

Organo-montmorillonite: Synthesis, characterization, and application in removal of perchlorate and related oxoanions

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論文内容の要旨

Perchlorate ion (ClO_4^-) is an emerging contaminant and has aroused widespread concern because it interferes with iodide uptake in tissues such as thyroid gland. Extensive contamination of perchlorate in groundwater, vegetables, rice, milk and bottled water has been detected. To develop techniques and methods to sequester perchlorate from aqueous solution is imperative. Montmorillonite (Mt) is one of the most abundant naturally occurring clay minerals, which can be used as a starting material for synthesis of organo-montmorillonite (OMt) through facile modification using surfactants. Alkyl quaternary ammonium compounds (QACs) are the most ubiquitous surfactants for Mt modification. Recently, several OMts were synthesized using different amounts of QACs with diverse alkyl-chain lengths and applied to remove perchlorate. However, influences of molecular structure and dosage of QACs on perchlorate adsorption have not yet been addressed. The relationships between molecular structure and dosage of QACs and performance of OMt on perchlorate adsorption were indentified in the present thesis. In addition to well-known ion exchange, a potential mechanism of perchlorate adsorption on OMt was explored. The generally ignored issue of QACs release was also taken into account. Finally, application of OMt for removal of other relevant anions was extended and the different selectivities were interpreted.

In **Chapter 1**, background information about perchlorate, including its toxicity and removal techniques were overviewed, and then applications of organically modified Mt in environmental remediation, especially for adsorption of anions were presented. Based on these background, the purposes and movitation of this thesis were elucidated.

Six QACs were deliberately selected and used to modify Mt to investigate the influence of their structures on adsorption characteristics of perchlorate using obtained OMt in **Chapter 2**. These six QACs possess different alkyl-chain lengths, head groups, and alkyl-chain numbers. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric and differential thermal analysis (TG-DTA), X-ray photoelectron spectroscopy (XPS), CHN analysis, field emission scanning electron microscopy (FESEM), and the measurement of zeta potential were applied to characterize the obtained OMts. Based on these characterization, the different performance of OMts in perchlorate adsorption, including adsorption capacity, kinetics and selectivity were interpreted. Longer or more numerous alkyl chain improved adsorption density and selectivity of perchlorate but decreased the adsorption rate, because of compact configuration resulting from high QACs content. Bulkier head groups resulted in more favorable adsorption capacity and selectivity of perchlorate. Hydrophobicity of the surroundings where ion-exchanging sites located governed the selectivity of OMts to perchlorate.

Based on **Chapter 2**, benzyl octadecyl dimethyl ammonium chloride (BODMA-Cl) showed better performance, therefore, it was used to examine the influence of BODMA-Cl dosage on perchlorate adsorption in **Chapter 3**. The amounts of BODMA-Cl corresponding to 0.5~4.0 times of cation exchange capacity (CEC) of Mt were applied to modify Mt, and the obtained composites were characterized by multiple techniques. BODMA-Cl content significantly increased in composite after the amount of initially added BODMA-Cl higher than 1.0 times CEC of Mt, and its increasing rate was remarkably slowed down once BODMA-Cl dosage was greater than 2.0 times CEC of Mt. In addition, effects of temperature, pH and co-existing anions on perchlorate adsorption were also investigated. A high adsorption capacity of perchlorate (ca. 0.9 mmol/g) on BODMA-4-Mt was stably maintained against variations in those parameters, suggesting that the composite would be promising for treatment of practical perchlorate-contaminated wastewater.

The amount of adsorbed perchlorate by OMt was generally larger than that of released counter ion (chloride) from OMt, which contradicts to ion exchange. In **Chapter 4**, latent mechanism of perchlorate adsorption was revealed according to the results of ^{13}C nuclear magnetic resonance and adsorption energy evaluated by the Dubinin-Radushkevich model. Desorption-adsorption would explain the gap in amounts between adsorbed perchlorate and released chloride. Moreover, in-situ method and unwashed wet OMt were designed for comparison with conventionally synthesized OMt in terms of adsorption capacity of perchlorate and release of hexadecyl pyridinium (HDPy). XRD and Attenuated Total Reflection (ATR)-FTIR were applied to characterize composites and elucidate inhibition of HDPy release in unwashed wet OMt. Although relatively high adsorption capacity of perchlorate and negligible HDPy release were obtained on unwashed wet OMt, re-dispersion of the composite paste in perchlorate-containing solution should be improved in the future.

Application of HDPy/Mt was extended to remove other 14 perchlorate-related oxoanions in **Chapter 5**. Unwashed and washed dry OMt were used to investigate their performance in anion adsorption and HDPy release. Washing process significantly decreased adsorption capacities of ReO_4^- , ClO_4^- , NO_3^- , and I^- , and release of HDPy was generally inhibited for all selected anions. Unwashed HDPy/Mt indicated higher selectivity to poorly hydrated monovalent anions because it presented a more hydrophobic environment resulting from higher HDPy content. In contrast, strongly hydrated divalent anions were more readily intercalated into less hydrophobic washed HDPy/Mt. Hydration of counter ion chloride is the driving force for anion adsorption on HDPy/Mt, whereas dehydration of anion consumed energy. Higher energy consumption required to peel off hydration shell of divalent anions accounted for their lower affinities to HDPy/Mt.

In **Chapter 6**, the main conclusions of this thesis were summarized to propose that more attention should be paid on suppression of surfactant release in the application of OMt. No release of surfactants avoids potential fouling of the highly porous adsorbents like activated carbon and/or resins, which is suitably arranged after OMt, resulting in extension of their life time. Physical encapsulation of OMt in gel may be an alternative to solve this problem. After further optimization, OMt will be a promising material in environmental remediation for perchlorate and the related oxoanions including radionuclide species.