Comparative assessment of modified bentonites as retardation barrier: adsorption performance and characterization

Dongdong Guo1,2 · Yong Wan1,2 · Jiangshan Li1,2,3 · Ruiqi Liu4 · Lei Liu1,2,3 · Qiang Xue1,2,3

Abstract
Modified bentonites for the anti-seepage system have been attracting global attention. At the same time, the performances of modified bentonite containing retardation barrier exposed to organic–heavy metal pollutants have not been fully reported. In this study, the adsorption performances (one of the key evaluation indicators of retardation barrier) of nine kinds of commonly used modified bentonites on multiple contaminants were comparatively investigated. The x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analyses were also performed to unravel the adsorption mechanisms. Results show that the adsorption of modified bentonites on phenol and Pb(II) follows the order of SB-16 > PVA > CTAB > APAM > CTAB + PAC > PAC > CPAM > CTAB + CPAM + PAC + APAM. Among all the samples, the bentonite modified with SB-16 showed the highest adsorption capacities for phenol and Pb(II). The surfactant molecules inserted in the interlayer space of montmorillonite increase the substrate spacing, which changes the structural properties of the bentonite from hydrophilic to hydrophobic and increases the adsorption of organic contaminants. On the other hand, the polymer has functional groups such as hydroxyl and carboxyl that can form a spatial three-dimensional cross-linking structure on the bentonite surface, providing more adsorption sites for heavy metal ions. These findings indicate the potential industrial applications of modified bentonite in a contaminant barrier system.

Keywords Bentonite · Modification · Heavy metal · Organic contaminant · Adsorption

Introduction
Urban industrial contaminated sites are characterized by complex contamination components, serious pollution degrees, and considerable impact depth, which seriously impact groundwater structure, ecological environment, and human health. This problem has also seriously hindered the national planning of new urbanization and the safe development of underground space (Abuabdou et al. 2020; Xue et al. 2020). Nevertheless, the leaching of organic compounds and heavy metals from the contaminated sites leads to the spread of contaminants to the adjacent soil and groundwater due to the process of erosion, dissolution, or others. The pollution plume from contaminated sites not only causes serious environmental problems but also threatens human health (Sparks 2003). Typical contaminants present in the adjacent soil or water of urban industrial contaminated sites include organic solutes such as phenol and benzene, and heavy metals such as lead, zinc, and cadmium, all of which are contaminants that need to be addressed and treated urgently (Sonne et al. 2018; Ying et al. 2017).

In order to control the risk of urban industrial contaminated sites, bentonite-based impermeable materials (e.g., geotechnical composite liner (GCL), soil-bentonite (SB) barrier, and compacted sand–bentonite mixture) are widely used in groundwater seepage and landfill barrier systems due to the high swelling capacity and very low permeability (Sharma and Reddy 2004; Sposito 1989; Sun et al. 2021; Scalia IV 2018; Rowe 2005). However, researchers have shown that the leaching of pollutants from contaminated
sites can cause structural failure of bentonite-based barrier structures (Xu et al., 2019; Touzefoltz et al., 2006; Vadlamudi and Mishra, 2018; Gupta et al., 2020; Zhang and Burns, 2010). Changes in engineering properties due to structural failure of bentonite impermeable materials can be attributed to: (1) contract of the diffusion double layer of bentonite particles due to increased ionic strength in the pore water (Benson and Meer, 2009; Wan et al., 2020) and (2) exhibit limited intrinsic adsorption capacity for organic solutes due to lacking an appreciable amount of soil organic carbon (Goodarzi et al., 2016; Malusis et al., 2010; Mendes et al., 2013). Therefore, the modification of bentonite to improve its chemical compatibility and service performance in complex environments is the focus of the current study.

The current study on modified bentonite in the geotechnical field mainly focuses on permeability and swelling (Keramatikerman et al., 2017; Xu et al., 2016; Xu et al., 2019). For the application of impermeability of contaminated sites, the hindrance of contaminants is also an important index to be examined. The retardation factor is proportional to the adsorption constant, so it is necessary to study the adsorption effect of modified bentonite on contaminants. The retardation factor can be estimated from the distribution coefficient $K_d$ (Freeze and Cherry, 1979). Hence, the adsorption constants obtained from the adsorption experiments conducted in this paper can indirectly show the barrier performance of bentonite against contaminants.

$$R = 1 + \frac{\rho_b}{n} \cdot K_d$$  \hspace{1cm} (1)

where $\rho_b$ = porous media bulk density (g/cm³) and $n$ = effective porosity of the media at saturation (%).

In the last decade, many modified bentonites have been developed, focusing on improving the adsorption capacity or reducing the permeability of heavy metal contaminants (de Paiva et al., 2008; Stumm and Morgan, 1996). The traditional organic modifier in the geoenvironmental field is the quaternary ammonium cation (QAC), which is also the most widely used organic cation. Usually, organic cations can be inserted into the interlayer space of montmorillonite through cation exchange reactions (Slade and Gates, 2004; Zhu et al., 2019). The interacting cations are then bound to the surface of montmorillonite mainly through electrostatic interactions (Xi et al., 2005; Israelachvili, 2011). Through hydrophobic interactions between the embedded surfactant cations and the alkyl chains of the external surfactant molecules, other surfactant molecules can be co-adsorbed into the interlayer space of montmorillonite. It was shown that modified bentonite could effectively remove hydrophobic organic contaminants from water, but its permeability coefficient in inorganic solutions increased (Sun et al., 2013; Soule and Burns, 2001). Hence, some scholars have improved the modification of bentonite by adding hydrophilic polymers to form a three-dimensional cross-linking structure among the bentonite particles to enhance the adsorption of heavy metal ions (Fan et al., 2020; Chen et al., 2020). Although organically modified bentonite is attracting more and more attention in various fields, adsorption properties and applicable engineering conditions of the synthetically modified bentonite in the previous literature are difficult to be compared due to the various raw materials. At present, the adsorption performances of modified bentonites prepared by different modification methods have not been compared and evaluated.

In summary, amounts of exciting research on the modification of bentonite have been investigated in the past decades, but there are still many problems that deserve further exploration. First, most studies are limited to a single type of contaminant, and there is lacking experimental research on multiple contaminants that are closer to actual engineering conditions. In addition, the current investigations do not have an evaluation of the performance of different types of modified bentonites and hence cannot provide valuable recommendations for the selection of engineering applications. Finally, the microscopic mechanism of removing contaminants by various types of composite-modified bentonite has not been extensively compared and explored.

Therefore, this paper mainly investigated the effects of multiple contaminants on the adsorption performance of different kinds of modified bentonites and explained in relation to the physicochemical characterization. Also, batch adsorption experiments and physicochemical property tests were conducted to reveal the interaction mechanism between heavy metal, organic compound, bentonite, and polymer. Calcium-based bentonite exhibits a lower swelling index than sodium-based bentonites, so they are rarely directly used in engineering. Given the extensive storage of calcium-based bentonite in the world, its modification and application prospects are promising. The results of this study can be used to optimize the doping of organic modifiers to optimize the engineering properties of calcium bentonite and provide a theoretical basis for the broad application of this high-performance modified bentonite in engineering and contaminant control.

**Materials and methods**

**Materials**

The raw calcium bentonite (Ca-B) was obtained from Shandong Province, China, with an estimated cation exchange capacity (CEC) of 64 mmol/100 g. It contains 62.68% montmorillonite, 32.65% anorthite, 2.16% quartz, and 2.51% calcite, calculated using a semiquantitative method on x-ray
diffraction (XRD) analysis. The index properties of Ca-B measured via ASTM standards are summarized in Table 1.

Phenol is an aromatic hydrocarbon and more hydrophilic than many common volatile organic compounds (VOC) pollutants. Phenol has higher solubility than benzene, toluene, and trichloroethene due to its functional –OH group, so phenol may have a more pollution source and harm in the soil–groundwater system than these hydrophobic pollutants. Phenol also has low octanol–water partition coefficient, so it is a more conservative alternative to most VOC pollutants tested (LaGrega et al. 2010; Malusis et al. 2010). Therefore, phenol may be considered a conservative surrogate compound in examining the adsorption performance of modified bentonite on organic contaminants (Malusis et al. 2010; Ocampo-Perez et al. 2011). Also, Pb(II) was selected as the representative heavy metal contaminant due to the toxicity and common occurrence in contaminated groundwater at industrial contaminated sites in China (Pal et al. 2014; Wang et al. 2018; Yang et al. 2019). Analytically pure phenol and Pb(NO_3)_2 used in tests were obtained from Aldrich Chemical Co.

All modifying reagents were analytical grade and used without further purification. The 3-(N,N-dimethylpalmitylammonio) propane sulfonate (SB-16) was purchased from Nanjing Robiot Co. Ltd. Cetyltrimethylammonium bromide (CTAB), polyanionic cellulose (PAC), polyvinyl alcohol (PVA), cationic polyacrylamides (CPAM), and anionic polyacrylamide (APAM) were of analytical purity, which were purchased from Aladdin Chemistry Co. Ltd. (Aladdin Chemistry Co. Ltd., Shanghai, China). Deionized water with a resistivity of 18.1 MΩ•cm was used for all experiments.

**Methods**

**Synthesis of modified bentonites**

Modified bentonites were prepared through the following steps: (1) A quantitative amount of the modifier was first added to 100 mL of deionized water at a temperature of 70 °C and stirred until completely dispersed and dissolved; (2) 10 g of bentonite was mixed in 100 mL of solution, and the mixture was shaken in a constant temperature mechanical shaker (180 r/min) for 24 h at 70 °C; and (3) the prepared organic bentonite was separated from the solid by centrifugation at 4000 r/min, washed several times with deionized water until no residue was detected, placed in an ultra-low-temperature refrigerator for freeze-drying to reach a constant weight (24 h), crushed, and passed through a No. 200-mesh sieve (75 μm). The specific modification methods, as well as the symbolic representation, are given in Table 2 (He and Zhu 2016; Zhu and Zhu 2008; Du et al. 2021; Norris et al. 2018; Yang et al. 2021; Zhu et al. 2011; Sanchez et al. 2019). It is worth noting that the composite-modified samples must be operated separately to obtain a significant change in the interlayer structure. The bentonite was modified by intercalation with organic cations and then re-modified with polymer.

The modification conditions can significantly affect the adsorption capacities of the modified bentonite toward contaminants (Parolo et al. 2014). First, when using surfactants for modification, the surface of the bentonite must be washed with deionized water. By measuring the adsorption of phenol and Pb(II) separately, the adsorption capacity of modified bentonite on heavy metal ions of the composite contaminants will significantly reduce without this step. Therefore, considering the combined effect of heavy metal–organic contaminant co-removal, the modified bentonite needs to be cleaned with deionized water during the preparation process to ensure that the hydroxyl groups (—OH) on the bentonite surface are not wrapped or covered by surfactants. Second, compound modifications, such as CTAB and CPAM, cannot be added together to the bentonite suspension. Therefore, surfactant intercalation followed by polymer addition must be used to achieve adsorption of the composite contaminants. The purpose is to prevent the modifiers from reacting with each other instead of binding in the raw bentonite structure. Third, the polymer must be heated and dissolved in water before adding the bentonite. Otherwise, it is difficult to form a uniformly dispersed modified environment.

**Batch adsorption experiments**

The stock phenol and Pb(II) solution (1000 mg/L) was prepared by dissolving analytical grade phenol and Pb(NO_3)_2 in deionized water; the desired concentration of Pb(II) solutions were obtained by diluting the stock solution. All adsorption experiments were performed by mixing a specific amount of modified bentonite with 80 mL Pb(II)/phenol-containing solution in a 100 mL polyethylene tube and then shaking at 180 rpm in a thermostatic shaker (SHA-B300).

The testing procedure for the batch sorption experiments followed the Chinese national standard GB/T 21851–2008 (SAC 2008) and the specific admixtures described in Table 2. The solid to liquid ratio was set at 1:100 (g/mL) to ensure that the adsorption capacity of the tested bentonite was between 20 and 85% (Jin et al. 2016; Lee et al. 2002; Wang et al. 2010). Three parallel samples of each type of bentonite were tested to eliminate errors. 0.8 g samples were first suspended in 80 mL Pb (II) and phenol-containing solutions (concentrations were 100, 200, 500, 800, and 1000 mg/L) in the centrifuge tubes. These tubes sealed with parafilm were shaken in a thermostatic shaker.
Table 1 Chemical compositions and index properties of Ca-B used

| Chemical compositions | Percentage (%) |
|-----------------------|----------------|
| SiO₂                  | 63.35          |
| Al₂O₃                 | 63.35          |
| CaO                   | 5.44           |
| MgO                   | 4.38           |
| Fe₂O₃                 | 7.50           |
| K₂O                   | 0.974          |
| Na₂O                  | 1.15           |
| TiO₂                  | 0.910          |
| P₂O₅                  | 0.184          |

| Property                | Value | Method       |
|-------------------------|-------|--------------|
| Swell index (ml/2 g)    | 7     | (ASTM, 2006) |
| pH                      | 8.39  | (ASTM, 2015) |
| Specific gravity, Gₛ    | 2.74  | (ASTM, 2010) |
| CEC (meq/100 g)         | 64    | (ASTM, 2010c) |
| Liquid limit, Wₐ (%)    | 112   | (ASTM, 2010b) |
| Plastic limit, Wₚ (%)   | 38    |              |

Characterization of modified bentonites

Analyses of the mineralogical compositions of the untreated bentonite and the synthesized modified bentonite samples were performed in an X-ray diffractometer Ultima IV (Rigaku, Tokyo, Japan) using Cu Kα radiation (λ = 1.5406 Å) generated at 40 kV and 40 mA, a scan range of 0.5°—10° 2θ, and a scan speed of 1° 2θ/min (Burnett 1995).

FTIR spectra in the range of 400–4000 cm⁻¹ of selected solid samples were determined by the Nicolet 6700 FTIR spectrometer (Thermo Scientific).

Brunauer, Emmett, and Teller (BET) surface areas of selected solid samples were measured by nitrogen adsorption at 77 K with an Asap 2460, Micromeritics Surface Area and Pore Size Analyzer. Prior to N₂ adsorption, the samples were degassed in a vacuum at 300 °C for 12 h. The specific surface area was determined by the ethylene glycol mono-methyl ether (EGME) method in the laboratory compared with the BET method.

Other physical and chemical tests were performed on the samples as follows. Total organic carbon (TOC) content of bentonites was measured using a Vario TOC analyzer (Elementer, Germany). The organic carbon content here consists of two components, in addition to the organic carbon inherent in the soil, and the organic carbon carried by the introduced modifiers, which can be used to calculate the contents of loaded surfactants (Ma et al. 2014). The SSA and pore volumes were tested using the Brunauer, Emmett, and Teller (BET) method, with the ASAP 2460 analyzer (Micromeritics, USA). Bentonite–water mixtures were also used to determine the zeta potentials using a Nano NS-90 Zetasizer (Malvern, UK).

Results and analyses

Characterization of modified bentonites

Optimization of modification conditions

The adsorption capacities of phenol and Pb(II) by different kinds of modified bentonites dosing and modification methods were compared. As shown in Fig. 1, it is easy to find that the adsorption capacity of modified bentonite on phenol can be easily improved by surfactant intercalation. No competitive adsorption between the composite contaminants was observed due to different adsorption mechanisms and no interfering effect between them.

The adsorption capacity of modified bentonite is greatly affected by the accumulation density of modifiers such as surfactants in the layer spacing. Research showed that more than 250% CEC would lead to a too dense accumulation of interlayer modifiers due to spatial
site resistance, resulting in a reduced adsorption effect (He et al. 2014). Furthermore, 100% CEC-modified bentonite is supposed to have a better adsorption performance, so this parameter was chosen for intercalation modifier in this study to evaluate different types of modified bentonite.

**X-ray diffraction (XRD)**

Figure 2 shows the small-angle XRD patterns of the untreated Ca-B and different types of modified bentonite specimens. From Fig. 2(a), it can be found that after the addition of organic cations, the characteristic peak centered at 5–7° of Ca-B shifts along a lower diffraction angle. According to the Bragg equation, the phenomenon that the layer spacing of montmorillonite gradually increases indicates that the modifier is effectively added into the interlayer of montmorillonite. It can be observed that the basal spacing of organic cation-intercalated bentonite is higher than Ca-B from Fig. 2(a), indicating that the organic cation has been effectively intercalated into the interlayer space of montmorillonite. An asymmetric first-order reflection for concentrations higher than 60% CEC–CTAB was observed, suggesting a random interstratification of surfactant molecule in the interlayer space. It should be clear that a particular concentration is required for the ion exchange reflection to occur, and it can be found that a significant exchange occurs after 60% CEC–CTAB, leading to a change in the interlayer, which is consistent with the findings in the literature (Zhu et al. 2011).

**Table 2** Modification methods for bentonites used in this study

| Samples   | Parameters | Dosage | References                  |
|-----------|------------|--------|-----------------------------|
| Modifier  | CTAB       | 100% CEC | (He and Zhu 2016; Zhu and Zhu 2008) |
| 1C        | CTAB       | 100% CEC | (Zhu et al. 2010)           |
| 1C4P      | CTAB       | 100% CEC |                             |
| 1C4CP     | CTAB       | 100% CEC |                             |
| 1C4CP4AP  | CTAB       | 100% CEC |                             |
| 4PAC      | PAC        | 4% Wt   | (Du et al. 2021; Norris et al. 2018) |
| 4CP       | CPAM       | 4% Wt   |                             |
| 4AP       | APAM       | 4% Wt   |                             |
| SB-16     | SB-16      | 100% CEC | (Yang et al. 2021; Zhu et al. 2011) |
| 2PVA      | PVA        | 2% Wt   |                             |

**Fig. 1** Comparison of adsorption performances of raw bentonite and different kinds of modified bentonites on composite and single contaminants: a phenol, b Pb(II)
and Zhu 2008; Zhu et al. 2010). Figure 2(b) shows the polymer-modified and the original bentonite layer spacing keeps the same \(d_{001}\), about 1.824 nm, which indicates that there is no intercalation behavior of organic polymer into the layer spacing of bentonite.

Combined with previous literature analyses (Chen et al. 2020; Kuo Tian et al. 2019), this type of hydrophilic polymer can only be combined on the external surface of the bentonite by physical interaction, thus resulting in modified bentonite with functional groups on the surface. What need to clarify is the classification of external and internal surface. External surface refers to the external surface and edge of clay particles, while internal surfaces mean the interlayer space of swelling clay minerals. The hydroxyl and the carboxyl groups of the polymer can be combined with each other in water into hydrogen bonds, forming a three-dimensional cross-linking structure. Figure 2(c) shows that the composite-modified bentonite still retains the intercalation behavior of the organic molecules. Therefore, the structure of the composite modified bentonite is also a comprehensive reflection of the two kinds of modifiers as observed by XRD, which will be further elucidated in the later sections.

Interestingly, through the detection of small-angle XRD, a slight fluctuation can be found in the 2\(^{\circ}\) diffraction angle position, but no one explained clearly; the peak here might be the internal microscopic pore structure of the sample, maybe in the grinding or testing process of the sample in contact with air to form an aerogel with pore structure aerogel (Ishii et al. 2013). It is initially speculated that it is caused by the artificial sample-making process, which does not affect the analysis of the mineral structure of montmorillonite, so the effect of the results of this study is not significant and can be ignored.

From Fig. 2(d), the effect of modifiers (on bentonite) is very distinguishable. These modifiers can be mainly divided into two kinds, organic cations and combined with a polymer. Among them, the organic cation involved in the modified bentonite samples will occur in intercalation and is not affected by the polymer. The addition of 100% CEC is the best according to the previous findings, as shown above. The organic modified samples with > 100% CEC will form a larger stacking density and decrease the adsorption capacity due to the spatial site resistance. In this study, 100% CEC was used as the best addition to focus on the role of modifier category, in which SB-16 has the best intercalation effect on bentonite; also it was an environmentally friendly, green, and non-hazardous biomass duality surfactant, and CTAB was the second. The other polymer modifiers maintained the same layer spacing with the untreated bentonite, and no intercalation behavior was observed, which indicated that polymer modification might occur only on the bentonite surface (Zhou et al. 2019).

### Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) analysis can also illustrate the internal structural changes of bentonite before and after modification (Yang et al. 2021; Yu et al. 2019; Zhu et al. 2005). Figure 3 shows the FTIR spectra of the untreated bentonite as well as various modified bentonites. There are six main characteristic peaks of bentonite, as listed below. In the spectral range below 600 cm\(^{-1}\), these bands are attributed to the structural octahedral and tetrahedral absorption bands in the montmorillonite lattice. The peak at 466 cm\(^{-1}\) can be assigned to the Si–O–Al bending vibration characteristic peak, and the peak at 519 cm\(^{-1}\) can be assigned to the Si–O–Mg bending vibration characteristic peak. Also, the peak at 1036 cm\(^{-1}\) can be designated as the Si–O–Si stretching vibration characteristic peak. The stronger absorption peak at 3623 cm\(^{-1}\) is attributed to the broad, and the strong absorption peak at 3431 cm\(^{-1}\) is attributed to the stretching vibration characteristic absorption peak of –OH on the carboxyl groups of adsorbed water or polymers located between bentonite layers. If the absorption peak is sharp, it indicates that the –OH group in water is not connected; otherwise, the –OH group in water has been linked. The weaker absorption peak at 1637 cm\(^{-1}\) is the bending vibration characteristic absorption peak of interlayer adsorbed water hydroxyl –OH, if the characteristic absorption peak at this place is stronger, it indicates that the interlayer of bentonite contains more interlayer adsorbed water.

The FTIR characteristic peaks of natural bentonite, which did not change significantly after modification, indicate that the mineral skeleton of bentonite was not changed after modification.

Compared with the FTIR spectra of natural bentonite, it can be found that the modified bentonite shows three new characteristic peaks located at nearly 1474 cm\(^{-1}\), 2853 cm\(^{-1}\), and 2926 cm\(^{-1}\), respectively. The peaks located at 1474 cm\(^{-1}\) can be attributed to the shear vibration characteristic absorption peak of –CH\(_3\) in the organic modifier molecules. Those located near 2853 cm\(^{-1}\) and 2926 cm\(^{-1}\) can be attributed to the symmetric and antisymmetric stretching vibration characteristic peaks of sub-methyl H–C–H in the –CH\(_3\) group on the organic modifier molecule, and their presence indicates that CTAB or SB-16 was introduced into the layer space of the bentonite. With the introduction of organic cations into the interlayer, the stretching and bending vibrational characteristic absorption peaks of the interlayer adsorbed water hydroxyl –OH located at 3431 cm\(^{-1}\) and 1637 cm\(^{-1}\) are weakened to different degrees, indicating that the interlayer adsorbed water is greatly reduced while the hydrophobicity of the surface is significantly enhanced. The characteristic absorption peak of structural water in the lattice located at 3623 cm\(^{-1}\) is also very different. For the modified bentonite...
sample with organic cation intercalation, the absorption peak here disappears, indicating that a large amount of interlayer adsorbed water is exchanged and removed from the bentonite due to the intercalation of organic modifiers. However, the polymer-modified samples still retain this peak, and the peak position is close to the untreated bentonite, indicating that the interlayer hydrophilicity is not affected. Combined with the XRD analyses of polymer-modified bentonite, it shows that the polymer introduced has no intercalation behavior.

Other physicochemical characteristics

Specific surface area (SSA) represents the degree of contact between the active sites of the modified clay and the contaminant, i.e., the space where the contaminant is adsorbed. The surface area is divided into the internal surface area and external surface area, where the BET method commonly used can only measure the external surface area for expansive clays, since the contraction between the layers occurs at low-temperature desorption, resulting in the inaccessibility of nitrogen molecules. In this case, it is necessary to measure the accurate specific surface area by the EGME method. It is not difficult to find from Fig. 4 that all modified samples involving organic cation intercalation have a reduced SSA, indicating that the CTAB or SB-16 molecule is mainly introduced in the mesopore space (Parolo et al. 2014). As proposed by Park et al. (2011), when the introduced molecules are densely intercalated in the structure of the bentonite, in both the interlayer spaces and interparticle pores, it results in a reduction in the specific surface area and pore volume of the tested bentonite samples. As a result, after the bentonite sample is intercalated, the interlayer space is almost completely enclosed, which leads to the entry of nitrogen and ethylene glycol monomethyl ether being blocked by organic molecules at the edges of individual platelets.

As shown in Fig. 5, the layer spacing and the total organic carbon content (organic carbon existed in soil and organic carbon introduced by the addition of modifier) have a high linear correlation, and the results are also consistent with the adsorption constants of modified bentonite for organic contaminants such as phenol, indicating that the adsorption capacity of modified bentonite for organic contaminants is related to the intercalation and the total organic carbon content. Total organic carbon is often associated with a high volume of aliphatic carbon as a partitioning medium. Therefore, the sorbent–water distribution coefficient $K_d$, which is the slope of the linear sorption isotherm, is inherently related to organic carbon, which is consistent with the conclusions in the literature (Zhao et al. 2017).

As shown in Fig. 6, the zeta potential ($\xi$) of the clay surface is widely used to measure the stability of clay dispersions, as well as to characterize the adsorption mechanism at the solid–liquid interface. It is not difficult to find that the zeta potential has a similar trend to the adsorption constant $K_F$, and the specific reasons and mechanism need further exploration (Zadaka et al. 2010).
Comparison of the adsorption effect on Pb(II) and phenol

To explore the adsorption of modified bentonite on composite contaminants in batch adsorption experiments, the composite contaminants were discussed separately. The intercalation effect of surfactants on the bentonite reduced the adsorption capacity of the untreated bentonite for heavy metal ions due to the occupation of a portion of the internal surface area. Figure 7 and Table 3 show the adsorption isotherms of Pb(II) onto the bentonites. Natural bentonite is very remarkable for removing heavy metal ions, such as Pb(II), through ion exchange reactions, because multivalent ions are effective competitors for the clay exchange sites occupied by monovalent ions. Meanwhile, cations with smaller hydration radii for the same valent ions have a stronger hydration ability to enter the interlayer of the clay mineral (Jo et al. 2001; Kolstad et al. 2004). The adsorption of Pb(II), however, gradually decreased as the mass of surfactant adsorbed by the bentonite increased, as shown in Fig. 7. The reason for this is that the molecular weight of organic molecules is much larger than inorganic metal ions, and so the Coulomb force generated is greater. Therefore, the organic molecules are more easily attracted to the interlayer of bentonite than inorganic ions, thus replacing the original inorganic metal ions, such as calcium and small amounts of sodium. In this way, the interlayer domains of bentonite are hydrophobic in nature and thus cannot be replaced by inorganic ions nor do they provide adsorption sites where inorganic metal ions can be adsorbed.

The adsorption of Pb(II) by modified bentonite was fitted using two nonlinear models, Langmuir and Freundlich, respectively, as given in Table 3, and it was found that the Freundlich model had a better fitting with the experimental data. From Fig. 8, PVA, 1.0 CTAB, and SB-16 are the three modified bentonites with relatively outstanding performance. The other modified bentonite samples with added polymers have a worse adsorption effect than the untreated bentonite. It seems that the hydrophilic polymers may easily lead to flocculation due to a large number of hydrogen bonds, which makes the effective surface area for contaminant adsorption decreases. The higher absolute value of the zeta potential indicates that the colloidal system is more dispersed, and the lower value means that the flocculation effect is greater. In addition, the surfactant of the intercalation layer must be cleaned with deionized water to retain the better adsorption of heavy metal ions by the bentonite itself, presumably due to a large number of functional groups on the surface of the bentonite, such as hydroxyl and carboxyl groups, which can be confirmed by FTIR, indicating that the adsorption of heavy metal ions is mainly contributed by the edges and external surface of the bentonite lamellae.

The adsorption results for phenol satisfy the Henry linear adsorption model, and the results are shown in Fig. 7 and Table 4. The linear adsorption isotherm curve indicates that the adsorption mechanism is mainly based on the hydrophobic partitioning of alkyl chains. The data circled in the figure show that the bentonite samples modified with different polymers have no adsorption effect on phenol in the full concentration range. The only way to adsorb phenol is organic molecular intercalation (like surfactant) intercalation, in which the adsorption effect of the samples modified with 1.0 CTAB first is basically the same, and the adsorption effect of the zwitterionic surfactant, SB-16, on phenol is much better than the other modified bentonite samples. Thereby, the organic carbon content normalized by adsorption coefficient ($K_{oc} = K_d f_{oc}$) has been suggested to be a more proper parameter for evaluating the adsorption efficiency of surfactant-modified adsorbents (Zhu et al. 2007; Bartelt-Hunt et al. 2003; Ma et al. 2016). The calculated $K_{oc}$ value of SB-16 was higher than that of others (Table 4). The results of $K_{oc}$ indicates that the adsorption capacity of SB-16 toward phenol is greatest, which was consistent with the calculated adsorption constants. The results also imply that the organic phase formed by SB-16 had better affinity toward phenol than other modified bentonite using surfactant in the interlayer space. The above experimental data indicate
that the adsorption of modified bentonite on the organic molecule can only contribute to the adsorption effect by intercalation of organic cations, and the specific adsorption mechanism is mainly hydrophobic interactions and distribution of organic phases. It is worth mentioning that SB-16 as a new green surfactant should attract greater attention and is
expected to be a complete replacement of monosubstituted surfactants, not only due to its superior adsorption effect but also because of its own adaptation to the environmental requirements of a future life as an environmentally friendly and economical green modifier.

In order to better evaluate the comprehensive performance of different types of modified bentonite, a comprehensive factor, $W$, the adsorption constant of organic contaminants, and heavy metal contaminants by normalization was proposed to establish a comprehensive index to describe the adsorption performance of the modified bentonites quantitatively, and the following mathematical model can be established:

$$W = \frac{x}{x_{\text{max}}} + \frac{y}{y_{\text{max}}}$$  \hspace{1cm} (3)

where $x$ is the $K_d$ of different samples; $x_{\text{max}}$ is the highest $K_d$ among different samples; $y$ is the $K_F$ of different samples; and $y_{\text{max}}$ is the highest $K_F$ among different samples.

From Table 5, the PVA-modified bentonite has the highest adsorption capacity for Pb(II), and the SB-16-modified bentonite has not only the highest adsorption capacity for phenol but also the highest combined adsorption capacity for both contaminants, with a $W$ index of 1.756. The adsorption performance of modified bentonite on both phenol and Pb(II) follows the ranking as SB-16 > PVA > CTAB > APA M > CTAB + PAC > PAC > CPAM > CTAB + CPAM > CTAB + CPA B + CPAM + APAM.

**Discussion**

**Modification mechanism of organic bentonite**

Due to the lattice substitution phenomenon of bentonite, excess negative charge is generated in its lattice. In order to maintain the charge balance of its cells, bentonite adsorbs exchangeable cations such as Na$^+$ and Ca$^{2+}$ into its interlayer domain. When cations with higher hydration capacity are introduced, and the concentration is changed to exceed a certain threshold, the cations in the interlayers of bentonite are easily exchanged by other cations, so some inorganic or organic cations can be introduced into the layer space of bentonite. In this paper, during the reaction process of bentonite modification using surfactants, ion exchange reactions occur between organic cations and the original inorganic cations between bentonite layers, resulting in the layer spacing of bentonite and the organic phase increasing, which has a great impact on the adsorption performance of bentonite.

Generally speaking, the organic modifier enters the interlayer space of bentonite through two stages: ion exchange adsorption and partitioning mechanism. Ion-exchange
adsorption refers to the process of ion exchange between the organic modifier and the exchangeable cations (such as Na\(^+\), Ca\(^{2+}\)) in the interlayer of bentonite. The partitioning mechanism refers to when the original exchangeable cations between the layers of bentonite are replaced by organic cations. The organic cations exchanged into the interlayer of the bentonite form a micro-organic distribution phase, which continues to adsorb organic modifiers through hydrophobic interaction.

The surface functional groups of the bentonite were analyzed by FTIR, combined with XRD to analyze the possible adsorption sites. FTIR analysis was performed on the untreated bentonite and modified bentonite samples. The adsorption amounts measured with the modifiers of different addition ratios were compared with the qualitative analysis of the crystal structure and its functional groups to explore the structural changes of bentonite before and after modification and the interaction between bentonite samples and the modifiers, which was verified by batch adsorption experiments.

In this paper, CTAB–PAC/PAM–composite-modified bentonite was prepared by a stepwise method. First, the cationic surfactant CTAB underwent ionic exchange with the exchangeable cation Ca\(^{2+}\) in the interlayer of calcium-based bentonite. The positively charged end of the surfactant was bound to the interlayer of bentonite to obtain the surfactant single modified organic bentonite CTAB–bentonite with a bottom spacing of 1.905 nm, indicating that the CTAB between the modified bentonite layers was arranged in a predominantly pseudo-trilayered manner. In addition, when the polymer (PAC or PAM) was further introduced into the single modified CTAB–bentonite structure, the polymer could not be adsorbed in the interlayer due to its hydrophilic structure. As observed from XRD findings, the polymer did not change the layer spacing of the modified bentonite.

![Adsorption isotherms of Pb(II) and phenol on modified bentonites](image)

**Table 3** Fitting parameters of adsorption isotherms for Pb(II)

| Samples | Freundlich isotherm | Langmuir isotherm |
|---------|---------------------|-------------------|
|        | Value | Standard deviation | Value | Standard deviation | Value | Standard deviation | Value | Standard deviation | Value | Standard deviation |
| 0       | 38.086 | 5.131 | 0.132 | 0.027 | 0.911 | 77.168 | 3.064 | 0.980 |
| 1C      | 31.068 | 4.543 | 0.176 | 0.030 | 0.952 | 86.853 | 20.666 | 0.572 |
| 1C4P    | 9.147 | 5.724 | 0.214 | 0.105 | 0.684 | 56.126 | 26.333 | 0.369 |
| 1C4CP   | 3.140 | 1.938 | 0.356 | 0.100 | 0.851 | 44.659 | 15.403 | 0.628 |
| 1C4CP4AP| 1.766 | 1.148 | 0.450 | 0.105 | 0.897 | 52.755 | 19.387 | 0.686 |
| 4PAC    | 15.424 | 3.167 | 0.240 | 0.038 | 0.953 | 60.851 | 7.064 | 0.821 |
| 4CP     | 11.946 | 3.617 | 0.256 | 0.057 | 0.936 | 69.136 | 14.767 | 0.753 |
| 4AP     | 22.773 | 4.353 | 0.162 | 0.031 | 0.928 | 62.218 | 7.340 | 0.583 |
| SB-16   | 31.197 | 4.320 | 0.177 | 0.028 | 0.956 | 86.036 | 19.658 | 0.583 |
| 2PVA    | 41.264 | 5.319 | 0.135 | 0.027 | 0.922 | 82.272 | 6.731 | 0.921 |
bentonite. Also, FTIR showed the modified bentonite with the introduction of special functional groups, so the polymer should be adsorbed on the external surface or edge of the bentonite through the hydroxyl and carboxyl groups.

The surfactant molecule entered the bentonite layers by ion exchange process, and the polymer added later was bound to the surface and edges of modified bentonite lamella by intermolecular forces. However, the weak interaction between polymer and the modified bentonite leads to the elution phenomenon in practical engineering, i.e., the polymer easily dissolves from the modified bentonite, leading to the failure of barrier performance, which has been a severe engineering problem.

**Mechanisms of contaminants removal**

As can be seen from Fig. 7, the natural calcium-based bentonite and polymer-modified bentonite have a weak adsorption capacity for phenol, which is due to their hydrophilic surface. But surfactants with organic cations have a positive charge and can adsorb partially deprotonated and dissociated phenol anions through electrostatic interaction, and organic bentonite has large layer spacing and good hydrophobicity

### Table 4  Fitting parameters of adsorption isotherms for phenol

| Samples | Linear isotherm | $K_d$ | $K_{oc}$ | $R^2$ |
|---------|-----------------|------|---------|-------|
|         |                 | Value| Standard deviation |       |
| 0       | –               | –    | –       | –     |
| 1C      | 0.041           | 0.001| 0.336   | 0.998 |
| 1C4P    | 0.043           | 0.001| 0.342   | 0.995 |
| 1C4CP   | 0.041           | 0.001| 0.317   | 0.996 |
| 1C4CP4AP| 0.041           | 0.001| 0.312   | 0.998 |
| 4PAC    | –               | –    | –       | –     |
| 4CP     | –               | –    | –       | –     |
| 4AP     | –               | –    | –       | –     |
| SB-16   | 0.063           | 0.006| 0.597   | 0.963 |
| 2PVA    | –               | –    | –       | –     |

### Table 5  Introduction of the new assessment factor $W$ combining the adsorption constants of pollutants by normalization

| Samples | $K_d$ | $x/x_{max}$ | $K_F$ | $y/y_{max}$ | $W^*$ |
|---------|------|-------------|------|-------------|-------|
| 0       | –    | –           | 38.086| 0.923       | 0.923 |
| 1C      | 0.041| 0.651       | 31.068| 0.753       | 1.404 |
| 1C4P    | 0.043| 0.683       | 9.147 | 0.222       | 0.904 |
| 1C4CP   | 0.041| 0.651       | 3.140 | 0.076       | 0.727 |
| 1C4CP4AP| 0.041| 0.651       | 1.766 | 0.043       | 0.694 |
| 4PAC    | –    | –           | 15.424| 0.374       | 0.374 |
| 4CP     | –    | –           | 11.946| 0.289       | 0.289 |
| 4AP     | –    | –           | 22.772| 0.552       | 0.552 |
| SB-16   | 0.063| 1.000       | 31.197| 0.756       | 1.756 |
| 2PVA    | –    | –           | 41.264| 1.000       | 1.000 |

* $W = x/x_{max} + y/y_{max}$
to form a "micro-organic distribution phase," resulting in a relatively strong organic distribution medium, so it has a better effect on adsorption and removal of phenol. The larger the layer spacing of modified bentonite, the larger the adsorption space for phenol, and the more prominent the phenol removal effect of modified bentonite.

The adsorption removal of heavy metal ions is generally accomplished by interlayer cation exchange and chelation on the surface. The adsorption capacity is related to the cation exchange capacity (CEC) of bentonite and the specific surface area of bentonite. From the XRD results, although the intercalation of surfactants leads to a larger layer spacing of bentonite, the hydrophobic effect makes it difficult for heavy metal ions to enter the interlayer domain, while the external surfaces of bentonite and surface-bound polymers contain many hydroxyl and carboxyl functional groups, which increase the adsorption sites for heavy metal ions. For the composite-modified bentonite, the adsorption capacity for heavy metal ions is slightly reduced than that of the single-polymer-modified bentonite due to the introduction of surfactant.

The linear adsorption isotherm curve indicates that the adsorption mechanism is mainly based on the hydrophobic partitioning of alkyl chains. The magnitude of the adsorption performance of organic montmorillonite not only depends on the magnitude of the adsorption interaction but also is closely related to its adsorption capacity.

The adsorption capacity of modified bentonite is greatly affected by the accumulation density of modifiers such as surfactants in the layer spacing. Research showed that more than 250% CEC would lead to a too dense accumulation of interlayer modifiers due to spatial site resistance, resulting in a reduced adsorption effect (He et al. 2014; Zhao et al. 2017). Furthermore, 100% CEC-modified bentonite is supposed to have a better adsorption performance, so this parameter was chosen for intercalation modifier in this study to evaluate different types of modified bentonite.

Partition of organic compounds into interlayer surfactant aggregates driven by hydrophobic interactions was believed to be the predominant adsorption mechanism of organoclay-loading long-chain surfactant (Johnston et al. 2012; Xu et al. 2014; Zhao and Burns 2012).

**Concluding remarks and future prospects**

Nine types of modified and untreated bentonites were prepared and characterized in this study. The adsorption performances of modified bentonites on Pb(II) and phenol were compared and evaluated, and also, the corresponding adsorption mechanism was analyzed. The following conclusions can be drawn:

- Modification improved the adsorption effectiveness of bentonites. The PVA-modified bentonite posed the highest adsorption capacity for Pb(II), and the SB-16-modified bentonite had not only the highest adsorption capacity for phenol but also the highest combined adsorption capacity for both contaminants. The adsorption performance of modified bentonites on both phenol and Pb(II) followed the ranking of SB-16 > PVA > CTAB > APAM > CTAB + PAC > PAC > CPAM > CTAB + APAM > CTAB + CPAM + APAM.
- The surfactant intercalation of the bentonite resulted in very effective adsorption of organic contaminants, and the main adsorption mechanism was the hydrophobic partitioning of alkyl chains. While the polymer formed a three-dimensional cross-linking structure with abundant functional groups, such as carboxyl and hydroxyl groups, on the bentonite surface and thus had a strong adsorption effect on heavy metal ions.

Attempts were made to optimize the effectiveness of multivariate approaches to bentonite modification in the simultaneous removal of complex contaminants to provide targeted and universal implementation solutions for varieties of engineering needs. To achieve these goals, future bentonite modification studies can be oriented to the following aspects: (1) Modification be even more specific to the contaminant in question. Polyphosphate-amended bentonite exhibited excellent containment of metal contamination, which can be designed to target contaminants like lead and hexavalent chromium (Yang et al. 2019). Organo-bentonites are extensively studied to enhance the adsorption of the organics, such as benzene and polycyclic, chlorinated benzene, and other hydrocarbons sorbates. (2) Combine the microstructure of modified clays with the engineering behavior to reveal the mechanism of modification under multiscale studies. Modified bentonites can be used in permeable reactive barriers as the wall material with extraordinary geochemical and physical behaviors. For example, the hydraulic conductivity of organic bentonites is not susceptible to freeze–thaw and wet–dry cycles. (3) It is necessary to explore the applicability of modified bentonites as adsorbents in real waters (e.g., mixed organic pollutants, dye and metal ion mixtures, or heavy metal ion mixtures). However, the studies were mostly performed in the laboratory, but the real wastewater contains a variety of cations/anions that may hamper the adsorption behavior of the modified clays. Therefore, there are several areas in need of more investigation. These results and analyses will provide a fundamental basis for the comparative assessment of modified bentonites.

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Declarations

Conflict of interest  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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