GA06 / P18

Investigation of imidazole bearing surfactant modified montmorillonite for the adsorption of perchlorate

Li Zhang, Srinivasarao Kancharla, Keiko Sasaki
Department of Earth Resources Engineering, Kyushu University, Fukuoka 819-0395, Japan
Email: keikos@mine.kyushu-u.ac.jp

Abstract: *Insoluble gemini surfactants 1,3-(3-alkyl imidzolium) xylene dichloride ($(C_xIm)_2Xy{\cdot}2Cl$) with different alkyl chain length as the hydrophobic "tail" of surfactants was used to modify montmorillonite (Mt) and the obtained nanocomposite was applied for removal of perchlorate in aqueous solutions. The $(C_xIm)_2Xy$-Mt nanocomposites with different length of the alkyl chain were characterized by XRD, FTIR, CHN analysis, SEM and TEM observation. These were supplied for batch adsorption experiments to obtain kinetic model and adsorption isotherm. Based on the XRD patterns, the molecular configuration of the surfactants in interlayer of Mt was illustrated. Kinetic data was fit to pseudo-second-order model and adsorption isotherm was well fit to Langmuir model, indicating that the adsorption mechanism is dominated by ion-exchange. No organic release of the modified nanocomposites during adsorption of perchlorate was observed, indicating that the highly chemical stability of $(C_xIm)_2Xy$-Mt nanocomposites is caused by the double positive charged sites on one $(C_xIm)_2Xy{\cdot}2Cl$ gemini surfactant to interact with Mt surfaces.*

Keywords: Imidazole, Gemini surfactant, Modifier release

1. INTRODUCTION

The toxicity of perchlorate (ClO_4^-) has been recognized in the public water system. The main health concern regarding perchlorate is that it interferes with iodide uptake in the thyroid gland. However, it is difficult to immobilize perchlorate compare with other anionic species, due to its large ionic size and small charge. Destruction technologies for the treatment of large hazardous anions need the assistance of catalysts, electricity, etc. The microbial reduction is limited by the environmental conditions pathology concern. Adsorption was extensively studied and applied to anion remediation. Compare to activated carbon, resin or membrane, modified montmorillonite is a more cost-effective material in water treatment.

Montmorillonite (Mt) is one of the most abundant clay minerals in nature. The isomorphic substitutions (e.g., Al^{3+} replaced by Mg^{2+} or Fe^{2+} in the octahedral sheet and Si^{4+} replaced by Al^{3+} in the tetrahedral sheet) creates permanent negative charge which is balanced by introducing exchangeable cations such as Na^+, K^+, and Ca^{2+} in the interlayer. These interlayer cations could be substituted by quaternary ammonium compounds (QACs) to expand the interlayer space and create a hydrophobic environment. Both QACs anchored on Mt by static electricity and hydrophobic interaction could be released during the adsorption of perchlorate leading to the second contamination to treated water [1].

In this study, Insoluble gemini surfactants 1,3-(3-alkyl imidzolium) xylene dichloride ($(C_xIm)_2Xy{\cdot}2Cl$) with different alkyl chain length as the hydrophobic "tail" of surfactants was used to modify montmorillonite by mixing montmorillonite and (CxIm)2Xy·2Cl gemini surfactant in methanol at 60℃. Differently from conventional cationic surfactants, the double positive charged sites on one $(C_xIm)_2Xy{\cdot}2Cl$ gemini surfactant anchored on montmorillonite can be expected to stabilize functional groups for perchlorate. X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) were used to interpret structural changes of PVBMeIm-Mt nanocomposites depending on the amounts of PVBMeImCl added. The corresponding maximum adsorption capacities of perchlorate were evaluated using adsorption isotherms and the adsorption kinetics was evaluated.

2. EXPERIMENTAL

$(C_xIm)_2Xy$-Mt were synthesized by mixing 1 CEC of $(C_xIm)_2Xy{\cdot}2Cl$ with Mt in methanol at 60℃, and the solid residue was lyophilized, ground and sieved. The loading amount of $(C_xIm)_2Xy{\cdot}2Cl$ was calculated from CHN analysis and TG-DTA. The configuration of $(C_xIm)_2Xy{\cdot}2Cl$ in the interlayer of Mt was characterized by XRD and FTIR. Adsorption isotherms were conducted in 0.001 mM to 0.3 mM ClO_4^- solution. Kinetics, and influence of pH and co-ion tests were operated with 0.2 mM ClO_4^-. The concentration of co-ions was fifty times higher. ClO_4^- and released Cl^- were determined by IC. The amount of adsorbed ClO_4^- (Q_e) and released Cl^- on materials was calculated by mass balance.

3. RESULTS AND DISCUSSION

3.1 Characterization of modified montmorillonites

TG-DTA and CHN analysis were utilized to calculate the loading amount of the gemini surfactants on the nanocomposites (Table. 1). It can be indicated that the loading of $(C_xIm)_2Xy{\cdot}2Cl$ gemini surfactant will increase as the chain length of the alkyl chain increase. Based on previous researches [2], this is because the improved hydrophobicity of the modifier promoted the loading processes. FTIR result indicated the successful intercalation of the modifier onto the Mt. the adsorption peak of perchlorate after adsorption experiment is located around 1200 cm^{-1}. The XRD pattern for $(C_xIm)_2Xy$-Mt nanocomposites showed two predominant peaks in those with modifier having alkyl chain length more than 16 carbons, the others showed single peak. Since the initial stoichiometric adding amount of the modifier were equal with any chain length, we can clearly predict how the chain length of the $(C_xIm)_2Xy{\cdot}2Cl$ gemini surfactant influence the loading behavior of itself. Both the peaks at

the lower angle in $(C_{18}Im)_2$Xy-Mt and $(C_{20}Im)_2$Xy-Mt are assigned as pseudo-trilayer pillaring configuration. As is illustrated in Fig. 1, two gemini surfactants overlapped together to expand the interlayer space of the Mt. because there are three layers of alkyl chains in this configuration, therefore, the definition of this configuration is made to continue with previous researches. Besides this configuration, the sufficient expanded space provided enough space for the formation of other configurations, for instance, a paraffin-like configuration but with twisted alkyl chain. In general, the pseudo-trilayer configuration is the dominant configuration in such case and is directly responsible for the pillaring of the Mt layer. The peaks at higher angle in $(C_{18}Im)_2$Xy-Mt and $(C_{20}Im)_2$Xy-Mt are ascribed as lateral monolayer configuration. As is shown in Fig. 1, one layer of $(C_xIm)_2$Xy-Mt lie in parallel with Mt layers. The only configuration in $(C_{16}Im)_2$Xy-Mt was determined as pseudo-trilayer configuration as described in $(C_{18}Im)_2$Xy-Mt and $(C_{20}Im)_2$Xy-Mt nanocomposites. however, the only configuration in the $(C_xIm)_2$Xy-Mt nanocomposites with shorter chain length are ascribed as lateral bilayer pillaring configuration (Fig. 1). Same as pseudo-trilayer pillaring configuration, the sufficient interlayer spaces due to the pillaring of this lateral bilayer configuration supported adequate possibility for the formation of other configurations but this lateral bilayer configuration is the predominant configuration.

3.2 Adsorption kinetics and isotherms

The adsorption kinetics of perchlorate onto $(C_xIm)_2$Xy-Mt nanocomposites could approximately reach to the equilibrium within 2 hours. Adsorption data was tried to fit to pseudo-second-order model and pseudo-first-order models. The equations are described as follows:

Pseudo-second-order: $dQ_t/dt = k_1(Q_e - Q_t)$ (2)

Pseudo-first-order: $dQ_t/dt = k_2(Q_e - Q_t)^2$ (3)

Where Q_e (mmol/g) is the adsorbed perchlorate at equilibrium and Q_t (mmol/g) is the adsorbed perchlorate at time t (min). The parameters k_1 (min^{-1}) and k_2 ($g \cdot mmol^{-1} \cdot min^{-1}$) are the rate constant of pseudo-first-order model and pseudo-second-order model. The initial sorption rate h ($mmol.g^{-1}.min^{-1}$) of pseudo-second-order model could be calculated by the equation: $h = k_2 Q_e^2$. The correlation coefficient for the pseudo-second-order models are larger than 0.99, in comparison, the correlation coefficient for the pseudo-first-order models are relatively lower. Pseudo-second-order model can correctly predict the kinetics. This model can be applied to reaction with limited reaction sites which is in good agreement with the assumed ion-exchange mechanism.

Adsorption data of perchlorate on the $(C_xIm)_2$Xy-Mt nanocomposites were fit to Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models were used:

Langmuir: $Q_e = Q_m b C_e / (1 + bC_e)$ (5)

Freundlich: $Q_e = K_F {C_e}^{1/n}$ (6)

Where Q_e (mmol/g) is the adsorbed perchlorate at equilibrium and C_e (mmol/L) is the equilibrium concentration of perchlorate (mM). Q_m (mmol/g) is the maximum adsorption capacity, b (L/mmol) is the Langmuir constant relating to adsorption intensity. K_F ((mmol/g) (L/mmol)), is the Freundlich constant and $1/n$ is a dimensionless exponent.

D-R: $Q_e = Q_m e^{-K_{DR}\varepsilon^2}$ (7)

Where K_{DR} (mol^2/J^2) is a DR constant and ε (J/mol) is a Polanyi potential, which is related to C_e by the following equation:

$\varepsilon = RT \ln(1 + 1/C_e)$ (8)

The adsorption data was best fit to Langmuir model. The Langmuir model assumes that the adsorption sites are distributed homogeneously and adsorption takes place at the specific surface. As expected, the ion-exchange of perchlorate with chloride is the dominant mechanism of adsorption. The highest adsorption capacity achieved on $(C_{20}Im)_2$Xy-Mt with the highest loading which was calculated by CHN analysis. The empirical Freundlich equation is applicable to the heterogeneous adsorption with multilayer of adsorbates is generated during adsorption, this model didn't fit the isotherms well. The D-R modeling is also related to the heterogeneous adsorption and is generally applied to distinguish physical adsorption from chemical adsorption by the mean free energy E (kJ/mol) expressed in (Eq. 9)

$E = (2K_{DR})^{-1/2}$ (9)

The E values of the materials are in the range of 8-16 kJ/mol that is correspondent to ion exchange. The value of the correlation coefficient for the D-R model were higher than 0.96, therefore, the mean free energy E could be taken as a reliable coefficient.

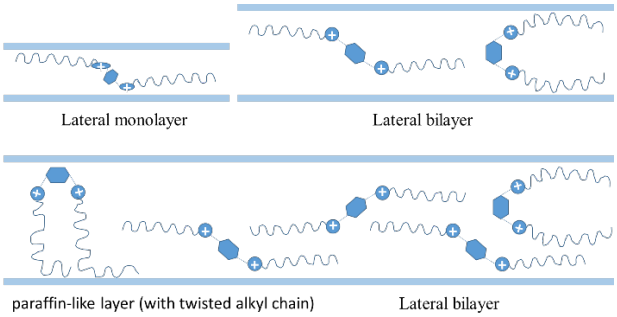

Fig. 1. Illustration of the intercalation modes of $(C_xIm)_2$Xy-Mt.

Table 1. Calculation of surfactant loading

Chain length	H_2O[1] (wt. %)	Adding (mmol/g)	Surfactant loading[2] mmol/g	meq/g
10	2.104	0.726	0.441	0.882
12	2.068	0.695	0.449	0.898
14	3.120	0.663	0.398	0.795
16	2.156	0.644	0.502	1.004
18	2.828	0.618	0.557	1.114
20	2.990	0.596	0.624	1.248

[1] Estimated from TG curves. Weight loss at 150℃.

[2] Estimated by mass balance based on CHN analysis.

4. REFERENCES

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