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Article

Influence of acid activation on the NH₃-adsorption properties of a Turkish bentonite

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Abstract

In this study, the adsorption of NH_3 gas on a bentonite from Ünye (Turkey) in its natural state and after acid treatments, was investigated experimentally at 298 K and up to 100 kPa. Bentonite was treated with HCl solutions of various concentrations (0.5–2.5 M) at 75°C for 4 h. X-ray diffraction (XRD), X-ray fluorescence (XRF), N_2 adsorption and thermogravimetric/differential thermal analysis (TG/DTA) were used to characterize the bentonite before and after acid treatment. The quantitative XRD analysis demonstrated that the bentonite sample was composed predominantly of smectite (75%), with abundant feldspar (20%) and minor opal-CT, analcime and quartz (5%). Increasing gas adsorption values of acid-treated bentonites were analysed depending on the structural changes of the clay. The NH_3-adsorption capacities of the bentonite samples (3.801–5.068 mmol g^{-1}) were also compared with previously studied clay-based materials (0.828–4.000 mmol g^{-1}) in terms of their textural and structural differences.

Our modern civilization is built on developments in technology and industry. However, from the last quarter of the twentieth century onwards, we have had to deal with the challenges of industrial and agricultural wastes, among other types of waste. Clays and clay minerals have been proven to be good candidates for pollution control. They have the ability to adsorb radionuclides (Krupskaya *et al.*, 2017), heavy metal ions (Ma *et al.*, 2016), dyes (Gök *et al.*, 2010), gases and volatile compounds (Volzone & Ortiga, 2009; Chen & Lu, 2015; Erdoğan Alver & Günal, 2016; Erdoğan Alver *et al.*, 2016; Erdoğan Alver, 2017; Mucha *et al.*, 2017). Bentonites are clays consisting essentially of smectites (Fontaine *et al.*, 2020). Smectites consist of repetitions of T–O–T layers, where T corresponds to tetrahedral sheets that consist of one T atom residing at the centre of the tetrahedron (T is usually Si^{4+}) and four O^{2-} atoms are at the corners of the tetrahedron, and O represents octahedral sheets that consist of a metal atom (generally Al^{3+}) and six O^{2-} atoms and OH^- (Brigatti *et al.*, 2006; Do Nascimento, 2016). Through isomorphic substitution, the Al atoms in the octahedral sheets may be replaced with divalent cations such as Fe^{2+} or Mg^{2+}, and in the tetrahedral sheets Al^{3+} atoms replace Si. These substitutions create a negative net charge, which is balanced with exchangeable interlayer cations (Erdoğan *et al.*, 2016). Despite their large cation-exchange capacity and basal swelling abilities, the structural properties of smectites need to be improved through the application of various techniques. The most common method is acid activation (Balci, 2019). Treatment with inorganic acids

changes the chemical composition and structure of smectites, leading to increases in their specific surface areas, Brønsted acidity and gas-adsorption capacity (Didi *et al.*, 2009; Sarıoğlan *et al.*, 2010; Çağlar *et al.*, 2013; Wang *et al.*, 2013).

Ammonia is a colourless and malodorous gas (Li *et al.*, 2010). It consists of three hydrogen atoms bonded to nitrogen with a H–N–H bond angle of ~107°. It has a molar mass of 17.0312 g mol^{-1} and a kinetic diameter of 2.6 Å. The ammonia molecule has a dipole moment (1.5 Debye) due to its asymmetrical shape (Appl, 2000). Agricultural activities produce various types of ecological pollutants, one of which is ammonia (Ciahotný *et al.*, 2002). In particular, ammonia released from livestock and poultry poses a serious environmental risk (Amon *et al.*, 1997), and the concentration of ammonia in the air directly affects worker health and production capacity. When the ammonia concentration reaches 50 ppm in poultry, the production capacity decreases and workers display eye irritation (Gülşen & Alagöz, 2010). In addition, ammonia may cause pharyngitis, laryngitis and pulmonary oedema (Appl, 2000). Consequently, the release of ammonia in livestock facilities must be controlled.

Clay minerals may be good candidates for dealing with the problem of controlling the concentration of ammonia in air due to their structural properties and significant gas-adsorbing capacities. Russell (1965) reported the ammonia-adsorption capacity of Wyoming montmorillonite to be 0.58 mmol g^{-1}. Ursu *et al.* (2008) used the Al^{3+}-doped K10 commercial clay and natural Romanian Na-bentonite in fixed and fluidized bed gas–solid reactors and reported ammonia-adsorption capacities of 2.09 and 1.07 mmol g^{-1} for K10 and Na-bentonite, respectively. Panasyugin *et al.* (2004) determined the ammonia-adsorption capacity of Fe^{3+}-modified montmorillonite to be ~4 mmol g^{-1}, and Belzunce *et al.* (1998) observed that the ammonia-adsorption

capacity of sepiolites modified with hydrofluoric acid at various concentrations and at 60°C increased up to 0.320 mmol g^{-1}. Exchangeable cations and moisture affect ammonia adsorption in clay soils (Dontsova *et al.*, 2005). Seredych *et al.* (2016) reported that the phenolic–formaldehyde resin/bentonite composite material exhibited an ammonia-adsorption capacity of 38 mg g^{-1} (~2.23 mmol g^{-1}). Liu *et al.* (2016) observed that the ammonia-adsorption capacity of bentonite treated with 4 M HCl solution for 1 h was 0.828 mmol g^{-1}. Based on previous studies in the literature, it is clear that there is limited work on ammonia adsorption by acid-treated bentonites. In addition, the presence of large bentonite deposits in Turkey would make this material advantageous for use in the removal of harmful gases such as ammonia in the future (İpekoğlu *et al.*, 1997). Therefore, the purpose of the present study is to investigate the effect of HCl treatment on bentonite for adsorbing ammonia at 298 K from environments such as poultry houses.

Materials

Natural bentonite (B) from the Ünye region was used in this study. The bentonite sample was ground and sieved to obtain the <63 µm fraction. A total of 5 g of each bentonite was activated with 100 mL of 0.5–2.5 M HCl solutions at 75°C for 4 h under reflux conditions. The suspensions were then filtered, and the solid samples were washed several times with deionized water at the approximate boiling point and dried at 100°C overnight. The dried bentonite samples were kept in a desiccator containing silica gel. Acid-treated bentonites were labelled as 'BH-*X*', where *X* indicates the acid molarity.

Experimental

The mineralogy of the samples was determined using X-ray diffraction (XRD) with a Panalytical Emperian device using Cu-*K*α radiation (λ = 1.54 Å) in the range 5–40°2θ with a step size of 0.02° at room temperature using the glass slide method. The chemical composition of the bentonites was determined using X-ray fluorescence (XRF) spectroscopy with a Rigaku ZSX Primus XRF spectrometer. Simultaneous thermogravimetric/differential thermal analysis (TG/DTA) was conducted using Setaram Setsys Evolution equipment in the temperature range 30–1000°C at a heating rate of 10°C min^{-1}. Approximately 35 mg of sample was used for each run. Nitrogen gas adsorption isotherms of the bentonites were obtained at 77 K using 3Flex equipment (Micromeritics, USA). The adsorption isotherms of ammonia were determined volumetrically at 298 K and up to 100 kPa using the same 3Flex instrument. The nitrogen- and ammonia-adsorption measurements were made after degassing in vacuum at 125°C for 12 h. The specific surface areas and the micropore data were calculated using the Brunauer–Emmett–Teller (BET) and *t*-plot methods, respectively.

Results and discussion

Chemical composition

The chemical compositions (mass% of metal oxides) of the raw bentonite and the acid-treated samples (BH-0.5, BH-1.0, BH-1.5, BH-2.0 and BH-2.5) are listed in Table 1. For the BH-0.5 sample, the Ca^{2+}, Na$^+$ and K$^+$ contents of the bentonite decreased rapidly due to the initial attack of the H$^+$ ions of HCl on the exchangeable interlayer cations (Na$^+$, Ca^{2+} and K$^+$) and

Table 1. Chemical composition (mass%) of the raw and acid-treated bentonite samples.

Sample	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	LOI
B	57.841	22.362	2.241	3.208	2.188	1.320	2.922	7.750
BH-0.5	61.739	20.766	2.534	3.448	0.722	0.769	2.504	7.323
BH-1.0	61.982	20.635	2.526	3.460	0.563	0.672	2.448	7.489
BH-1.5	62.624	20.358	2.561	3.597	0.465	0.710	2.331	7.137
BH-2.0	63.680	19.226	2.352	3.279	0.563	0.967	2.636	7.115
BH-2.5	63.955	19.354	2.164	3.238	0.613	0.881	2.718	6.900

LOI = loss on ignition.

the resulting cation exchange (Carrado & Komadel, 2009). However, CaO, Na$_2$O and K$_2$O were not totally depleted from the acid-treated samples due to the presence of impurities such as feldspar, which resisted leaching (Bendou & Amrani, 2014). These results are consistent with the XRD data (Fig. 1).

As the acid concentration increased, the SiO$_2$ content of acid-modified bentonites increased, while the abundances of octahedral cations (Al^{3+}, Fe^{3+} and Mg^{2+}) decreased. This is due to the resistance of Si tetrahedral sheets in acid solution. Although the acid molarity increased up to 2.5 M (Fig. 1f), the Si–O network was not fully destroyed in accordance with previous studies (Brindley & Youell, 1951; Erdoğan Alver *et al.*, 2016). The dissolution behaviour of bentonites at low acid concentrations depends largely on the experimental conditions (e.g. acid concentration and contact time). For example, Timofeeva *et al.* (2015) found that the Al contents of 0.25 and 0.50 M HCl acid-activated bentonites from Russia and Kazakhstan increased slightly. On the other hand, Arus *et al.* (2018) determined that the Fe content of the bentonite first increased and then decreased, while the Al content of a commercial bentonite decreased continuously. In the present study, low acid concentrations generally affected the exchangeable cations more substantially, and the SiO$_2$/Al$_2$O$_3$ ratio increased with increasing acid molarity (Table 1), in accordance with similar previous studies (Venaruzzo *et al.*, 2002; Amari *et al.*, 2010; Bendou & Amrani, 2014; Erdoğan Alver *et al.*, 2016; Komadel, 2016; Alexander *et al.*, 2018).

X-ray diffraction

The XRD traces of the original and acid-treated samples are shown in Fig. 1. Sample B consists predominantly of smectite, feldspar, opal-CT and quartz. The identification of the clay minerals and non-clay minerals in the raw bentonite followed Moore & Reynolds (1997). The 001 reflection was mainly affected by acid treatment and the intensity of this peak decreased significantly after treatment with 0.5 M HCl solution (Fig. 1). As the acid concentration increased to 2.5 M, the intensities of the non-basal reflections of montmorillonite (4.43 and 2.56 Å) also decreased. The presence of feldspar, quartz and analcime in the sample treated with 2.5 M HCl indicates that these phases are more resistant to acid attack than smectite (Venaruzzo *et al.*, 2002). As the acid concentration increased, the crystal order of smectite decreased. Moreover, the XRD traces of the acid-treated samples show the characteristic hump between 19 and 30°2θ, which becomes clearer due to partial destruction of the smectite structure and precipitation of amorphous SiO$_2$. A similar characteristic hump for acid-treated bentonites has also been reported in previous works (Gonzales-Pradas *et al.*, 1991; Christidis *et al.*, 1997; Venaruzzo *et al.*, 2002). Acid treatment caused significant changes in the smectite structure, especially at HCl molarities greater than 1.0 M.
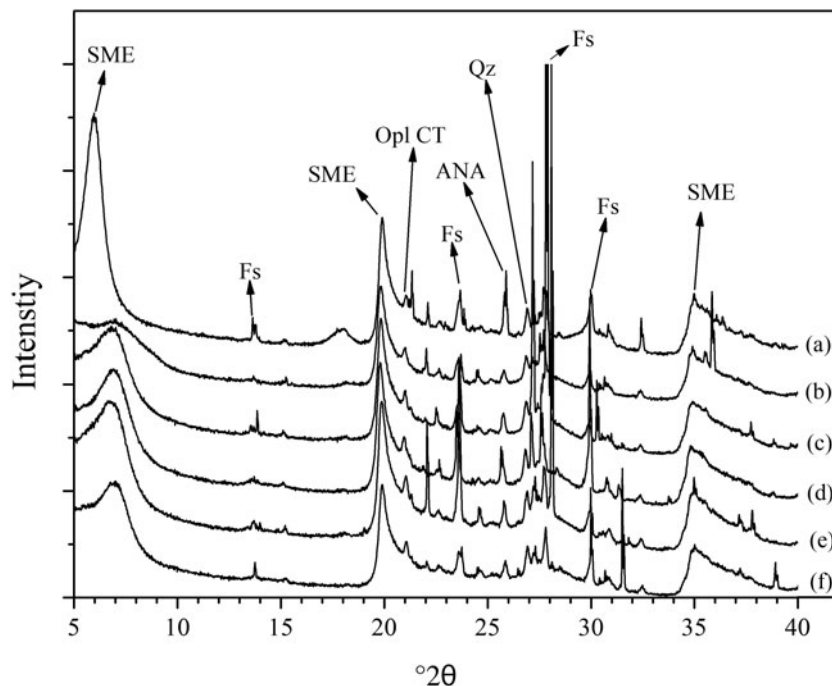
Fig. 1. XRD traces of (a) the original bentonite sample, (b) BH-0.5, (c) BH-1.0, (d) BH-1.5, (e) BH-2.0 and (f) BH-2.5. ANA = analcime; Fs = feldspar; Opl CT = opal-CT; Qz = quartz; SME = smectite.

Thermal properties

The TG/DTA curves of the original and the acid-treated bentonites are shown in Fig. 2. The shoulder at 68°C and endothermic events at ~140°C and 198°C correspond to the removal of adsorbed water. The double endotherm in the original bentonite at 142°C and 198°C is associated with the presence of exchangeable divalent cations (Fontaine *et al.*, 2020), and its intensity decreased in the acid-activated bentonites. The lower abundances of CaO after acid treatment (Table 1) support the relationship between the presence of divalent cations and double-peak behaviour. The endothermic peak at 651°C is attributed to the dehydroxylation of smectite. Increasing acid concentration affected the thermal behaviour of the bentonite samples. The dehydroxylation peaks of samples BH-0.5, BH-1.0, BH-1.5, BH-2.0 and BH-2.5 became more diffuse and shifted to lower temperatures (623–629°C) compared to the original bentonite sample (651°C). This result may be attributed to the easier loss of hydroxyl units from the broken edges of the acid-treated bentonites (Srasra *et al.*, 1989; Çağlar *et al.*, 2013). The endothermic peak at 869°C indicates collapse of the structure and recrystallization.

The total mass-loss values of all bentonite samples were determined using TG analysis (Fig. 2). The first mass-loss event of the bentonite samples due to removal of adsorbed interlayer water occurred between 30 and 200°C. In addition, the total mass losses of the BH-0.50, BH-1.0, BH-1.5, BH-2.0 and BH-2.5 samples (6.463–7.325%) were smaller than that of the original bentonite sample (8.915%). This result is due to the loss of exchangeable cations and disorganization of the tetrahedral and octahedral layers as a result of acid activation (Srasra *et al.*, 1989; Christidis *et al.*, 1997; Önal *et al.*, 2002; Çağlar *et al.*, 2013).

N₂ adsorption

The N₂ adsorption isotherms of the original and acid-treated bentonite samples are presented in Fig. 3. The isotherms of bentonites are of type II (Gregg & Sing, 1982; Lowell *et al.*, 2004). Table 2 presents some important parameters obtained from the

analysis of the nitrogen-adsorption isotherms. The *t*-plot method ($P/P_0 > 0.1$) was used to evaluate the micropore surface areas and micropore volumes of the samples. The specific surface areas were calculated using data in the interval $0.05 < P/P_0 < 0.35$ (Table 2). As the acid concentration increased, the N₂-adsorption capacities gradually increased. The specific surface area of natural bentonite increased from 55 to 129 m² g⁻¹ after acid treatment with 2.5 M HCl solution (BH-2.5). The increase in specific surface area is due to the gradual disruption of the smectite structure and the formation of amorphous SiO₂, generating greater microporosity (Venaruzzo *et al.*, 2002; Horri *et al.*, 2020). However, it was not possible to increase the micropore surface area by increasing the acid concentration beyond a certain value. In addition, the sample modified with 2.5 M HCl had a smaller micropore surface area (39.61 m² g⁻¹) and micropore volume (0.0161 cm³ g⁻¹) than the BH-2.0 sample (48.50 m² g⁻¹ and 0.0197 cm³ g⁻¹, respectively). This is attributed to an increase in average pore diameter, condensations of silanol groups and a partial collapse of the smectite crystal structure (Gonzalez-Pradas *et al.*, 1991; Horri *et al.*, 2020), in accordance with the XRF data (Table 1) and the XRD data (Fig. 1).

NH₃ adsorption

The ammonia-adsorption isotherms for the original and acid-treated bentonites are shown in Fig. 4, and the amounts of adsorbed NH₃ per gram of bentonite are listed in Table 2. NH₃, an extremely polar molecule, penetrates easily between the smectite layers. In addition, its relatively small kinetic diameter (2.6 Å) should render it available to the whole clay surface (Siegel, 1956). Slightly greater amounts of ammonia were adsorbed on acid-treated bentonites at lower partial pressures. The difference in adsorption of ammonia between different samples decreased with increasing partial pressure. Sorption of ammonia gas on all of the bentonites increased in the following sequence: B < BH-2.5 < BH-2.0 < BH-0.5 < BH-1.5 < BH-1.0 (Table 2). The NH₃-adsorption capacities of acid-treated bentonite samples varied
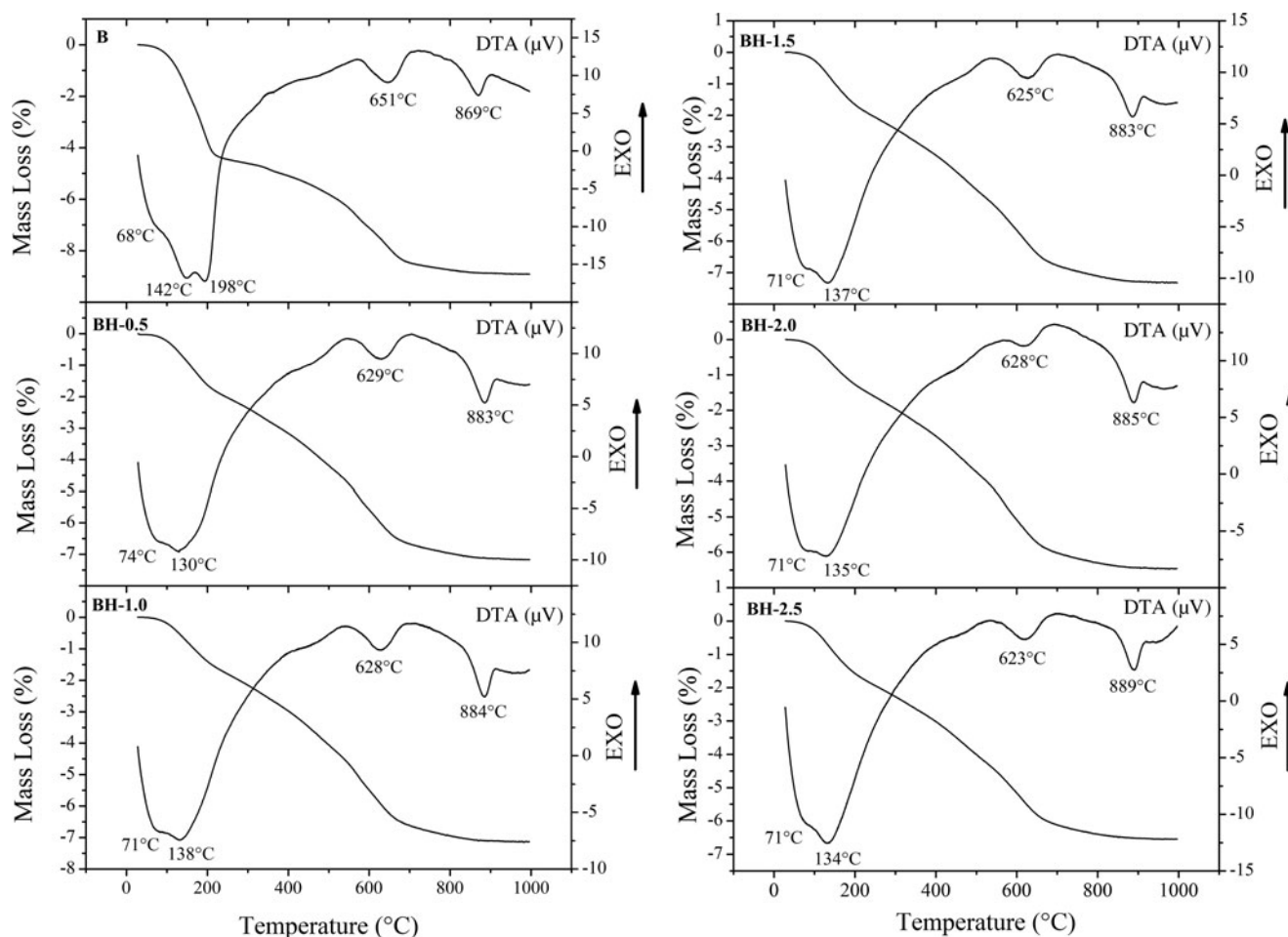
Fig. 2. TG/DTA curves for the raw and acid-activated bentonite samples.
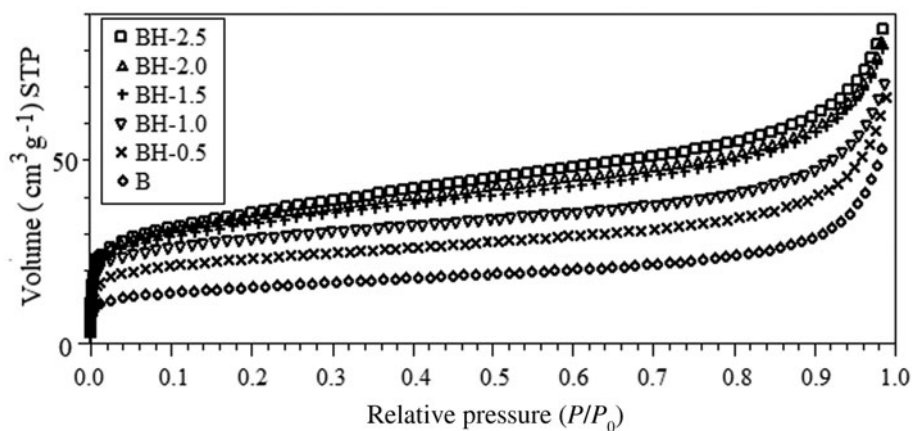

Fig. 3. N_2-adsorption isotherms of the raw and acid-activated bentonite samples. STP = standard temperature and pressure.

from 4.000 to 5.068 mmol g^{-1}. Sample B (3.801 mmol g^{-1}) demonstrated a much lower adsorption capacity compared to the acid-treated forms. The stronger affinity for ammonia of acid-treated bentonites is attributed to the presence of active acidic sites, which attract basic ammonia molecules (Siegel, 1956).

Increasing the acid concentration to greater than 1.0 M did not further increase the NH$_3$-adsorption capacity (Fig. 4).

Sample BH-1.0 showed the highest NH$_3$-adsorption capacity (5.068 mmol g^{-1}) compared to the remaining samples (Table 2). In addition to the removal of exchangeable cations and the loss of octahedral cations, acid treatment increases the number of Brønsted and Lewis acid sites in the clay structure and leads to the formation of Si-OH, Al-OH and (SiO$_3$) Si–OH groups. Thus, interaction of ammonia with silanol groups and surface

Table 2. N$_2$- and NH$_3$-adsorption data of the raw and acid-treated bentonite samples.

Sample	BET surface area (m^2 g^{-1})	Micropore surface area (m^2 g^{-1})	Micropore volume (cm^3 g^{-1})	NH$_3$ adsorption (mmol g^{-1}) at 298 K
B	55	21.43	0.0088	3.801
BH-0.5	85	43.34	0.0176	4.343
BH-1.0	104	47.01	0.0189	5.068
BH-1.5	118	47.12	0.0193	4.485
BH-2.0	126	48.50	0.0197	4.139
BH-2.5	129	39.61	0.0161	4.000

oxygens is more probable for acid-modified bentonites (Ashworth, 1978; Christidis *et al.*, 1997; Venaruzzo *et al.*, 2002). However, although the density of the Brønsted acid sites increased with the acid concentration, the total number of acid sites on the montmorillonite surface decreased due to dealumination (Flessner *et al.*, 2001).

The ammonia-adsorption capacities of the bentonite samples were not directly proportional to their specific surface areas (Fig. 5). Although the specific surface area values of BH-1.5, BH-2.0 and BH-2.5 (118–129 m^2 g^{-1}) were greater than that of BH-1.0 (104 m^2 g^{-1}), the ammonia-adsorption capacities were lower (4.000–4.485 mmol g^{-1}) owing to the greater extent of dealumination and partial destruction of the structure (Fig. 1 & Table 1). This is probably because ammonia adsorption is associated with specific sites on the surface. Retention of ammonia by sample BH-1.0 (5.068 mmol g^{-1}) was greater than those of the commercial adsorbent K10-montmorillonite (2.09 mmol g^{-1}) and Na-bentonite (1.07 mmol g^{-1}) (Ursu *et al.*, 2008), carbon/bentonite composites (14.8 mg g^{-1}, 0.869 mmol g^{-1}) (Seredych *et al.*, 2008), phenolic–formaldehyde resin/bentonite composites (~2.23 mmol g^{-1}) (Seredych *et al.*, 2016), Fe^{3+}-modified montmorillonite (~4.0 mmol g^{-1}) (Panasyugin *et al.*, 2004) and bentonite treated with 4 M HCl solution for 1 h (0.828 mmol g^{-1}) due to the structural and textural differences in the origin, the mineral and impurity contents and the conditions of acid treatment. The abundance and large sorption capacity of the bentonite-type clay mineral contribute to low-cost and eco-friendly solutions. Therefore, bentonite treated with 1.0 M HCl solution is a promising material for removing ammonia from the air in livestock facilities.
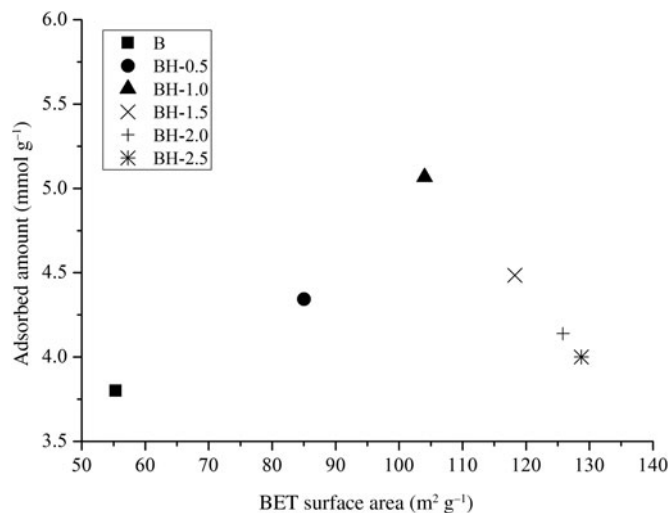
Fig. 5. NH$_3$-adsorption *vs* BET surface area values of the bentonite samples.

Summary and conclusions

The adsorption characteristics of bentonite and its acid-activated counterparts towards NH$_3$ were investigated. All samples were examined using XRF, XRD, TG/DTA and N$_2$ adsorption techniques to determine their structural, chemical and thermal properties, and the following conclusions were drawn:

(1) Significant structural changes occurred as a result of the acid activation, and the smectite structure dissolved significantly with increasing acid molarity.
(2) All chemical elements except for Si decreased with increasing HCl concentration.
(3) HCl concentrations up to 1.0 M increased the micropore surface area and volume.
(4) Thermal analysis of bentonite samples showed that the total mass losses of the acid-treated samples were lower than that of the natural form of bentonite.
(5) The acid-treated forms of bentonite were more efficient in terms of ammonia adsorption than the raw material. Although the specific surface area of the acid-modified samples increased as
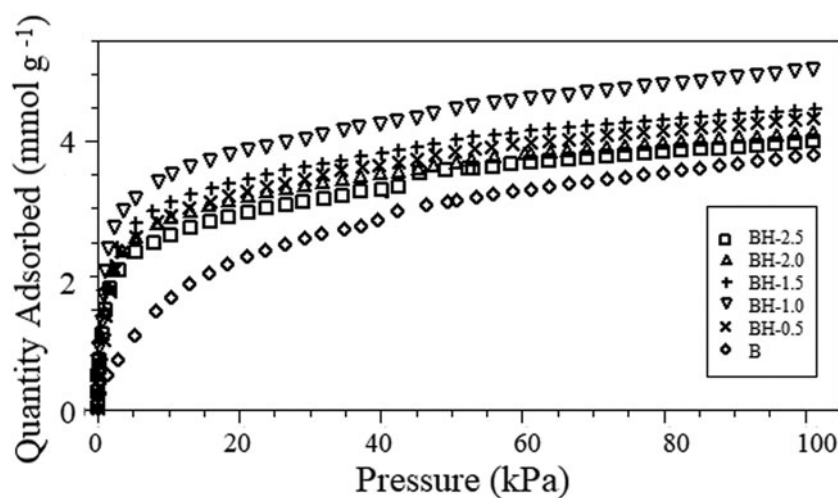
Fig. 4. NH$_3$-adsorption isotherms of the raw and acid-activated bentonite samples.

the acid concentration increased, treatment with HCl concentrations greater than 1.0 M did not increase the uptake of ammonia gas. Consequently, the BH-1.0 sample with the greatest ammonia-adsorption capacity ($5.068 \, \mathrm{mmol \, g^{-1}}$) is recommended as an effective adsorbent of ammonia gas in environments such as poultry houses.

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