



Research paper

Metakaolin geopolymer characterization and application for ammonium removal from model solutions and landfill leachate

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ABSTRACT

Geopolymers are aluminosilicate compounds that are amorphous analogues of zeolites, and thus possess similar cation-exchange properties. Geopolymers have been successfully applied to remove toxic metals and organic dyes from aqueous solutions. In this study, geopolymer was synthesized from metakaolin and applied to remove ammonium (NH_4^+) from model solutions and landfill leachate. Geopolymerization increased the ammonium removal capacity, surface area and average pore width and changed the chemical structure of metakaolin. The maximum NH_4^+ removal capacity of the geopolymer was 21.07 mg g^{-1} which was 46% higher than the capacity of the reference clinoptilolite–heulandite zeolite (14.42 mg g^{-1}). The adsorption data of the geopolymer and zeolite fitted best to the Langmuir–Freundlich isotherm and the removal kinetics followed the pseudo-second order kinetic equation. The spent geopolymer adsorbent was regenerated efficiently using 0.2 M NaCl and 0.1 M NaOH as a regenerant. A small-scale continuous field experiment with landfill leachate was performed and further indicated that the metakaolin-based geopolymer could be a feasible NH_4^+ removal adsorbent.

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1. Introduction

The accumulation of nitrogen in the aquatic environment can lead to eutrophication and subsequently oxygen depletion. Therefore, the removal of nitrogen from municipal and industrial wastewaters before discharge has become obligatory in many countries. Aqueous nitrogen commonly exists as ammonium (NH_4^+), which is likely the most serious nitrogen species from the viewpoint of eutrophication. In Finland, the discharge limit for municipal wastewater treatment plants is typically a maximum of $4 \text{ mg L}^{-1} \text{ NH}_4^+$ when the water temperature is higher than $+12^\circ\text{C}$. At lower temperatures, the kinetics of the commonly applied biological nitrogen removal process (nitrification–denitrification) is hindered substantially. Alternative removal methods include air stripping of ammonia, reverse osmosis, ion exchange or adsorption. Of these methods, ion exchange and adsorption have received attention since many potentially effective and low-cost materials are emerging. These methods are also less affected by temperature or variation in wastewater quality.

Natural zeolites, such as clinoptilolite (Saltali et al., 2007; Jorgensen and Weatherley, 2003; Langwaldt, 2008; Alkas et al., 2013; Sprynsky et al., 2005; Wang et al., 2006; Karadag et al., 2006; Wang et al., 2008;

Weatherley and Miladinovic, 2004), mordenite (Weatherley and Miladinovic, 2004) and chabazite (Langwaldt, 2008), have been successfully applied to remove ammonium. However, synthetic zeolites have a higher zeolite content and a lower Si/Al ratio, and thus exhibit better pollutant-removing abilities (Wang et al., 2008). Synthetic zeolites for removing ammonium have been prepared from fly ash (Zhang et al., 2011a; Zhang et al., 2011b; Juan et al., 2009), rice husk ash (Yusof et al., 2010) and halloysite mineral (Zhao et al., 2010a), for example. However, zeolite synthesis frequently involves a high temperature (Querol et al., 2002). Alternative synthesis at room or only slightly elevated temperature produces amorphous analogues known as geopolymers (Davidovits, 1991).

Alkaline synthesis of geopolymers involves a solid aluminosilicate source (such as fly ash, blast furnace slag or metakaolin) and concentrated aqueous alkali (typically Na or K) hydroxide and/or silicate solution. Tetrahedral AlO_4^- and SiO_4^- monomers are formed that subsequently polycondensate into a three-dimensional polymer structure that has a net negative charge arising from the valency difference between Si and Al. The charge balancing cations (e.g., Na^+ or K^+) of geopolymers have been shown to be exchangeable (Skorina, 2014; O'Connor et al., 2010).

Depending on the synthesis and curing conditions, the resulting geopolymer materials are amorphous or partly crystalline with zeolite-like nanocrystallite structures (Provis et al., 2005). Zeolite formation is promoted by a low Si/Al ratio, high water content or elevated

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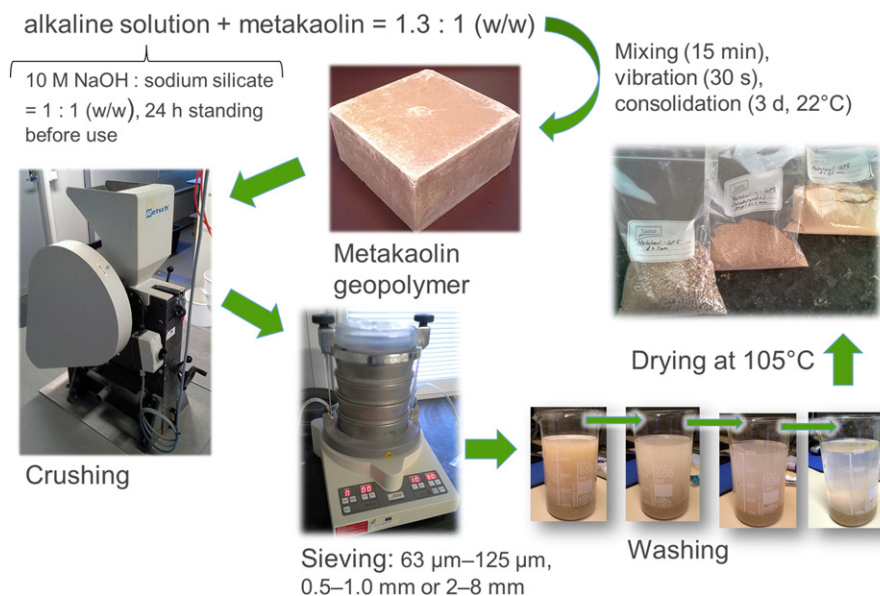


Fig. 1. A pictorial presentation of the synthesis procedure.

curing temperatures (Provis and Van Deventer, 2009; Brew and Mackenzie, 2007). Geopolymers have several useful properties including a quick compressive strength development, acid and fire resistance, fast setting, good resistance to freeze–thaw cycles and a tendency to decrease the mobility of heavy metals. These properties have resulted in a wide range of potential applications such as low-CO₂-producing cement, waste encapsulation, fire- and corrosion resistant coatings, porous insulators and filters (Davidovits, 2011). One interesting application area is the utilization of geopolymers in wastewater treatment.

Coal fly ash geopolymers have been studied for the adsorption of organic dyes (methylene blue and crystal violet) and metals such as Cu²⁺, Pb²⁺ and Cd²⁺ (Javadian et al., 2013; Li et al., 2006; Wang et al., 2007b; Mužek et al., 2014; Ge et al., 2015; Al-Zboon et al., 2011). Additionally, this geopolymer has been used as a photocatalyst for methylene blue degradation under UV irradiation (Zhang and Liu, 2013). Metakaolin geopolymer has been studied for the adsorption of Pb²⁺, Cu²⁺, Cr³⁺, Cd²⁺ and Cs⁺ (López et al., 2014a; López et al., 2014b; Cheng et al., 2012). Zeolite can be used as a filler in geopolymer concrete to produce a material with good mechanical properties combined with a high adsorption capacity (Yousef et al., 2009; Alshaaer et al., 2014). Geopolymerization typically significantly improves the adsorption capacity of the raw material. O'Connor et al. (2010) showed that the Ag⁺ exchanged halloysite geopolymer has anti-microbial properties, which could potentially also have water treatment applications. Additionally, geopolymers have been studied as a substrate for a fixed-film wastewater treatment process (biofilm reactor) (Silva et al., 2012).

The literature concerning the adsorption applications of geopolymers for water treatment is still limited. The adsorbates used in previous studies have been metal cations or organic dyes. Although

some studies mention NH₄⁺ as a possible charge-balancing cation (O'Connor et al., 2010), no studies on utilizing geopolymers in removing NH₄⁺ from aqueous solutions have been conducted.

In this paper, a geopolymer was prepared from calcined clay mineral kaolinite (i.e. metakaolin), characterized and tested for NH₄⁺ removal from aqueous solutions. Batch adsorption experiments with model NH₄⁺ solutions were performed to determine the effects of the pH, adsorbent dose, initial NH₄⁺ concentration and contact time on the removal efficiency. Isotherm and kinetic models were applied to describe the collected data. Finally, a small scale continuous field experiment with landfill leachate was performed to test the performance in a real wastewater matrix in an authentic environment. The results indicate that a metakaolin-based geopolymer is a technically feasible alternative for removing NH₄⁺ from wastewater. Metakaolin itself is a poor NH₄⁺ adsorbent, but geopolymerization substantially increases the NH₄⁺ removal capacity (600–900%).

2. Materials and methods

2.1. Synthesis of the geopolymer

A NaOH solution (10 M, technical grade, VWR International) was mixed with sodium silicate solution (technical grade, SiO₂:Na₂O = 3.1–3.4, VWR International) in the weight ratio of 1:1 and the resulting alkaline solution was allowed to stand for 24 h before use. Metakaolin (obtained from Aquaminerals Finland Ltd) was mixed with the alkaline solution in the weight ratio of 1.3:1. The formed paste was mixed for 15 min and vibrated for 2 min to remove gas bubbles. The paste was allowed to consolidate at room temperature (approximately 22 °C) for 3 days. The geopolymers were synthesized according to Cheng et al.'s

Table 1

Parameters for testing the effects of pH, adsorbent dose, ammonium concentration and contact time on ammonium removal. The temperature was 22 °C, and the adsorbent particle size was 63–125 μm.

Test	Initial solution pH ^a	Initial NH ₄ ⁺ [mg L ⁻¹]	Contact time [h]	Adsorbent dose [g L ⁻¹]
Effect of pH	4.0, 6.0 or 8.0	50	24	5
Effect of adsorbent dose	6.0	50	24	0.2–15
Effect of contact time	6.0	50	0.016–6	5
Effect of initial concentration	6.0	10–1000	24	5

^a Adjusted with 0.1 M NaOH or 0.1 M HCl.

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