



# Copper-complexed clay/poly-acrylic acid composites: Extremely efficient adsorbents of ammonia gas



Erming Liu <sup>\*</sup>, Binoy Sarkar <sup>\*</sup>, Liang Wang <sup>1</sup>, Ravi Naidu <sup>\*\*</sup>,<sup>1</sup>

*Environmental Science and Engineering Strand, Future Industries Institute, University of South Australia, Adelaide, SA 5095, Australia*

*CRC for Contamination Assessment and Remediation of the Environment (CRC CARE), Environmental Science Building, Mawson Lakes, Adelaide, SA 5095, Australia*

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## ABSTRACT

Work reported in this manuscript takes into consideration the possible use of NH<sub>3</sub> gas by terrorists and the potential for an effective and rapid removal of such toxic substance from air using a modified clay material. In this study, a series of clay/polymer composites were synthesised for ammonia gas (NH<sub>3</sub>) adsorption. The adsorbents were prepared by polymerisation of acrylic acid with N,N'-methylenebisacrylamide (MBA) as cross-linker in the presence of a large amount of highly dispersed clay nanoparticles, followed by interaction with copper ions (Cu<sup>2+</sup>). Two kinds of clays were used. One was an acid-treated bentonite that had a specific surface area (SSA) of 395 m<sup>2</sup>/g and the other was natural palygorskite with a SSA of 87 m<sup>2</sup>/g. The materials were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption-desorption and Fourier transform infrared spectroscopy (FTIR). The materials' ability to remove NH<sub>3</sub> was investigated using NH<sub>3</sub> breakthrough dynamic test while the strength of NH<sub>3</sub> retention was characterised by Thermogravimetric Analysis (TGA) coupled with FTIR. The results indicate that clay/poly-acrylic acid composites are highly efficient adsorbents of NH<sub>3</sub> after binding with Cu<sup>2+</sup>. Trapping NH<sub>3</sub> on such adsorbents can lead to colour change and this makes it possible to predict the lifetime of the adsorption bed visually. In addition, the result of NH<sub>3</sub> release from the material following adsorption showed that majority of the adsorbed NH<sub>3</sub> desorbed at temperature above 180 °C. The clay/polymer composites can potentially be used in air filters. They may provide an effective and cheap way for removing NH<sub>3</sub> from contaminated air.

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## 1. Introduction

Developing a highly efficient and commercially feasible material for the removal of ammonia (NH<sub>3</sub>) from air is very important for addressing point-source emissions possibly during a terrorist attack or an industrial accident causing significantly excess NH<sub>3</sub> concentration in the atmosphere (ApSimon et al., 1987; Renard et al., 2004). Ammonia is very harmful to humans and exposure to 750 µL/L (ppm) of NH<sub>3</sub> in the air for up to 1 h can be life-threatening. Even a concentration of 150 ppm can result in irreversible or serious outcomes that may impair an individual's ability to take protective action (Chemwatch Material Safety Database).

The materials usually used as NH<sub>3</sub> adsorbents predominantly include zeolites (Valyon et al., 1998), alumina (Sharonov and Aristov,

2005; Saha and Deng, 2010b), acid-treated clay (Ursu et al., 2008), activated carbon modified by inorganic acid, and some metal salts (Petit et al., 2007; Petit and Bandosz, 2007; Fortier et al., 2008; Huang et al., 2008; Smith et al., 2011). Ammonia gas has a relatively low boiling point and small molecular size (Linders et al., 2007). Retaining NH<sub>3</sub> by physical adsorption on an adsorbent with large specific surface area (SSA) and microporous texture has proven to be ineffective and unsafe (Nickolov and Mehandjiev, 2004; Petit et al., 2007; Petit and Bandosz, 2007; Huang et al., 2008). Ammonia molecules can only be strongly trapped by particular functional groups and specific sites, including carboxylic group (Kim and Park, 2007; Seredych and Bandosz, 2007a), epoxy group (Seredych et al., 2010), amino group (Britt et al., 2008; Johnson et al., 2012), inorganic acids (Huang et al., 2008; Grant Glover et al., 2012) or chemically adsorbed by transitional metal ions such as copper (Smith et al., 2009), chromium (Le Leuch and Bandosz, 2007) and silver (Brown and Jayson, 1989).

Recently, promising results for NH<sub>3</sub> removal under dry conditions have been reported by adsorption on to graphite oxide materials (Seredych and Bandosz, 2007b; Petit and Bandosz, 2009; Seredych and Bandosz, 2012). The adsorption process on graphite oxide is mainly governed by interactions between NH<sub>3</sub> and carboxylic or epoxy groups of graphite oxide. Metal-organic frameworks (MOF) (Britt et al., 2008;

<sup>\*</sup> Corresponding authors at: Environmental Science and Engineering Strand, Future Industries Institute, University of South Australia, Adelaide, SA 5095, Australia.

<sup>\*\*</sup> Correspondence to: R. Naidu, Global Centre for Environmental Remediation, ATC Building, University of Newcastle, Callaghan, NSW 2308, Australia.

E-mail addresses: [erming.liu@hotmail.com](mailto:erming.liu@hotmail.com) (E. Liu), [binoy.sarkar.clay@gmail.com](mailto:binoy.sarkar.clay@gmail.com), [binoy.sarkar@unisa.edu.au](mailto:binoy.sarkar@unisa.edu.au) (B. Sarkar), [ravi.naidu@newcastle.edu.au](mailto:ravi.naidu@newcastle.edu.au) (R. Naidu).

<sup>1</sup> Current address: Global Centre for Environmental Remediation, ATC Building, University of Newcastle, Callaghan, NSW 2308, Australia.

Peterson et al., 2009; Petit et al., 2010; Grant Glover et al., 2011; Petit et al., 2011; Petit and Bandosz, 2011) also exhibit very effective  $\text{NH}_3$  adsorption, resulting from the combination of functional groups of complex organic molecules and coordinately unsaturated metal sites on MOF frameworks (Britt et al., 2008). However, the stability of MOF materials under moist condition is a serious problem (Saha and Deng, 2010a).

The objective of this work is to develop an effective and relatively inexpensive, commercially feasible material that can adsorb  $\text{NH}_3$ . Clays are relatively inexpensive natural materials composed of naturally occurring nanoparticles. Clays usually possess large SSA, unique swelling behaviour and intercalation characteristics (Zhou et al., 2011; Sarkar et al., 2012). Clay modification using functional polymers could produce a relatively inexpensive porous composite which could potentially adsorb and neutralise gas contamination. In this work, the clay/polymer composite adsorbents were prepared by polymerisation of acrylic acid with *N,N'*-methylenebisacrylamide (MBA) as a cross-linker in the presence of a great excess of highly dispersed clay nanoparticles, followed by reaction with  $\text{Cu}^{2+}$ . Cross-linked polymer acrylic acid was used for clay functionalisation not only because it contains a great amount of acidic carboxyl groups, which are efficient in adsorbing  $\text{NH}_3$ , but also because it is non-toxic and non-corrosive to humans (Liu and Rempel, 1997). It can be quickly synthesised in very mild conditions.

The effect of clay types on the adsorption capacities of  $\text{NH}_3$  was investigated. Two kinds of clays were used. They were acid-treated bentonite and untreated palygorskite. The clay to polymer proportion was varied from 50% to 75% to find the optimum adsorption performance for  $\text{NH}_3$ . The main mechanism of  $\text{NH}_3$  entrapment on the composite adsorbent was clarified and the retention strength of  $\text{NH}_3$  trapped on the adsorbent was also studied.

## 2. Experimental section

### 2.1. Materials

Acrylic acid (AA) was used as the monomer and *N,N'*-methylenebisacrylamide (MBA) was used as a cross-linker. The radical initiator was ammonium persulphate (APS). They were all purchased from Sigma-Aldrich and used without further purification. The clays used in this work were an Australian bentonite supplied by Bentonite Products Western Australia, and an Australian palygorskite supplied by Hudson Resources Limited, Western Australia.

### 2.2. Clay treatment

The bentonite clay was used after acid treatment. The porosity of untreated bentonite resulting from the turbostratic stacking of individual clay layers was not very high due to the strong inter-lamellar attraction generated by the negatively charged layers and intercalated cations. Acid treatment could eliminate the inter-lamellar attraction which was useful to expose the individual clay layers. This was important for the penetration of polymer guest molecules into the clay structure. Bentonite (30 g) was dispersed into 150 mL of 4 M HCl solution in a glass beaker. The suspension was kept at 25 °C with continuous stirring for 1 h. The acid-treated clay was recovered by filtration and then repeatedly washed with hot deionised water until the filtrate was neutral (pH = 7) in reaction. Finally, the sample was dried at 60 °C overnight. The acid-treated clay possessed a SSA of 395  $\text{m}^2/\text{g}$  and cation exchange capacity (CEC) of 0.21 meq/g measured by 0.01 M Cu-triethylenetetramine (Meier and Kahr, 1999; Ammann et al., 2005). The sample is referred to as “A-Bent” in this report. On the other hand, palygorskite has a unique fibrous morphology. The randomly stacked clay fibres are able to create a macroporous network which may be suitable for polymer modification. Acid treatment of palygorskite would only increase the microporosity, which is too small to incorporate organic functional groups. Therefore, the natural palygorskite was used without any

further treatment and is referred to as “Pal”. The SSA of natural palygorskite is 87  $\text{m}^2/\text{g}$  and its CEC is 0.17 meq/g.

### 2.3. Preparation of clay/poly-acrylic acid (clay/PAA) composites

Acrylic acid (7.2 g) was dissolved in 20 mL of distilled water and then neutralised at 5 °C with 12 mL of 5 M sodium hydroxide solution in a flask equipped with a condenser, a thermometer and a nitrogen ( $\text{N}_2$ ) line (the apparatus schematic is provided in Supporting Information). Clay powder was dispersed in the above partially neutralised monomer solution. The mass of clay was predetermined to be 7.2 g, 14.4 g and 21.6 g, which corresponded respectively to 50%, 66% and 75% of total mass of the resultant products. The cross-linker MBA (16.0 mg  $\approx$  0.1 mol.%) was added under a nitrogen atmosphere to the AA-clay mixture and the mixed suspension was stirred in an oil bath at room temperature for 30 min. The radical initiator APS (82.2 mg  $\approx$  0.36 mol.%) was added to the mixture and the oil bath was then heated slowly to 70 °C with vigorous stirring, and then kept at 70 °C for 3 h. The resulting product was washed several times with distilled water and then dried in an oven at 60 °C to a constant mass. Finally, the dried product was pulverized and ground using a laboratory ball mill (Noah NQM-0.4 Planetary Ball Mill, Yangzhou Nuoya Machinery Co. Ltd., China). Stainless steel balls (diameter: 6 mm) with ball to powder ratio 4 were used for 1 h in the air in a stainless steel sample holder. The maximum proportion of clay achieved in the products was 75% because it is difficult to disperse a greater amount of clay into the polymerisation system under laboratory conditions.

### 2.4. Preparation of copper-complexed clay/PAA composites

Ion-complexation was performed using  $\text{CuCl}_2$  solution: 40 mL of 0.5 M  $\text{CuCl}_2$  was mixed with 5 g of clay/PAA composites. After stirring for half an hour the mixture was transferred to an oven at 60 °C and heated for 24 h. The powder was collected by centrifugation and washed with deionised water three times. Finally, all samples were dried at 60 °C. The amount of copper loaded on the composites was calculated by measuring the copper remaining in the supernatant using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Agilent), and shown in Table 1.

### 2.5. $\text{NH}_3$ breakthrough dynamic test

A micro-scale breakthrough apparatus was developed to assess the  $\text{NH}_3$  adsorption behaviour of the samples. The gas stream was 1550 ppm  $\text{NH}_3$  (1080  $\text{mg}/\text{m}^3$ ) prepared by diluting 1%  $\text{NH}_3$  in  $\text{N}_2$  with dry air. The flow of 1%  $\text{NH}_3$  was controlled by a mass flow meter. The flow rate of air was monitored by a rotameter. The two flow meters were calibrated with a bubble meter. The total flow rate of inlet gas was fixed at 115 mL/min. About 1 mL of samples was packed into a 1.0 cm inner diameter glass column. The  $\text{NH}_3$  concentration in the outlet gas was measured using a Dräger XAM7000 system equipped with an electrochemical sensor for  $\text{NH}_3$ . The flow of  $\text{NH}_3$  was arbitrarily stopped when the breakthrough concentration was 100 ppm, following which desorption process was studied by purging the sample with dry air only. The entire adsorption experiments were replicated three times. The adsorption capacity of each adsorbent was calculated by integrating

**Table 1**  
The concentration of copper in clay/poly-acrylic acid (PAA) composites.

Sample	Copper uptake (mg/g)
CuPAA ABent 50%	132
CuPAA ABent 66%	102
CuPAA ABent 75%	86
CuPAA Paly 50%	150
CuPAA Paly 66%	147
CuPAA Paly 75%	139

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