculated using ratios of existing young and old leachates

[d] Initial 10 mg/L BPA added

Raw landfill leachate

Raw landfill leachate was obtained from a municipal landfill in Laem Chabang City in the East Seaboard of Thailand. The landfill has been receiving municipal waste generated in Laem Chabang City and its surrounding municipalities since 2004 and was operational during the leachate sampling. Its estimated area and capacity are 59,000 m^2 and 530,000 m^3, respectively. Characteristics of the raw leachate are summarized in Table 2. The BPA concentration in the leachate was 0.51 mg/L, and an additional 10 mg/L of BPA was added to the raw leachate for the adsorption experiments.

Table 2 Characteristics of raw landfill leachate

Parameters	Unit	Values
pH	(−)	6.4
COD	mg/L	36,350
DOC	mg/L	12,800
Suspended solids	mg/L	890
NH_4^+-N	mg/L	1,680
Mg^{2+}	mg/L	270
Ca^{2+}	mg/L	1,310
Na^+	mg/L	1,940
K^+	mg/L	420
Formic acid	mg/L	N.D.
Acetate acid	mg/L	6,510
Propionic acid	mg/L	2,560
n-Butyric acid	mg/L	428
iso-Butyric acid	mg/L	4,160
n-Valeric acid	mg/L	988
iso-Valeric acid	mg/L	1,180

N.D. not detected

Adsorption experiments

Adsorption kinetic studies were conducted by adding 30 mg HSZ-385 powder into the BPA solution (10 mg/L, 500 mL) in a glass vessel at 25 °C. The BPA concentration was measured at predetermined time intervals. The adsorption isotherm was obtained by changing the amount of HSZ-385 powder (10–60 mg) added into the BPA solution (10 mg/L, 1 L) and the solution was stirred for 4 h and 25 °C. Preliminary kinetic studies confirmed that the reaction time of 4 h is sufficient for the solution to reach a pesudo-equilibrium state of sorption. The amount of BPA adsorbed onto the HSZ-385 zeolite was calculated as follows:

$$q = (C_0 - C_t) \cdot \frac{V}{m} \tag{1}$$

where q is the amount of BPA adsorbed per gram of zeolite at a time period (mg/g); C_0 and C_t are the concentrations at the beginning and end of a time period (mg/L), respectively; V is the reaction volume (L); and m is the amount of zeolite (g).

The effect of pH on the adsorption of BPA by HSZ-385 was studied with an initial BPA concentration of 10 mg/L at a pH from 5.0 to 11.0 at 25 °C. The solution pH was measured and controlled using a portable pH meter (D-51, Horiba, Tokyo, Japan).

The effect of ionic strength was studied by adding NaCl (50–400 mmol/L) into 10 mg/L BPA solution at 25 °C and a pH of 5.0.

The effect of DOC was carried out by the addition of sodium acetate (200–2,000 mgC/L) and HA (25–200 mgC/L) into 10 mg/L BPA solution at 25 °C and pH 5.0.

The effect of leachate type was examined by the addition of various synthetic (Table 1) and raw (Table 2) landfill leachates with 10 mg/L BPA at 25 °C.

All experiments were conducted in triplicate to determine the reproducibility of the results, and data are reported as a mean value±standard deviation.

Analytical methods

Aqueous BPA solutions were filtered through a membrane filter (Dismic-13HP; pore size, 0.20 μm; Toyo Roshi Kaisha Ltd., Tokyo, Japan.) and measured by ultraperformance liquid chromatography (UPLC; Acquity UPLC, Waters, Milford MA, USA). The UPLC analysis was performed using a BEH C18 chromatographic column with a linear gradient at a constant flow rate of 0.3 mL/min. The mobile phases used were (A) acetonitrile as solvent and (B) 0.05 % formic acid in Milli-Q water as solvent. The elution steps were 10 % acetonitrile at 0 min, held for 0.5 min, increased to 90 % solvent A from 0.5 to 5 min, decreased to 10 % solvent A from 5 to 10 min, and held for 2 min (total run time 12 min). BPA was detected with a photodiode array detector at 280 nm. The BPA in the raw landfill leachate was extracted by the solid-phase extraction method (Waters Oasis HLB, Waters, Milford MA, USA), and the eluent was analyzed using the UPLC system.

Sample DOC was determined as non-purgeable organic carbon using a Shimadzu total organic carbon analyzer (TOC-5000A, Shimadzu, Kyoto, Japan) based on CO_2 quantification by non-dispersive infrared analyses after high temperature catalytic combustion. Ion concentrations were determined using an ion chromatograph system (DX-120; Dionex, Sunnyvale, CA, USA). The acetate concentration was measured by high-performance liquid chromatography (GL-Science, Tokyo, Japan) equipped with a C18 column.

Statistical analysis

The effects of pH, NaCl, and DOC on the BPA removal efficiency were analyzed by a one-way analysis of variance using SigmaPlot version 12.5 statistical software (Systat Software Inc., San Jose, CA, USA). Statistical differences in the means of the BPA removal efficiency were detected by Tukey's test at the 0.05 probability level.

Results and discussion

Effect of pH on BPA adsorption

pH dependency of BPA adsorption

BPA that contains phenolic compounds is usually present as a weak acid in nature and can be ionized into its mono- or divalent anionic form at sufficiently high pH according to its pK_a value (Fig. S1). Because of its variable appearance in the environment, it is more complex than other permanently ionic or non-ionizable compounds (Dong et al. 2010). A pH-dependent adsorption model has been reported in which the adsorption capacity of sulfa drugs onto silica zeolite varies according to pH level (Fukahori et al. 2011). In this study, the effect of pH on BPA adsorption was investigated from pH 5.0 to 11.0, which represents almost all pH conditions from young to old landfill leachates.

Figure 1 illustrates the effect of pH on BPA adsorption. At pH 5.0 and 7.0, the BPA removal efficiencies can reach up to 84.4±0.3 and 84.1±0.7 %, respectively. The efficiency slightly decreased to 80.0±6.1 % with an increase of pH to 9.0. A lower BPA removal efficiency of 64.6±3.6 % was obtained at pH 10.0, and the lowest BPA removal efficiency of 15.2±3.0 % resulted at pH 11.0. The BPA removal efficiencies at pH 10.0 and 11.0 were significantly lower than those at pH 5.0–9.0 ($p<0.05$). High adsorption efficiencies were achieved at a

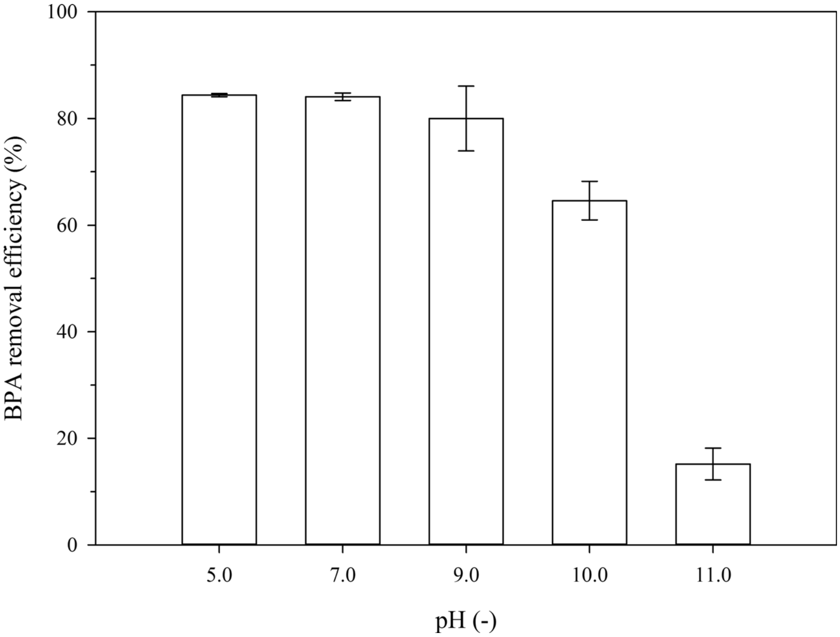


Fig. 1 Effect of solution pH on BPA adsorption by HSZ-385

pH less than the p$K_{a,1}$ value of BPA at 9.6 where almost all of the BPA exists in neutral form. Therefore, neutral BPA is more easily adsorbed onto HSZ-385 than the mono- or divalent anions of BPA.

Adsorption kinetic study of BPA

The adsorption rate is important in the design of optimal treatment processes. Figure 2 shows the rate of BPA adsorption by HSZ-385 at different pH values. Almost identical adsorption behavior was obtained. Adsorption equilibrium was achieved in 60 min when the solution pH ranged from 5.0 to 9.0, where the BPA exists in neutral form. The BPA adsorption efficiency decreased because of partial BPA ionization at pH 10.0, although rapid BPA adsorption was observed in the initial stages of the adsorption process. Some BPA adsorbed on the HSZ-385 was desorbed after 60 min at pH 11.0 since the HSZ-385 zeolites collapsed partially and dissolved at a pH above 10.0 (data not shown).

A pseudo-second-order model as shown in Eq. (2) was applied to analyze the adsorption kinetics.

$$\frac{t}{q_t}=\frac{t}{q_e}+\frac{1}{k_2q_e^2} \qquad (2)$$

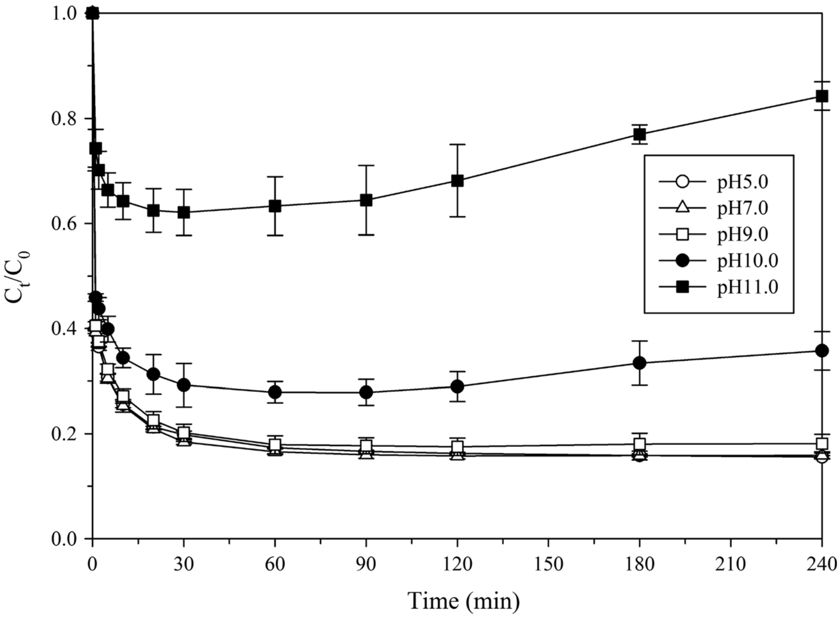


Fig. 2 Time course of BPA adsorption by HSZ-385 at different pH levels

where k_2 (g/mg/min) is the rate constant of the pseudo-second-order adsorption, and q_t (mg/g) and q_e (mg/g) are the amount of adsorbed BPA at time t (min) and the equilibrium state, respectively. (t/q_t) versus t was plotted and the rate constant, k_2, was calculated. The half-life time ($t_{1/2}$) (time required to adsorb half of the q_e is used frequently and can be calculated by inserting $t = t_{1/2}$ and $q_t = \frac{q_e}{2}$ into Eq. (2):

$$t_{1/2} = \frac{1}{k_2 q_e} \tag{3}$$

The values of k_2, q_e, R^2, and $t_{1/2}$ are shown in Table 3.

The high values of R^2 for the pseudo-second-order fitting can be explained by the adsorption behavior of BPA on HSZ-385. The adsorption capacity of BPA (q_e) decreases with increasing pH. The highest q_e was 146±2 mg/g at pH 5.0, and the lowest was 29.5±5.3 mg/g at pH 11.0 because of the zeolite collapse.

Adsorption isotherms of BPA

BPA adsorption onto HSZ-385 was analyzed using two different isotherm models:

$$\text{Langmuir model}: q_e = q_{\max} \frac{b \cdot c_e}{1 + b \cdot c_e} \tag{4}$$

$$\text{Freundlich model}: q_e = K_f \cdot {C_e}^{1/n} \tag{5}$$

where q_e is the equilibrium solid-phase concentration (mg/g); C_e is the equilibrium liquid-phase concentration (mg/L); $q_{\max}$ is the maximum adsorption capacity (mg/g); b is the Langmuir fitting parameter (L/mg); K_f is the Freundlich affinity coefficient $[(\text{mg/g})/(\text{mg/L})^{(1/n)}]$; and n is a dimensionless number related to surface heterogeneity.

Table 3 Pseudo-second-order kinetic parameters for BPA adsorption by HSZ-385 at different pH levels (mean±standard deviation, n=3)

pH (−)	$q_\in$ (mg/g)	k_2 (g/g/min)	$t_{1/2}$ (min)	R^2 (−)
5.0	146±2	5.78±0.63	1.20±0.11	1.000
7.0	141±2	7.99±0.64	0.89±0.07	1.000
9.0	137±2	10.2±1.1	0.64±0.07	1.000
10.0	112±9	4.98±0.23	2.20±1.39	0.997
11.0	29.5±5.3	2.23±0.38	15.8±3.1	0.900

Figure 3 displays the adsorption isotherms of BPA onto HSZ-385 at different pH values. Langmuir and Freundlich isotherm models were used to fit the obtained experimental data. Table 4 lists the fitting parameters for both isotherms under various pH conditions. The Freundlich isotherm is an empirical model while the Langmuir isotherm is a theoretical single-layer adsorption model. The coefficients of determination (R^2) for the Langmuir model were higher than those for the Freundlich model, suggesting that single-layer adsorption of BPA on HSZ-385 may have occurred. As mentioned previously, the neutral form of BPA was adsorbed easily onto HSZ-385. Consequently, the adsorption ability at pH 10.0 was lower than that at pH 5.0–9.0. An isotherm study at a pH higher than 10.0 was not conducted because of the collapse of the HSZ-385.

Effect of ionic strength

The ionic strength is determined mainly by the cation concentrations (such as Ca^{2+}, Mg^{2+}, Fe^{2+}, Na^+, and Mn^{2+}), which changes with landfill age. It is high in the leachate during the acetogenic phase and decreases in the methanogenic phase because of the higher pH and lower levels of total organic carbon in the leachate. The effect of ionic strength on BPA adsorption by HSZ-385 was studied at different NaCl concentrations. The BPA adsorption efficiency decreased slightly to 82.2±1.3 % with the addition of 50 mmol/L NaCl (Fig. 4). With a 100–400 mmol/L NaCl solution addition, BPA removal efficiencies increased to 89.6±6.2 %. There was no significant difference in BPA adsorption with HSZ-385 (p>0.05).

Effect of DOC

During landfill waste decomposition stabilization, the operational stage is indicated by a wide variety of organic components in the leachate ranging from VFAs to humic- and fulvic-like compounds. Figure 5 shows the effect of acetate concentration on BPA adsorption by HSZ-385. An increase in acetate concentration from 200 to 2,000 mgC/L did not have a significant effect on the adsorptive removal of BPA, which varied from 81.7±2.2 to 82.4±1.1 % as shown in Fig. 5a (p>0.05). With the addition of 25 mgC/L HA solution as the DOC source, the BPA removal efficiency decreased to 81.7±0.7 % but the effect was insignificant (p>0.05). The BPA removal efficiency was reduced to between 76.8±0.3 and 77.5±1.6 % when the HA concentrations ranged from 50 to 200 mgC/L as shown in Fig. 5b, and the effect of HA addition was statistically significant (p<0.05). The adsorptive removal of BPA by HSZ-385 may therefore not be affected in the young leachate since this leachate contains simple organic compounds, such as acetic acid instead of HA. It would, however, be inhibited in the old leachate, which contains coexisting HA.

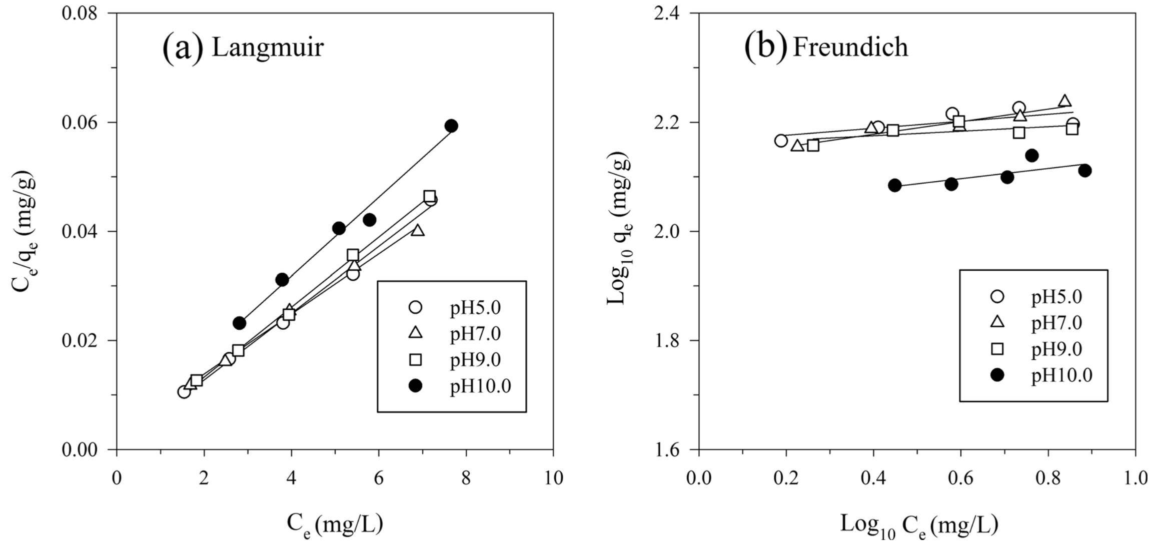


Fig. 3 Langmuir and Freundlich isotherms for BPA adsorption by HSZ-385 at different pH levels

Adsorption behavior of BPA in landfill leachates

Many factors affect leachate quality, e.g., landfill age, precipitation, seasonal weather variation, waste type, and composition, with the landfill leachate composition varying depending on landfill age (Renou et al. 2008). Parameters in the synthetic leachate were considered based on leachate composition according to landfill age. The concentration and complexity of pollutants in the leachate may affect EDC adsorption. pH values of 5.0 and 9.0 were used to produce the youngest (type A) and oldest (type E) synthetic leachates, respectively. Sodium acetate and HA were used to represent the simple and complex DOCs in the young and old leachates, respectively, to determine the effect on the adsorptive removal of BPA by HSZ-385.

Figure 6 shows the rate of BPA adsorption in various synthetic leachates. BPA adsorption reached equilibrium after 60 min in all synthetic leachates. There was no obvious difference in BPA adsorption among the type A, B, and C synthetic leachates, while BPA adsorption differed for the other two synthetic leachates, types D and E. The kinetic parameters of a pseudo-second-order study on BPA adsorption for all synthetic leachates are summarized in Table 5. The adsorptive capacity (q_e) varied from 111 to 145 mg/g. The half-life time increased from the type A to type E synthetic leachates implying that BPA adsorption by the HSZ-385 in the young leachate was more rapid than in the old leachate.

Table 4 Langmuir and Freundlich model fitting parameters of BPA adsorption by HSZ-385 at different pH levels

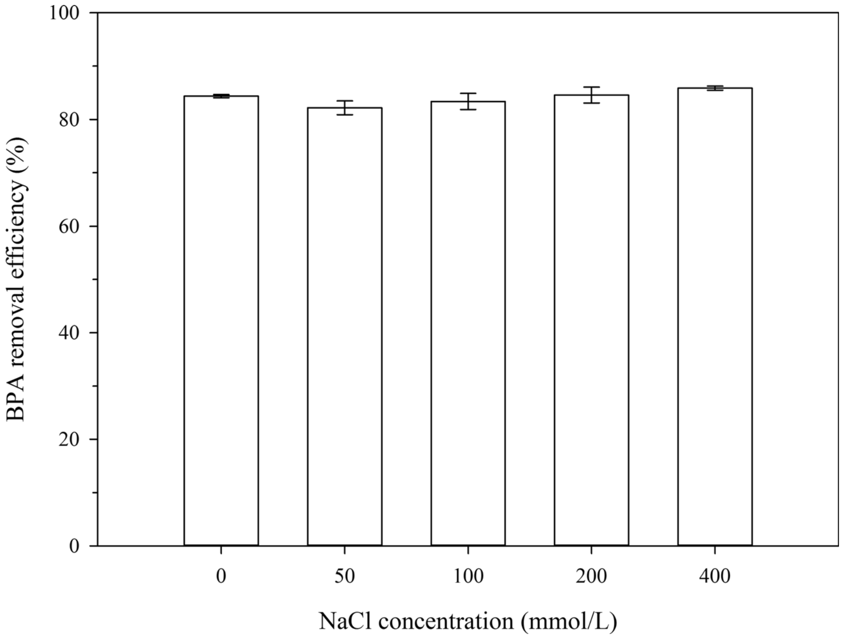
pH	Langmuir			Freundlich		
(−)	$q_{\max}$ (mg/g)	b L/mg	R^2 (−)	$\log K_f$ (mg L)/(mg/g)$^{(1/n)}$	$1/n$ (−)	R^2 (−)
5.0	182	0.45	0.980	2.14	0.128	0.984
7.0	196	0.80	0.992	2.12	0.138	0.907
9.0	204	0.92	0.984	2.12	0.155	0.816
10.0	139	0.40	0.987	2.04	0.094	0.499

The raw landfill leachate composition appears to be more complex, and BPA removal by HSZ-385 was examined. Figure 7 presents the BPA removal efficiencies in the synthetic and raw leachates after 4-h adsorption. High BPA removal efficiencies from 82.8±0.6 to 86.9±1.1 % were obtained in the type A, B, and C synthetic leachates, while the BPA removal efficiencies decreased to 76.6±0.6 and 69.1±1.7 % in types D and E, respectively. As shown in Table 2, the amount of acetic acid in the raw leachate was 6,510 mg/L, and all VFAs share 63 % of the total chemical oxygen demand value (36,350 mg/L). The raw leachate characteristics from Thailand are different from those in Japan, where municipal solid waste (MSW) landfill contains low amounts of organic compounds and has a low VFA concentration, while the MSW landfill in Asian countries contains mostly organic matter (Urase et al. 2007). At pH 6.4, this raw leachate has characteristics of a young leachate. Most BPA in the raw leachate would present in the neutral form. As a result, 81.8 ±0.2 % adsorptive removal of BPA was achieved despite the more complex compositions in the raw leachate than in the synthetic leachates.

Adsorption mechanism of BPA by HSZ-385

Higher BPA removal efficiencies were obtained under wide range of pH (pH 5.0–9.0) because most BPA exists in neutral form. The hydrophobic interaction between the molecular BPA and HSZ-385 may be the dominant adsorption

Fig. 4 Effect of ionic strength on BPA adsorption by HSZ-385



mechanism, judging from the large octanol/water partition coefficient ($\log K_{ow}=3.32$) for BPA and the high SiO_2/Al_2O_3 ratio of HSZ-385, which possesses hydrophobic characteristics. Fukahori et al. reported that sulfa drugs in neutral form could be more readily adsorbed onto HSZ-385 than those in cationic and anionic forms based on hydrophobic interactions (Fukahori et al. 2011). The reduction of adsorption capacity under alkaline conditions (pH 10.0–11.0) may be because of repulsive electrostatic interactions, since BPA is partly ionized into bisphenolate form at high pH and the surfaces of hydrophobic zeolites are negatively charged (Tsai et al. 2006). Previous studies on BPA adsorption by activated carbon suggest that adsorption is enhanced with increasing ionic strength (Bautista-Toledo et al. 2005; Liu et al. 2009a). One possible reason is that the screening effect from higher ionic strength could favor adsorbate–adsorbent dispersion interactions (Bautista-Toledo et al. 2005). Another possible reason is that a salting-out effect caused by the presence of NaCl decreases the BPA solubility and enhances BPA adsorption onto activated carbon (Bautista-Toledo et al. 2005; Liu et al. 2009a). In this study, there was no significant difference in BPA removal efficiency by NaCl addition. This suggests that the screening and salting-out effects were weaker than the hydrophobic interactions between the HSZ-385 zeolite and neutral BPA. The adsorptive removal of BPA from synthetic leachates also confirmed that no significant effect resulted from salts coexisting at high concentration in the leachate.

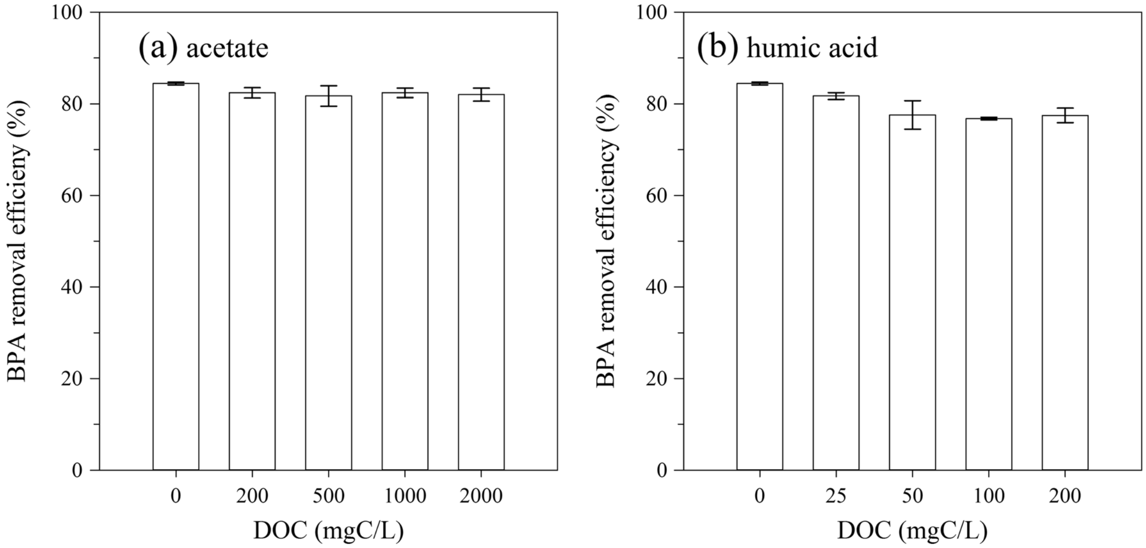
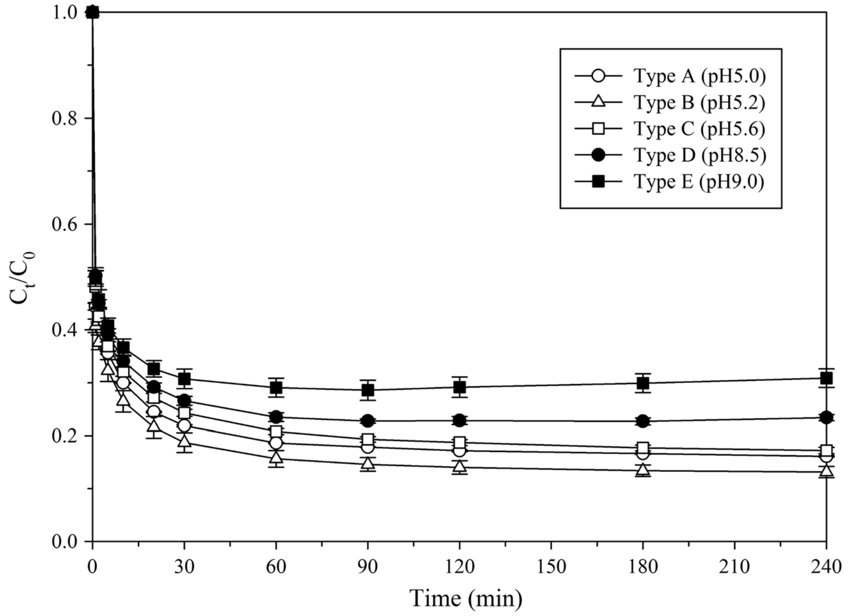


Fig. 5 Effect of DOC on BPA adsorption by HSZ-385: **(a)** acetate and **(b)** humic acids

Fig. 6 Time course of BPA adsorption by HSZ-385 in various synthetic leachates



The good agreement in isotherm data with the Langmuir model suggests that neutral BPA is adsorbed on a single-layer-specific HSZ-385 surface site. A study on the effect of DOC indicated that the presence of HA decreased BPA adsorption. Such an effect may be induced by the hydrophobicity of HA and may compete directly with the adsorption surface sites of HSZ-385 with neutral BPA. The application of HSZ-385 to remove BPA from synthetic and raw leachates indicated that the BPA removal efficiency in young leachates was higher than that in old leachates. Because young leachates contain less HA under acid conditions, most of the neutral BPA was adsorbed onto the HSZ-385 by hydrophobic interactions and the HA inhibition was weak.

Adsorptive capacity of BPA by HSZ-385

The adsorption capacities of BPA by HSZ-385 are compared with literature information in Table 6. The maximum adsorption capacities by the Langmuir model were 182 mg/g at pH 5.0 and 196 mg/g at pH 7.0, respectively. These were much higher than those achieved by application of two kinds of commercial activated carbon to remove BPA (Nakanishi et al. 2002; Asada et al. 2004) and lower than those obtained by two activated carbons that were modified to remove inorganic matter (Bautista-Toledo et al. 2005). Although activated carbon is a well-established adsorbent and is often used for water or wastewater treatment, its easy adsorptive saturation and difficult regeneration may limit its application in treating landfill leachate because of the pollutant complexity. Carbon nanotubes (Pan et al. 2010a; Pan et al. 2010b; Joseph et al. 2011) and graphene (Xu et al. 2012) materials also have high BPA removal capacities, but when operating costs are considered, BPA removal from landfill leachate treatment with HSZ-385 may be more effective and useful in practice.

Table 5 Pseudo-second-order kinetic parameters on BPA adsorption in various synthetic leachates with HSZ-385 (mean±standard deviation, $n=3$)

Leachate type (−)	pH (−)	q_e (mg/g)	k_2 (g/g/min)	$t_{1/2}$ (min)	R^2 (−)
A	5.0	143±0	4.06±0.08	1.72±0.03	1.000
B	5.2	145±2	4.37±0.61	1.60±0.24	1.000
C	5.6	133±2	3.63±0.25	2.08±0.12	1.000
D	8.5	124±5	3.63±1.05	2.17±0.14	1.000
E	9.0	111±2	3.63±0.44	2.48±0.03	1.000

To regenerate the adsorbent after saturation, some researchers combined adsorption and photocatalysis properties by the synthesis of photocatalyst/adsorbent composites (Matos et al. 1998; Yap and Lim 2012; Yap et al. 2012; Ito et al. 2014; Fukahori and Fujiwara 2014). The superior adsorption capacity in the composite materials can increase the surface contact during photocatalysis, and simultaneously, the degradation of pollutants by photocatalysis can regenerate the adsorption sites of the adsorbent. One of these studies demonstrated this technique in the regeneration of powdered activated carbon using photocatalysis during the removal of contaminants of emerging environmental concern (Yap and Lim 2012). A TiO_2/HSZ-385 composite was synthesized to remove sulfamethazine in secondary effluent, and the adsorbed sulfamethazine was decomposed by photocatalysis. The composites could therefore be regenerated and their adsorptive ability without reaching adsorption equilibrium be recovered (Ito et al. 2014). The application of TiO_2-zeolite composites for BPA removal from landfill leachate will be evaluated in the future.

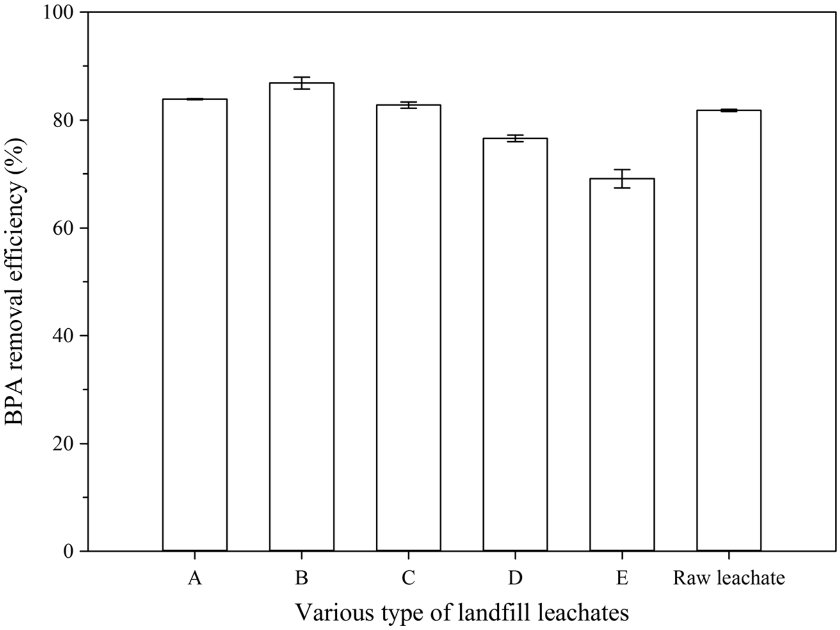


Fig. 7 BPA removal efficiency in various type landfill leachates by HSZ-385

Conclusions

The adsorptive removal of BPA from landfill leachates by high silica Y-type zeolite (HSZ-385) has been demonstrated in this study. Among the leachate characteristics (e.g., pH, ionic strength, DOC, and type of leachate) according to landfill age, pH was the most important factor in BPA adsorption by HSZ-385. The dominant adsorption mechanism was a hydrophobic interaction between neutral BPA and HSZ-385 with hydrophobic characteristics. High removal efficiencies of BPA were obtained at wide range of pH (5.0–9.0). The variation in ionic strength with increasing NaCl concentration had

Table 6 Adsorption capacity of BPA in comparison with literature values

Adsorbent	pH	*T* (°C)	S_{BET} area (m^2/g)	Initial BPA conc. (mg/L)	MAC (mg/g)[a]	Reference
High silica Y-type zeolite (HSZ-385)	5.0	25	600	10	182	This study
High silica Y-type zeolite (HSZ-385)	7.0	25	600	10	196	This study
Hydrophobic zeolite	7.0	25	500	10–90	19–125	Tsai et al. (2006)
Single-walled carbon nanotubes	NA[b]		540	0.1–40	455	Pan et al. (2010b)
Multi-walled carbon nanotubes	NA[b]		95–172	0.1–40	61.6–102	Pan et al. (2010b)
Graphene	6.0	29	327	10	181.6	Xu et al. (2012)
Surface modified zeolite from coal fly ash	9.6–10.4	25	50.6–91.5	100	56.8–114.9	Dong et al. (2010)
Zeolite from coal fly ash	10.5–11.2	25	1–2.8	100	1.4–3.5	Dong et al. (2010)
Activated carbon purchased from Takeda	NA[b]	25	1,119	NA[b]	23.5	Nakanishi et al. (2002)
Activated carbon purchased from Wako	NA[b]	25	1,350	NA[b]	56.5	Asada et al. (2004)
Commercial charcoal-based activated carbon purchased from Sorbo Norit (S)	6.5–7.0	25	1,225	50–350	129.6	Bautista-Toledo et al. (2005)
Commercial charcoal-based activated carbon purchased from Merck (M)	6.5–7.0	25	1,084	50–350	263.1	Bautista-Toledo et al. (2005)
Activated carbon prepared from almond shells	6.5–7.0	25	1,216	50–350	188.9	Bautista-Toledo et al. (2005)
Activated carbon (S) with removing the inorganic matters	6.5–7.0	25	1,277	50–350	285.7	Bautista-Toledo et al. (2005)
Activated carbon (M) with removing the inorganic matters	6.5–7.0	25	1,158	50–350	303.0	Bautista-Toledo et al. (2005)

[a] Maximum adsorption capacity obtained from Langmuir model or from adsorption capacity at highest initial concentration

[b] Data not available

a negligible effect because of the weak inhibition. Adding HA decreased the BPA adsorption slightly, possibly because of the competition for surface adsorption sites on the HSZ-385 by neutral BPA.

In young acidic leachates that contain simple organic compounds, the use of HSZ-385 for the adsorptive removal of BPA appears to be more effective than that in old alkaline leachates, which contain large amounts of HA. The HSZ-385 adsorbed the BPA selectively from the raw leachate that contained various contaminants. Results from the factors affecting the adsorptive removal of BPA from landfill leachate in this study will promote the application of HSZ-385. Rapid and selective BPA removal may enable treatment of accidental BPA pollutant spills.

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