

Original Research

# Chromium (VI) Adsorption Characteristics of Bentonite Under Different Modification Patterns

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## Abstract

We investigated the Cr(VI) adsorption characteristics of bentonite under different modification patterns by using a mixture of BS-12 (dodecyl dimethyl betaine) and DTAB (dodecyl trimethyl ammonium bromide). DTAB was used to compositely modify 25%, 50%, and 100% BS-12-modified bentonite (three modified modes of bentonite with BS-12). In addition to these modification modes, variations as functions of pH value, temperature, and ionic strength were compared. Results showed:

1. Cr(VI) adsorption capacity of bentonite compositely modified with BS (short for BS-12) + DT (short for DTAB) rapidly increased compared with that of BS-modified bentonite, and the adsorption capacity of 100%BS+100%DT-modified bentonite was the highest among the samples surveyed and 23-fold higher than that of CK (raw bentonite).
2. Cr(VI) adsorption on bentonite exhibited saturated adsorption in ion exchange (*IE*) mode, distributive adsorption in ion exchange and hydrophobic bond coexisting (*IE+HB*) pattern, and synergistic adsorption in the hydrophobic bond (*HB*) pattern.
3. Effects of rising temperature on Cr(VI) adsorption appeared in the *IE* mode, while negative temperature effect was observed in the *HB* mode. Higher pH value and ionic strength were unfavorable for Cr(VI) adsorption. 100%BS+100%DT compositely modified bentonite exhibited the optimal adsorption of Cr(VI) at 10°C, pH = 4, and ionic strength of 0.01 mol L<sup>-1</sup>.

**Keywords:** modification pattern, bentonite, Cr(VI), adsorption capacity

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## Introduction

Development of methods to dispose and remediate heavy metal pollution was an extremely urgent endeavor [1]. Previous studies showed that clays could be easily modified [2], and that TOC (total organic carbon) content [3], interlayer spacing [4], surface hydrophobicity [5, 6], and adsorption ability of organic contaminants and heavy metal salt ions [7-9] on the modified clays were proven to increase significantly.

Heavy metal cations were well adsorbed by natural clays owing to the special surface charge characteristics of these clays, but heavy metal anions were hardly adsorbed on clays. Many experiments were performed to study the adsorption characteristics of differently modified clays or soils to heavy metal anions. Data from Haggerty and Bowman [10] and Li and Bowman [11, 12] indicated that clays such as kaolin and montmorillonite, modified with CTMAB (cetyl trimethyl ammonium bromide), provided sufficient adsorption capacity to nitrate, arsenate, chromate, and other oxygen-containing acid anions. These modified clays exhibited the best adsorption ability when the modification ratio was set to be 200% CEC (cation exchange capacity) of clay, and the heavy metal anions were mainly adsorbed by electrostatic interactions on modified clays [13]. Bentonite was modified by CTMAB [14] or HTMAC (hexadecyl trimethyl ammonium chloride) [15], presenting a Cr(VI) removal rate of over 74%. Akar [16] confirmed that clay modified by HTMAC showed excellent Cr(VI) removal capacity at pH = 4. Brum [17] also found that the removal rate of Cr(VI) exceeds 98% in CTMAB-modified bentonite at pH = 4. Physical and chemical effects coexisted during Cr(VI) adsorption in modified clays. By increasing the modified ratio of these clays, their ability to adsorb Cr(VI) improved [18].

Cr(VI) adsorption capacity of clays modified by two mixed surfactants showed considerable progress. Lou soil was simultaneously modified with anionic and cationic modifiers, and Cr(VI) adsorption capacity of this soil sharply improved [19]. Two cationic modifiers were also used to modify natural bentonite, and the result showed apparent improvement in Cr(VI) adsorption [20]. Amphoteric modifiers BS-12 (dodecyl dimethyl betaine) and BS-18 (octadecyl dimethyl betaine) were proposed to perform similar functions in the adsorption of heavy metal salt ions [21, 22].

Clay modified with an initial modifier transformed the clay surface from hydrophilic to hydrophobic. Then a second modifier combined with the soil surface via hydrophobic chains and exposed hydrophilic ends to air. Consequently, the modified clays showed great electrostatic adsorption of ionic pollutants [23, 24]. Studies showed that a strong relationship existed between the modification patterns of clays and their capacity in adsorbing pollutants. Hydrophobic modification of clays began at the modification ratio of 50% CEC of clay, and this modification was dominant at the modification ratio beyond 100% CEC [25, 26]. Such modification improved the adsorptive effects of the clay. Previous research

showed that 25%, 50%, and 100% CEC BS-12 modified bentonites began to appear in hydrophobic modification mode at DTAB (dodecyl trimethyl ammonium bromide)-modified ratios of 30%, 20%, and 0% CEC of bentonite [27]. Moreover, the adsorption of pollutants by bentonite was improved under hydrophobic modification mode. However, studies of the relationship between the modification modes and the pollutant adsorption characteristics of clays were rare.

To achieve excellent Cr(VI) adsorption capacity of clay compositely modified with amphoteric and cationic modifiers and establish the relationship between the modification modes and adsorption characteristics, DTAB was used to compositely modify BS-12-modified bentonite with three modification modes (i.e., ion exchange, hydrophobic bond and ion exchange coexisting, hydrophobic bond). Different modification proportions of bentonite were designed based on the results of a previous study [27]. Cr(VI) adsorption characteristics and capacity of bentonite under different modification modes and variations such as temperature, pH value, and ionic strength were analyzed. This study provided a theoretical foundation for future heavy metal anions adsorption research with the application of compositely modified clay.

## Materials and Methods

### Materials

Analytical reagent (AR)-grade DTAB in water [96% (w/v)] was selected as the cationic modifier in this experiment and provided by Tianjin Zhiyuan Chemical Reagent Co., Ltd. AR-grade dodecyl dimethyl betaine (BS-12) in water [30% (w/v)] was used as the amphoteric modifier and provided by Xingguang Auxiliary Factory, Tianjin City, China.

Sodium bentonite was collected from Xinyang City, Henan Province, China. Raw clay samples were purified with wet cleaning process [28] before use. The basic characteristics of bentonite after purification are as follows: pH = 10.3, CEC = 1000.33 mmol kg<sup>-1</sup>, and TOC = 4.98 g kg<sup>-1</sup>.

Cr(VI) was used as the anionic heavy metal pollutant and prepared using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (AR).

### Preparation of Modified Bentonite

A wet process [29] was used to modify bentonite. In this process, a certain weight of purified bentonite was acquired, slowly added to the prepared BS-12 solution at a soil/water ratio of 1:10, and then dispersed by ultrasound at 60°C for 3 h. The samples were centrifuged at 4,800 rpm for 20 min, and the supernatant was separated. BS-12 modified bentonite (BS bentonite) could be obtained after washing thrice with deionized water. BS bentonite was dried at 60°C for 12 h and then passed through a 0.25 mm sieve.

BS bentonite was added to the prepared DTAB solution at a soil/water ratio of 1:10. The same preparation method was repeated with BS (short for BS-12) + DT (short for DTAB)-modified bentonite.

The weight of BS-12 or DTAB for a certain weight of clay minerals can be obtained by using the following equation (1):

$$W = m \times CEC \times M \times 10^{-6} \times \frac{R}{b} \quad (1)$$

...where  $W$  is the weight (g) of BS-12 or DTAB,  $m$  is the weight (g) of the clay minerals that will be modified,  $CEC$  is the CEC ( $\text{mmol kg}^{-1}$ ) of the clay minerals,  $M$  is the molecular mass ( $\text{g mol}^{-1}$ ) of BS-12 or DTAB,  $R$  is the proportion of modification, and  $b$  is the product content of the modifier (mass fraction).

## Experimental Design

### Adsorption of Cr(VI) under Differently Modified Bentonites

According to the mechanism of bentonite modified with BS-12 found by Meng [21], 25% BS bentonite was in ion exchange (*IE*) modified mode, 50% BS bentonite showed hydrophobic bond and ion exchange coexisting (*IE+HB*) modification mode, and 100% BS bentonite was in hydrophobic bond (*HB*) modification mode. BS bentonite was compositely modified with DTAB, showing that 25%, 50%, and 100% BS bentonite began to appear *HB* modification at the DTAB modified ratios of 30%, 20%, and 0% CEC of bentonite, respectively [27]. These modified ratios that began to appear in *HB* modification mode were used as turning points. One-half turning point (*IE* mode), turning point (*IE+HB* mode), and two-times turning point (*HB* mode) were chosen as modification ratios (100% BS except). The modification proportions of bentonite were as follows: raw bentonite (CK): 25%, 50%, and 100%, BS-modified bentonite; 25% BS+15DT, 25%BS+30DT, and 25%BS+60 DT; 50% BS+10DT, 50% BS+20DT, and 50% BS+40DT; 100% BS+25DT, 100% BS+50DT, and 100% BS+100DT compositely modified bentonite. Bentonite was compositely modified in all 13 samples.

Cr(VI) aqueous solutions of 5, 10, 20, 50, 100, 200, 300, 400, and 500  $\mu\text{g mL}^{-1}$  were prepared.  $\text{KNO}_3$  was used as the ion background to maintain a constant ionic strength among the samples. Each reaction was performed in triplicate. The temperature was set to 20°C, the pH value was set to 7, and the ionic strength was set to 0.1 mol  $\text{L}^{-1}$ .

### Effects of Temperature, pH Value, Ionic Strength on Cr(VI) Adsorption

Experimental temperatures were set to be at 10°C, 20°C, and 30°C (pH value of the initial solution is 7; ionic strength is 0.1 mol  $\text{L}^{-1}$ ).

The pH values of the initial Cr(VI) solution were set to be at 4, 7, and 10 (temperature is 20°C; ionic strength is 0.1 mol  $\text{L}^{-1}$ ).

The ionic strengths of the background solution were set to be at 0.01, 0.1, and 0.5 mol  $\text{L}^{-1}$  (temperature is 20°C; pH value of the initial solution is 7).

## Experimental Method

0.2500 g of modified samples were taken into nine 50 mL centrifuge tubes. Twenty ml from each of the nine Cr(VI) solutions was added into separate tubes, and the tubes were capped tightly. Equilibrium was achieved by shaking the suspensions for 12 h (an early dynamic experiment showed that adsorption equilibrium was achieved at 12 h) at 20°C using the batch method with a temperature-regulated thermostat shaker. Subsequently, samples were centrifuged at 4,800 rpm for 20 min. Last, the Cr(VI) concentrations in the supernatant were measured. The amount of Cr(VI) adsorbed by the modified sample was calculated as the difference between the initial and final concentrations of Cr(VI) in the supernatant.

The Cr(VI) concentration in the supernatant was determined by measuring absorbance with an SP-1200 UV-VIS spectrophotometer at 540 nm using the diphenylcarbazide method. Background absorption was corrected with a reagent blank.

## Data Processing

The Freundlich model ( $S = kc^{(1/n)}$ ) was used to fit the adsorption isotherms obtained. Here,  $S$  is the equilibrium adsorption amount ( $\text{mmol kg}^{-1}$ ) of Cr(VI) on the solid adsorbent,  $c$  is the equilibrium concentration ( $\text{mmol L}^{-1}$ ) of Cr(VI) in the supernatant fluid,  $k$  is a parameter related to the adsorption capacity, and  $n$  – which refers to affinity – is a parameter reflecting the binding capacity of the adsorbate on the adsorbent.

Curve Expert 1.3 fitting software was used for linear fitting, and SigmaPlot 10.0 software was adopted to improve data plotting.

## Results and Discussion

### Adsorption of Cr(VI) on Bentonite Modified in Different Patterns

#### *Cr(VI) Adsorption Ability of Bentonite*

The adsorption isotherms in Fig. 1 show that the adsorption amounts of Cr(VI) on different modified bentonites increased with increasing equilibrium concentration of Cr(VI). The adsorption amounts of Cr(VI) changed from 3.67 to 80.92  $\text{mmol kg}^{-1}$  at 20°C, pH 7, and ionic strength of 0.1 mol  $\text{L}^{-1}$ . The adsorption ability of Cr(VI) on the original bentonite was the lowest among the samples observed. The adsorption amount of

Cr(VI) on BS bentonite was greatly improved. Moreover, the adsorption amount of 25%, 50%, and 100% BS bentonites increased by 2.30-fold, 6.64-fold, and 8.82-fold, respectively, compared with that of CK.

For DTAB+BS-12 compositely modified samples, bentonite compositely modified on 25% BS+15% DT, 30% DT and 60% DT all exhibited greater Cr(VI) adsorption capacity than 25% BS bentonite. In particular, adsorption amounts of Cr(VI) on these 25% BS+DTAB compositely modified samples improved by 1.75-fold, 2.98-fold, and 3.64-fold, respectively, compared with that of 25% BS bentonite. All of these values were more than four times greater than that of CK. Bentonite was modified with 50% BS+10%, 20%, and 40% DT, showing insignificant changes in the adsorption of Cr(VI). These treatments presented Cr(VI) adsorption amounts 1.4-1.6 times greater than that of 50% BS bentonite and nine times

greater than that of CK. Bentonites compositely modified with 100% BS+DTAB showed significant improvement in Cr(VI) adsorption, and its adsorption amount was 1.2-2.5 times greater than that of 100% BS bentonite and 23 times (maximum) greater than that of CK. The ranking order of different modification patterns based on Cr(VI) adsorption was *HB* modification mode > *IE+HB* modification mode > *IE* modified mode.

#### *Cr(VI) Adsorption Properties of Bentonite*

The Freundlich model was adopted to fit the adsorption isotherms of Cr(VI) in different modified bentonites (Fig. 1) and fitting parameters were obtained (Table 1). Results showed the correlations of the adsorption isotherms, each of which was significant ( $p<0.01$ ). With increasing modification ratios of BS bentonite, the

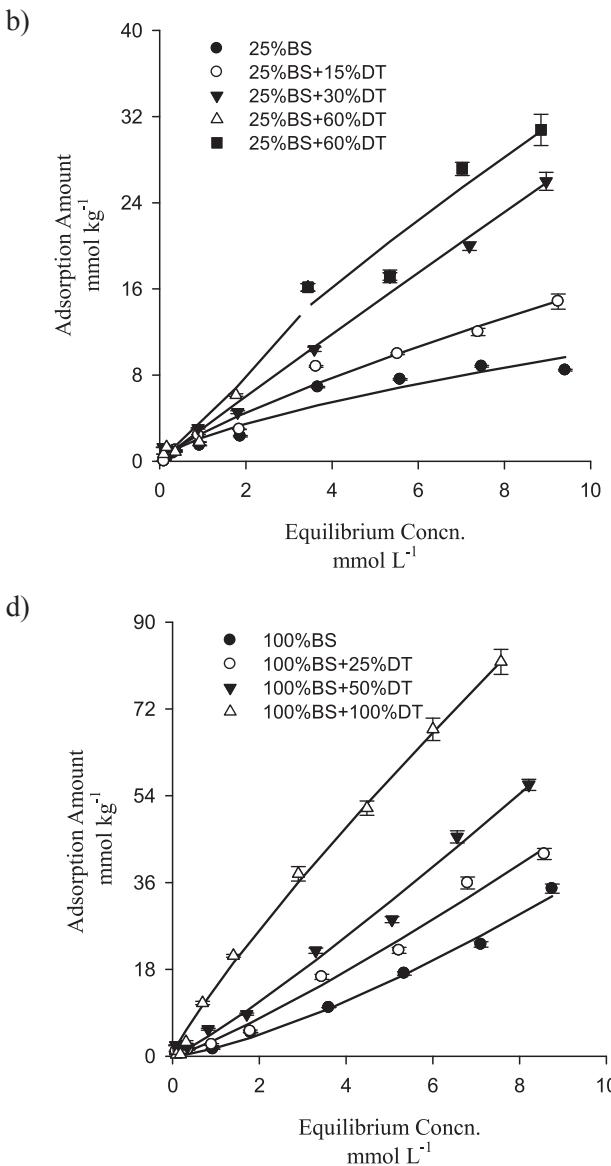
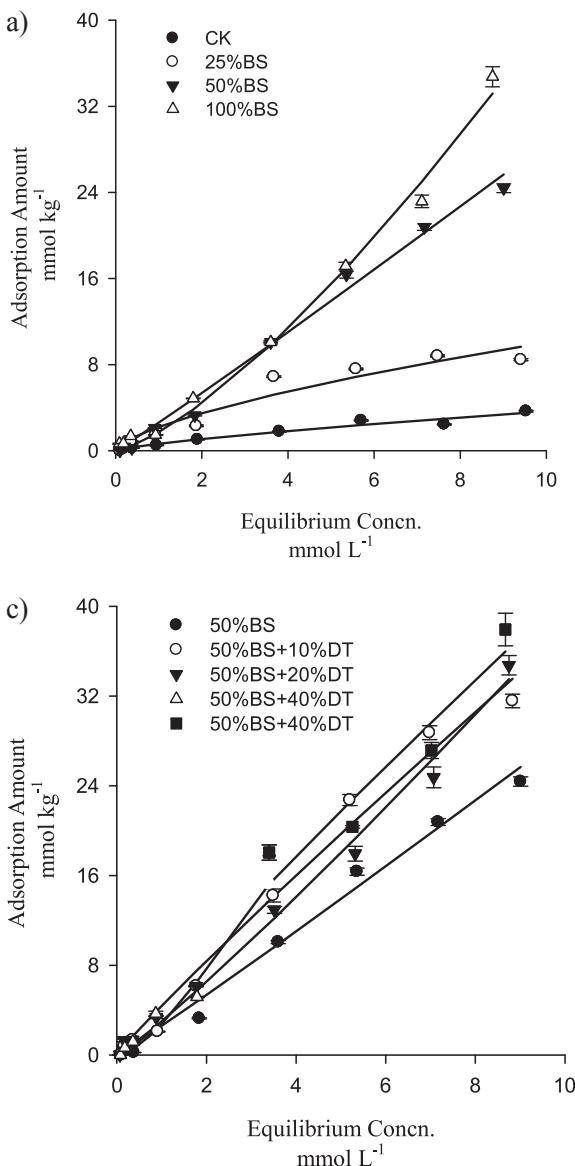


Fig. 1. Adsorption isotherms of Cr(VI) on different modified bentonites, with CK the natural bentonite; 25% BS, 50% BS, and 100% BS are bentonites modified with BS-12; 25% BS+DT, 50% BS+DT, and 100% BS+DT are BS-12 bentonites compositely modified with DTAB. The temperature was set to 20°C, the pH value was set to 7, and the ionic strength was set to 0.1 mol L⁻¹.

Table 1. Freundlich isotherm parameters of Cr(VI) adsorption on different modified bentonites;  $r$  and  $S$  are the correlation coefficient and standard deviation of each fitting isotherm,  $k$  is a parameter related to adsorption capacity, and  $n$  is referred to as affinity.

Modified samples	Correlation coefficients/ $r$	Standard deviations/ $S$	$k$	$n$
CK	0.9817**	0.2698	0.63	1.31
25% BS	0.9684**	0.9997	2.21	1.52
50% BS	0.9951**	1.0163	2.60	0.96
100% BS	0.9965**	1.0889	1.70	0.73
25% BS+15% DT	0.9903**	0.8267	2.62	1.28
25% BS+30% DT	0.9969**	0.8097	3.07	1.03
25% BS+60% DT	0.9957**	0.6397	2.57	0.67
	0.9456**	2.8963	5.28	1.24
50% BS+10% DT	0.9930**	1.6035	4.38	1.07
50% BS+20% DT	0.9965**	1.0970	3.01	0.90
50% BS+40% DT	0.9890**	1.1209	2.62	0.64
	0.9493**	3.4354	4.96	1.09
100% BS+25% DT	0.9945**	1.7874	3.44	0.85
100% BS+50% DT	0.9952**	2.1359	5.12	0.88
100% BS+100% DT	0.9985**	1.8285	10.45	1.17

Note: \*\*indicates that the correlation coefficient is significant at the  $p = 0.01$  level ( $r = 0.765$  when the degree of freedom  $f = 8$  and the level of significance  $p = 0.01$ ).

adsorption strength ( $n$ ) consistently decreased. For CK and 25% BS-modified bentonite (*IE* modified mode), the adsorption strength ( $n$ ) was greater than 1, as the preferential adsorption and adsorption curves tended to reach saturated adsorption type. For 50% BS-modified bentonite, hydrophobic bonding began to appear ( $n$  was close to 1). Adsorption was approximately linear and the adsorption curve demonstrated distributive adsorption. 100% BS-modified bentonite showed an *HB*-modified mode ( $n < 1$ ), which indicated non-preferential adsorption as well as a synergistic adsorption curve.

Bentonite was compositely modified with 25% BS+15% DT and 50% BS+10% DT, revealing an *IE* modification mode with  $n > 1$ , and preferential adsorption and saturated adsorption curves. Bentonite compositely modified with 25% BS+30% DT and 50% BS+20% DT showed the *IE+HB* modification mode and the values of  $n$  approximately equal to 1.25% BS+60% DT, and 50% BS+40% DT presented the *HB* modification mode, but revealed both synergistic adsorption and distribution adsorption. 100% BS bentonite compositely modified with DTAB all demonstrated the *HB* modification mode and synergistic adsorption. At some point, however, 100% BS+100% DT began to show saturated adsorption.

Results demonstrated a certain relationship between modification modes and the adsorption properties of bentonite. The *IE* mode of clay tended to promote saturated adsorption of Cr(VI). When modification began to appear *HB* mode on clay, Cr(VI) adsorption changed to the distributive type. Lastly, the *HB* mode led to synergistic adsorption.

$k$  values related to adsorption capacity were shown in the following order: 100% BS+100% DT > 100% BS+50% DT > 25% BS+60% DT > 50% BS+40% DT > 50% BS+10% DT > 100% BS+25% DT > 25% BS+30% DT > 50% BS+20% DT > 25% BS+15% DT > 50% BS > 25% BS > 100% BS > CK. Cr(VI) adsorption capacity of clay basically maintained an increasing trend with increasing total modification ratios of BS+DT, and 100% BS bentonite compositely modified by DTAB maintained a high adsorption capacity of Cr(VI). Hydrophobic modification can lead positively charged groups of BS-12 and DTAB to be outward, which forms an electrical (physical) adsorption of Cr(VI), this process is exothermic and spontaneous. These results were consistent with those of previous studies on Cr(VI) adsorption [19].

#### Effects of Temperature on Cr(VI) Adsorption

Cr(VI) adsorption on BS and BS+DT-modified bentonite at different temperatures was shown in Fig. 2. The adsorption amount of Cr(VI) on CK increased over 50% from 10°C to 30°C. By comparison, adsorption amount on the 25%, 50%, and 100% BS-modified bentonites under the same conditions increased by 15%, 5%, and 4%, respectively. The adsorption amount of Cr(VI) also increased by 2% to 7% on the different 25% BS+DT-modified bentonites. These results showed that CK- and BS-modified bentonite and 25% BS+DT compositely modified samples presented better Cr(VI) adsorption capacity with increasing temperature, and this indicated that the chemical adsorption and endothermic

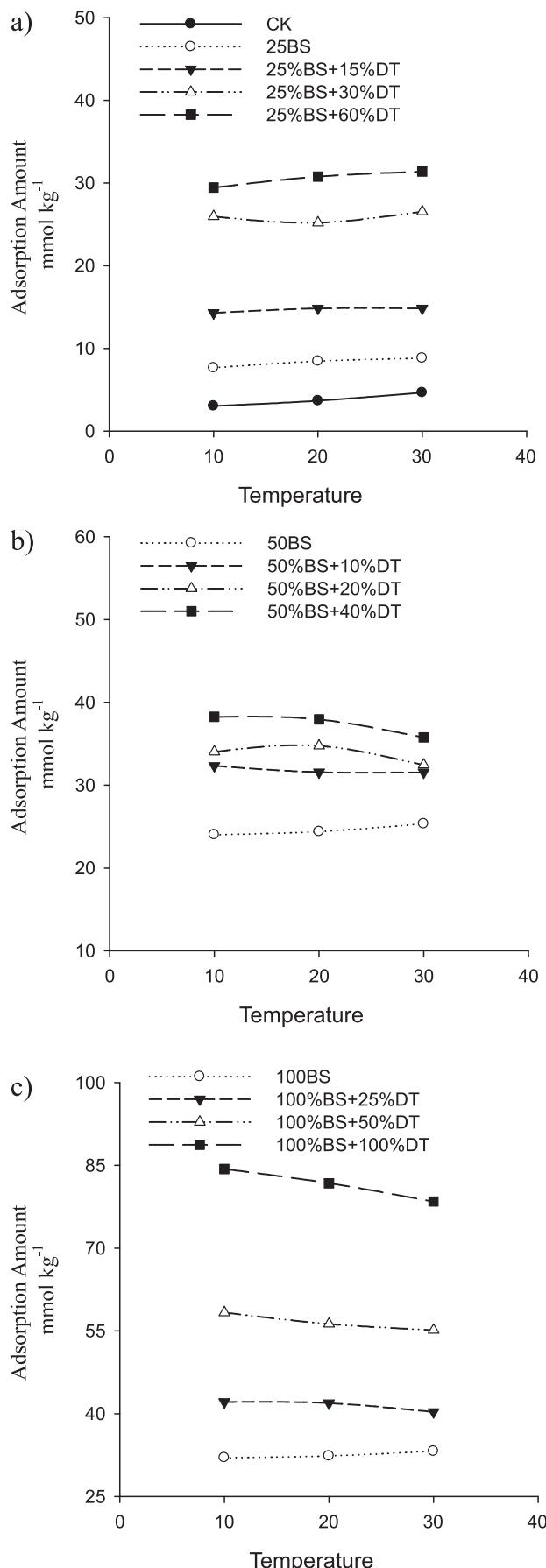


Fig. 2. Effects of temperature on Cr(VI) adsorption of different modified bentonite with pH value was set to 7 and ionic strength set to  $0.1 \text{ mol L}^{-1}$ .

reaction were presented in the process of Cr(VI) adsorbing bentonite under the *IE* modification mode.

For bentonites compositely modified by 50% BS+DT and 100% BS+DT, the adsorption amount of Cr(VI) decreased by approximately 2-7% from 10-30°C. This result revealed the negative influence of temperature [30] on Cr(VI) adsorption and was associated with the covering effect of the modifier on the surface of bentonite. The hydrophobic carbon chain of the modifier inhibited Cr(VI) adsorption on the surface of the soil sample and weakened the endothermic reaction. By contrast, positively charged hydrophilic groups on the surface of BS-12 and DTAB compositely modified bentonite enhanced the electrical charge of bentonite and improved the physical adsorption of  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  and exothermic functions, which changed the temperature effect from positive to negative. The results were completely consistent with the findings by Sarkar [18], who demonstrated that the adsorption of Cr(VI) on bentonite occurred through both physical and chemical effects and the adsorption amount increased with increasing modification ratios.

Therefore, the adsorption amount of Cr(VI) on modified bentonite increased with increasing temperature in the *IE* modification mode. The rising temperature effect of Cr(VI) adsorption was reduced with the appearance of *HB* modification mode. Negative temperature effect was observed in the *HB* modification mode.

#### Effects of pH Value on Cr(VI) Adsorption

The effects of pH values on Cr(VI) adsorption on differently modified bentonites are presented in Table 2. At the range of pH value from 4 to 7, the adsorption amount of Cr(VI) on CK decreased and had a significant distinction among these three pH values. Cr(VI) adsorption of differently modified BS-12 bentonite all decreased with the pH values from 4 to 7, and no significant distinction of 25% and 100% BS bentonite existed. However, with the pH value from 4 to 10, adsorption of Cr(VI) in 50% BS bentonite had a significant distinction. Different BS+DT compositely modified bentonites, except for 25% BS+30% DT and 50% BS+20% DT-modified bentonite, had the highest Cr(VI) adsorption at pH = 10 and pH = 7, respectively, and other bentonites all presented the highest absorption at the pH value of 4. With the pH value from 4 to 7, Cr(VI) adsorption on 25% BS+15% and 30% DT-, 50% BS+10% and 40% DT-, and 100% BS+25% DT- and 50% DT-modified bentonite all showed insignificant distinction, while 100% BS+100% DT- and 50% BS+20% DT-modified bentonite had significant adsorption differences in pH values of 4, 7, and 10 treatments.

Under high pH conditions, high  $\text{OH}^-$  concentration in the balance liquid and variable negative charge of BS-12 on bentonite all leads to competitive adsorption with  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ . By contrast, when the  $\text{OH}^-$  concentration was low in the balance liquid, competitive adsorption with  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  was weakened. Increasing  $\text{H}^+$  in the balance liquid can enhance the electrical adsorption

Table 2. Effects of pH value on Cr(VI) adsorption on modified bentonite with temperature set to 20°C and ionic strength set to 0.1 mol L<sup>-1</sup>.

Treatments	Adsorption amounts/mmol kg <sup>-1</sup>		
	pH = 4	pH = 7	pH = 10
CK	3.75±0.06a	3.56±0.03b	3.36±0.03c
25% BS	8.20±0.12a	8.15±0.14a	8.04±0.02a
50% BS	25.22±0.70a	24.13±0.58ab	22.27±0.73b
100% BS	34.53±1.46a	32.52±1.45a	32.14±0.66a
25% BS+15% DT	15.23±0.71a	14.27±0.47a	14.36±0.37a
25% BS+30% DT	25.69±1.19a	25.06±1.05a	25.82±0.98a
25% BS+60% DT	33.48±1.43a	30.34±0.77ab	27.54±0.58b
50% BS+10% DT	35.56±2.05a	31.32±0.76a	30.67±0.96a
50% BS+20% DT	34.00±0.72a	34.25±0.58a	33.37±0.79b
50% BS+40% DT	40.22±1.28a	37.71±1.56a	34.43±1.40a
100% BS+25% DT	41.04±0.96a	41.67±1.18a	40.35±0.20a
100% BS+50% DT	60.79±2.19a	56.22±1.28a	55.87±1.08a
100% BS+100% DT	87.81±2.20a	80.92±2.26a	71.59±1.50b

Note: The different lowercase letters indicate significant difference among treatments at 0.05 levels.

of HCrO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>2-</sup>, and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. All of the results were consistent with the findings of Akar [16] and Brum [17].

#### Effects of Ionic Strength on Cr(VI) Adsorption

The results of Cr(VI) adsorption under three different ionic strengths (Table 3) showed that the adsorption of Cr(VI) in the ionic strength range of 0.01–0.5 mol L<sup>-1</sup> gradually decreased for differently modified bentonites, excluding 25% BS+30% DT treatment. Cr(VI) adsorption in CK-, BS-, and BS+DT-modified bentonites all showed no significant distinction under the three ionic strengths.

This result was consistent with observations made during Cr(VI) adsorption on bentonite simultaneously modified with amphoteric and cationic modifiers [31]. With increasing KNO<sub>3</sub> concentration, competitive adsorption occurred between CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and negative charge on bentonite. Bentonite surfaces had an electric double-layer structure and its diffusion layer was gradually compressed by adding KNO<sub>3</sub>. Consequently, Cr(VI) adsorption decreased with increasing ionic strength.

Comparison of Cr(VI) adsorption rates at different modification ratios, pH, temperatures, and ionic strengths

revealed that 100% BS+DT (the HB modification mode) compositely modified bentonite showed superior adsorption capacity among the samples tested. 100% BS+100% DT-modified bentonite showed the best adsorption of Cr(VI) at 10°C, pH 4, and ionic strength of 0.01 mol L<sup>-1</sup>.

#### Adsorption Mechanisms of Cr(VI) on Modified Bentonites

Exchangeable cations on natural clay surfaces rendered clay negatively charged. Negative charges on bentonite surfaces resulted in electrical repulsion of CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> [2]. However, Cr(VI) can only combine with bentonite by covalent bonding. Chemical adsorption was the main adsorption mechanism for Cr(VI) on CK.

The positive end of BS-12 can be combined on the bentonite surface via ionic exchange with cations on bentonite. With increasing ionic exchange of BS-12, more carbon chains of BS-12 were covered on the surface of bentonite, and the hydrophobic combination of carbon chains gradually appeared on the surface. When sufficient BS-12 was combined with the organic phase on the surface of bentonite, modification completely followed the hydrophobic-modified mode, and positive groups on the outside surface of bentonite produced more electrical attractions toward CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. Bentonite in hydrophobic modification mode presented strong adsorption ability for CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. Negatively charged groups on the exterior of bentonite resulted in electrical repulsion of CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. Thus, clay with both negative and positive charges were formed, so there was a competition effect of Cr(VI) adsorption on bentonite modified with BS-12. BS-12-modified bentonites showed no significant improvement in Cr(VI) adsorption compared with CK.

When BS-12 bentonite was compositely modified with DTAB, the positive end of DTAB can combine with the negative group of BS-12 and the hydrophobic carbon chains of DTAB can combine with the hydrophobic phase of the bentonite surface. This can lead more positive ends of DTAB to the outside surface and further enhance the physical adsorption of Cr(VI). Thus, 25% BS (the IE modification mode), 50% BS bentonite (the IE+HB mode), and 100% BS bentonite (the HB modification mode) compositely modified with DTAB increased positive charges on the surface of bentonite and enhanced Cr(VI) adsorption ability by more than 9-fold, 11-fold, and 23-fold, respectively.

A certain relationship existed between the total BS+DT modification ratios of bentonite and the adsorption amount of Cr(VI) on modified bentonite. With increasing total DT+BS modification ratios of bentonite, the number of positive charges increased and the negative charges on the surface of bentonite were neutralized. This phenomenon promoted Cr(VI) adsorption on the modified bentonite, and caused physical adsorption to be gradually dominated by the adsorption mode [19]. The adsorption rate showed a considerable relationship with charge-neutralization

Table 3. Effects of ionic strength (IS) on Cr(VI) adsorption under different modified bentonites with temperature set to 20°C pH set to 7.

Treatments	Adsorption amounts /mmol kg <sup>-1</sup>		
	IS = 0.01 mmol L <sup>-1</sup>	IS = 0.1 mmol L <sup>-1</sup>	IS = 0.5 mmol L <sup>-1</sup>
CK	3.78±0.28a	3.56±0.21a	3.26±0.15a
25%BS	8.42±0.24a	8.15±0.09a	7.59±0.34a
50%BS	25.23±0.71a	24.13±0.65a	23.46±0.84a
100%BS	35.40±1.39a	32.52±1.45a	30.45±1.41a
25%BS+15%DT	15.57±0.90a	14.27±0.16a	14.01±0.58a
25%BS+30%DT	25.02±0.59a	25.06±0.61a	24.17±0.10a
25%BS+60%DT	31.35±0.78a	30.34±1.35a	28.90±1.10a
50%BS+10%DT	32.22±1.28a	31.32±0.76a	30.56±0.32a
50%BS+20%DT	35.06±0.61a	34.25±1.30a	32.80±1.04a
50%BS+40%DT	42.56±1.48a	37.71±1.56a	36.31±1.33a
100%BS+25%DT	43.04±1.76a	41.67±0.96a	40.64±1.52a
100%BS+50%DT	61.45±0.84a	56.22±1.86a	54.42±1.97a
100%BS+100%DT	86.11±2.37a	80.92±1.69a	78.25±1.88a

by DTAB and the total BS+DT modification ratios of bentonite. When 25% BS, 50%, and 100% bentonite were compositely modified by DTAB with proportions of 15-60%, 10-40% and 25-100%, respectively, the neutralization ability of negative charges increased. Thus, the *HB* modification mode of BS+DT-modified bentonite exhibited superior adsorption ability toward Cr(VI). Furthermore, the total number of positive charges on bentonite indicated its adsorption efficiency and capacity.

## Conclusions

The absorption capacity of CK was the lowest among the samples surveyed. The amount of Cr(VI) adsorbed by BS bentonite showed 2.30-fold to 6.64-fold higher than that of CK. 25% and 50% BS+DT bentonite revealed absorption amounts were 4-fold and 9-fold higher than that of CK, respectively. The amount adsorbed by 100% BS+100% D-modified bentonite was 23-fold higher than that of CK. Cr(VI) adsorption amount under different modification patterns showed the following order: *HB* modification mode > *IE+HB* modification mode > *IE* modification mode. The *IE* modification mode of clay tended to promote saturated adsorption of Cr(VI). When modification started to appear as hydrophobic bonding on clay, adsorption of Cr(VI) changed to the distributive type and the hydrophobic modification mode led to synergistic adsorption. The amount of Cr(VI) adsorbed by modified bentonite increased with increasing temperature in the *IE* mode. However, the rising temperature effect of Cr(VI) adsorption was reduced with the appearance of the *HB* mode. Negative temperature effect was observed in *HB* modification mode. An increase in solution pH and ionic

strength gradually reduced Cr(VI) adsorption capacity of the modified samples. 100% BS+100% DT compositely modified bentonite showed the optimal adsorption of Cr(VI) at the 10°C, pH = 4, and ionic strength of 0.01 mol L<sup>-1</sup>.

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