Adsorptive removal of ammonium ion from aqueous solution using surfactant-modified alumina

Tien Duc Pham,[A,D] Thi Trang Do,[A] Van Lau Ha,[A] Thi Hai Yen Doan,[A] Thi Anh Huong Nguyen,[A] Thanh Duc Mai,[B] Motoyoshi Kobayashi[C] and Yasuhisa Adachi[C]

[A]Faculty of Chemistry, VNU – University of Science, Vietnam National University, Hanoi, 19 Le Thanh Tong, Hoan Kiem, Hanoi 10000, Vietnam.
[B]Centre for Environmental Technology and Sustainable Development (CETASD), VNU – University of Science, Vietnam National University, Hanoi, 334 Nguyen Trai, Thanh Xuan, Hanoi 10000, Vietnam.
[C]Faculty of Life and Environmental Sciences, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8572, Japan.
[D]Corresponding author. Email: tienduchphn@gmail.com

Environmental context. Ammonium ion, an inorganic pollutant in agricultural land, can induce eutrophication, impacting on water quality. We investigate the adsorption of ammonium ion on surfactant-modified alumina and demonstrate highly efficient removal of ammonium ions by the alumina from two agricultural water samples. Adsorption mechanisms are also proposed based on adsorption isotherms, surface modification and the change in surface charge.

Abstract. The adsorptive removal of ammonium ions (NH_4^+) from aqueous solution using surfactant-modified alumina (SMA) was investigated. The optimum NH_4^+ adsorption removal conditions on SMA were systematically studied and found to be pH 4, contact time 180 min, adsorbent dosage 30 mg mL^{-1} and ionic strength 1 mM NaCl. The equilibrium concentration of NH_4^+ was measured by capillary electrophoresis with capacitively coupled contactless conductivity detection (CE-C^{4}D) and spectrophotometry. Surface modification of α-Al$_2$O$_3$ with the anionic surfactant sodium dodecyl sulfate (SDS) at high salt concentration induced a significant increase of removal efficiency. The change in surface charge and surface modification of α-Al$_2$O$_3$ by pre-adsorption of SDS and subsequent adsorption of NH_4^+ were evaluated by zeta potential measurements and Fourier-transform infrared spectroscopy. Under optimum adsorption conditions, NH_4^+ removal from two agricultural water samples achieved very high removal efficiencies of 99.5 and 96.5 %. The adsorption of NH_4^+ onto SMA increases with decreasing NaCl concentration because desorption of SDS from the α-Al$_2$O$_3$ surface is minimised. Experimental results of NH_4^+–SMA adsorption isotherms at different ionic strengths can be represented well by a two-step adsorption model. Based on adsorption isotherms, surface charge effect and surface modification, we suggest that the adsorption mechanism of NH_4^+ onto SMA was mainly electrostatic attraction between cationic NH_4^+ and the negatively charged SMA surface.

Introduction

The increase of nitrogen contamination in water results mainly from agricultural activities, industrial effluent, or natural disasters. One of the inorganic pollutants in aqueous solution is the ammonium ion (NH_4^+), which can cause eutrophication and impair self-purification of the water environment.[1] Therefore, many projects focus on the removal of ammonium ions to protect water resources and maintain ecology.

Various treatment techniques have been used for NH_4^+ removal from the aquatic environment, such as adsorption, biological nitrification, air stripping and chemical precipitation,

and electrochemical oxidation.[2–6] Among them, adsorption is one of the most common technologies for removing ammonia. Adsorptive removal of ammonia is easily applied in the gas phase by using novel adsorbents, whereas adsorption of ammonium ions from aqueous solutions is still a challenge.[7–10] In this case, novel solid adsorbents are needed.[11–19] Also, adsorption can be applicable for developing countries by the use of inexpensive or modified adsorbents.[20–32] To enhance the removal efficiency of the NH_4^+ ion by modified adsorbent surfaces, an understanding of the adsorption characteristics of the NH_4^+ ion onto charged solid surfaces is needed. Recently,

some groups have investigated the adsorptive removal of ammonium ions by using solid adsorbents such as zeolites, activated carbon, silicates and related materials. Numerous studies have focussed on the modification of solid surface adsorbents using ionic surfactants and polyelectrolytes to remove both organic and inorganic pollutants.[7,9,33–36] Nevertheless, the removal of NH_4^+ by surfactant-modified metal oxide has not been reported.

Alumina is a common adsorbent that can be easily collected and synthesised from natural minerals. Alumina with high specific surface area has been widely used for the removal of many pollutants from aqueous solution.[37] Adsorption of NH_4^+ onto alumina has been investigated previously.[7,38] In order to increase the adsorptive removal efficiency, alumina surface modification is necessary. Adsorption is normally carried out under isothermal conditions so that adsorption isotherms can be fitted by theoretical models to better understand adsorption mechanisms and to explain the interactions between the alumina surface and NH_4^+. Adsorption characteristics of inorganic pollutants are frequently described by Langmuir and Freundlich isotherms.[39,40] Such isotherms cannot be applied to adsorption of surfactants. Thus, adsorption of inorganic pollutants onto surfactant-modified alumina (SMA) could not be fitted by Langmuir and Freundlich models. Fortunately, a two-step model presented by Zhu et al.[41] with a general adsorption isotherm equation was successfully applied to various types of surfactant, polymer and dye adsorption isotherms for numerous systems.[41–46] Adsorptive removal of both organic and inorganic pollutants using SMA was thoroughly studied by Anjali Pal and coworkers,[47–52] who indicated that SMA is a novel adsorbent. However, a two-step model was not used to fit adsorption isotherms of all pollutants onto SMA. Also, they did not study the adsorption of NH_4^+ onto SMA.

In order to study the adsorption of the ammonium ion, the analytical method used for determination of NH_4^+ concentration is important. Although spectrophotometry is a common method to quantify the concentration of NH_4^+ in aqueous media,[53] it requires the preparation of many chemicals and may suffer from interference at high salt concentrations. Fortunately, capillary electrophoresis (CE) with capacitively coupled contactless conductivity detection (C^4D) is a simple, fast and inexpensive method that can be applied to simultaneously determine NH_4^+ and alkaline ions in aqueous media.[54,55] This method, which is a 'green' technique, is also useful for determining low concentrations of NH_4^+ in a complex matrix. Owing to the advantageous properties of CE-C^4D for determining NH_4^+ in solutions, the effects of experimental adsorption conditions such as pH, contact time, adsorbent dosage and ionic strength can be easily evaluated. CE-C^4D is a separation method with high efficiency so that it can be used to determine NH_4^+ in complex matrices to evaluate removal efficiency after adsorption in agricultural water samples.

In the present research, we investigate adsorptive removal of NH_4^+ using SMA. This is the first systematic study of the adsorption of ammonium ions from aqueous solution on SMA by CE-C^4D, spectroscopic and electrokinetic methods. The optimum parameters for adsorptive removal of NH_4^+ using SMA are systematically studied. Surface modification and the change in surface charge are investigated by Fourier-transform infrared spectroscopy (FT-IR) and zeta potential measurements respectively. An adsorption mechanism is also proposed on the basis of adsorption isotherms, surface modification and the change in zeta potential.

Experimental

Materials

High-purity (99.99 %) α-Al$_2$O$_3$ (AKP-30, Sumitomo, Chuo-ku, Osaka, Japan), diameter ~300 nm, was used. Specific surface area was determined by the Brunauer–Emmett–Teller (BET) method using a surface area analyser (Micromeritics, Gemini VII 2390 – Micromeritics Instrument Corp., Norcross, GA, USA) and found to be 7.85 m^2 g^{-1}. The α-Al$_2$O$_3$ was treated before measurements as follows: the original α-Al$_2$O$_3$ was washed several times with 0.2 M NaOH before washing with ultrapure water to neutral pH, then dried at 110 °C and reactivated at 600 °C for 2 h. The treated α-Al$_2$O$_3$ was cooled in a desiccator at room temperature and stored in a polyethylene container. The α-Al$_2$O$_3$ that was modified with 0.01 M sodium dodecyl sulfate (SDS) (solid-to-liquid ratio 30 mg mL^{-1}) in 0.1 M NaCl at pH 4 by shaking for 3 h, and then washed with ultrapure water, was called surfactant-modified alumina (SMA).

Pure analysis-grade ammonium chloride (NH$_4$Cl, CAS number 12125-02-9) was supplied by Merck (Germany). The anionic surfactant SDS (purity >95 %; Wako Pure Chemical Industries) was used to modify the surface of α-Al$_2$O$_3$. All chemicals for determination of ammonium ions by spectrophotometry such as thymol, sodium nitroprusside dihydrate, sodium carbonate, sodium bicarbonate and sodium hydroxide were analytical reagents, purchased from Merck or Scharlau (Spain). Commercial hypochlorite solution, 3 % available chloride, was also used to determine the concentration of ammonium ions spectrophotometrically. The cationic dye methylene blue (purity >98.5 %) and organic solvent CHCl$_3$ (HPLC grade) from Merck were used to determine the concentration of SDS spectrophotometrically. The effect of ionic strength was studied by the addition of NaCl (Merck). In order to adjust solution pH, HCl and NaOH (Merck) were used. Buffers of histidine and acetic acid (His/Ace) in the presence of 18-crown-6 were prepared from chemicals purchased from Merck or Scharlau (Spain) of analytical reagent grade. An ultrapure water system (Labconco, USA) with resistivity 18.2 MΩ cm was used to produce ultrapure water for preparing all aqueous solutions.

Adsorption studies

All adsorption experiments were conducted in batches. Initially, 10^{-2} M ammonium stock solution was prepared by dissolving a precisely calculated amount of ammonium chloride. Then, the stock solution was appropriately diluted based on experimental requirements.

A known amount of adsorbent solution was thoroughly mixed with 10 mL of 10^{-4} M aqueous ammonium solution (NH_4^+) in 15-mL Falcon tubes at 25 ± 2 °C (air-conditioned laboratory). The effect of operating conditions (pH, adsorbent dosage, contact time, ionic strength and initial absorbate concentration) on removal of NH_4^+ was studied. The concentration of NH_4^+ was determined by CE-C^4D. The removal efficiency (% RE) of NH_4^+ was calculated with Eqn 1.

$$\% \, RE = \frac{C_i - C_f}{C_i} \times 100 \, \%$$ (1)

where C_i and C_f are initial concentrations and final concentrations of NH_4^+ respectively. The experimental adsorption studies were carried out in triplicate.

To measure adsorption isotherms, the concentration of NH_4^+ was varied from 10^{-5} M to 6×10^{-3} M and pH was adjusted to

the desired value. The adsorption capacity of NH_4^+ (ΓNH_4^+) onto α-Al_2O_3 and onto SDS-modified α-Al_2O_3 was determined by the concentration difference of NH_4^+ solutions before adsorption and after equilibration by CE-C⁴D. All adsorption isotherms were measured twice.

CE-C⁴D

The concentration of NH_4^+ was determined using a portable semi-automated CE-C⁴D detection (3Sanalysis JSC, Hanoi, Vietnam). Fig. 1 shows a photograph of the CE-C⁴D instrument.

The background electrolyte solutions were prepared with a His/Ace buffer (pH 4) in the presence of 18-crown-6. Solution pH was measured using an HI 2215 Hanna Instruments pH meter (Woonsocket, RI, USA). Fused silica capillaries of 50-μm internal diameter (ID) and 365-μm outer diameter (OD) with a total length (L_t) of ~50 cm and effective length (L_{eff}) of 40 cm (purchased from Polymicro Technologies, Phoenix, AZ, USA) were used for determination. The capillaries were preconditioned with 1 M NaOH for ~10 min and then ultrapure water for 10 min before flushing with buffer solutions. Table 1 summarises the CE-C⁴D operating parameters used.

A linear standard curve with a correlation coefficient of 0.9988 between the peak area and concentrations of NH_4^+ was observed. The limit of detection (LOD) and limit of quantification (LOQ) for NH_4^+ were calculated from signals of six replicates of peak area corresponding to 3 and 10 times the baseline noise ($s/n = 3$ and 10) respectively. The LOD was 5×10^{-6} M while the LOQ was 5×10^{-6} M. Method validity was confirmed by spectrophotometry based on the colour change of indothymol blue formed between ammonia in nitroprusside and thymol [53]. The differences in determination of NH_4^+ concentration by the two methods did not exceed 5% (Table S1, available as supplementary material to this paper).

Spectrophotometry

The concentration of the anionic surfactant SDS used for α-Al_2O_3 surface modification was determined by spectrophotometry using an ion-paired complex of SDS and methylene blue dye in chloroform solvent. The procedure followed our previous paper.[45]
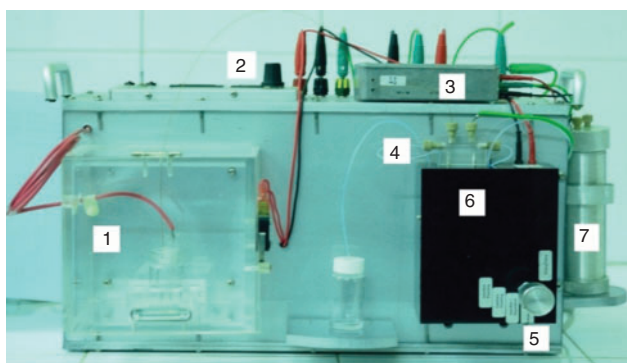
Fig. 1. Photograph of the capillary electrophoresis with capacitively coupled contactless conductivity detection (CE-C⁴D) instrument. (1) Safety cage for application of high voltage (HV); (2) HV controller board, on/off and magnitude controls, and two digital screens for the monitoring voltage and current; (3) miniaturised HV conductively coupled contactless conductivity detector; (4) flow-cell interface housing one capillary and the ground electrode; (5) rotary selector switch; (6) box containing solenoid valves; (7) gas-pressurised buffer container.

Spectrophotometry was also used to validate the determination of ammonium ions in the presence of thymol. Details of the procedure are as follows: an aqueous sample of 10 mL was transferred into a 25-mL volumetric flask with 1 mL of 1% sodium nitroprusside solution, 2 mL of carbonate buffer (pH 10 prepared from appropriate amounts of sodium carbonate and sodium bicarbonate) and 0.2 mL of 0.1% hypochlorite solution and the solution was thoroughly mixed. After mixing, 2 mL of 3% thymol solution in 2 M NaOH was added to the solution. Then, the solution was diluted to the mark with ultrapure water and incubated for 5 min. The absorbance was measured at 693 nm with a glass 10-mm path-length cuvette using a spectrophotometer (UV-1650 PC, Shimadzu, Japan).

The linear relationship between the absorbance and concentrations of NH_4^+ had a correlation coefficient of at least 0.997.

Zeta potential measurements

Zeta potential measurement was used to evaluate the change in α-Al_2O_3 surface charge before and after pre-adsorption with SDS and subsequent adsorption of NH_4^+. The zeta potential is calculated from the electrophoretic mobility using Smoluchowski's equation[56]

$$\zeta = \frac{u_e \eta}{\varepsilon_{rs} \varepsilon_0} \tag{2}$$

where ζ is the zeta potential (mV), u_e is the electrophoretic mobility ($m^2 \ s^{-1} \ V^{-1}$), η the dynamic viscosity of the liquid (mPa s), ε_{rs} the relative permittivity constant of the electrolyte solution and ε_o is the electric permittivity of vacuum ($8.854 \times 10^{-12} \ F \ m^{-1}$).

The electrophoretic mobility was measured using a Zeta phoremeter IV (CAD Instrumentation, France) at a temperature of 25 °C, pH 4.0, and with a background electrolyte of 1 mM NaCl.

FT-IR spectroscopy

To confirm surface modification of α-Al_2O_3 and to reveal the adsorption mechanism of NH_4^+ onto SMA, FT-IR spectroscopy was performed with an Affinity-1S spectrometer (Shimadzu, Japan). The FT-IR spectra of α-Al_2O_3, SMA, SMA after adsorption of NH_4^+ at the maximum level and NH_4Cl were obtained under at the same conditions: 25°C, atmospheric pressure, and resolution of 4 cm^{-1}.

Modelling by general isotherm equation

The isotherms obtained were fitted by a general isotherm equation. The equation was derived by assuming that two adsorption steps can occur at the solid–liquid interface.[41]

Table 1. Operating conditions of capillary electrophoresis with capacitively coupled contactless conductivity detection (CE-C⁴D) system for determine NH_4^+ in aqueous media

Background electrolyte composition	Histidine/acetic acid buffer adjusted to pH 4, 2 mM 18-crown-6
High voltage	20 kV
Detection	C⁴D
Capillary	365 μm OD, 50 μm ID; L_t 50 cm; L_{eff} 40 cm; pre-conditioned
Hydrodynamic injection	20 s at 15-cm height

The general isotherm equation is

$$\Gamma = \frac{\Gamma_\infty k_1 C\left(\frac{1}{n} + k_2 C^{n-1}\right)}{1 + k_1 C\left(1 + k_2 C^{n-1}\right)} \qquad (3)$$

where Γ is the amount of NH_4^+ adsorbed, Γ_∞ is the maximum adsorption amount, $k1$ and k_2 are equilibrium constants for the first layer adsorption and clusters of n molecules or multilayer adsorption. C denotes the equilibrium concentration of NH_4^+ in solution.

The selected fitting parameters are described in our previously published papers.[44–46]

Results and discussion

Surface modification of α-Al₂O₃ by SDS

The measurement of the anionic surfactant SDS adsorption isotherm on $\alpha\text{-}Al_2O_3$ is reported in Fig. S1. The maximum adsorption capacity of SDS on $\alpha\text{-}Al_2O_3$ was obtained at high NaCl concentration when the concentration of SDS in bulk solution was higher than the critical micelle concentration (CMC). Thus, SDS with a concentration of 0.01 M was used to modify the surface of $\alpha\text{-}Al_2O_3$ in 0.1 M NaCl (pH 4). Because the point of zero charge of $\alpha\text{-}Al_2O_3$ is $\sim$8.0,[57,58] SDS adsorption on $\alpha\text{-}Al_2O_3$ is enhanced at low pH. The maximum adsorption capacity of SDS onto $\alpha\text{-}Al_2O_3$ (with a solid–liquid ratio of 30 mg mL^{-1}) is 0.293 mmol g^{-1}, which is in good agreement with published papers.[59–61] The loading implies the presence of a bilayer and/or admicelles of SDS.[45] As a result, the surface charge of $\alpha\text{-}Al_2O_3$ is negative, which can enhance adsorption of inorganic cationic pollutants such as NH_4^+. Fig. 2 indicates that the removal efficiency of NH_4^+ in 1 mM NaCl (pH 4) with an initial concentration of 10^{-4} M increases significantly from 18.1 to 94.4 % after the surface modification of $\alpha\text{-}Al_2O_3$ by SDS.

The results of surface modification and the change in surface charge on SDS pre-adsorption and adsorption of NH_4^+ evaluated by FT-IR spectroscopy and zeta potential measurement are given below.

FT-IR spectroscopy

FT-IR is widely used to characterise adsorbed functional groups.[62] Fig. 3 shows the ex situ FT-IR spectra of $\alpha\text{-}Al_2O_3$ particles without adsorbate, $\alpha\text{-}Al_2O_3$ after pre-adsorption with SDS (SMA), and SMA after NH_4^+ adsorption with peaks assigned in the wavenumber range 400–4000 cm^{-1}. The FT-IR spectrum of NH_4Cl, which was also recorded from 400 to 4000 cm^{-1}, is given in Fig. 4.

Fig. 3 shows that the relative intensity of asymmetrical and symmetrical stretching of $-CH_2-$ present at 2924 and 2854 cm^{-1} decreases dramatically in SMA compared with SDS powder (data not shown). This confirms that hydrophobic interaction occurs on the surface of $\alpha\text{-}Al_2O_3$. In addition, the characteristic peaks of SO_4^{2-} at $\sim$1247 and 1218 cm^{-1} appear very strongly in spectra of SDS whereas all bands disappear in the spectra of SMA. This demonstrates that SDS has sulfate head groups in contact with the surface of $\alpha\text{-}Al_2O_3$ through electrostatic attraction. Admicelles in an SDS bilayer containing both a first layer head-on towards $\alpha\text{-}Al_2O_3$ and second layer head-out towards solution were formed.[45] In other word, the modification of $\alpha\text{-}Al_2O_3$ was successful owing to the presence of admicelles at the surface of $\alpha\text{-}Al_2O_3$.
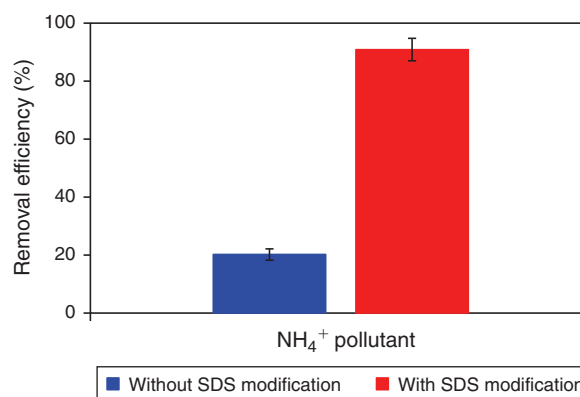

Fig. 2. The removal efficiency of NH_4^+ pollutant starting from an initial concentration of 10^{-4} M in 1 mM NaCl (pH 4) using $\alpha\text{-}Al_2O_3$. Error bars show the standard deviations of three replicates.

As can be seen in Figs 3 and 4, a comparison between the spectra of NH_4Cl and SMA after NH_4^+ adsorption indicates that the characteristic peak of N–H at $\sim$1402 cm^{-1} appears in the NH_4^+ spectrum (Fig. 4)[9,63] but it disappears after adsorption onto SMA (Fig. 3). In addition, the peaks of $-CH_2-$ present at 2924 and 2854 cm^{-1} in the SMA spectra could not be seen after NH_4^+ adsorption. These results suggest the adsorption of ammonium ion onto SMA through N–H bonding.

Zeta potential measurements

Electrophoretic mobility measurement is useful for characterising the charging behaviour of many nano- and microsized materials.[64,65] Zeta potential calculated from electrophoretic mobility of $\alpha\text{-}Al_2O_3$ particles, $\alpha\text{-}Al_2O_3$ modified with SDS (SMA) and SMA after adsorption of ammonium ions was measured in 1 mM NaCl background electrolyte at pH 4.

Fig. 5 shows that the ζ potential of $\alpha\text{-}Al_2O_3$ significantly changes after pre-adsorption with SDS and after adsorption of ammonium ion. Although the value of the ζ potential of $\alpha\text{-}Al_2O_3$ in the present study is small compared with other work,[58,66,67] the surface of $\alpha\text{-}Al_2O_3$ still has a positive charge ($\zeta = 12.95$ mV). As SDS is an anionic surfactant, the pre-adsorption of SDS onto $\alpha\text{-}Al_2O_3$ (SMA) induces negative surface charge ($\zeta = -17.05$ mV). This implies that the admicelles occur with negative SDS head groups towards the solution, indicating charge reversal occurs. However, after adsorption of ammonium ions (cations), the net negative charge is decreased so that the ζ potential is less negative ($\zeta = -11.29$ mV) than without NH_4^+ adsorption. These results agree well with FT-IR measurements.

Adsorptive removal of ammonium ion using surfactant-modified alumina

Effect of pH

Solution pH plays an important role in the adsorption of NH_4^+ onto SMA because it can influence the surface charge of SMA and charging behaviour of ammonia. As $pK_a = -\log K_a$, pK_a of NH_4^+ is 9.25 so that at pH $<$9.25, over half of the ammonia species have a positive charge. This implies that the negatively charged SMA surface can electrostatically attract NH_4^+. The effect of initial pH on the adsorption of NH_4^+ by SMA was investigated in the pH range 3–8 in 1 mM NaCl while the initial concentration of NH_4^+ was kept constant.

As can be seen in Fig. 6, the removal efficiency decreases with increasing solution pH from 4 to 8 because of the
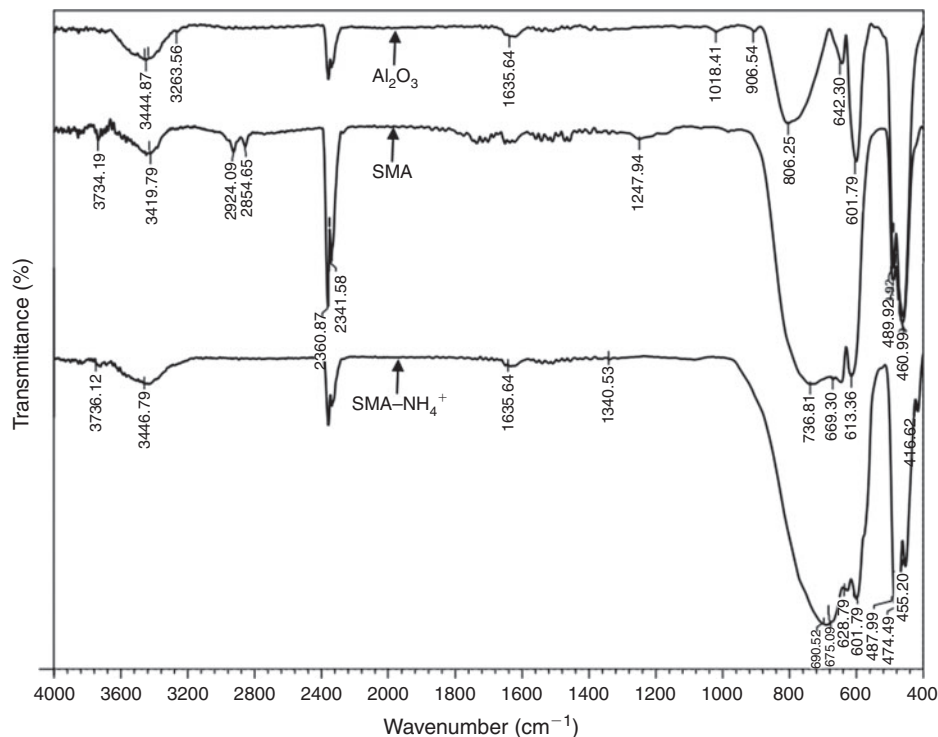
Fig. 3. Fourier-transform (FT)-IR spectra for α-Al$_2$O$_3$ particles without adsorption (Al$_2$O$_3$) and after pre-adsorption (surfactant-modified alumina, SMA) and SMA after adsorption of ammonium ions (SMA–NH$_4^+$) in the range 400–4000 cm^{-1}.
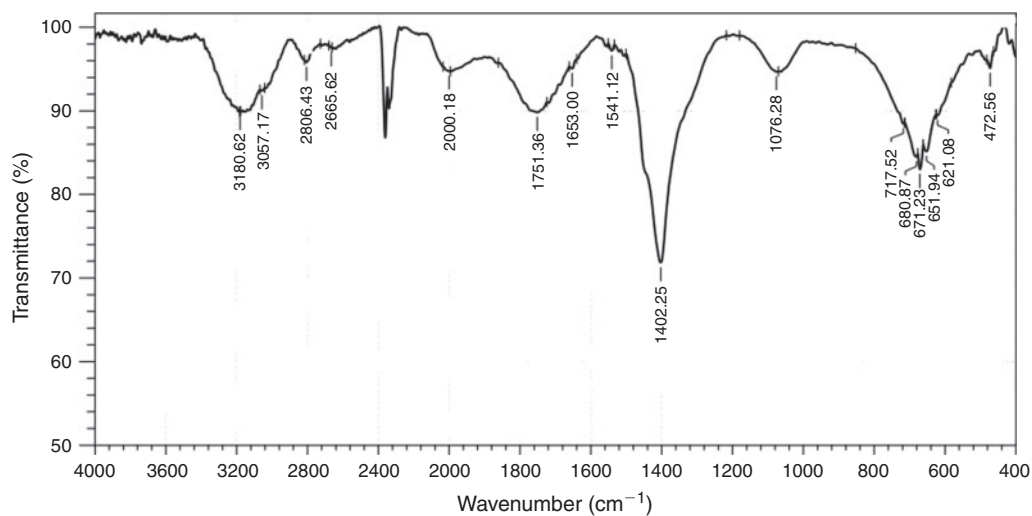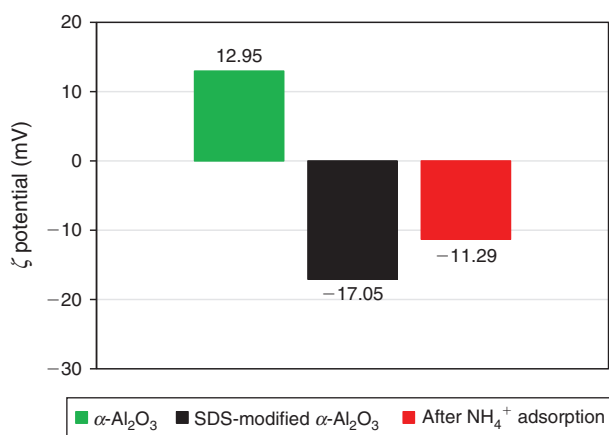

**Fig. 4.** Fourier-transform (FT)-IR spectra of NH$_4$Cl recorded from 400 to 4000 cm^{-1}.

competition between OH$^-$ (at high pH) and SDS sulfate groups on the surface of α-Al$_2$O$_3$. As a consequence, the desorption of SDS increases at higher pH (see Fig. S2), so that the removal efficiency of NH$_4^+$ decreases. Also, the error bars show higher standard deviations when increasing pH in the range 4–8. The increase of SDS desorption due to pH results in high variation in experimental replicates. However, dissolution of α-Al$_2$O$_3$ can take place at pH 3[57,58] (the error bar is quite high) and therefore, the removal efficiency seems to be a little lower than at pH 4. Thus, the optimum pH for removal of NH$_4^+$ by SMA is pH 4.

Effect of contact time

Contact time affects the completeness of adsorption equilibration. The effect of contact time on the adsorptive removal of NH$_4^+$ using SMA is presented in Fig. 7, which shows the removal efficiency grows with time from 10 to 180 min. This suggests that adsorption reaches equilibrium at 180 min. After equilibrium, the removal efficiency decreases because of NH$_4^+$ desorption at high ionic strength. Equilibration takes longer than when NH$_4^+$ is adsorbed using Fe$_3$O$_4$ nanoparticles (only 40 min) and the removal of NH$_4^+$ by coconut shell activated carbon (120 min).[1,68] However, it is somewhat faster than

331

Fig. 5. The ζ potential of α-Al$_2$O$_3$ without adsorption (α-Al$_2$O$_3$) and after modification with sodium dodecyl sulfate (SDS) (SDS-modified α-Al$_2$O$_3$) and after adsorption of ammonium ion (after NH$_4^+$ adsorption) in 1 mM NaCl (pH 4).
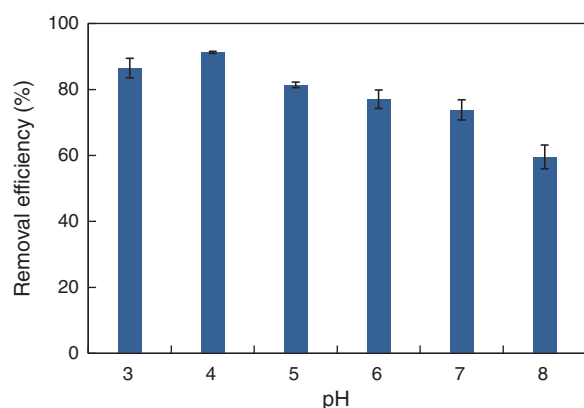
Fig. 6. Effect of pH on the removal of NH$_4^+$ by surfactant-modified alumina (SMA). (Initial concentration C_i (NH$_4^+$) = 10^{-4} M, contact time 180 min, adsorbent dosage 30 mg mL^{-1}, 1 mM NaCl). Error bars show the standard deviations of three replicates.

Fig. 7. Removal efficiency of NH$_4^+$ by surfactant-modified alumina (SMA) with different contact times (initial concentration C_i (NH$_4^+$) = 10^{-4} M, pH 4, adsorbent dosage 30 mg mL^{-1}, 1 mM NaCl). Error bars show the standard deviations of three replicates.

Fig. 8. Effect of adsorbent dosage on the removal efficiency of NH$_4^+$ by surfactant-modified alumina (SMA) (initial concentration C_i (NH$_4^+$) = 10^{-4} M, pH 4, contact time 180 min, 1 mM NaCl). Error bars show the standard deviations of three replicates.

adsorption of NH$_4^+$ by natural zeolite (2880 min).[28] Thus, 180 min is acceptable and was selected as the optimum contact time for removal of NH$_4^+$ using SMA in 1 mM NaCl (pH 4).
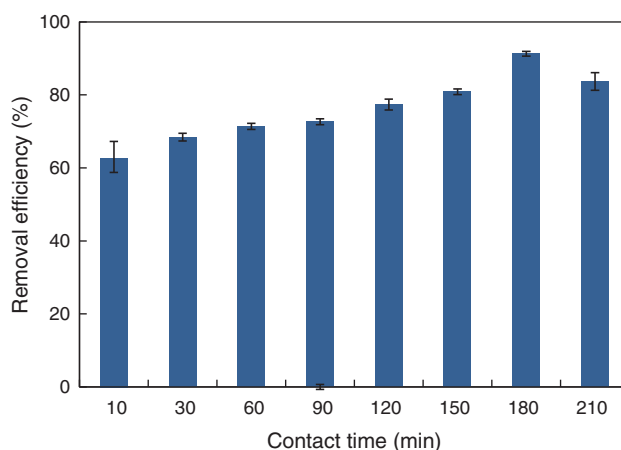
Effect of adsorbent dosage

The adsorbent dosage has a significant effect on the adsorption process because it can influence the total surface area of adsorbent and number of binding sites. The amount of SMA was varied from 5 to 40 mg mL^{-1}.
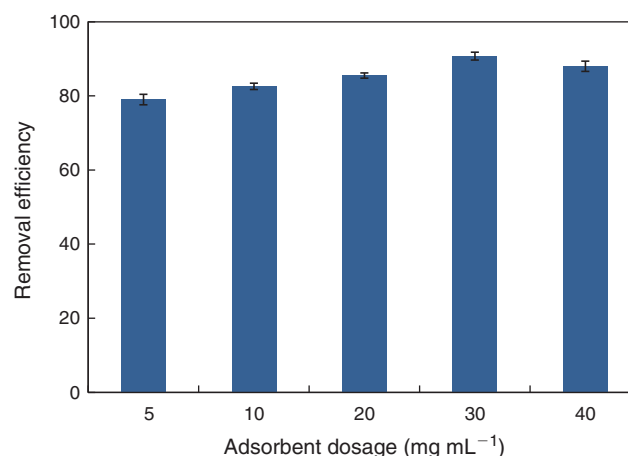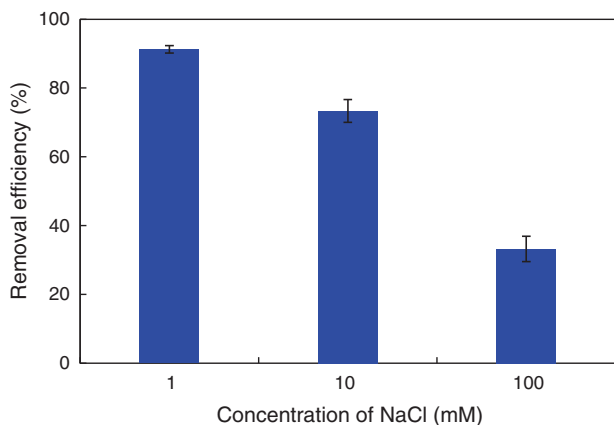
Fig. 8 shows that the removal efficiency of NH$_4^+$ by SMA increases with increasing adsorbent dosage from 5 to 30 mg mL^{-1}. This may be explained by the increasing number of available binding sites or increasing net specific surface area with increased dosage.[28] However, further increase in adsorbent dosage over 30 mg mL^{-1} causes a decrease of removal efficiency due to the aggregation of colloidal particles.[69] The optimum adsorbent dosage was found to be 30 mg mL^{-1} and was fixed for the remaining studies.

Effect of ionic strength

Ionic strength affects electrostatic attraction between ionic adsorbates and charged surface adsorbent. For the adsorption of
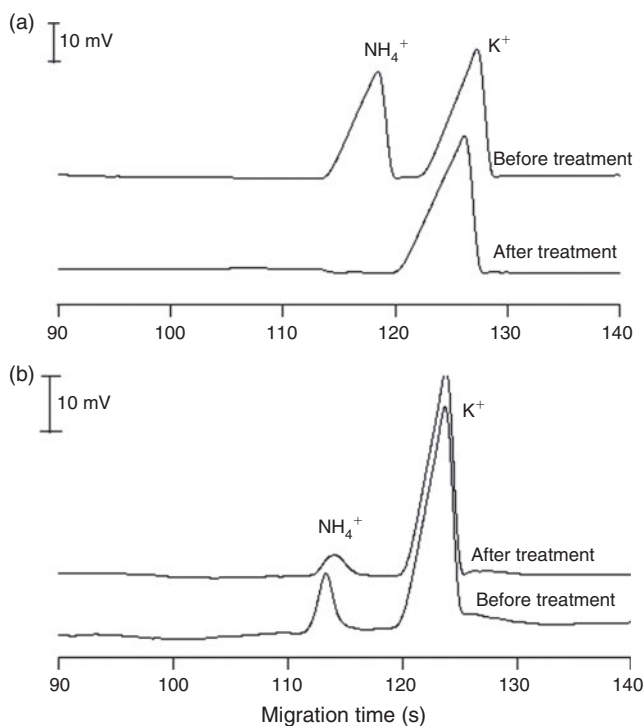
NH$_4^+$ onto SMA, ionic strength also induces a change in SDS load on the α-Al$_2$O$_3$ surface. As can be seen in Fig. 9, the removal efficiency increases with a decrease of NaCl concentration. This result can be explained by desorption of SDS at high salt concentration.[70] Also, increasing concentration of NaCl reduces the attraction of SDS and NH$_4^+$ so that error bars of replicate experiments increase with increasing salt concentration. In addition, Mazloomi and Jalali[28] indicated that the removal efficiency of NH$_4^+$ was strongly influenced by the presence of Cl$^-$ ion. When increasing salt concentration, the concentration of Cl$^-$ is high so that the removal efficiency is decreased dramatically. The effect of salt concentration will be discussed in the adsorption isotherms section.

Removal of ammonium ions from agricultural water using SDS-modified α-Al$_2$O$_3$

We applied the optimum conditions for removal of NH$_4^+$ to treat raw water samples. Two water samples were collected at Thuong Tin of Hanoi city (W1) and at Phu Tho province (W2).

Fig. 9. Effect of ionic strength on the removal efficiency of NH_4^+ by surfactant-modified alumina (SMA) (initial concentration $C_i(NH_4^+) = 10^{-4}$ M, pH 4, contact time 180 min, adsorbent dosage 30 mg mL^{-1}). Error bars show the standard deviations of three replicates.

Fig. 10. Electropherograms of removal of NH_4^+ from two agricultural water samples, W1 (a), and W2 (b), using sodium dodecyl sulfate (SDS)-modified α-Al$_2$O$_3$ (surfactant-modified alumina, SMA).

Table 2. The treated performance of two real agricultural water samples containing high concentrations of NH_4^+ using surfactant-modified alumina (SMA)

LOQ, limit of detection

Water sample	Concentration of NH_4^+ (M)		Removal efficiency (%)
	Before treatment	After treatment	
W1[A]	191×10^{-6}	<LOQ (10^{-6})	>99.5
W2[B]	234×10^{-6}	8.3×10^{-6}	96.5

[A]Water sample was collected at Thuong Tin, Hanoi city, Vietnam.
[B]Water Sample was collected at Phu Tho province, Vietnam.

(4.21 mg L^{-1}) to 8.3×10^{-6} M (0.15 mg L^{-1}) respectively. This corresponds to 99.5 and 96.5 % removal efficiency of NH_4^+ ion for W1 and W2 respectively. The achieved removal efficiencies are close to the performance of the removal of NH_4^+ by membrane filtration.[71] It should be noted that European Union standards limit the concentration of ammonia in drinking water below 0.5 mg L^{-1}.[72] Our results indicate that W1 and W2 samples reached pure water standards. Although the procedure for wastewater treatment is hard to apply continuously, the batch method using SMA as a treatment technique seems to be a very promising method to remove NH_4^+ from aqueous solutions.

Characteristics of ammonium ion adsorption isotherms

Adsorption isotherms of ammonium ion on α-Al$_2$O$_3$ and on SDS-modified α-Al$_2$O$_3$

Adsorption isotherms of NH_4^+ on α-Al$_2$O$_3$ and on SDS-modified α-Al$_2$O$_3$ (SMA) were obtained under the same conditions. Fig. 11 shows that the adsorption capacity of NH_4^+ on SMA is much higher than that on α-Al$_2$O$_3$ without surface modification by SDS although the error bar in the case without SDS is smaller than the case with it. Also, the slope of the adsorption isotherm for NH_4^+ onto SMA is greater than the slope for NH_4^+ onto α-Al$_2$O$_3$ in the absence of SDS. It should be noted that these operating conditions are optimum parameters for NH_4^+ adsorption on SMA. However, when changing the conditions (pH and ionic strength), the adsorption capacity did not change significantly (data not shown). These results can be explained by the low adsorption capacity of many adsorbates on α-Al$_2$O$_3$ with small net charge and low specific surface area.[73] However, SDS-modified α-Al$_2$O$_3$ significantly increased the α-Al$_2$O$_3$ surface charge, so that the adsorption increased dramatically. This implies that SMA can be used at higher concentration and at different pH as a more potent adsorbent than α-Al$_2$O$_3$ without modification by SDS.

Adsorption isotherms of ammonium ion on SDS-modified α-Al$_2$O$_3$ by a two-step adsorption model

The effect of ionic strength on adsorption of NH_4^+ on SMA is clearly demonstrated in Fig. 12. At pH 4, the NH_4^+ adsorption capacity decreases with increasing ionic strength. At high salt concentration (100 mM), the adsorption capacity decreases dramatically (5.4 times) compared with adsorption in 10 mM NaCl, whereas the adsorption decreases only 1.24 times from 1 to 10 mM NaCl. The increase in salt concentration increases the number of Na$^+$ cations (counter-ions) on the negatively charged SMA layer, reducing the electrostatic effect of SMA on NH_4^+ ion. It is quite different from the case of adsorption of NH_4^+ on strawberry leaf powder,[27] in which the effects of Na$^+$, K$^+$,

Heavy use of nitrogen fertiliser on agricultural land in Vietnam results in high concentrations of NH_4^+ in surface water. As can be seen in Fig. 10, after applying the SMA treatment procedure, the concentration of NH_4^+ in the two water samples decreased greatly. After treatment, NH_4^+ cannot be detected in sample W1 while the concentration of NH_4^+ in W2 is quite small. Fig. 10 also shows that the removal of NH_4^+ is not affected by the presence of high amounts of K$^+$-containing mineral salts. Table 2 indicates that NH_4^+ concentrations of W1 and W2 samples decreased from 191×10^{-6} M (3.44 mg L^{-1}) to less than 10^{-6} M (0.018 mg L^{-1}) and from 234×10^{-6} M

Mg^{2+} and Ca^{2+} on ammonium adsorption were not significant. In our case, the electrostatic attraction between the NH_4^+ cation and the negatively charged SMA surface is effectively suppressed by increasing salt concentrations. Other interactions such as hydrophobic, hydrogen-bonding, surface complexation and Van der Waals interactions are probably important in the adsorption of inorganic anions on the surface of alumina.[73] However, adsorption of NH_4^+ on SMA is mainly controlled by electrostatic attraction so that adsorption decreases with
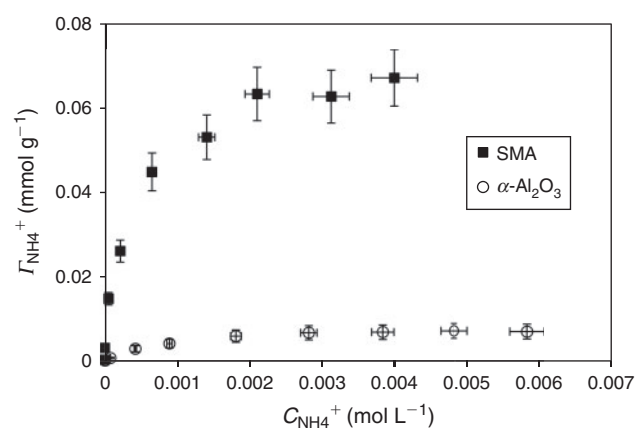
Fig. 11. Adsorption isotherms of NH_4^+ onto α-Al$_2$O$_3$ and onto sodium dodecyl sulfate (SDS)-modified α-Al$_2$O$_3$ (surfactant-modified alumina, SMA) as a function of equilibrium concentration of NH_4^+. Error bars show root-mean-square error of two replicates.
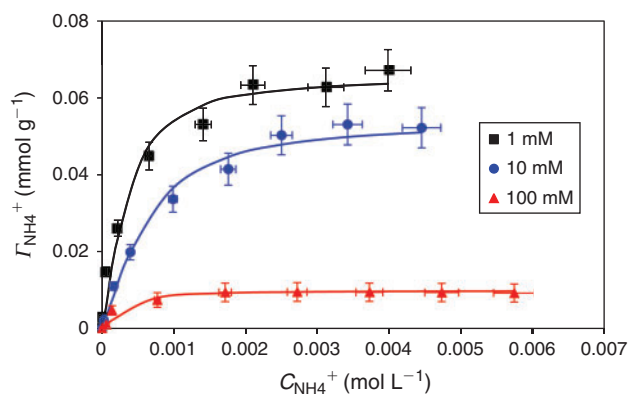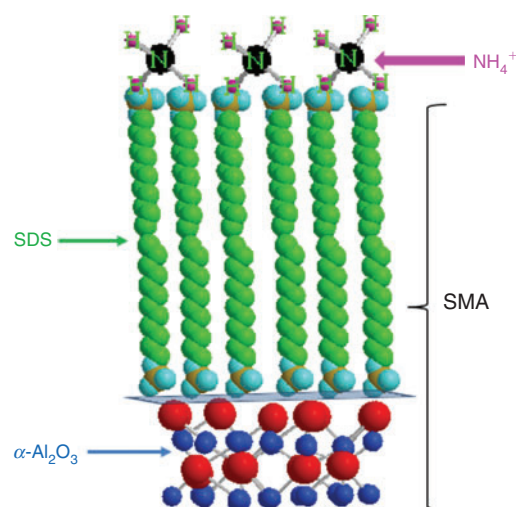

Fig. 12. Adsorption isotherms of NH_4^+ onto sodium dodecyl sulfate (SDS)-modified α-Al$_2$O$_3$ (surfactant-modified alumina, SMA) as a function of equilibrium concentration of NH_4^+ at different NaCl concentrations. Points are experimental data; solid lines are fitted by the two-step adsorption model. Error bars show the root-mean-square error of two replicates.

increasing NaCl concentration. In other words, the SDS bilayer formation on the surface α-Al$_2$O$_3$ seems to be easily eliminated with increasing ionic strength, and SDS–NH_4^+ attraction is reduced so that the NH_4^+ adsorption on SMA is decreased. These results agree well with the effect of ionic strength on the removal of NH_4^+ using SMA shown in the previous section.

Fig. 12 indicates that at different salt concentrations, the experimental results can be represented well by the general isotherm Eqn 3 with the fitting parameters in Table 3. As shown in Table 3, increasing ionic strength from 1 to 100 mM causes a decrease in k_{1,NH_4^+} while the changes in k_{2,NH_4^+} and the number of NH_4^+ clusters are not significant ($k_{2,NH_4^+} \approx 7.0 \times 10^3$ g mmol^{-1} and $n_{NH_4^+} \approx 2$). The value of k_{1,NH_4^+} is also related to the slope of isotherm. As a result, at high salt concentration, the slope is lower than that at low salt concentration. This suggests that desorption of SDS from the bilayer of admicelles is enhanced by increasing salt concentration. Thus, the net charge of SMA is less negative so that the adsorption of NH_4^+ is decreased (see zeta potential measurements).

Adsorption mechanisms of ammonium ion onto SDS-modified α-Al$_2$O$_3$

Adsorptive removal of NH_4^+ is greatly enhanced by using anionic surfactant SDS-modified α-Al$_2$O$_3$ (SMA). The effective conditions for adsorption of NH_4^+ ions by SMA were systematically examined by CE-C^{4}D, which is was inexpensive, fast and easily operated. A two-step model was established to

Fig. 13. Schematic representation of structure of the adsorbed NH_4^+ onto sodium dodecyl sulfate (SDS)-modified α-Al$_2$O$_3$ (surfactant-modified alumina, SMA).

Table 3. The fit parameters for NH_4^+ adsorption onto surfactant-modified alumina (SMA): maximum adsorbed amount Γ_{∞,NH_4^+}, equilibrium constants k_{1,NH_4^+} and k_{2,NH_4^+} for first-layer adsorption and multilayer adsorption respectively and the number of cluster of NH_4^+ ion, $n_{NH_4^+}$

Concentration salt (mM NaCl)	Γ_{∞,NH_4^+} (mmol g^{-1})	k_{1,NH_4^+} (g mmol^{-1})	k_{2,NH_4^+} (g mmol^{-1})$^{n-1}$	$n_{NH_4^+}$
1	0.066	3.0×10^3	7.0×10^3	2.1
10	0.054	2.0×10^3	7.1×10^3	2.2
100	0.010	1.5×10^3	7.0×10^3	2.0

describe NH_4^+ adsorption onto SMA, suggesting that the adsorption of NH_4^+ ion could replace admicellar bilayers of SDS molecules on the α-Al_2O_3 surface. Adsorption of NH_4^+ decreases with an increase in NaCl concentration because desorption of SDS is enhanced by increasing salt concentration. It is well represented by the two-step adsorption model with decreasing k_{1,NH_4^+} when increasing NaCl concentration.

During SDS pre-adsorption and NH_4^+ adsorption, pH 4 was fixed so that concomitant protonation effects were negligible and the surface charge of α-Al_2O_3 without adsorption was positive (ζ potential > 0).[58] After surface modification with SDS to form SMA, the surface charge of α-Al_2O_3 was dependent on the amount of NH_4^+ adsorbed. As previously noted, bilayer formation and/or SDS admicelles occur on the surface of α-Al_2O_3,[45] reversing surface polarity (ζ potential < 0 or $u_e < 0$).[74] Most previous studies of NH_4^+ adsorption in aqueous media showed the change in surface charge on NH_4^+ adsorption.[1,7–9,25–28,36–38,75] In our case, a decrease of surface charge or a reduction of ζ potential was obtained by measuring electrophoretic mobility that was in accordance with cationic NH_4^+ adsorption on SMA.

The predominance of the electrostatic NH_4^+ adsorption mechanism onto SMA is also supported by FT-IR spectra. The main peaks of the asymmetric N–H bonding in the NH_4^+ spectra disappeared after adsorption onto SMA while CH_2– bands of SMA were also not evident. This is consistent with electrostatic adsorption of positively charged tetrahedral NH_4^+ (pH < 9.25) onto the negatively charged sulfate groups of SMA. Fig. 13 shows a schematic representation of the adsorbed structure of NH_4^+ on SMA. In Fig. 13, the ammonium ions adsorbed onto SMA through electrostatic attraction create bonds between the N–H bonding of cationic NH_4^+ ions and the negative sulfate group of SDS. This is different from the case of NH_4^+ on graphite oxide–aluminium polycations and graphite oxide–zirconium–aluminium polyoxycation composites in which the interaction is through hydrogen bonding with surface structure oxygen and functional groups.[9] However, our results are close to the adsorption of ammonia on metal oxide surfaces.[76] These results are also in good agreement with adsorption isotherms and ζ potential measurements, demonstrating that the main interaction between the positive charge of NH_4^+ and negatively charged SMA must be electrostatic attraction.

Conclusions

In the present paper, we studied the adsorption of the ammonium ion (NH_4^+) onto surfactant-modified alumina (SMA) from aqueous solution. The adsorption experiments were quantified using CE-C^{4}D and spectrophotometry. The optimum conditions for adsorptive removal of NH_4^+ using SMA were found to be pH 4, contact time 180 min, and adsorbent dosage 30 mg mL^{-1}. We applied the optimum adsorption parameters to treat two agricultural water samples and obtained high removal efficiencies of 99.5 and 96.5 %. Adsorption isotherms of NH_4^+ on SMA at different NaCl concentrations were fitted well by a two-step adsorption model. The adsorption of NH_4^+ onto SMA decreased with an increase of NaCl concentration owing to the enhancement of SDS desorption with increasing salt concentration. Based on adsorption isotherms, surface charge effects as measured by zeta potential, and surface modification as measured by FT-IR, we suggest that adsorption of NH_4^+ onto SMA is mainly controlled by electrostatic attraction between the positive charge of NH_4^+ and the negatively charged layer SMA.

Supplementary material

Comparison between CE-C^{4}D and spectrophotometric method for determining ammonium ion concentration, and adsorption isotherm of SDS on α-Al_2O_3 and desorption of SDS with ammonium ion adsorption are available from the Journal's website.

References

[1] K. Zare, H. Sadegh, R. Shahryari-ghoshekandi, M. Asif, I. Tyagi, S. Agarwal, V. K. Gupta, Equilibrium and kinetic study of ammonium ion adsorption by Fe$_3$O$_4$ nanoparticles from aqueous solutions. *J. Mol. Liq.* **2016**, *213*, 345. doi:10.1016/J.MOLLIQ.2015.08.045

[2] A. Almutairi, L. R. Weatherley, Intensification of ammonia removal from waste water in biologically active zeolitic ion exchange columns. *J. Environ. Manage.* **2015**, *160*, 128. doi:10.1016/J.JENVMAN.2015.05.033

[3] D. Bejan, T. Graham, N. J. Bunce, Chemical methods for the remediation of ammonia in poultry rearing facilities: a review. *Biosyst. Eng.* **2013**, *115*, 230. doi:10.1016/J.BIOSYSTEMSENG.2013.03.003

[4] H. Liu, Y. Yang, J. Kang, M. Fan, J. Qu, Removal of tetracycline from water by Fe-Mn binary oxide. *J. Environ. Sci.* **2012**, *24*, 242. doi:10.1016/S1001-0742(11)60763-8

[5] N. Liu, M.-x. Wang, M.-m. Liu, F. Liu, L. Weng, L. K. Koopal, W.-f. Tan, Sorption of tetracycline on organo-montmorillonites. *J. Hazard. Mater.* **2012**, *225–226*, 28. doi:10.1016/J.JHAZMAT.2012.04.060

[6] M. Uğurlu, M. H. Karaoğlu, Adsorption of ammonium from an aqueous solution by fly ash and sepiolite: isotherm, kinetic and thermodynamic analysis. *Microporous Mesoporous Mater.* **2011**, *139*, 173. doi:10.1016/J.MICROMESO.2010.10.039

[7] C. Petit, T. J. Bandosz, Activated carbons modified with aluminium–zirconium polycations as adsorbents for ammonia. *Microporous Mesoporous Mater.* **2008**, *114*, 137. doi:10.1016/J.MICROMESO.2007.12.029

[8] C. Petit, T. J. Bandosz, Enhanced adsorption of ammonia on metal–organic framework/graphite oxide composites: analysis of surface interactions. *Adv. Funct. Mater.* **2010**, *20*, 1118. doi:10.1002/ADFM.200900880

[9] M. Seredych, T. J. Bandosz, Adsorption of ammonia on graphite oxide/aluminium polycation and graphite oxide/zirconium–aluminium polyoxycation composites. *J. Colloid Interface Sci.* **2008**, *324*, 25. doi:10.1016/J.JCIS.2008.04.062

[10] M. Seredych, T. J. Bandosz, Graphite oxide/AlZr polycation composites: surface characterization and performance as adsorbents of ammonia. *Mater. Chem. Phys.* **2009**, *117*, 99. doi:10.1016/J.MATCHEMPHYS.2009.05.004

[11] H. Khani, M. K. Rofouei, P. Arab, V. K. Gupta, Z. Vafaei, Multi-walled carbon nanotubes–ionic liquid–carbon paste electrode as a super selectivity sensor: application to potentiometric monitoring of mercury ion(II). *J. Hazard. Mater.* **2010**, *183*, 402. doi:10.1016/J.JHAZMAT.2010.07.039

[12] T. A. Saleh, V. K. Gupta, Functionalization of tungsten oxide into MWCNT and its application for sunlight-induced degradation of Rhodamine B. *J. Colloid Interface Sci.* **2011**, *362*, 337. doi:10.1016/J.JCIS.2011.06.081

[13] T. A. Saleh, V. K. Gupta, Photo-catalyzed degradation of hazardous dye methyl orange by use of a composite catalyst consisting of multi-walled carbon nanotubes and titanium dioxide. *J. Colloid Interface Sci.* **2012**, *371*, 101. doi:10.1016/J.JCIS.2011.12.038

[14] T. A. Saleh, V. K. Gupta, Processing methods, characteristics and adsorption behavior of tire derived carbons: a review. *Adv. Colloid Interface Sci.* **2014**, *211*, 93. doi:10.1016/J.CIS.2014.06.006

[15] R. Saravanan, F. Gracia, M. M. Khan, V. Poornima, V. K. Gupta, V. Narayanan, A. Stephen, ZnO/CdO nanocomposites for textile effluent degradation and electrochemical detection. *J. Mol. Liq.* **2015**, *209*, 374. doi:10.1016/J.MOLLIQ.2015.05.040

[16] R. Saravanan, V. K. Gupta, V. Narayanan, A. Stephen, Comparative study on photocatalytic activity of ZnO prepared by different methods. *J. Mol. Liq.* **2013**, *181*, 133. doi:10.1016/J.MOLLIQ.2013.02.023

[17] R. Saravanan, N. Karthikeyan, V. K. Gupta, E. Thirumal, P. Thangadurai, V. Narayanan, A. Stephen, ZnO/Ag nanocomposite: an efficient catalyst for degradation studies of textile effluents under visible light. *Mater. Sci. Eng. C* **2013**, *33*, 2235. doi:10.1016/J.MSEC.2013.01.046

[18] R. Saravanan, M. Mansoob Khan, V. K. Gupta, E. Mosquera, F. Gracia, V. Narayanan, A. Stephen, ZnO/Ag/CdO nanocomposite for visible light-induced photocatalytic degradation of industrial textile effluents. *J. Colloid Interface Sci.* **2015**, *452*, 126. doi:10.1016/J.JCIS.2015.04.035

[19] R. Saravanan, E. Sacari, F. Gracia, M. M. Khan, E. Mosquera, V. K. Gupta, Conducting PANI stimulated ZnO system for visible light photocatalytic degradation of coloured dyes. *J. Mol. Liq.* **2016**, *221*, 1029. doi:10.1016/J.MOLLIQ.2016.06.074

[20] M. M. Barbooti, H. Su, P. Punamiya, D. Sarkar, Oxytetracycline sorption onto Iraqi montmorillonite. *Int. J. Environ. Sci. Technol.* **2014**, *11*, 69. doi:10.1007/S13762-013-0361-6

[21] V. K. Gupta, R. Kumar, A. Nayak, T. A. Saleh, M. A. Barakat, Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. *Adv. Colloid Interface Sci.* **2013**, *193–194*, 24. doi:10.1016/J.CIS.2013.03.003

[22] V. K. Gupta, A. Mittal, V. Gajbe, Adsorption and desorption studies of a water soluble dye, quinoline yellow, using waste materials. *J. Colloid Interface Sci.* **2005**, *284*, 89. doi:10.1016/J.JCIS.2004.09.055

[23] V. K. Gupta, A. Nayak, Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe$_2$O$_3$ nanoparticles. *Chem. Eng. J.* **2012**, *180*, 81. doi:10.1016/J.CEJ.2011.11.006

[24] V. K. Gupta, S. K. Srivastava, D. Mohan, S. Sharma, Design parameters for fixed bed reactors of activated carbon developed from fertilizer waste for the removal of some heavy metal ions. *Waste Manag.* **1998**, *17*, 517. doi:10.1016/S0956-053X(97)10062-9

[25] V. K. Gupta, Suhas, Application of low-cost adsorbents for dye removal – a review. *J. Environ. Manage.* **2009**, *90*, 2313. doi:10.1016/J.JENVMAN.2008.11.017

[26] H. Liu, Y. Dong, Y. Liu, H. Wang, Screening of novel low-cost adsorbents from agricultural residues to remove ammonia nitrogen from aqueous solution. *J. Hazard. Mater.* **2010**, *178*, 1132. doi:10.1016/J.JHAZMAT.2010.01.117

[27] H. Liu, Y. Dong, H. Wang, Y. Liu, Ammonium adsorption from aqueous solutions by strawberry leaf powder: equilibrium, kinetics and effects of coexisting ions. *Desalination* **2010**, *263*, 70. doi:10.1016/J.DESAL.2010.06.040

[28] F. mazloomi, M. jalali, Ammonium removal from aqueous solutions by natural Iranian zeolite in the presence of organic acids, cations and anions. *J. Environ. Chem. Eng.* **2016**, *4*, 1664. doi:10.1016/J.JECE.2015.11.031

[29] A. Mittal, D. Kaur, A. Malviya, J. Mittal, V. K. Gupta, Adsorption studies on the removal of coloring agent phenol red from wastewater using waste materials as adsorbents. *J. Colloid Interface Sci.* **2009**, *337*, 345. doi:10.1016/J.JCIS.2009.05.016

[30] A. Mittal, J. Mittal, A. Malviya, V. K. Gupta, Adsorptive removal of hazardous anionic dye 'Congo red' from wastewater using waste materials and recovery by desorption. *J. Colloid Interface Sci.* **2009**, *340*, 16. doi:10.1016/J.JCIS.2009.08.019

[31] A. Mittal, J. Mittal, A. Malviya, V. K. Gupta, Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials. *J. Colloid Interface Sci.* **2010**, *344*, 497. doi:10.1016/J.JCIS.2010.01.007

[32] A. Mittal, J. Mittal, A. Malviya, D. Kaur, V. K. Gupta, Decoloration treatment of a hazardous triarylmethane dye, Light Green SF (Yellowish) by waste material adsorbents. *J. Colloid Interface Sci.* **2010**, *342*, 518. doi:10.1016/J.JCIS.2009.10.046

[33] Y. G. Mishael, P. L. Dubin, Uptake of organic pollutants by silica–polycation-immobilized micelles for groundwater remediation. *Environ. Sci. Technol.* **2005**, *39*, 8475. doi:10.1021/ES050763S

[34] Y. G. Mishael, T. Undabeytia, O. Rabinovitz, B. Rubin, S. Nir, Sulfosulfuron incorporated in micelles adsorbed on montmorillonite for slow release formulations. *J. Agric. Food Chem.* **2003**, *51*, 2253.

[35] Y. G. Mishael, T. Undabeytia, G. Rytwo, B. Papahadjopoulos-Sternberg, B. Rubin, S. Nir, Sulfometuron incorporation in cationic micelles adsorbed on montmorillonite. *J. Agric. Food Chem.* **2002**, *50*, 2856. doi:10.1021/JF011496M

[36] Y.-C. Song, B. Subha, J. H. Woo, H. J. Lim, P. Senthilkumar, Surface modification of sediment with surfactant for capping material on contaminated coastal sediment. *Water, Air, Soil Pollut.* **2014**, *225*, 2067. doi:10.1007/S11270-014-2067-X

[37] V. K. Gupta, P. J. M. Carrott, M. M. L. Ribeiro Carrott & Suhas, Low-cost adsorbents: growing approach to wastewater treatment – a review. *Crit. Rev. Environ. Sci. Technol.* **2009**, *39*, 783. doi:10.1080/10643380801977610

[38] D. Saha, S. Deng, Characteristics of ammonia adsorption on activated alumina. *J. Chem. Eng. Data* **2010**, *55*, 5587. doi:10.1021/JE100405K

[39] H. M. F. Freundlich. *Z. Phys. Chem.* **1906**, *57*, 385.

[40] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361. doi:10.1021/JA02242A004

[41] B.-Y. Zhu, T. Gu, Surfactant adsorption at solid–liquid interfaces. *Adv. Colloid Interface Sci.* **1991**, *37*, 1. doi:10.1016/0001-8686(91)80037-K

[42] I. Hoffmann, C. Oppel, U. Gernert, P. Barreleiro, W. von Rybinski, M. Gradzielski, Adsorption isotherms of cellulose-based polymers onto cotton fibers determined by means of a direct method of fluorescence spectroscopy. *Langmuir* **2012**, *28*, 7695. doi:10.1021/LA300192Q

[43] R. Ndong, W. Russel, Linear viscoelasticity of ZrO$_2$ nanoparticle dispersions with associative polymers. *Rheol. Acta* **2012**, *51*, 771. doi:10.1007/S00397-012-0633-Y

[44] T. D. Pham, M. Kobayashi, Y. Adachi, Adsorption of polyanion onto large alpha alumina beads with variably charged surface. *Adv. Phys. Chem.* **2014**, *2014*, 460942. doi:10.1155/2014/460942

[45] T. D. Pham, M. Kobayashi, Y. Adachi, Adsorption of anionic surfactant sodium dodecyl sulfate onto alpha alumina with small surface area. *Colloid Polym. Sci.* **2015**, *293*, 217. doi:10.1007/S00396-014-3409-3

[46] T. D. Pham, M. Kobayashi, Y. Adachi, Adsorption characteristics of anionic azo dye onto large α-alumina beads. *Colloid Polym. Sci.* **2015**, *293*, 1877. doi:10.1007/S00396-015-3576-X

[47] A. Adak, M. Bandyopadhyay, A. Pal, Removal of crystal violet dye from wastewater by surfactant-modified alumina. *Separ. Purif. Tech.* **2005**, *44*, 139. doi:10.1016/J.SEPPUR.2005.01.002

[48] A. Adak, M. Bandyopadhyay, A. Pal, Fixed bed column study for the removal of crystal violet (C. I. Basic Violet 3) dye from aquatic environment by surfactant-modified alumina. *Dyes Pigments* **2006**, *69*, 245. doi:10.1016/J.DYEPIG.2005.03.009

[49] A. Adak, A. Pal, M. Bandyopadhyay, Removal of phenol from water environment by surfactant-modified alumina through adsolubilization. *Colloids Surf. A Physicochem. Eng. Asp.* **2006**, *277*, 63. doi:10.1016/J.COLSURFA.2005.11.012

[50] A. K. Das, S. Saha, A. Pal, S. K. Maji, Surfactant-modified alumina: an efficient adsorbent for malachite green removal from water environment. *J. Environ. Sci. Health. Part A: Toxic/Hazard. Subst. Environ. Eng.* **2009**, *44*, 896.

[51] M. U. Khobragade, A. Pal, Fixed-bed column study on removal of Mn (II), Ni(II) and Cu(II) from aqueous solution by surfactant bilayer supported alumina. *Sep. Sci. Technol.* **2016**, *51*, 1287.

[52] M. U. Khobragade, A. Pal, Adsorptive removal of Mn(II) from water and wastewater by surfactant-modified alumina. *Desalination Water Treat.* **2016**, *57*, 2775. doi:10.1080/19443994.2014.982195

[53] M. Okumura, K. Fujinaga, Y. Seike, S. Honda, A simple and rapid visual method for the determination of ammonia nitrogen in environmental waters using thymol. *Fresenius J. Anal. Chem.* **1999**, *365*, 467. doi:10.1007/S002160051642

[54] A. J. Gaudry, M. C. Breadmore, R. M. Guijt, In-plane alloy electrodes for capacitively coupled contactless conductivity detection in poly (methylmethacrylate) electrophoretic chips. *Electrophoresis* **2013**, *34*, 2980.

[55] T. D. Mai, T. T. T. Pham, H. V. Pham, J. Sáiz, C. G. Ruiz, P. C. Hauser, Portable capillary electrophoresis instrument with automated injector and contactless conductivity detection. *Anal. Chem.* **2013**, *85*, 2333. doi:10.1021/AC303328G

[56] A. V. Delgado, F. González-Caballero, R. J. Hunter, L. K. Koopal, J. Lyklema, Measurement and interpretation of electrokinetic phenomena. *J. Colloid Interface Sci.* **2007**, *309*, 194. doi:10.1016/J.JCIS.2006.12.075

[57] G. Lefèvre, M. Duc, M. Fédoroff, Effect of solubility on the determination of the protonable surface site density of oxyhydroxides. *J. Colloid Interface Sci.* **2004**, *269*, 274. doi:10.1016/S0021-9797(03)00653-2

[58] T. D. Pham, M. Kobayashi, Y. Adachi, Interfacial characterization of α-alumina with small surface area by streaming potential and chromatography. *Colloids Surf. A Physicochem. Eng. Asp.* **2013**, *436*, 148. doi:10.1016/J.COLSURFA.2013.06.026

[59] K. Esumi, N. Fujimoto, K. Torigoe, Simultaneous adsorption of poly (amidoamine) dendrimers with surface carboxyl groups and sodium dodecyl sulfate at the alumina/water interface. *Langmuir* **1999**, *15*, 4613. doi:10.1021/LA981664D

[60] K. Esumi, Y. Yamanaka, Interaction between sodium dodecyl poly (oxyethylene) sulfate and alumina surface in aqueous solution. *J. Colloid Interface Sci.* **1995**, *172*, 116. doi:10.1006/JCIS.1995.1232

[61] J. J. Lopata, K. M. Werts, J. F. Scamehorn, J. H. Harwell, B. P. Grady, Thermodynamics of mixed anionic/non-ionic surfactant adsorption on alumina. *J. Colloid Interface Sci.* **2010**, *342*, 415. doi:10.1016/J.JCIS.2009.10.072

[62] A. R. Hind, S. K. Bhargava, A. McKinnon, At the solid/liquid interface: FTIR/ATR – the tool of choice. *Adv. Colloid Interface Sci.* **2001**, *93*, 91. doi:10.1016/S0001-8686(00)00079-8

[63] J. G. Amores, V. S. Escribano, G. Ramis, G. Busca, An FT-IR study of ammonia adsorption and oxidation over anatase-supported metal oxides. *Appl. Catal. B* **1997**, *13*, 45. doi:10.1016/S0926-3373(96)00092-6

[64] M. Kobayashi, Electrophoretic mobility of latex spheres in the presence of divalent ions: experiments and modeling. *Colloid Polym. Sci.* **2008**, *286*, 935. doi:10.1007/S00396-008-1851-9

[65] A. Yamaguchi, M. Kobayashi, Quantitative evaluation of shift of slipping plane and counterion binding to lysozyme by electrophoresis method. *Colloid Polym. Sci.* **2016**, *294*, 1019. doi:10.1007/S00396-016-3852-4

[66] G. V. Franks, Y. Gan, Charging behavior at the alumina–water interface and implications for ceramic processing. *J. Am. Ceram. Soc.* **2007**, *90*, 3373.

[67] G. V. Franks, L. Meagher, The isoelectric points of sapphire crystals and alpha-alumina powder. *Colloids Surf. A Physicochem. Eng. Asp.* **2003**, *214*, 99. doi:10.1016/S0927-7757(02)00366-7

[68] R. Boopathy, S. Karthikeyan, A. B. Mandal, G. Sekaran, Adsorption of ammonium ion by coconut shell-activated carbon from aqueous solution: kinetic, isotherm, and thermodynamic studies. *Environ. Sci. Pollut. Res. Int.* **2013**, *20*, 533. doi:10.1007/S11356-012-0911-3

[69] J. K. Wolterink, L. K. Koopal, M. A. C. Stuart, W. H. Van Riemsdijk, Surface charge regulation upon polyelectrolyte adsorption, hematite, polystyrene sulfonate, surface charge regulation: theoretical calculations and hematite–poly(styrene sulfonate) system. *Colloids Surf. A Physicochem. Eng. Asp.* **2006**, *291*, 13. doi:10.1016/J.COLSURFA.2006.04.053

[70] A. M. Blokhus, K. Djurhuus, Adsorption of poly(styrene sulfonate) of different molecular weights on α-alumina: effect of added sodium dodecyl sulfate. *J. Colloid Interface Sci.* **2006**, *296*, 64. doi:10.1016/J.JCIS.2005.08.038

[71] H. Kurama, J. Poetzschke, R. Haseneder, The application of membrane filtration for the removal of ammonium ions from potable water. *Water Res.* **2002**, *36*, 2905. doi:10.1016/S0043-1354(01)00531-0

[72] L. A. Huetter, *Wasser und Wasseruntersuchung* **1992** (Salle und Sauerlaender: Frankfurt).

[73] B. Kasprzyk-Hordern, Chemistry of alumina, reactions in aqueous solution and its application in water treatment. *Adv. Colloid Interface Sci.* **2004**, *110*, 19. doi:10.1016/J.CIS.2004.02.002

[74] L. K. Koopal, E. M. Lee, M. R. Böhmer, Adsorption of cationic and anionic surfactants on charged metal oxide surfaces. *J. Colloid Interface Sci.* **1995**, *170*, 85. doi:10.1006/JCIS.1995.1075

[75] V. K. Gupta, I. Ali, T. A. Saleh, A. Nayak, S. Agarwal, Chemical treatment technologies for waste-water recycling – an overview. *RSC Advances* **2012**, *2*, 6380. doi:10.1039/C2RA20340E

[76] G. A. Blomfield, L. H. Little, Adsorption of ammonia on oxide surfaces. *J. Catal.* **1971**, *21*, 149. doi:10.1016/0021-9517(71)90132-1

Handling Editor: Kevin Wilkinson