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Research paper

Organoclays of high-charge synthetic clays and alumina pillared natural clays: Perchlorate uptake

Sridhar Komarneni [a,*], Amir Reza Aref [a], Siqi Hong [b], Young Dong Noh [a], F.S. Cannon [b], Yujue Wang [c]

[a] *Materials Research Institute, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA*
[b] *Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA 16802, USA*
[c] *School of Environment, Tsinghua University, Beijing 100084, China*

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ABSTRACT

Several organoclays were synthesized from different types of high charge synthetic clays using octadecyltrimethylammonium (ODTMA) chloride or polyethylenimine (PEI). Two alumina pillared clays were also prepared using two naturally occurring montmorillonites. These organic–clay and inorganic–clay nanocomposites were characterized by powder X-ray diffraction (XRD) and tested for perchlorate uptake. The results showed that the highest perchlorate uptake capacity of 0.436 ± 0.001 was achieved with ODTMA Na-3-mica followed by 0.269 ± 0.016 meq/g with ODTMA Na-2-mica. The uptake of perchlorate by synthetic Na-n-micas is as follows: ODTMA Na-3-mica > ODTMA Na-2-mica > ODTMA Na-1-mica > ODTMA Na-4-mica. Perchlorate uptake isotherms were determined for both ODTMA Na-3-mica and ODTMA Na-2-mica as a function of perchlorate concentration but apparently equilibrium was not achieved in both cases. The uptake of perchlorate by the ODTMA Na-n-micas could be attributed to exchange with chloride ions of the neutral surfactant occluded in between cationic chains during the cation exchange process. Organoclays prepared with PEI and hydroxy Al polymer pillared clays and their calcined counterparts showed little or no uptake because excess positive charge was not created in the interlayers in these nanocomposites unlike in the organoclays with Na-n-micas.

1. Introduction

Perchlorate (ClO_4^-) is a highly oxidized (+7) chlorine oxy-anion manufactured for use as the oxidizer in solid propellants for rockets, missiles, explosives, roadside flares etc. (Xu et al., 2003). Their use leads to the release of perchlorate into the environment (Bardiya and Bae, 2011). The perchlorate ion is similar in size to an iodide ion, and can, therefore, be taken up in place of iodide ions by the mammalian thyroid gland. In this way, perchlorate ions can disrupt the production of thyroid hormones and may disrupt metabolism in the human body and the effects can be significant in case of pregnant women and fetuses (Srinivasan and Sorial, 2009; Urbansky, 2002). According to these findings, drinking water standards for perchlorate have been proposed. For example, The National Academy of Engineers has recommended a reference dose (RfD) of 0.7 μg/kg · day, which yields a drinking water equivalent limit of 24.5 μg/l assuming a relative source contribution (RSC) of 100% and a 2.0-L daily water intake for a 70-kg adult (Ye et al., 2012). Therefore, it is essential to find an effective method to remove perchlorate from drinking water and wastewater. A considerable amount of research has been carried out to evaluate treatment alternatives for perchlorate remediation in drinking water. Several materials and technologies have been used for removal of perchlorate ions from water. These technologies can be classified into removal or destruction. The major removal technologies are adsorption with activated carbon, ion-exchange and filtration. Destruction technologies for perchlorate include biological treatment, chemical reduction, and electrochemical reduction (Srinivasan and Sorial, 2009). Currently ion-exchange is an effective and commonly used technology to remove perchlorate from drinking water due to its simplicity (Parette and Cannon, 2005; Parette et al., 2005). We have recently discovered that organosilicas and organoclays exchange perchlorate selectively (Kim et al., 2011; Komarneni et al., 2010; Seliem et al., 2010, 2011, 2013). Subsequent work by Chitrakar et al. (2012) using montmorillonite modified with hexadecylpyridinium chloride confirmed our findings of selective uptake of perchlorate by organo-clays (Kim et al., 2011; Seliem et al., 2010, 2011, 2013). Excess exchange of organic ammonium cations exceeding the exchange capacity of the clay has been suggested previously and the electroneutrality is apparently maintained by adsorption of anions in the interlayers (Cowan and White, 1958). The charge on the organic ammonium cations is balanced by chloride or other anions which can be exchanged as proposed by us previously for organosilicas and organoclays (Kim et al., 2011; Komarneni et al., 2010; Seliem et al., 2010, 2011, 2013). Organoclays have been used previously for the uptake of anions such as chromate, CrO_4^{2-} (Dultz et al., 2012; Krishna et al., 2001; Mahadevaiah et al., 2008),

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* Corresponding author at: 205 Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA. Tel.: +1 814 865 1542; fax: +1 814 865 2326.
E-mail address: komarneni@psu.edu (S. Komarneni).

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molybdate, MoO_4^{2-} (Mahadevaiah et al., 2007), pertechnetate, TcO_4^- (Bors et al., 2000), iodide, I^- (Behnsen and Riebe, 2008; Kaufhold et al., 2007) and perrhenate, ReO_4^-, bromide, Br^-, sulfate, SO_4^{2-} and selenite, SeO_3^{2-} and bromate, BrO_3^- (Chitrakar et al., 2011) and nitrate, NO_3^- (Chitrakar et al., 2011; Xi et al., 2010). However, there are no studies of organoclays for anion uptake prepared from clays with wide charge density differences.

In addition to conventional organoclays, clay–organic nanocomposites based on the intercalation of chitosan in Na-montmorillonite also exhibited anion exchange based on the following mechanism (Darder et al., 2005): When the chitosan biopolymer amount exceeds the cationic exchange capacity (CEC) of the clay, the biopolymer is intercalated as a bilayer in interlayers of clay by cation exchange and hydrogen bonding processes (Darder et al., 2005). The excess of $-NH_3^+$ groups on the biopolymer do not interact electrostatically with the negatively charged clay but these positive groups are balanced by acetate ions from the initial chitosan solution. Thus the bidimensional nanocomposite material with anionic exchange sites ($-NH_3^+$ X^- [acetate]) exhibits anion exchange (Darder et al., 2003, 2005). When this type of a nanocomposite was used as an anion sensor, the selectivity for anions is as follows (Darder et al., 2003): $NO_3^-–CH_3COO^-–Cl^- >>> SO_4^{2-}–Cr_2O_7^{2-} \gg Fe(CN)_6^{3-}$. Intercalation of cationic polyelectrolytes such as polyethylenimine (PEI) and poly(allylamine hydrochloride) (PAH) in the interlayers of fluoromica is possible but the conformation of the intercalated polycation plays an important role in anion uptake (Hata et al., 2007). Monolayer intercalation of PEI in which the polymer adopted an extended rather than coiled conformation did not accommodate anionic guests (Hata et al., 2007). However, intercalation of quaternary ammonium polycation poly(diallyldimethylammonium) (PDDA) resulted in an excess of cationic sites within the interlayers of the fluoromica polysilicate due to coiled conformation and these cationic sites exchange anionic blue dye (Hata et al., 2007) in the expanded interlayers. The PEI polyelectrolyte–clay nanocomposites, however, have not been tested for inorganic anion exchange. In addition to clay–organic nanocomposites, inorganic oxide-clay nanocomposites i.e., pillared clays have been prepared extensively by us (Malla and Komarneni, 1990) and others by intercalating polymeric cations such as Al_{13} with a 7^+ charge. Do these polymeric cations intercalate in excess of the cation exchange capacity of the clay? If so, the pillared clays may also show anion exchange just as in the case of organoclays and clay–polyelectrolyte nanocomposites described above.

Thus, the main objectives of this work were (a) to synthesize and characterize organoclays prepared from synthetic clays with different charge densities and investigate their perchlorate exchange properties (b) to synthesize clay–polyethylenimine nanocomposites and investigate their perchlorate uptake properties and (c) to synthesize alumina pillared clays i.e., Al_{13} polymer–clay nanocomposites and determine perchlorate uptake, if any.

2. Materials and methods

2.1. Materials

Synthetic swelling Na-n-micas, $Na_nSi_{8-n}Al_nMg_6O_{20}F_4 \cdot yH_2O$ (n = 1, 2, 3 and 4 with theoretical cation exchange capacities, CECs of 117, 234, 351 and 468 meq/100 g or mmol/100 g, respectively) of different compositions and charge densities were prepared by a solid state method as has been described previously (Noh et al., 2013). All these micas and two other synthetic micas, Na–tetrasilicic mica (Na-TS), $NaSi_4Mg_{2.5}O_{10}(F)_2$ and lithium taeniolite (Li-TN), $LiSi_4Mg_2LiO_{10}(F)_2$ supplied by commercial companies were used in this study. Two montmorillonites, one from Wyoming, USA (designated as Mt) and one from Kunimine Industries, Kunimine, Japan (designated as Kunipea) were also used for making alumina pillared clays i.e., inorganic oxide–clay nanocomposites.

2.2. Methods

2.2.1. Preparation of organo-swelling micas of Na-1-mica, Na-2-mica, Na-3-mica and Na-4-mica using octadecyltrimethylammonium (ODTMA) cation

The cation exchange reactions between octadecyltrimethylammonium chloride (Fluka, ≥95% ODTMA Cl) and Na-n-micas were carried out to prepare organo-micas. An excess amount of ODTMA Cl (i.e., an amount equal to 2 CEC of each Na-n-mica) was put into 80 ml deionized (DI) water in a Teflon vessel. After dissolving the ODTMA Cl in the Teflon vessel, 0.2 g of Na-1-mica, Na-3-mica or Na-4-mica was added into the vessel under stirring and then the mixture was hydrothermally heated at 120 °C for 1 day to facilitate the exchange reaction of ODTMA into the interlayer space of Na-n-mica. In the case of Na-2-mica, the synthesis of organo-mica was accomplished at 65 °C under stirring on a hot plate. The different Na-n-micas are designated from hereinafter as ODTMA Na-1-mica, ODTMA Na-2-mica, ODTMA Na-3-mica and ODTMA Na-4-mica for Na-1-mica, Na-2-mica, Na-3-mica and Na-4-mica, respectively. Afterwards, the solid was washed with DI water several times by centrifugation and dried at room temperature.

2.2.2. Preparation of polyethylenimine (PEI) intercalated swelling micas

Intercalation of PEI into three micas (Na-TS, Li-TN, Na-1-mica) was attempted by a procedure previously described by Hata et al. (2007). Dry samples of each mica (75 mg) were first dispersed separately in distilled water (75 ml) by stirring for 1 day at room temperature. A stoichiometric amount of PEI corresponding to five times the cation exchange capacity of each of the mica was dissolved in water at pH 12 first and then added to the clay dispersion. The suspension was then vigorously agitated on a shaker for 1 day at 298 K. PEI is not soluble in water, therefore, it was first stirred in water for 2 h and then the pH of the suspension was adjusted to 12 with 10 N NaOH before adding it to the clay suspension as has been described previously (Hata et al., 2007). After the reaction, the suspension was centrifuged to separate solids and solutions. The solid products were washed with distilled water and ethanol several times to remove any remaining soluble salts. The solids were dried in an oven at 65 °C. The dried samples were gently ground and homogenized in an agate mortar with a pestle prior to characterization and perchlorate adsorption studies.

2.2.3. Preparation of Al-pillared montmorillonites

First, Al polymer pillaring precursor solution was prepared as follows: 500 ml of 0.4 M NaOH was titrated into 250 ml of 0.4 M $Al(NO_3)_3 \cdot 9H_2O$ at 2.5 ml per min under vigorous stirring (Na:Al = 2:1). At the end of titration, the solution was stirred for 1 h followed by heating at 65 °C for 4 h in a sealed container. This pillaring solution was stored at room temperature before use in the pillaring process as described below.

2.2.3.1. Pillaring process with Al_2O_3. A 0.2 g of Na-montmorillonite, Wyoming (Mt) or a sodium montmorillonite supplied by Kunimine (Kunipia) was added slowly to 20 ml of deionized water for dispersion of the clay. After 30 min of stirring of the clay in water, 20 ml of the above pillaring solution was added into the clay dispersion. This dispersion was then stirred for 8 h to complete the pillaring process and then centrifuged to separate the solid from liquid. In order to make sure that the Al pillar intercalation was complete with the clay, the above solid was again treated with 20 ml of deionized (DI) water and 20 ml of the pillaring solution under stirring for 1 day. The resulting alumina pillared clays were washed with DI water several times and finally with ethanol. The final product was dried in air. The above preparation of Al_2O_3-pillared montmorillonite was based on a previously described procedure by Malla and Komarneni (1990). The Al_2O_3-pillared montmorillonites (Mt) are hereinafter referred to as Al-pillared Kunipia and Al-pillared Na-Mt. The above as-prepared pillared clays with