Application of Dithiocarbamate Chitosan Modified SBA-15 for Catalytic Reductive Removal of Vanadium(V)

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Abstract: We have successfully synthesized dithiocarbamate chitosan modified SBA-15 (CS2C@SBA) composites, with promise in vanadium (V(V)) elimination. Among the three composites using different mass ratios of dithiocarbamate chitosan to SBA-15, CS2C@SBA−3, which had the highest CS2 substitution, showed the best performance on V(V) removal of which the maximum adsorption capacity could achieve 218.00 mg/g at pH 3.0. The adsorption kinetics were best fitted with a pseudo-second order reaction model, suggesting a chemisorption mechanism. Meanwhile, the Langmuir model fitted better with the adsorption isotherm, revealing a monolayer adsorption behavior. Through FTIR and XPS analysis, the functional group −SH was identified as dominating reduction sites on this composite, which reduced 73.1% of V(V) into V(IV) and V(III). The functional group −NH− was the main adsorption site for vanadium species. This reaction followed a catalytic reduction coupled adsorption mechanism reducing most of V(V) into less toxic vanadium species. Furthermore, CS2C@SBA−3 showed great selectivity towards V(V) in the presence of various co-existing ions in synthetic wastewater and real water samples. Moreover, CS2C@SBA−3 could retain a removal efficiency over 90% after five adsorption−desorption cycles. Based on the aforementioned results, we can conclude that CS2C@SBA−3 has great potential to be applied in efficient remediation of vanadium water pollution.

Keywords: vanadium elimination; adsorption; catalytic reduction; thiol function group; dithiocarbamate chitosan modified SBA-15

1. Introduction
Vanadium pollution has become a worldwide problem with the extending process of industrialization, such as steelmaking, battery manufacturing, and medicinal processing [1−3]. Vanadium is a potential toxic contaminant that may cause pulmonary tumors and oxidative cell damage if it is over ingested [4]. There exist various valence states of vanadium including +2, +3, +4 and +5 [5,6]. The higher the valence state of vanadium is, the more toxicity and stability it has [7]. Over the past, a variety of methods including ion exchange, surface complexation and electrostatic interaction have been applied for the elimination of V(V). Anion exchange resins such as D201, D314 and 711 were employed for the removal of V(V), achieving a removal efficiency up to 99.0% [8]. Lactococcus raffinolactis was proved to have promising prospects in the elimination of V(V), offering microbial resources for the bioremediation of a V(V)−polluted environment [9]. Among aforementioned traditional technologies for the remediation of V(V), adsorption was the most widely used, due to its high removal efficiency and low cost. For example, surface modified pine bark was investigated with the maximum adsorption capacity of 35.00 mg/g with quaternary nitrogen groups on its surface as the dominant adsorption sites [10]. Kong et al. synthesized a double hydroxide−supported nanoscale zero−valent iron (nZVI@LDH)
for the elimination of vanadium, which achieved the maximum adsorption capacity of 93.70 mg/g at initial pH of 3.0 [11].

Chitosan is a natural and linear copolymer comprised of β-(1,4)-glucopyranose units containing randomly distributed N-acetyl-glucosamine and glucosamine residues [12,13]. The application of pristine chitosan to the removal of heavy metals is limited by its low surface area and restricted accessibility of surface functional groups [14,15]. Thus, various physical and chemical synthetic methods have been adopted to modify chitosan into more application-worthy composites with improved adsorption properties [16–18]. Due to the presence of abundant heteroatoms and polar functional groups serving as potential complexation sites with metal ions, derivatives of chitosan can be considered as potential remediation agents for the elimination of heavy metals [19]. A dithiol functional terminal may be introduced to chitosan (CS₂−chitosan) [20]. The successfully grafted thiol functional groups (−SH) may then serve as reactive sites to reduce vanadium at high valence states into lower valence states. It is well known that the −SH/−SS− redox couple displays a standard oxidation potential of 0.420 V [21,22], while the standard reduction potential of a V(V/IV) couple is 1.420 V [23]. Thus, thiol groups (−SH) are a promising reducing site theoretically to donate electrons to V(V). Furthermore, the abundance of −NH₂ and −OH may promote the adsorption process due to their coordination with V(V). Thus, CS₂−chitosan may preclude the desorption of vanadium species back into the water matrix due to its folder configuration. Applications of chitosan alone may be limited in neutral or alkaline conditions by the difficulty of convoluted separation procedures, since it is hydrophobic in nature [24]. Thus, coating CS₂−chitosan on a stable support may be feasible to synthesize a promising heterogeneous adsorbent for practical applications to the remediation of vanadium contaminated wastewater. As is acknowledged, Santa Barbara Amorphous type 15 material (SBA-15) is one of the most popular support materials for the development of heterogeneous composites in which the 2D hexagonal array of uniformly distributed mesopores plays a vital role in the easy diffusion of substrate molecules [25]. Due to the distinctive properties, high surface area and abundance of hydroxyl groups on its surface [26], SBA-15 can compensate for the disadvantages of CS₂−chitosan, facilitating the rafting of polymers.

Inspired by the aforementioned facts, we proposed a dithiocarbamate chitosan modified SBA-15 (CS₂C@SBA) composite as a heterogeneous remediation agent for the catalytic reduction coupled adsorption of V(V) in this work. During this research, we investigated the impacts of various parameters including pH value, the dosage of CS₂C@SBA, contact time, initial concentration of V(V) and coexisting anions on the elimination of V(V). Afterwards, recycling and regeneration studies were carried out. As the mechanism of catalytic reduction of V(V) by −SH functional groups is not clear, a series of characterization techniques such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscope combined with an electron dispersive X-ray (SEM−EDS) and X-ray photoelectron spectroscopy (XPS) were employed to analyze the change of the physicochemical properties of CS₂C@SBA before and after the reaction. Three CS₂C@SBA materials with distinct ratios of SBA-15 and modified dithiocarbamate chitosan were tested to disclose the structure−performance relationships. Finally, the performance was tested in real waters to further evaluate the potential of CS₂C@SBA in future practical applications. By all the aforementioned efforts, we aim to shed light on the adsorption and catalytic reduction mechanism of V(V) by CS₂C@SBA, and to confirm the potential of its future applications.

2. Result and Discussion

2.1. Structural Characterizations of Modified CS₂C@SBA − 1,2,3

Three CS₂C@SBA materials which were synthesized with the mass ratios of CS₂−chitosan to SBA-15 of 2:1, 1:1 and 1:2 were named as CS₂C@SBA − 1, CS₂C@SBA − 2 and CS₂C@SBA − 3, respectively. The elemental compositions of the synthesized materials, which were confirmed by elemental analyzer, are listed in Table 1. The elemental contents of N (weight percentage) of CS₂C@SBA − 1, CS₂C@SBA − 2 and CS₂C@SBA − 3 were 4.50%, 3.52% and 2.62%, while the
The physical properties of SBA-15 and CS₂C@SBA–3 are shown in Table S1 and Figure S1. As the successful hybrid of CS₂–chitosan, the Brunauer–Emmett–Teller (BET) surface areas of SBA-15 and CS₂C@SBA–1, CS₂C@SBA–2 and CS₂C@SBA–3 were calculated as 632.6, 121.4, 223.4 and 309.2 m²/g (Table S1), respectively. The BET surface area increased with the increasing mass ratio of CS₂–chitosan to SBA-15. Furthermore, the pore width increased from 2.04 to 2.28 nm while the pore volume increased from 0.1637 to 0.1762 cm³/g, respectively (Table S1 and Figure S1). CS₂C@SBA was mainly micro–mesopore structure (>2 nm). The X-ray diffraction (XRD) patterns revealed the ordered mesoporous structure of SBA-15 and CS₂C@SBA–3 (Figure S2). The peak at 2θ° was assigned for the amorphous SiO₂. Typical peaks at 0.8° (100), 1.6° (110) and 1.8° (200) indicated the mesopore structure of SBA-15 [31–34]. Furthermore, SEM images (Figure 2A–F) clearly showed the surface morphology of SBA-15, CS₂–chitosan and CS₂C@SBA–3 [35,36]. In the SEM image of CS₂C@SBA–3, it can be found that SBA-15 was uniformly wrapped by CS₂–chitosan (Figure 2E,F). To sum up, all the analyses above from the different characterizations proved the coating of CS₂–chitosan on the surface of SBA-15 [37]. TEM images (Figure S3) of SBA-15 exhibited cylindrical silicate layer morphologies [21,35]. After reaction with CS₂–chitosan, TEM images of CS₂C@SBA–3 (Figure S3) exhibited a core–shell structure which indicated the successful hybrid of CS₂–chitosan and SBA-15 [21]. Besides, after the reaction with V(V), CS₂–chitosan was still coated on the surface of SBA-15 (Figure S4). The phenomena suggested a robust nature of CS₂C@SBA–3 in the adsorption coupled catalytic reduction processes.
Figure 1. FTIR spectra of synthesized composites (A); Zeta potential plots of SBA-15, CS$_2$ chitosan and CS$_2$C@SBA−3 (B). The XPS survey spectra of CS$_2$C@SBA−3 before reaction (C). High resolution XPS spectra S 2p of CS$_2$C@SBA−3 (D).

Figure 2. SEM images of SBA-15 (A,B); CS$_2$−chitosan (C,D); CS$_2$C@SBA−3 (E,F).
2.2. Adsorption Properties on Vanadium (V) Elimination

2.2.1. Effects of pH

The solution pH is one of the most important influence factors in the removal of heavy metal since it can change not only the surface charge properties of adsorbents but also the distribution of metal ions species [38,39]. As is acknowledged, the distribution of V(V) oxyanions exists in different forms at different solution pH values [40,41]. Taking those facts into consideration, we decided to determine the removal of V(V) by CS2C@SBA−1, CS2C@SBA−2 and CS2C@SBA−3 at a specific pH ranging from 2.0 to 10.0.

Figure 3 showed the effects of pH value on the removal of V(V). CS2C@SBA−1, CS2C@SBA−2 and CS2C@SBA−3 achieved V(V) removal of 62.2%, 72.1% and 98.2% at pH 3.0, respectively (Figure 3). CS2C@SBA−3 demonstrated the highest efficiency in the removal of V(V). Furthermore, the removal of V(V) can be strongly influenced by the mass ratio of SBA−15/CS2−chitosan. With the increase of SBA−15/CS2−chitosan mass ratio, the removal efficiency was remarkably enhanced since there were more functional groups grafted on the surface of the composites, which acted as reactive sites to remove V(V). However, the removal efficiency of V(V) by CS2C@SBA−3 decreased from 98.2% to 4.6% with the increase of solution pH from 2.0 to 10.0, while it decreased from 62.2% and 72.1% to 4.5% and 4.6% for CS2C@SBA−1 and CS2C@SBA−2, respectively (Figure 3). Hence, the optimum pH value for the removal of V(V) was determined as 3.0. The pHzpc of CS2C@SBA−3 is 6.9 (Figure 1B) which suggested a negative surface charge at pH over 6.9. Vanadium anions were reported to mainly exist as H2V10O284−, H2VO4− and H3V10O283− at pH 3.0 [2]. Therefore, positively charged CS2C@SBA−3 should have an electrostatic attraction with V(V) oxyanions at solution pH 3.0, favoring the adsorption of V(V) oxyanions. The analysis above suggests a strong co−relationship between pH value and the removal of V(V). An acidic environment favored the immobilization of V(V) by CS2C@SBA−3.

![Figure 3](image-url)

**Figure 3.** Effects of pH on V(V) elimination. Conditions: V(V) initial concentration = 100 ppm, CS2C@SBA dosage = 1.0 g/L, experimental temperature = 298 K, contact time = 24 h.

2.2.2. Effects of the Dosage of CS2C@SBA−3

To determine the effects of the dosage of CS2C@SBA−3, a series of different dosages were examined in a 100 ppm V(V) solution. As the dosage increased from 0.1 to 2.0 g/L, the removal efficiency of V(V) increased from 31.2% to 99.7% (Figure 4). This might be attributed to the increase of the density of reactive sites on the surface. However, the removal efficiency of V(V) increased only slightly with increases in dosage from 1.0 to 1.5 and 2.0 g/L. The phenomena suggested that the removal of V(V) attained an equilibrium with the dosage of CS2C@SBA−3 higher than 1.0 g/L. Thus, the adsorption
capacity decreased from 312.44 to 49.85 mg/g along with the increase of the dosage of CS$_2$C@SBA−3 (Figure 4). The moles ratio of V(V) to CS$_2$C@SBA−3 higher than 1.0 g/L. Thus, the adsorption capacity decreased from 312.44 to 49.85 mg/g along with the increase of the dosage of CS$_2$C@SBA−3 did not reach saturation point in those cases.

![Figure 4](image-url)

**Figure 4.** Effects of the dosage of CS$_2$C@SBA−3 on the removal of V(V). Conditions: V(V) initial concentration = 100 ppm, pH value = 3.0, experimental temperature = 298 K, contact time = 24 h.

2.3. Adsorption Kinetics

Figure 5A–C and Table 2 show the kinetics of the elimination of V(V). The effects of reaction time were investigated in a 100 ppm V(V) solution. Within the initial 5 min, 48.9% of V(V) was removed by CS$_2$C@SBA−3 (Figure 5A). The elimination rate was fast in the first 10 min. These results might be attributed to the abundance of reactive sites on the surface of CS$_2$C@SBA−3 which were quickly enriched with V(V). After 360 min of reaction, an equilibrium was reached, with 98.2% removal of V(V) due to the saturation of reactive sites (Figure 5A). Based on the data, the maximum adsorption capacity was calculated as 98.24 mg/g. The kinetics data were carefully fitted by both pseudo–first–order model and pseudo–second–order models. The regression coefficient ($R^2$) values of pseudo–second–order model were higher (0.9999) compared with pseudo–first–order model ($R^2 = 0.9851$) and Elovich model ($R^2 = 0.8788$) (Figure 5B–D). Hence, the pseudo–second–order kinetic model fitted better than the pseudo–first–order kinetic model and Elovich model did. The phenomena indicated that the elimination of V(V) by CS$_2$C@SBA−3 was primarily directed by the chemisorption [37,40,42,43].

| Models                        | Parameters | $R^2$   |
|-------------------------------|------------|---------|
| Pseudo–first–order model      | $K_1$ (min$^{-1}$) 0.014 | $Q_e$ (mg·g$^{-1}$) 39.813 | $R^2$ 0.9851 |
| Pseudo–second–order model     | $K_2$ (mg·g$^{-1}$·min$^{-1}$ 0.001 | $Q_e$ (mg·g$^{-1}$) 98.045 | $R^2$ 0.9999 |
| Elovich model                 | $\alpha$ (mg·min$^{-1}$·g$^{-1}$ 41.341 | $\beta$ (mg·g$^{-1}$) 9.057 | $R^2$ 0.8788 |
| Langmuir model                | $Q_m$ (mg·g$^{-1}$) 221.193 | $K_L$ (L·mg$^{-1}$) 0.260 | $R^2$ 0.9982 |
| Freundlich model              | $n$ 4.252 | $K_f$ (mg$^{1-n}$·L$^n$·g$^{-1}$) 65.663 | $R^2$ 0.9218 |

Table 2. The parameters of kinetic and thermodynamics models for the adsorption of V(V) on CS$_2$C@SBA−3.
Figure 5. Kinetics studies. (A) V(V) removal percentage versus time; (B) fitted results for linearized pseudo-first order; (C) pseudo-second order kinetic models; and (D) Elovich model. Conditions: V(V) initial concentration = 100 ppm, CS\textsubscript{2}C@SBA–3 dosage = 1.0 g/L, pH value = 3.0, experimental temperature = 298 K.

2.4. Adsorption Isotherm

To identify the adsorption interaction and the type of adsorption, adsorption isotherms were investigated at a series of initial V(V) concentrations (10–500 ppm). Figure 6 and Table 2 show the isotherm results of V(V) removal. The V(V) removal efficiency decreased from 98.6% to 43.6% while the adsorption capacity increased from 8.64 to 218.00 mg/g along with the increase of V(V) concentration from 10 to 500 ppm (Figure 6A). Two different isotherm models including Langmuir and Freundlich ones were used to fit the data [44,45]. From the parameters listed in Table 2, the Langmuir model fitted better than Freundlich models, since their correlation coefficient (R\textsuperscript{2}) were 0.9982 and 0.9218, respectively (Figure 6B and Table 2). From the calculation results of the Langmuir model, Q\textsubscript{m} of CS\textsubscript{2}C@SBA–3 is 221.19 mg/g which is appropriately equal to the measured experimental value (218.00 mg/g) (Table 2). The phenomena suggested that the adsorption of V(V) by CS\textsubscript{2}C@SBA–3 was based on the assumption of monolayer distribution of V(V) on the surface of CS\textsubscript{2}C@SBA–3 and no lateral interaction between V(V) and CS\textsubscript{2}C@SBA–3 [46,47]. As long as a molecule occupies the reactive site on CS\textsubscript{2}C@SBA–3, there is no adsorption that can take place at this site any more.
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Figure 6. Isotherm studies. (A) removal efficiency versus V(V) initial concentration, (B) adsorption capacity versus equilibrium concentration. Conditions: CS_{2}C@SBA−3 dosage = 1.0 g/L, pH value = 3.0, experimental temperature = 298 K, contact time = 24 h.

2.5. Effects of Competing Anions

In real wastewater or groundwater, there are abundant co–existing anions which may have negative impacts on the removal of V (V). The co–existing anions may compete with V(V) for the reactive sites on the surface of composites. Thus, to simulate the real groundwater, the effects of co–existing anions (60 ppm PO_{4}^{3−}, 600 ppm SO_{4}^{2−}, 400 ppm NO_{3}^{−}, 400 ppm HCO_{3}^{−}) and 60 ppm Cu^{2+} and ionic strength (0.01, 0.1, and 0.3 M) on the removal of V(V) were studied [11,48].

Figure 7A,B indicate the impacts of various of co–existing anions and ionic strength on the elimination of V(V) by CS_{2}C@SBA−3. CS_{2}C@SBA−3 showed a predominant selectivity for the uptake of V(V). Despite of the presence of the competing anions, over 98.0% of V(V) could be removed from the solution except for two cases in the presence of 600 ppm SO_{4}^{2−} and 400 ppm HCO_{3}^{−}. The removal efficiency rates of V(V) were 95.9% and 97.2% in the presence of SO_{4}^{2−} and HCO_{3}^{−}, respectively (Figure 7A). This could be attributed to slight competition on reactive sites between V(V) and the two anions. Furthermore, the ionic strength demonstrated only slight impacts on the elimination of V(V) by CS_{2}C@SBA−3 because V(V) removal efficiency could achieve over 98.0% in a wide range of NaCl concentrations from 10 to 300 ppm (Figure 7B). All the aforementioned results suggest a promising performance of CS_{2}C@SBA−3 in the presence of common anions in wastewater or groundwater.

Figure 7. Effects of co–existing ions (A), effects of ionic strength (B) and the elimination of V(V) in real water samples (C). Conditions (A,B): V(V) initial concentration = 100 ppm V(V), and 60 ppm PO_{4}^{3−}, 600 ppm SO_{4}^{2−}, 400 ppm NO_{3}^{−}, 400 ppm HCO_{3}^{−} and 60 ppm Cu^{2+}, CS_{2}C@SBA−3 dosage = 1.0 g/L, experimental temperature = 298 K, contact time = 24 h; Condition(C): V(V) initial concentration = 10 ppm, CS_{2}C@SBA−3 dosage = 1.0 g/L, experimental temperature = 298 K, contact time = 24 h.
2.6. The Elimination of V(V) in Real Waters

In order to evaluate the practical potential of CS$_2$C@SBA−3, the elimination of V(V) was tested in three types of real water samples including lake, pond and tap waters. At pH 3.0, the removal efficiency of V(V) from lake, pond and tap waters was 99.5%, 99.8% and 99.3% respectively (Figure 7C). The results indicated that CS$_2$C@SBA−3 was highly efficient in real water bodies. However, V(V) removal efficiency by CS$_2$C@SBA−3 decreased to 77.5%, 75.2% and 75.4% in lake, pond and tap waters, respectively, at a local pH of 8.0 (Figure 7C). Hence, we can conclude that pH value has a significant impact on the removal of V(V), which was consistent with our previous results in Section 2.2.1. The dramatic decrease of V(V) removal may be attributed to the electrical repulsion between negatively charged CS$_2$C@SBA−3 and V(V) oxyanions at pH 8.0. The results suggest that CS$_2$C@SBA−3 can be successfully employed for the remediation of V(V) in real wastewater with appropriate adjustment of pH value.

2.7. Mechanism for V(V) Removal by CS$_2$C@SBA−3

SEM−EDS analysis was conducted to investigate the morphology and elemental composition of CS$_2$C@SBA−3 before and after the remediation of V(V). Figure 8A–E and Figure S4 show the structure and morphology of CS$_2$C@SBA−3 after the reaction. Comparing with Figure 2E,F, SBA-15 was still coated with CS$_2$−chitosan uniformly and there was nearly no obvious change on the morphology after treatment with 100 ppm V(V) for 24 h. Table 3, Figures S5 and S6 show the results of EDS elemental mapping of CS$_2$C@SBA−3 before and after the reaction. The results are consistent with the results of elemental analysis which can be considered as solid evidence supporting the successful complexation of the composites (Tables 1 and 3). Before the reaction, no signal of V was detected (Figure 8F). After treatment with large amounts of vanadium ions, CS$_2$C@SBA−15 was enriched with V which accounted for 12.2 wt% of the composite (Figure 8G and Table 3). The results once again indicated that large amounts of V(V) were adsorbed on the surface of CS$_2$C@SBA−3.

Figure 8. SEM−EDS images of CS$_2$C@SBA−3 before adsorption with V(V) (A) and EDS elemental mapping images (B,F), SEM−EDS images of CS$_2$C@SBA−3 after adsorption with V(V) (C) and EDS elemental mapping images (D,E,G). Conditions: V(V) initial concentration = 100 ppm, CS$_2$C@SBA−3 dosage = 1.0 g/L, pH value = 3.0, experimental temperature = 298 K, contact time = 24 h.
were 51.2% and 48.8%. After the reaction with V(V), a new S 2p XPS peak appeared at 163.1 and 161.8 eV could be attributed to the sulphur species of CS 2C@SBA. The results indicated that 73.1% of V(V) was reduced to V(IV) and V(III) on the surface of CS 2C@SBA–3 (Figure 9B, Figures S7 and S8 show the XPS survey spectra of CS 2C@SBA–3 before and after the reaction. Comparing these two XPS results, there was a distinct signal of V 2p at 516.8 eV which could prove the adsorption of V(V) on the surface of CS 2C@SBA–3 (Figure 9B) [39]. To illustrate the mechanism of the reduction of V(V) by CS 2C@SBA–3, XPS spectra of V 2p, V 2p1/2 and V 2p2/3 are provided in Figure 9C, D and E, respectively. There were three peaks at binding energies of 524.0, 516.8, and 513.3 eV, which occupied 26.9%, 66.9% and 6.6% of peak area, respectively (Figure 9C). The three peaks in XPS spectra of V 2p were characteristic of V 2O5, V(IV), and V(III) respectively [52,53]. The results indicated that 73.1% of V(V) was reduced to V(IV) and V(III) on the surface of CS 2C@SBA–3 (Figure 9C–E).

Table 3. Elemental composition of CS 2C@SBA–3 before adsorption and after adsorption.

| Adsorbent | Elemental Composition a (wt %) |
|-----------|--------------------------------|
| CS 2C@SBA–3 before adsorption | C Si O N S V |
| 52.5 | 4.5 | 32.7 | 5.5 | 1.8 | 0.0 |
| CS 2C@SBA–3 after adsorption b | 46.3 | 5.8 | 32.6 | 2.7 | 0.4 | 12.2 |

a determined by EDS. b Conditions: V(V) initial concentration = 100 ppm, CS 2C@SBA–3 dosage = 1.0 g/L, pH value = 3.0, experimental temperature = 298 K, contact time = 24 h.

FTIR and XPS measurement was further conducted to uncover the deeper mechanisms at work. Figure 9A–F reveals the results of FTIR spectra and XPS spectra of CS 2C@SBA–3 before and after the reaction with V(V). The bands stretching at 3454, 2924, 2854, 1632 and 1465 cm−1 represents the presence of –OH/–NH2/–SH, –CH3, –CH2, –CNH, and –C=S, respectively, on CS 2C@SBA–3 after the reaction (Figure 9A) [49–51]. Figure 9B, Figures S7 and S8 show the XPS survey spectra of CS 2C@SBA–3 before and after the reaction. The XPS results, there was a distinct signal of V 2p at 516.8 eV which could prove the adsorption of V(V) on the surface of CS 2C@SBA–3 (Figure 9B) [39]. To illustrate the mechanism of the reduction of V(V) by CS 2C@SBA–3, XPS spectra of V 2p, V 2p1/2 and V 2p2/3 are provided in Figure 9C, D and E, respectively. There were three peaks at binding energies of 524.0, 516.8, and 513.3 eV, which occupied 26.9%, 66.9% and 6.6% of peak area, respectively (Figure 9C). The three peaks in XPS spectra of V 2p were characteristic of V 2O5, V(IV), and V(III) respectively [52,53]. The results indicated that 73.1% of V(V) was reduced to V(IV) and V(III) on the surface of CS 2C@SBA–3 (Figure 9C–E).

The successful synthesis of CS 2C@SBA–3 introduced organic functional groups including –SH, –OH, –NH2 to the composite which can enable the adsorption coupled reduction of V(V). Figures 1D and 9F demonstrate the results of the XPS spectra of S 2p before and after the elimination of V(V), respectively. Before the reaction with V(V), S 2p XPS peaks at 163.1 and 161.8 eV could be attributed to the sulphur species of CS 2C@SBA–3. Figures 1D and 9F demonstrate the results of the XPS spectra of S 2p before and after the elimination of V(V), respectively. Before the reaction with V(V), S 2p XPS peaks at 163.1 and 161.8 eV could be attributed to the sulphur species of CS 2C@SBA–3. Figures 1D and 9F demonstrate the results of the XPS spectra of S 2p before and after the elimination of V(V), respectively. Before the reaction with V(V), S 2p XPS peaks at 163.1 and 161.8 eV could be attributed to the sulphur species of CS 2C@SBA–3. Figures 1D and 9F demonstrate the results of the XPS spectra of S 2p before and after the elimination of V(V), respectively. Before the reaction with V(V), S 2p XPS peaks at 163.1 and 161.8 eV could be attributed to the sulphur species of CS 2C@SBA–3. Figures 1D and 9F demonstrate the results of the XPS spectra of S 2p before and after the elimination of V(V), respectively. Before the reaction with V(V), S 2p XPS peaks at 163.1 and 161.8 eV could be attributed to the sulphur species of CS 2C@SBA–3.
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XPS peaks at 163.1 and 161.8 eV could be attributed to the sulphur species of CS2H and CS2H+ or CS2H2+. The new peak at 529.8 eV indicated the presence of V2O5, as illustrated in Figure 9D [53]. The weak peak at 540 cm−1 in FTIR spectra also confirmed the formation of disulfide bonds (−S−S−) in this catalytic reduction process.

The decrease of the density of −OH was most likely attributable to the formation of hydrogen bonds between the V species and hydroxyl groups. As discussed above, the reaction between the CS2C@SBA−3 and V(V) species is a catalytic reduction process in which most of V(V) (73.1%) is reduced into V(IV) and V(III) species which are less toxic. A small amount of V(V) was transformed into V(V) oxide, V2O5. Meanwhile, the abundance of functional groups −NH− dramatically decreased from 80.6% to 3.2% after the elimination of V(V). The results suggest that large amounts of V(V) occupied −NH−. We could conclude that −NH− constituted the dominant adsorption site for V(V) among the nitrogen functional groups. Furthermore, O 1s XPS spectra located at binding energies of 533.4, 532.6 and 531.8 eV corresponded to C−O−C, −CH2OH and −C−O−Si, respectively (Figure 10C,D) [56].

The functional group −SH is the dominant reactive site for reducing V(V) and was oxidized into disulfide bonds (−S−S−) in this catalytic reduction process.

Figure 10. The XPS high-resolution of N 1s of CS2C@SBA−3 before adsorption (A), and after adsorption (B). The XPS high-resolution of O 1s of CS2C@SBA−3 before adsorption (C), and after adsorption (D). Conditions: V(V) initial concentration = 100 ppm, CS2C@SBA−3 dosage = 1.0 g/L, pH value = 3.0, experimental temperature = 298 K, contact time = 24 h.
2.8. Recycling Application

As recyclability is one of the most important factors to judge the practical potential of these findings, a series of recycling application experiments were conducted. Figure 11 shows the removal efficiency of V(V) in five consecutive adsorption–desorption cycles. The removal efficiency of V(V) by CS$_2$C@SAB–3 decreased from 98.2% to 90.8% from the first to the fifth cycle of application. The results suggested that a V(V) removal up to 90.0% could be achieved after five adsorption–desorption cycles. Thus, CS$_2$C@SAB–3 can be regarded as a promising composite for the elimination of V(V) via catalytic reduction coupled adsorption process with satisfying reusability and good practical potential.

![Figure 11. Effects of recyclability of CS$_2$C@SAB–3 on V(V) removal. Condition: V(V) initial concentration = 100 ppm, CS$_2$C@SBA–3 dosage = 1.0 g/L, pH value = 3.0, experimental temperature = 298 K, contact time = 24 h.](image)

3. Materials and Methods

3.1. Materials

Deionized water (DI water, 18.2 MΩ·cm$^{-1}$) was obtained from Lichen water purifier UPTA. Chitosan was purchased from Meryer (Shanghai, China) without any purification. NaOH (≥96.0%), HCl (38.0%), NH$_3$·H$_2$O (28%), Na$_3$PO$_4$·12H$_2$O (98%), NaNO$_3$ (99.0%), NaHCO$_3$ (≥99.8%), Na$_2$SO$_3$ (99%) and CS$_2$ (99.9%) were purchased from Hushi (Shanghai, China). Glutaraldehyde (50% v/v) and sodium metavanadate (NaVO$_3$, 99.9%) were obtained from Aladdin. All the chemicals mentioned above were used at analytical grade without further purification.

3.2. Preparation of SBA-15, CS$_2$–Chitosan and CS$_2$C@SBA

SBA-15 and modified dithiocarbamate chitosan (CS$_2$–Chitosan) was synthesized based on the methods in previous literature [49]. Details can be found in Texts S1 and S2 respectively. CS$_2$C@SBA was synthesized by the following method. Initially, 0.60 g CS$_2$–chitosan was dissolved in 100 mL acetic acid solution (1.2% v/v). Then, different dosages of SBA-15 were added (mass ratios SBA-15: CS$_2$–chitosan = 1:2, 1:1 and 2:1). According to these mass ratios, CS$_2$C@SBA composites are named as CS$_2$C@SBA–1, CS$_2$C@SBA–2 and [57,58] CS$_2$C@SBA–3, respectively. Afterwards, the above mixture was stirred for 30 min at 313 K, followed by the addition of 0.50 mL glutaraldehyde (50.0% v/v) and further stirred for 2 h. After that, the pH of the mixture was adjusted to 9.0 by adding 0.1M NaOH, and stirred for 30 min. Finally, the solid suspension was filtered, washed several times with distilled water and dried at 333 K overnight.
3.3. Characterizations

Fourier Transform Infrared Spectra (FTIR) was measured by Nicolet 5700 spectrometer through the KBr pellet method over a wavelength range from 400 to 4000 cm$^{-1}$ under a 4 cm$^{-1}$ resolution. The Scanning Electron Microscopy (SEM) was performed on SEM Virion 200 combined with an electron dispersive X-ray (EDS) analyzer. The Transmission Electron Microscopy (TEM) was conducted on JEM-2100. The Brunauer–Emmett–Teller (BET) pore properties of materials were measured via Belsorp–mini. Before the N$_2$ adsorption–desorption measurement, the composite was dried and degassed at 373 K under vacuum for 24 h. The X-ray diffraction (XRD, MiniFlex600, Japan) was conducted with radiation of Cu K$\alpha$ and scanning rate of 0.2°/min from 0.6° to 2.5° and 5°/min from 10° to 80°. Zeta potentials of the materials were measured by the Zetasizer Nano series at different pH (2.0–9.0). Firstly, 150 mg of composite was added into a plastic conical flask containing 65 mL DI water. Then the flask was mechanically shaken for 24 h. The resultant suspension was collected for zeta potentials determination in 0.01 mM NaCl solution. The pH was adjusted with 0.01 mM NaOH and HCl. The point of zero charge (pH$_{ZPC}$) was calculated by the zeta potentials under different pHs. The X-ray photoelectron spectroscopy (XPS) equipped with Al/Mg K$\alpha$ X-ray source with 30 eV pass energy in 0.5 eV step over an area of 650 mm $\times$ 650 mm to the samples was carried out (ESCALAB 250Xi) at vacuum of 10$^{-9}$ Torr, and the results were corrected by a reference of the C 1s peak from adventitious carbon at 284.8 eV and fitted with the Shirley method of background subtraction on XPSpeak4.1 Software.

3.4. Adsorption Experiments

The stock solution of V(V) (1000 ppm) was prepared by dissolving NaVO$_3$ with DI water. The effects of pH (2.0–10.0) on vanadium removal was conducted by adding 30 mg CS$_2$C@SBA composites into 30 mL of V(V) solution (100 ppm) under stirring (200 rpm) at normal temperature for 24 h. The pH of solutions was adjusted by 0.1 M HCl and NaOH. The effect of adsorbent dosage was conducted in 25 mL V(V) solution (100 ppm) with varying adsorbent dosages (0.1, 0.3, 0.5, 1.0, 1.5 and 2 g/L). The kinetics experiment was conducted by adding 30 mg CS$_2$C@SBA composites into 30 mL of V(V) solution (100 ppm) at pH 3.0 under stirring (200 rpm) at 298 K. The contact time was studied from 5 min to 12 h. The adsorption isotherm experiment was conducted by adjusting the concentration of V(V) from 10 to 500 ppm adding 1 g/L CS$_2$C@SBA. In all experiments, the residual concentration of total V was measured by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP–AES, Agilent 5110). Adsorption capacity ($q_t$) (mg/g) and percentage removal (%) were calculated by the following equations [41,59,60].

$$q_t = \left( C_0 - C_t \right) \frac{V}{m}$$  \hspace{1cm} (1)

$$\% \text{Removal} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100$$  \hspace{1cm} (2)

where $C_0$ and $C_t$ are, respectively, the initial concentration and equilibrium concentration of total V (ppm); $V$ is the solution volume (mL) while m is the adsorbent amount (g).

The results of the adsorption kinetic data were fitted by two models, pseudo–first–order, pseudo–second–order and Elovich models, as indicated below [10,61,62].

$$\ln(q_e - q_t) = \ln q_t - k_1 t$$  \hspace{1cm} (3)

$$\frac{t}{q_t} = \frac{1}{k_2 q_t^{2/3}} + \frac{t}{q_e}$$  \hspace{1cm} (4)

$$q_t = \frac{1}{\beta} \ln(1 + \beta t)$$  \hspace{1cm} (5)
where $q_e$ and $q_t$ are, respectively, the adsorbed capacity of V(V) on CS$_2$C@SBA$-3$ at equilibrium time and time t. $k_1$ (1/min) and $k_2$ (g/mg·min) are, respectively, the adsorption rate constants for pseudo—first—order and pseudo—second—order models. $a$ (mg·min/g) is the initial rate constant and $\beta$ (mg/g) is the desorption constant for Elovich model;

To determine the adsorption isotherm, Langmuir and Freundlich models are fitted to calculate the adsorption data, as indicated as the following equations [63]:

$$\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m}$$  \hspace{1cm} (6)

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$  \hspace{1cm} (7)

where $q_e$ and $q_m$ are, respectively, the adsorption capacity at equilibrium and the maximum adsorption capacity of V(V) by CS$_2$C@SBA$-3$. $C_e$ (ppm) is the concentration of V(V) at equilibrium. $K_L$ (L/mg) and $K_f$ ((mg/g)/(mg/L)$^{1/n}$) are, respectively, the Langmuir and Freundlich constants.

3.5. Regeneration and Recycle Experiments

To explore the recyclability of the material, the desorption was performed by using 25 mL NaOH solution (0.50 M) as the eluent at 298 K with 1 g/L CS$_2$C@SBA$-3$, and then using 0.01 M Na$_2$S$_2$O$_3$ solution to regenerate the oxidized disulfide bonds. The regenerated CS$_2$C@SBA$-3$ was employed to eliminate V(V) again, followed by the regeneration procedures. The experiment was repeated for five cycles. During the recycle experiments, the removal of V(V) was measured.

3.6. Effects of Groundwater Impurities

To investigate the effects of co—existing anions (60 ppm PO$_4^{3-}$, 600 ppm SO$_4^{2-}$, 400 ppm NO$_3^-$, 400 ppm HCO$_3^-$) and 60 ppm Cu$^{2+}$, based on the typical concentration of common ions in ground water, 1 g/L CS$_2$C@SBA$-3$ was tested in 100 ppm V(V) solution at pH 3.0 for 24 h at 298 K. The effects of ionic strength were studied in 100 ppm V(V) solution at pH 3.0 for 24 h at 298 K with varying NaCl concentrations (10, 100 and 300 mM).

3.7. V(V) Elimination Assays in Spiked Real Water

The applicability of the adsorbent was also tested in spiked real water samples (10 ppm V(V)) including lake water, pond water and tap water collected from Wuhan at pH 3.0 and at their local pH 8.0. The physical and chemical properties of these samples are listed in Table S2.

4. Conclusions

In this study, dithiocarbamate chitosan modified SBA-15 (CS$_2$C@SBA) was successfully synthesized via a facile and robust procedure. Among the three CS$_2$C@SBA composites, CS$_2$C@SBA$-3$ which embraced the highest mass ratio of dithiocarbamate chitosan showed the most efficient performance in the elimination of V(V). At 298 K, a V(V) removal efficiency of 98.2% was achieved by 1 g/L CS$_2$C@SBA$-3$ in a solution containing 100 ppm of V(V). In that case, the adsorption capacity by CS$_2$C@SBA$-3$ was 218.00 mg/g. The adsorption kinetics fitted better with pseudo—second—order model ($R^2 = 0.9999$), indicating that the elimination of V(V) by CS$_2$C@SBA$-3$ was primarily triggered by chemisorption. The adsorption isotherm followed the Langmuir model ($R^2 = 0.99981$), revealing the monolayer adsorption on the surface of CS$_2$C@SBA$-3$. FTIR, SEM—EDS and XPS characterization results demonstrated that the functional group —SH played a vital role, acting as a proton—coupled electron donor to reduce 73.5% V(V) into V(IV) and V(III) and transformed residual V(V) into V(V) oxide V$_2$O$_5$. Via the reduction of high—valent vanadium, its toxicity was reduced significantly. Furthermore, CS$_2$C@SBA$-3$ displayed high selectivity towards V(V) elimination in the presence of various co—existing ions in synthetic and spiked real water samples which could be attributed to the abundant —NH— on its surface.
Hence, we can conclude that CS₂C@SBA−3 is a promising composite to eliminate V(V) via an adsorption coupled catalytic reduction mechanism, with good practical potentials. CS₂C@SBA−3 can be applied in the reductive elimination of high–valent heavy metals in efficient remediation of water pollution.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12111469/s1. Text S1: Details of synthesis procedures of SBA-15; Text S2: Details of synthesis procedures of CS₂−chitosan; Figure S1: Nitrogen sorption isotherms of SBA-15 and CS₂C@SBA−3; Figure S2: The XRD patterns of preparation composite; Figure S3: TEM images of SBA-15 and CS₂C@SBA−3; Figure S4: SEM images of CS₂C@SBA−3 after reaction with V(V); Figure S5: EDS elemental mapping images of CS₂C@SBA−3 before reaction with V(V); Figure S6: EDS elemental mapping images of CS₂C@SBA−3 after reaction with V(V); Figure S7: The XPS survey spectra of CS₂C@SBA−3 before reaction; Figure S8: The XPS survey spectra of CS₂C@SBA−3 after reaction; Table S1: Porous properties of SBA-15 and CS₂C@SBA−3; Table S2: Physico-chemical properties of water samples used in this study.

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**Abbreviations**

Santa Barbara Amorphous type 15 material (SBA-15); Dithiocarbamate chitosan (CS₂−chitosan); Dithiocarbamate chitosan modified SBA-15 (CS₂C@SBA); Vanadium(V) [V(V)]; Fourier Transform Infrared Spectra (FTIR); Scanning Electron Microscopy with an electron dispersive X-ray (SEM-EDS); Brunauer-Emmett-Teller (BET); X-ray diffraction (XRD); Transmission Electron Microscopy (TEM); X-ray photoelectron spectroscopy (XPS).

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