

Utilization of by-products from mine industry as sorbents in water treatment

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Abstract Ammonium removal from explosive agent residues containing mining effluents represents a challenge, especially in cold climate. As environmental agencies are demanding ammonium removal at mine sites in e.g. Finland and Sweden, new methods are required. Natural zeolites are the most studied sorbents for ammonium removal and one promising material is a mining industry by-product, analcime. In this study, the ammonium removal capacity of analcime was improved by using geopolymerization. Four types of geopolymers were prepared and tested as an ammonium sorbent by using model solutions at different temperatures. Finally, the material could be regenerated or utilized e.g. as a fertilizer.

Key words ammonium removal, analcime, geopolymer, sorbent

Introduction

Zeolites are crystalline-hydrated aluminosilicate minerals with a three-dimensional framework, which consists of SiO_4 and AlO_4 tetrahedra linked with shared oxygen atoms. Zeolites possess large surface area and high cation exchange capacity. Zeolites are as cation exchangers and consequently they have been frequently applied as sorbents in water and wastewater treatment (Wang and Peng 2012). The most common types of zeolites are clinoptilolite, mordenite, dachiardite, analcime, phillipsite and heulandite. Zeolites have been reported to be effective in removing cations with widely variable size, such as dyes (Karadag et al. 2007; Wang and Zhu 2006), organics (Bowman 2003; Huttenloch et al. 2001), ammonium (Lei et al. 2008; Luukkonen et al. 2016) and metal ions (Cincotti et al. 2006; Oter and Akcay 2007) from wastewaters. Zeolite mineral, analcime [$\text{Na}_{16}(\text{Al}_{16}\text{Si}_{32}\text{O}_{96}) \cdot 16\text{H}_2\text{O}$], is formed as a by-product when lithium carbonate is produced from spodumene ($\text{LiAlSi}_2\text{O}_6$) using sodium pressure leaching process (Chen et al. 2011). Analcime has also been reported to be a sorbent in the wastewater treatment (Atta et al. 2012; Mallah et al. 2012; Montalvo et al. 2012).

Ammonium (NH_4^+) in mining effluents originates mainly from explosive agents such as ammonium nitrate-fuel oil explosives (ANFO) which contains 33% (w/w) of nitrogen (Forsyth et al. 1995). Ammonium is a major contributor to the eutrophication of water bodies in those cases when nitrogen is the nutrient in shortest supply. In fact, ammonium is more severe in term of eutrophication than the other common nitrogen species nitrate (NO_3^-) (Wet-

zel 2001). Therefore, several countries have set limit values to the nitrogen removal from wastewaters, also in small-scale wastewaters, and more commonly also from mining effluents. Typically, mines have a maximum annual nitrogen release amount. Currently sorption-based technologies are not widely applied for mining effluents but they have potential since the process is generally little affected by temperature or variations on concentration. Metakaolin geopolymer (Luukkonen et al. 2016) and natural zeolites (of which clinoptilolite is the most widely studied) or wollastonite (Hedström 2006a; Hedström 2006b), for example, have been developed earlier to ammonium removal.

Geopolymers consist of an anionic framework of corner-sharing SiO_4 and AlO_4 , and the exchangeable cations are located in the voids in the same way as in zeolites (Davidovits 2015). However, geopolymers are x-ray amorphous unlike zeolites. Geopolymers are most commonly prepared by a synthesis method in which aluminosilicate raw material (such as metakaolin) and alkaline activator (typically sodium hydroxide and/or silicate) react at room temperature and pressure (Luukkonen et al. 2016).

In the present study, the industrial waste material, analcime, was applied as a sorbent in the ammonium removal. Based on the literature, analcime removes ammonium at elevated temperature but water treatment should occur at ambient temperature which is, for example in Finland, typically low. Therefore, analcime was geopolymerized by four types of processes. Sorbent was studied for ammonium removal in batch experiments with synthetic wastewater with a high ammonium concentration. Sorption was studied at room (22 °C) temperature and elevated (80 °C) temperatures and the effect of ammonium solution concentration was assessed. In addition, experiments with analcime without geopolymerization were performed for comparison.

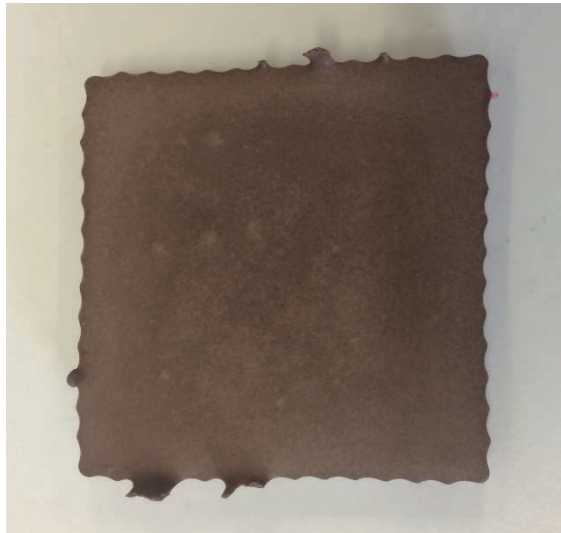
Materials and methods

Preparation of geopolymers

Analcime was provided by Keliber Oy, Finland (Keliber Oy 2016). Two geopolymer precursors were prepared. In the first, analcime was first acid-washed with 2 M HCl for 24 h and dried at 105 °C for 24 h. Acid washing causes dealumination and renders the mineral into more reactive form (Jozefaciuk and Bowanko 2002). Calcination was performed at 400 °C or 700 °C for 2 h. The second precursor was prepared by mixing analcime and metakaolin (3:1 w/w) and drying at 105 °C for 24 h. Geopolymers were synthesized by mixing precursors (analcime or analcime and metakaolin mixture) with 10 M sodium hydroxide (NaOH) and sodium silicate (VWR International, $\text{SiO}_2:\text{Na}_2\text{O}=3.1\text{-}3.4$) 1:1 (w/w) mixture. The formed pastes were mixed for 5 min and poured into molds and they were allowed to consolidate at 22 °C for 2–4 weeks to ensure complete reaction. Before sorption experiments, the geopolymers were crushed and sieved to a particle size <500 µm and washed with deionized water. The compositions and sample names of the analcime geopolymers synthesized in this study are presented in Table 1. The example of the synthesized geopolymers is presented in Fig 1. Dried and sieved analcime was used as a reference material to analcime-geopolymers.

Table 1 *Analcime geopolymers preparation conditions.*

Sample	Precursor	Pre-treatment	Calcination temperature	Alkali activator	Precursor-alkali activator ratio (w/w)
GP1	Analcime	Washed with 2 M HCl, 10 g/200 mL, 24 h. Dried at 105°C for 24 h.	-	10 M NaOH + sodium silicate (1:1 w/w)	0.9:1
GP2	Analcime	Washed with 2 M HCl, 10 g/200 mL, 24 h. Dried at 105°C for 24 h.	400°C, 2 h	10 M NaOH + sodium silicate (1:1 w/w)	0.9:1
GP3	Analcime	Washed with 2 M HCl, 10 g/200 mL, 24 h. Dried at 105°C for 24 h.	700°C, 2 h	10 M NaOH + sodium silicate (1:1 w/w)	0.9:1
GP4	Analcime + metakaolin (3:1 w/w)	Dried at 105°C for 24 h	-	10 M NaOH + sodium silicate (1:1 w/w)	1.36:1

**Figure 1** *Analcime-metakaolin geopolymer GP4.*

Ammonium sorption experiments

The effect of temperature on the ammonium removal efficiency of four analcime geopolymers and unreacted analcime was studied. Experiments were conducted in batch mode with synthetic wastewater. Sorbent dosage was 20 g/L, concentration of ammonium solution was 1000 mg/L, volume of solution 50 mL and initial pH 2 (adjusted with HCl). Sorption

temperatures were 22 °C at 80 °C in water bath. Samples were shaken during contact time with laboratory shaker at 300 rpm. All sorption experiments were performed as duplicate. Solids were separated from ammonium solution by centrifuging before measurement of ammonium concentration with a Hach Lange IntelliCal ammonium ISE- electrode.

Results and discussion

Yuan et al. (2016) found that ammonium removal with analcime was increased at elevated temperatures and therefore, experiments were conducted at 80 °C in addition to the room temperature (22 °C): the results are shown in Tables 2 and 3, respectively. Sorption efficiencies of materials at different temperatures are compared in Figure 2. At the room temperature, GP2 is the most efficient material with a removal efficiency of 15 % and a sorption capacity of 5 mg/g. Results indicate that the ammonium removal efficiencies are much higher at elevated temperatures than at the room temperature. At 80 °C the removal efficiencies are at the same level approx. 50-60% ($q = 10-13$ mg/g) with all sorbent materials except GP3 (removal approx. 15 % and $q = 1$ mg/g). Analcime without geopolymerization removes ammonium ions at elevated temperature as well as analcime-geopolymers but at room temperature ammonium removal efficiency is much higher for analcime-geopolymers (except GP3) compared to with analcime. In literature has been reported that analcime has two types of ion exchange: at room temperature and at elevated temperatures. Since, ion exchange occurs easier at elevated temperature because of small pores of analcime (Barrer and Hinds 1953; Sakizci 2016).

Before sorption experiments, initial pH was adjusted to value 2 to ensure that ammonium was present as NH_4^+ and not as NH_3 . During experiments, pH increased due to alkalinity of analcime (pH approx. 11).

Table 2 Results of ammonium sorption experiments at elevated temperature (80 °C)

Sample	Sorbent dosage [g/L]	Temperature [°C]	Concentration of NH_4^+ [mg/L]	pH. Initial	pH. Final	Removal [%]	Sorption capacity [mg/g]
Blank	-	80	507	-	-	-	-
Analcime	20	80	261	2.4	7.7	50.2	12.4
GP1	20	80	298	2.3	8.4	56.8	11.0
GP2	20	80	234	2.3	8.5	54.0	10.1
GP3	20	80	419	2.3	2.9	20.1	1.65
GP4	20	80	258	2.5	7.2	52.7	9.9

Table 3 Results of ammonium sorption experiments at room temperature (22 °C)

Sample	Sorbent dosage [g/L]	Temperature [°C]	Concentration of NH ₄ ⁺ [mg/L]	pH, Initial	pH, Final	Removal [%]	Sorption capacity [mg/g]
Blank	-	22	705	2.4	2.5	-	-
Analcime	20	22	679	2.5	7.8	3.8	1.3
GP1	20	22	614	2.2	8.4	13.0	4.6
GP2	20	22	595	2.2	8.0	15.6	5.5
GP3	20	22	754	2.1	2.3	0.5	0.2
GP4	20	22	636	2.9	5.4	9.8	3.4

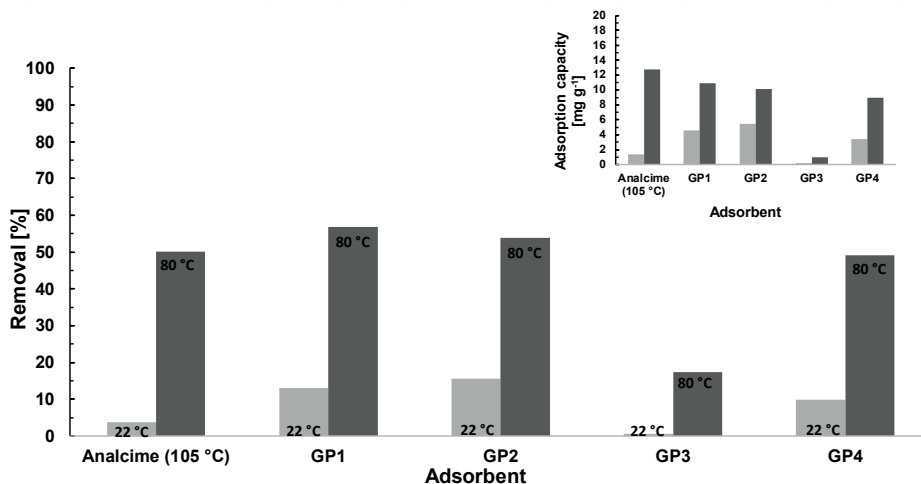


Figure 2 Comparison of removal efficiencies for analcime and analcime-geopolymers at room temperature and at 80 °C. The small figure presents sorption capacity (mg/g) for studied samples at room temperature and at 80 °C.

Conclusions

Different types of analcime-based geopolymers were prepared and tested as a sorbent in ammonium removal. Ammonium removal efficiencies were clearly higher at elevated temperature comparing with room temperature. Results from batch experiments with powdered analcime-geopolymer indicated that the maximum ammonium sorption capacity was 11 mg/g at 80 °C and 5.5 mg/g at room temperature. For analcime these results were

12.4 mg/g and 1.3 mg/g, respectively. Therefore, the analcime seems to have higher affinity to ammonium at elevated temperatures. Wastewater purification materials should act at wide temperature range and therefore, geopolymerization with 10 M NaOH and sodium silicate solution is a suitable treatment method to increase ammonium adsorption capacity at room temperature.

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