Preparation of Modified Calcium Bentonite for the Prevention of Heavy Metal Ion Transport in Groundwater

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Vertical engineered barriers are often used to prevent the transport of heavy metal ions in groundwater, and barrier layers are the key to pollution control. In this study, modified calcium-based bentonite (CB) was prepared via the modification of CB with sodium carboxymethyl cellulose (CMC) and sodium hexametaphosphate (SHMP) for the prevention of heavy metal ions transport. CMC-SHMP@CB composites were prepared by pulping, drying and grinding. Structural characterization was performed by using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The swelling, permeability and adsorption properties of the CMC-SHMP@CB composites were further evaluated. The results show that these CMC-SHMP@CB composites have a hybrid microstructure from the intercalation and exfoliation action during modification. The swell index in deionized water of the CMC-SHMP@CB composites is 24.4 mL/2 g, which is 4.8 times that of the original CB index. Modification of CB with CMC and SHMP significantly improves its anti-permeation performance. In the presence of Cd^{2+} and Ni^{2+} ions, the hydraulic conductivity of the CMC-SHMP@CB composites still reaches ~ 3×10^{-11} m/s, which is much lower than the value of untreated CB. The adsorption capacity values of CMC-SHMP@CB for Ni^{2+} and Cd^{2+} were 11.01 mg/g and 13.82 mg/g, which are 5.6 times and 7.2 times the values before modification. CMC-SHMP@CB composites have great potential for use as the barrier layers for the prevention of heavy metal ions transport in groundwater.

1. Introduction

Groundwater heavy metal pollution poses a serious threat to public health, this pollution is becoming an environmental issue of global concern. Vertical engineered barriers are a promising technology for preventing the transport of heavy metal ions in groundwater and bentonite is widely used as the barrier layer, such as geosynthetic clay liner (GCL) (Malusis et al., 2013) and soil-bentonite barrier walls (Katsumi et al., 2018). The barrier capacity is mainly attributed to the low hydraulic conductivity of bentonite (Koistad et al., 2004). However, the hydraulic conductivity generally increases in the presence of the pollutant, and the barrier performance is reduced. To address this issue, modified bentonite has been developed to improve the pollution resistance, including organoclay (Scalia et al., 2014), multi-swellable bentonite (MSB) (Onikata et al., 2009), dense-prehydrated GCL (DPH-GCL) (Mazzieri et al., 2013) and HYPER Clay (Di Emidio, 2010). Among these materials, research on organic modified bentonite is mainly focused on sodium-based bentonite (NaB). Compared with NaB, calcium-based bentonite (CB) has a less negative charge and lower specific surface area, so CB has poor expansion ability and high hydraulic conductivity. However, the known reserve of CB is much higher than that of NaB, so CB is easily available and has a low cost.

Previous studies have demonstrated that sodium hexametaphosphate (SHMP) as a dispersant can reduce the particle size of aggregates (Yang, 2017) and improve the dispersibility of CB (Yang et al., 2018). However, there is no significant increase in the swelling ability for the SHMP-modified CB. As a hydrophilic anionic macromolecule, sodium carboxymethylcellulose (CMC) has been used to improve the swelling ability (Fan et al., 2019) and chemical compatibility of NaB in the presence of K^+ and Ca^{2+} (Van Impe et al., 2015). In this

study, CMC-SHMP@CB composites were prepared via the modification of CB with CMC and SHMP. The structure of CMC-SHMP@CB was characterized by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The swelling ability, hydraulic conductivity and the adsorption of heavy metal ions were evaluated.

2. Materials and Methods

2.1 Materials

Sodium-based bentonite (NaB) was purchased from Real & Lead Chemical (Tianjin). Calcium-based bentonite (CB) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin). Sodium hexametaphosphate (SHMP, AR) and sodium carboxymethyl cellulose (CMC, AR) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin). Hydrochloric acid (HCl, 36 wt.%), sodium hydroxide (NaOH, AR), calcium chloride ($CaCl_2$, 99 wt.%), nickel sulfate ($NiSO_4$, AR) and cadmium sulfate ($CdSO_4$, AR) were purchased from Chemart Chemical Technology Co., Ltd. (Tianjin).

2.2 Preparation of CMC-SHMP@CB composites

First, 800 g of CB was added into 1,600 mL of an aqueous solution containing 16 g of sodium SHMP. The resulting mixture was stirred at 200 rpm for 5 min and then left to stand for 24 h. After oven drying at 105 °C, the sample was ground, screened through a 200 mesh sieve and named SHMP@CB. Subsequently, 100 g of SHMP@CB was added into 1,000 mL of an aqueous solution containing 3 wt.% ~ 12 wt.% CMC based on the dry weight. The resulting mixture was stirred at 200 rpm for 2 h, and then left to stand for 24 h. After drying, the CMC-SHMP@CB composites were ground and screened through a 200 mesh sieve.

2.3 Characterizations

The X-ray diffraction (XRD) patterns for the samples were recorded using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. The scanning range was 0 ~ 14° (2θ), and the scanning speed was 2 °/min. The interlayer distance (d) is calculated by Bragg's law:

$$d=n\lambda/2sin\theta \tag{1}$$

where d (nm) is the crystal layer spacing; n is the diffraction order, which is 1 for the first-order diffraction; λ is the X-ray wavelength of Cu Kα radiation (0.154 nm); and θ (°) is the half-angle of diffraction.

The Fourier transform infrared (FTIR) spectroscopy spectra of the samples were recorded by a Nicolet 6700 Fourier transform infrared spectrometer with a scanning range of 4,000 - 400 cm^{-1}. The sample was prepared by the potassium bromide tablet method.

2.4 Swell index test

Deionized water (DW) was used as a swelling medium to measure the free swelling index according to the JG/T193-2006 standard. Specimens of 2 g of NaB, CB, SHMP@CB or CMC-SHMP@CB (treated with 3 ~ 12 wt.% CMC) were poured into a 100 mL graduated cylinder containing 90 mL of DW. After 2 g of clay was added, the cylinders were filed up to 100 mL with additional DW solution. The mixtures were allowed to equilibrate for 24 h, and the final volumes of swollen bentonite were recorded. To evaluate the swelling performance durability in the presence of salt and heavy metal ions, an aqueous swelling medium containing Ca^{2+}, Ni^{2+} or Cd^{2+} with a concentration of 500 mg/L, instead of DW, was used for measurement of the swell index. It is worth noting that the swelling time for the electrolyte solutions is 168 h.

2.5 Hydraulic conductivity test

The hydraulic conductivity (the osmotic permeability coefficient for water) was measured in a Nanjing Soil Instrument TST-55 modified rigid-wall permeameter according to the JG/T193-2006 and GB/T 50123 - 2019 standards. The sample (Φ 61.8 mm*10 mm) containing 7.26 g of CMC-SHMP@CB with a mass per unit area of 4,000 g/m^2 was prepared. The sample was pre-saturated with water and placed in the container. Permeable stones were used to fill the cavity of the container, and Vaseline was used to seal the gap. The container was then connected with the water head device, and a small amount of edible oil was dripped onto the solution to reduce its evaporation. All the permeation tests were conducted until a steady state was achieved.

2.6 Adsorption of Ni²⁺ and Cd²⁺ ions

In a typical experiment, 0.1 g of CB, SHMP@CB, or 6 wt.% CMC-SHMP@CB was added to an aqueous solution (20 mL, pH 6.0) of Ni^{2+} or Cd^{2+} ions with an initial concentration of 100 mg/L. The resulting mixture was then stirred at 1200 rpm for 12 h. After adsorption, the supernatant was collected by centrifugation at 8,000rpm for 10 min. The contents of Ni^{2+} or Cd^{2+} ions in the supernatant was measured by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer ELAN DRC-E).

3. Results and discussion

3.1 Material characterization

Figure 1a shows the XRD patterns of CB, SHMP@CB and CMC-SHMP@CB. The interlayer distance of CB is 1.52 nm as calculated from formula (1), indicative of a typical nano-layered structure. The positions of the characteristic peaks of SHMP@CB and CMC-SHMP@CB exhibit a shift in the peak position and a broader peak width relative to that of the untreated CB, indicating that the original crystalline structure is disrupted. The FTIR spectra of CB, SHMP@CB and CMC-SHMP@CB are shown in Figure 1b. For CB, the broad bands at 3,610 and 3,450 cm⁻¹ are assigned to O-H stretching vibrations. The strong band at 1,040 cm⁻¹ represents Si-O-Si stretching vibrations of the tetrahedral sheet, while the spectral band at 920 cm⁻¹ reflects the stretching vibration of Al-O-(OH)-Al. In comparison with CB, SHMP@CB and CMC-SHMP@CB have a similar FTIR spectrum. A slight shift from 1,040 cm⁻¹ to 1,042 cm⁻¹ was observed, suggesting that a vibrational transition of Si-O-Si stretching occurred. In addition, the shifts from 920, 523, and 471 cm⁻¹ to 921, 524, and 472 cm⁻¹, reflects the chemical adsorption of phosphate in SHMP by CB (Olu-owolabi et al., 2011). Both the XRD and FTIR results suggested that the layered structure of CB was separated due to the modification of CB with SHMP and CMC; that is, SHMP and CMC were inserted into the layers of CB by destroying its crystal structure. The CMC-SHMP@CB composites exhibit a hybrid microstructure derived from the intercalation and exfoliation action during modification.
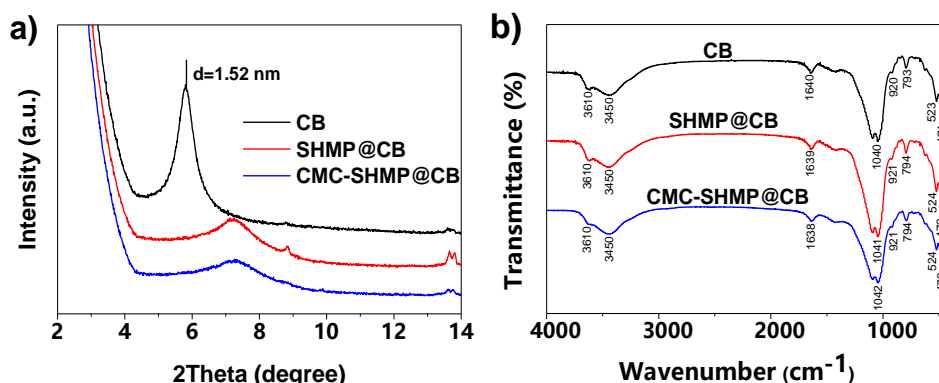

Figure 1: (a) XRD patterns and (b) FTIR spectra of CB, SHMP@CB and CMC-SHMP@CB.

3.2 Evaluation of swelling ability and hydraulic conductivity

The swelling ability of untreated and treated bentonite was quantified by means of the standard swell index test. Swell index values of CB, SHMP@CB and CMC-SHMP@CB in DW and aqueous solutions containing Ca^{2+}, Ni^{2+} or Cd^{2+} ions are given in Figure 2. As shown in Figure 2a, the swell index of CB in DW was 4 mL/2 g, and that of SHMP@CB was 9 mL/2 g. After treating the SHMP@CB with 3 wt.% CMC, an increased swell index to 20 mL/2 g was observed. When increasing the CMC dosage from 3 wt.% to 12 wt.%, the swell index further increased from 20 to 35 mL/2 g, which is 400 % - 775 % higher than that of CB. In particular, the swell index of 6 wt.% CMC-SHMP@CB in DW was 23.5 mL/2 g, which is higher than that of NaB (21 mL/2 g). The results indicate that CMC significantly improves the swelling ability of CB.

The swell index tests were conducted in electrolyte solutions containing Ca^{2+}, Ni^{2+} or Cd^{2+} ions. As shown in Figures 2a-c, when increasing the dosage of CMC from 3 wt.% to 12 wt.%, the swell index increased from 18 to 26 mL/2 g in the presence of Ca^{2+}, Ni^{2+} or Cd^{2+} ions, which is 75 % - 91 % that of the original value obtained in DW. The results indicated that all of these ions can reduce the swelling ability of CMC-SHMP@CB, and that the type of ions has little effect on the change in the swell index. To demonstrate the effect of CMC dosage on

the sensitivity to salt and metal ions, the salt sensitivity results are summarized in Figure 2d. In the presence of Ni^{2+} ions, the salt sensitivity of CMC-SHMP@CB slightly increased from 2.5 mL/2 g to 3 mL/2 g when the CMC dosage increased from 3 wt.% to 6 wt.%. When the CMC dosage further increased to 12 wt.%, the salt sensitivity quickly increased to 9 mL/2 g. The results indicated that an increase in the CMC dosage did not improve the salt sensitivity of the modified bentonite. Similar phenomena were also found in the presence of Ca^{2+} and Cd^{2+} ions. In view of the change in the swell index and salt sensitivity, together with the cost and swelling ability of the composite being comparable with those of NaB, the 6 wt.% CMC was the dosage chosen for further experiments.
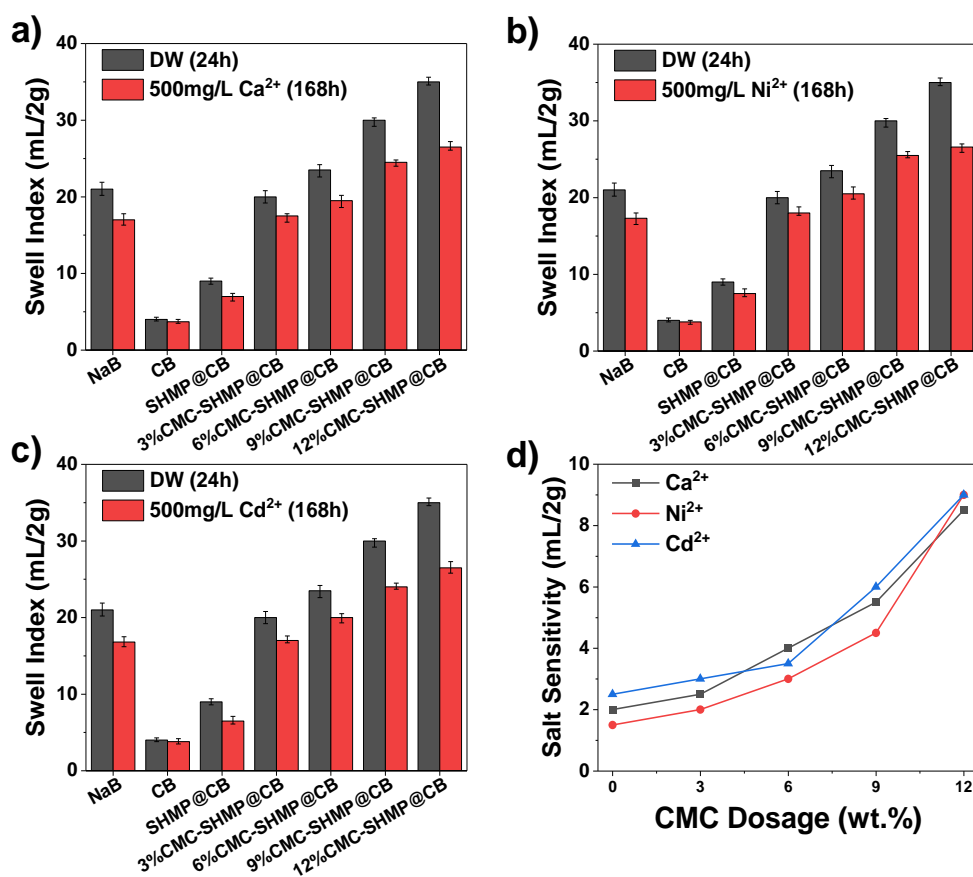

Figure 2: The change in the (a-c) swell index and (d) salt sensitivity in DW and in the presence of ions. The concentrations of Ca^{2+} Ni^{2+} and Cd^{2+} ions are each 500 mg/L.

Figure 3 summarizes the hydraulic conductivity of CB and 6 wt.% CMC-SHMP@CB in DW and an aqueous solution of 500 mg/L Ni^{2+}, 500 mg/L Cd^{2+} or 500 mg/L Ni^{2+} and 500 mg/L Cd^{2+} (denoted as $Ni^{2+}+Cd^{2+}$). As expected, the hydraulic conductivity of CB in the heavy metal ion solutions was higher than that in DW. As shown in Figure 3, the hydraulic conductivity of CB in DW was 1.9×10^{-10} m/s, the hydraulic conductivity in the solution of heavy metal ions increased to 3.6×10^{-10} - 9.1×10^{-10} m/s. This increase is probably attributed to the replacement of Na^+ of the bentonite with the heavy metal ions in the solution and the consequent compression of the double layer thickness. It is worth noting that in the presence of Ni^{2+} and Cd^{2+} ions, the hydraulic conductivity of CB was 9.12×10^{-10} m/s, which is close to the upper limit of the commonly used hydraulic conductivity of 1×10^{-9} m/s. In comparison with CB, 6 wt.% CMC-SHMP@CB has a lower hydraulic conductivity (1.6×10^{-11} - 3.4×10^{-11} m/s) in all of the solutions. In the presence of heavy metal ions, there is a slight increase in the hydraulic conductivity, indicating that 6 wt.% CMC-SHMP@CB exhibits better resistance to heavy metal ions. The reason was that the heavy metal ions preferentially exchange and coordinate with carboxylate groups in the CMC molecular chain (Papageorgiou et al., 2010), reducing the metal exchange volume directly involved in exchangeable cations in CB. The compression of the electronic double layer of bentonite was restrained, and the agglomeration of CB was avoided.
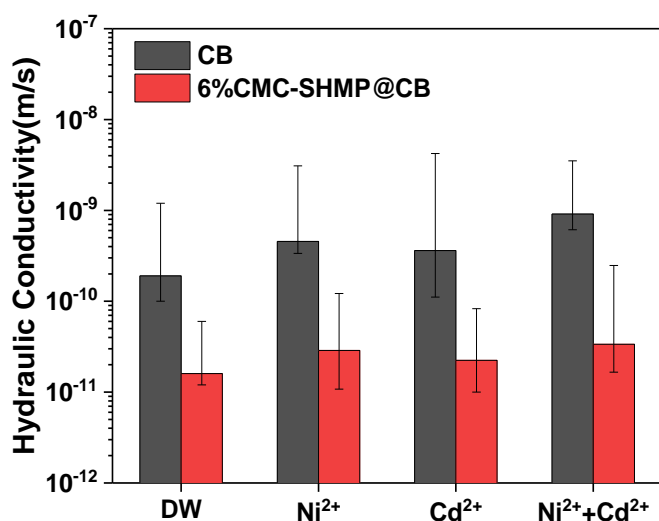
Figure 3: The change in the hydraulic conductivity of CB and 6 wt.% CMC-SHMP@CB

3.3 Evaluation of the adsorption of Ni^{2+} and Cd^{2+} ions

The prevention of heavy metal ion transport in groundwater by a barrier layer depends on the adsorption capacity of the barrier material. Adsorption experiments were carried out using Ni^{2+} and Cd^{2+} as the model. As shown in Figure 4, the adsorption capacity of CB for Ni^{2+} and Cd^{2+} was 1.98 mg/g and 1.92 mg/g. After modification by SHMP, the adsorption capacity of SHMP@CB for Ni^{2+} and Cd^{2+} slightly increased to 2.5 mg/g and 4.03 mg/g. When CMC was introduced into the modification, the adsorption capacity of 6 wt.% CMC-SHMP@CB for Ni^{2+} and Cd^{2+} significantly increased to 11.01 mg/g and 13.82 mg/g, which was 5.6 and 7.2 times that of the values for CB. The increased adsorption of heavy metal ions is mainly attributed to the action of CMC. The adsorption modes of CB are electrostatic adsorption, interlayer cation exchange and hydroxyl coordination. In addition to these three types of interactions, CMC-SHMP@CB exhibits coordination complexation of its carboxylate groups with heavy metal ions to form complexes. The modification of CB with SHMP and CMC made the CB agglomerates smaller and more well-dispersed than those of unmodified CB, leading to an increase in the specific adsorption area.
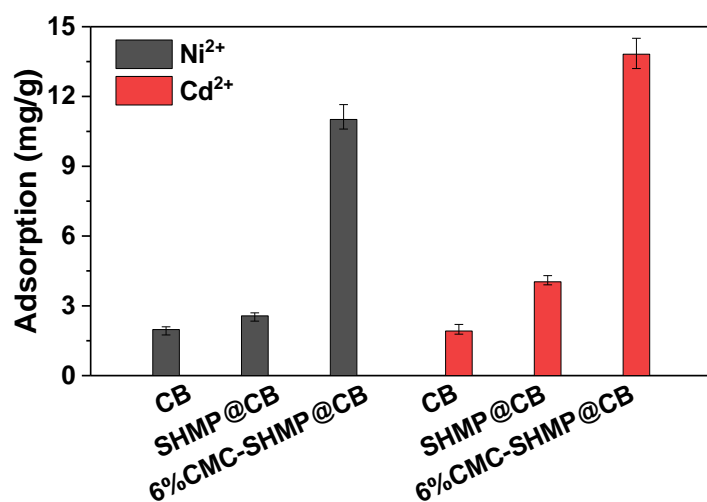

Figure 4: Adsorption capacity of CB, SHMP@CB and 6 wt.% CMC-SHMP@CB for Ni^{2+} and Cd^{2+}

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4. Conclusions

In summary, CMC-SHMP@CB composites were successfully synthesized via the modification of CB with SHMP and CMC. The as-prepared CMC-SHMP@CB composites have a higher swell index (24.4 mL/ 2g *vs* 4 mL/2 g) and better anti-permeation performance (1.6×10^{-11} m/s *vs* 1.9×10^{-10} m/s) than the original CB. The composites exhibited better resistance to heavy metal ions. In the presence of heavy metal ions, there is a slight increase in hydraulic conductivity. The CMC-SHMP@CB composites also exhibit increased adsorption of heavy metal ions from 1.92 - 1.98 mg/g to 11.01 - 13.82 mg/g in comparison with the values for CB. In addition, the cost of CMC-SHMP@CB was calculated as 650 - 730 RMB/t including the cost of raw materials and preparation, while the cost of NaB is generally 1,000 - 1,200 RMB/t. In view of the simple technique and low cost, these CMC-SHMP@CB composites have great potential for use as a barrier layer for the prevention of heavy metal ions transport in groundwater. To overcome the limitation of multistep operation, a facile and one-pot approach is required for the preparation of modified CB in future.

References

Di Emidio G., 2010, Hydraulic and chemico-osmotic performance of polymer treated clays, PhD Thesis, Ghent University, Ghent, Belgium.

Fan R D., Liu S Y., Du Y J., Reddy K.R., Yang Y L., 2019, Chemical compatibility of CMC-treated bentonite under heavy metal contaminants and landfill leachate, In: Zhan L., Chen Y., Bouazza A. (Ed.), Proceedings of the 8th international congress on environmental geotechnics, Vol 2, Springer Singapore, Singapore, 421-429.

Katsumi T., Takai A., Inui T., 2018, Soil–Bentonite cutoff walls for geoenvironmental containment. In: Krishna A., Dey A., Sreedeep S. (Ed.), Geotechnics for Natural and Engineered Sustainable Technologies, Springer Singapore, Singapore, 207-224.

Kolstad D. C., Benson C. H., Edil T. B., 2004, Hydraulic conductivity and swell of nonprehydrated geosynthetic clay liners permeated with multispecies inorganic solutions, Journal of Geotechnical and Geoenvironmental Engineering, 130, 1236-1249.

Malusis M. A., McKeehan M. D., 2013, Chemical compatibility of model soil-bentonite backfill containing multiswellable bentonite, Journal of Geotechnical and Geoenvironmental Engineering, 139, 189-198.

Mazzieri F., Di Emidio G., Fratalocchi E., Di Sante M., Pasqualini E., 2013, Permeation of two GCLs with an acidic metal-rich synthetic leachate, Geotextiles and Geomembranes, 40, 1-11.

Olu-Owolabi B. I., Unuabonah E. I., 2011, Adsorption of Zn^{2+} and Cu^{2+} onto sulphate and phosphate-modified bentonite, Applied Clay Science, 51, 170-173.

Onikata M., Kondo M., Hayashi N., Yamanaka S., 2009, Complex formation of cation-exchanged montmorillonites with propylene carbonate: osmotic swelling in aqueous electrolyte solutions, Clays and Clay Minerals, 47, 672-677.

Papageorgiou S. K., Kouvelos E. P., Favvas E. P., Sapalidis A. A., Romanos G. E., Katsaros F. K., 2010, Metal–carboxylate interactions in metal–alginate complexes studied with FTIR spectroscopy, Carbohydrate Research, 345, 469-473.

Scalia J., Benson C. H., Bohnhoff G. L., Edil T. B., Shackelford C. D., 2014, Long-term hydraulic conductivity of a bentonite-polymer composite permeated with aggressive inorganic solutions, Journal of Geotechnical and Geoenvironmental Engineering, 140, 4013025.

Van Impe W., Di Emidio G., Verastegui-Flores R. D., Mazzieri F., Bezuijen A., 2015, Polymer-treated bentonite clay for chemical-resistant geosynthetic clay liners, Geosynthetics International, 22, 125-137.

Yang Y. L., 2017, Contaminnntant conatainment performances of soil-phosphate amended calcium bentonite vertical cutoff walls, PhD Thesis, Southest University, Nanjing, China.

Yang Y.L, Reddy K. R., Du Y J., Fan R D., 2018, Sodium hexametaphosphate (SHMP)-amended calcium bentonite for slurry trench cutoff walls: workability and microstructure characteristics, Canadian Geotechnical Journal, 55, 528-537.