Efficient Removal of Cr(VI) Ions by a Novel Magnetic 4-Vinyl Pyridine Grafted Ni₃Si₂O₅(OH)₄ Multiwalled Nanotube

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**ABSTRACT:** The contamination of water systems by heavy metals greatly threatens human health and ecological safety. An efficient adsorbent is critical for the removal of these contaminants. In this work, magnetic Ni₃Si₂O₅(OH)₄ nanotubes (NTs) have been synthesized via in situ hydrothermal reduction and further functionalized by grafting poly(4-vinyl pyridine) (P4VP) brushes on its surface via atom transfer radical polymerization. Characterizations by Fourier transform infrared, X-ray diffraction, thermogravimetric analysis, transmission electron microscopy, and X-ray photoelectron spectroscopy proved that P4VP was successfully grafted on the surface of magnetic Ni₃Si₂O₅(OH)₄ NTs. The resultant Ni₃Si₂O₅(OH)₄-g-P4VP NTs are efficient nanosorbents for removing Cr(VI) anions from water. The Cr(VI) adsorption capacity of Ni₃Si₂O₅(OH)₄-g-P4VP NTs reaches 1.49 mmol/g at a pH of 3. The pseudo-second-order kinetic model and the Freundlich isothermal model are suitable to describe the adsorption process. The analysis using Weber−Morris and Boyd models indicates that both intraparticle diffusion and external film diffusion affect the Cr(VI) adsorption process. The adsorption enthalpy is estimated to be 18.37 kJ/mol. More than 90% of the Cr(VI) adsorption capacity of the Ni₃Si₂O₅(OH)₄-g-P4VP NTs remains after eight adsorption and desorption cycles.

1. INTRODUCTION

Chromium has been widely used in many industries, such as plating, ore smelting, leather, wood preserving, paper production, printing, and dyeing industries, which results in a large amount of chromium-contaminated effluents. Chromium exists in trivalent (Cr(III)) and hexavalent (Cr(VI)) states in aqueous solution. Excessive intake of chromium can cause various severe diseases, although chromium(III) is one of the essential microelements in the human body. Chromium(VI) is highly toxic due to its mutagenic and carcinogenic activity. The allowable maximum content of total chromium in drinking water has been limited to 100 and 50 μg/L by the United States Environmental Protection Agency and the World Health Organization, respectively. It is critical to reduce the discharge of chromium species into the water environment for environmental safety.

Chemical precipitation, ion exchange, membrane separation, and adsorption have been studied extensively for the removal of chromium contaminants. Adsorption of chromium species has been considered as one of the most promising and feasible methods due to its availability and efficiency. An efficient adsorbent is the primary factor for a successful adsorption process. An ideal adsorbent for wastewater treatment should satisfy the following criteria: (1) environmentally benign, (2) a high sorption capacity and high selectivity to contaminants particularly in extremely low concentration, (3) easy regeneration and recycling, (4) easy separation, and (5) rich and cheap in resources. Various adsorbents including synthetic polymers, biomass/biocomposites, waste tires, hydrogels/hydrogel composites, graphene oxide, and nanomaterials have been investigated in Cr(VI) removal. Each of them has its own advantages, for example, microgels are eco-friendly, biocompatible, and environmental stimuli-responsive; biomaterials derived from agricultural waste are abundant and of low-cost. However, few adsorbents were found meeting all criteria. Therefore, the development of an efficient Cr(VI) adsorbent with low cost is still a great challenge. Inorganic nanomaterials such as porous hematite nanoparticles, mesoporous MnFe₂O₄, carbon beads, and hydroxyapatite nanopowders have shown excellent adsorption performance to remove Cr(VI) and Pb(II) contaminants from water. However, the selectivity and capacity of these materials are limited by the availability of the adsorption sites. Furthermore, the separation of the nanophase...
adsorbents from water is also challenging. Functional modification is a promising way to improve the adsorption performance of the porous substrates. Polythiophene–Al2O3-based nanosorbent for Pb(II), Cd(II), and Zn(II) ions, silica nanopowders/alginate composite for Pb(II) ions, functionalized single-walled carbon nanotube (NT) for Cd(II), Cu(II), Pb(II), and Hg(II) ions, nano Uio-66-NH2 MOFs for Cr(VI) ions, and PAMPS-grafted-Ni3Si2O5(OH)4 NTs for the removal of Pb(II) ions are all excellent examples.

Chromium(VI) mainly exists in the form of anions. The one lone pair of electrons on the nitrogen atom of 4-vinylpyridine (4-VP) can either coordinate with heavy metal cations or be protonated to adsorb the oxygenated anions of the heavy metals. Grafting of 4-VP onto the polyethylene terephthalate fiber, divinylbenzene copolymer, and vinyltriethoxysilane-cellulose has been found to enhance the removal of Cr(VI) and U(VI). As to the difficulty in the separation of those nano-adsorbents from the treated water, introducing magnetism to the adsorbents or substrates has been proved to facilitate the separation process. Silicates, such as magnesium silicate, aluminum silicate, nickel silicate, and so forth, are promising adsorbent substrates due to large surface area and richness in surface hydroxyl groups. Introducing nickel, a known ferromagnetic metal, to the Ni3Si2O5(OH)4 NTs substrate by controlled reduction would endow the substrate with magnetism.

This work focuses on the preparation and evaluation of 4-vinylpyridine (4-VP)-modified magnetic Ni3Si2O5(OH)4 NTs for the efficient removal of Cr(VI). Various characterizations were employed to reveal the structure and properties of Ni3Si2O5(OH)4-g-4VP NTs. In Cr(VI) removal, batch experiments were conducted to investigate the dependent adsorption behavior including solution pH, contact time, and temperature on Cr(VI) removal efficiency. Furthermore, the adsorption kinetics, isotherms, and mechanisms were evaluated.

2. RESULTS AND DISCUSSION

2.1. Characterization of Ni3Si2O5(OH)4-g-4VP NTs.

The characterization results revealed the structure of the adsorbents, which indicates the successful preparation of Ni3Si2O5(OH)4-g-4VP NTs. Comparing the X-ray diffraction (XRD) patterns of Ni3Si2O5(OH)4 NTs before and after reduction, it is found that the reduced Ni3Si2O5(OH)4 NTs (Figure 1) show a new diffraction peak of nickel crystal phase. Transmission electron microscopy (TEM) images reveal that the NTs are well encapsulated inside the poly(4-vinyl pyridine) (P4VP) layers, and the thickness of P4VP brushes that grafted on the silicate NTs are circa 5 nm (Figure 2).

The FTIR peak at 1262 cm\(^{-1}\) (Figure 3b) observed on the salinized magnetic Ni3Si2O5(OH)4-g-4VP NTs is corresponding to the antisymmetric stretching vibration of –CH2Cl on (p-chloromethyl) phenyltrichlorosilane (CTS). The X-ray photoelectron spectroscopy (XPS) spectrum (Figure 4a) shows two peaks at about 197 eV and 230 eV corresponding to Cl 2p and Cl 2s, respectively. The ratio of [C]/[Cl] estimated from the peak areas of C 1s and Cl 2p is about 7.0:1.05, close to the theoretical value of CTS 7:1. The split peaks of C 1s at 284.6 and 286.2 eV (Figure 4b) are corresponding to C–C/C–H and C–Cl, respectively. The peaks at 200 and 202 eV corresponding to Cl 2p (Figure 4c) are due to the spin orbit splitting doublet of Cl 2p\(_{1/2}\) and Cl 2p\(_{3/2}\) in the benzyl chloride part of the silanization reagent. These characterizations prove the formation of CTS-salinized Ni3Si2O5(OH)4 NTs which provided an alkyl chlorine-terminated atom transfer radical polymerization (ATRP) initiator.
New peaks at 1601, 1556, 1418, and 1221 cm\(^{-1}\) (Figure 3c) corresponding to the stretching vibration of C=C and C=N in pyridine ring are observed on Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)-g-P4VP NTs. This indicates that the P4VP polymer brushes are successfully bound to the surface of magnetic Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\) NTs. The peak at 825 cm\(^{-1}\) is corresponding to the in-plane bending.
vibration of C−H in the polymer chain. The presence of nitrogen atoms, particularly the pyridine functional group in the samples, is evidenced by the N 1s peak at about 398.4 eV in XPS spectra (Figure 5). The peaks at 284.13 and 285.6 eV (Figure 5b) prove the presence of both the C−C chain and C−N groups in the sample. The decomposition temperature of magnetic Ni3Si2O5(OH)4-P4VP NTs (Figure 6d) is about 350 °C, which is coincident with the decomposition temperature of P4VP. The above characterizations illustrate the successful grafting of 4VP to magnetic Ni3Si2O5(OH)4 NTs which leads to the formation of Ni3Si2O5(OH)4-g-P4VP NTs. The reduced Ni3Si2O5(OH)4-g-P4VP NTs exhibit ferromagnetic behavior with a hysteresis loop. The value of the saturate magnetization (M) reaches circa 5.3823 emu·g−1 (Figure 7). The resultant reduced Ni3Si2O5(OH)4-g-P4VP NTs can be separated from water by applying an external magnetic field.

2.2. Effect of P4VP and the pH of Water on Cr(VI) Removal. Figure 8 compares the Cr(VI) capacity of both Ni3Si2O5(OH)4 NTs and Ni3Si2O5(OH)4-g-P4VP NTs. It clearly shows that P4VP greatly enhances adsorption of the Cr(VI) in a wide pH range. The pH of waste water from different sources could vary from one case to another, which somehow determines both the surface charge of the adsorbent and the form of chromium ions. The pH of water could control the chromium adsorption in turn. Figure 8 shows that the adsorption capacity of Ni3Si2O5(OH)4-g-P4VP NTs increases as the pH of the solution increases from 1 to 3 and reaches the maximum at the pH of 3. Without P4VP, the adsorption capacity of Ni3Si2O5(OH)4 NTs decreases monotonously with the increasing pH values. The equilibrium adsorption capacity of Cr(VI) on Ni3Si2O5(OH)4-g-P4VP NTs is 1.49 mmol/g, which is about 16 times higher than that of the magnetic Ni3Si2O5(OH)4 without P4VP. The grafting of 4-VP on magnetic Ni3Si2O5(OH)4 significantly improves the adsorption performance of the original substrate.

The equilibrium between the four forms of Cr(VI) in aqueous solution, H2CrO4, CrO42−, HCrO4−, and Cr2O72−, was examined at various pH values. The four existing forms are highly related to the pH value and Cr(VI) ion concentration of the solution, and the interconversion between these four forms are shown by eqs 1−3. Figure 9 shows the equilibrium concentration of these chrome ions at various pH values. Chromic acid (H2CrO4) dominates at a pH of less than 1; however, the dissociation of H2CrO4 increases significantly as the pH increases from 1 to 3. HCrO4− and CrO42− prevail in a pH of 3 to 5, while Cr2O72− dominates at pH above 7.

\[
\begin{align*}
H_2CrO_4 & \rightleftharpoons H^+ + HCrO_4^- \\
HCrO_4^- & \rightleftharpoons H^+ + CrO_4^{2-}
\end{align*}
\]

Figure 8. Effect of initial pH on adsorption of Cr(VI) by the magnetic Ni3Si2O5(OH)4 and the Ni3Si2O5(OH)4-g-P4VP NTs.

Figure 9. Distribution profiles of various Cr(VI) ions at different pH.
2HCrO$_4^-$ $\rightleftharpoons$ H$_2$O + Cr$_2$O$_7^{2-}$  

On the other hand, the surface charge of the adsorbents was examined by zeta potential measurement (Figure 10). Figure 10 shows that the surface of Ni$_3$Si$_2$O$_5$(OH)$_4$-g-P4VP NTs is positively charged at pH less than 3.8, while the surface of Ni$_3$Si$_2$O$_5$(OH)$_4$ NTs is positively charged only at pH less than 2.8. The presence of pyridine groups in P4VP provides the protonation sites for the adsorbent surface, which facilitates the adsorption of HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ at higher pH. The drastic decrease of the Cr(VI) adsorption capacity at pH above 4 suggests that the electrostatic attraction between the protonated pyridine group and the Cr(VI) anions is responsible for the high Cr(VI) adsorption capacity of Ni$_3$Si$_2$O$_5$(OH)$_4$-g-P4VP NTs. The behavior of Ni$_3$Si$_2$O$_5$(OH)$_4$ NTs under low pH is similar to that of other silicates, such as clay and bentonite. The dissolution of Ni$_3$Si$_2$O$_5$(OH)$_4$ NTs at pH less than 4 was observed. However, no nickel leaching of Ni$_3$Si$_2$O$_5$(OH)$_4$-g-P4VP NTs was detected by inductively coupled plasma-atomic emission spectroscopy after being treated with an acidic solution at pH of 1 for 3 h, which suggests that the P4VP polymer also acts as a protection coating for Ni$_3$Si$_2$O$_5$(OH)$_4$ NTs and prevents it from acid leaching.

2.3. Adsorption Kinetics. Adsorption kinetics has an important significance in the practical application of adsorbents, since it can help in determining the operation conditions of the adsorption process. The adsorption curve of Cr(VI) ions by the Ni$_3$Si$_2$O$_5$(OH)$_4$-g-P4VP NTs with time is illustrated in Figure 11. The Cr(VI) adsorbed on the Ni$_3$Si$_2$O$_5$(OH)$_4$-g-P4VP NTs increased rapidly in the initial 30 min, which accounts for about 75% of the equilibrium adsorption amount and then it slowly approaches an adsorption equilibrium. This is due to the large number of available adsorption sites on the surface of the adsorbent and the high solute concentration at the initial adsorption stage. As the adsorption progresses, more adsorption sites are occupied by Cr(VI) ions, and less adsorption vacancies and even lower Cr(VI) ion concentration in the solution lead to lower adsorption rate of the residual Cr(VI).

Typical kinetic models, the pseudo-first-order (PFO) model and pseudo-second-order (PSO) model, are represented by eqs 4 and 5, respectively. They are applied to analyze the adsorption kinetics data.

$$q_t = q_e (1 - e^{-kt})$$  

(4)

$$q_t = rac{q_e^2 k_2 t}{1 + q_e k_2 t}$$  

(5)

where $k_1$ (min$^{-1}$) and $k_2$ (g mmol$^{-1}$ min$^{-1}$) are the rate constants for PFO and PSO, respectively, while $q_e$ (mmol g$^{-1}$) and $q_t$ (mmol g$^{-1}$) are the amount of Cr(VI) removed by Ni$_3$Si$_2$O$_5$(OH)$_4$-g-P4VP NTs at time $t$ and equilibrium, respectively.

The kinetic model simulation results for the adsorption of Cr(VI) on the Ni$_3$Si$_2$O$_5$(OH)$_4$-g-P4VP NTs are shown in Figure 11. The adsorption kinetics constants, determination coefficient values ($R^2$), and chi-square ($\chi^2$) are given in Table 1. The values of $R^2$ for the PSO model are higher than those of the PFO model (Table 1). Furthermore, the values from theoretical calculation ($q_{cal}$) of the PSO kinetics model are found to be consistent with the experimental ones ($q_{exp}$). It suggests that the PSO kinetics model is more suitable to represent the Cr(VI) adsorption kinetics on the Ni$_3$Si$_2$O$_5$(OH)$_4$-g-P4VP NTs.

2.4. Adsorption Isotherms. The isothermal adsorption was employed to determine the capacity, strength, and state of the adsorbent in the adsorption process, which is helpful to further understand the adsorption mechanism. The adsorption curves of Cr(VI) ions by the Ni$_3$Si$_2$O$_5$(OH)$_4$-g-P4VP NTs at various temperatures are illustrated in Figure 12. It clearly shows that increasing both the equilibrium concentration and temperature favors the adsorption of Cr(VI) ions.

Two most important adsorption isotherm models, the Langmuir and Freundlich isotherm models as shown in eqs 6 and 7, respectively, are employed to analyze the adsorption of Cr(VI) ions on the magnetic Ni$_3$Si$_2$O$_5$(OH)$_4$-g-P4VP NTs.
experimental data better. The values of the Freundlich isotherm model is about 4.5 (Table 2), which takes place on heterogeneous surfaces. The exponent \( n \) of the empirical equation assuming that the adsorption process is better for this adsorption process. The Freundlich isotherm is closer to the experimental values, while the Langmuir isotherm somehow diverges at higher equilibrium concentrations. This also suggests that the Freundlich model is the maximum adsorption loading against the pollutants, \( q_{\text{max}} \), which is the ideal adsorption capacity toward Cr(VI). Compared with other magnetic nano-adsorption materials (Table 3), the preparation process of the Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)g-P4VP NTs is simpler, and the magnetic property can be achieved via in situ hydrothermal reduction without introducing additional magnet species.

### 2.5. Sorption Thermodynamics

The Cr(VI) adsorption capacity is found decreasing with the increase of temperature (Table 4). The thermodynamic analysis shows the exothermic nature of the Cr(VI) adsorption process.\(^7\) The Gibb’s free-energy change (\( \Delta G^0 \)) can be evaluated from eq 8. The Gibbs free-energy change is also related to enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)) at constant temperature by eq 9.

\[
\Delta G^0 = -RT \ln K_L
\]

\[
\ln K_L = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]

where \( K_L \) (L·mmol\(^{-1}\)) and \( K_F \) (mmol\(^{-1/\alpha}\)·L\(^{1/n}\)·g\(^{-1}\)) represent the Langmuir and Freundlich constants, respectively. \( q_e \) (mmol·g\(^{-1}\)) is the amount of Cr(VI) loaded on Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)g-P4VP NTs at equilibrium, \( q_{\text{max}} \) (mmol·g\(^{-1}\)) is the maximum adsorption loading against the pollutants, \( C_e \) (mmol·L\(^{-1}\)) is the residual Cr(VI) concentration, and \( n \) is the Freundlich heterogeneity factor.

The parameters of Langmuir and Freundlich isotherm models for Cr(VI) adsorption onto the Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)g-P4VP NTs at various temperatures are summarized in Table 2. The Cr(VI) adsorption on the adsorbents is spontaneous and favorable in the whole considered temperature range.\(^7\) The Cr(VI) adsorption entropy is 86.51 J·mol\(^{-1}\)·K\(^{-1}\), which indicates that the randomness of Cr(VI) at the solid/solution interface increased during the adsorption process.\(^77,78\) The negative values of the free-energy changes (\( \Delta G \)) confirm that the adsorption of Cr(VI) on the adsorbents is spontaneous and favorable in the whole considered temperature range.\(^7\) The Cr(VI) adsorption is more favorable at higher temperature since the free-energy change at higher temperature is more negative.\(^80\) The positive value of \( \Delta H \) indicates that Cr(VI) adsorption is endothermic and the Cr(VI) uptake increases with increasing temperature of the solution. This is consistent with the experimental findings. Similar results have been also observed using other adsorbents in Cr(VI) adsorption.\(^73,81\)

### 2.6. Regeneration and Recycling

The regeneration efficiency of the adsorbent is one of the key factors that affects industrial application. The magnetic Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)g-P4VP NTs possess abundant imine groups which exhibit electrostatic interaction with Cr(VI). The spent adsorbents are expected to be regenerated by ion exchange with OH\(^-\) in the base solution.
Morris model (eq 10) and Boyd model (eq 11) are employed to evaluate the rate-determining step in the adsorption process

\[ q_t = K_{id}t^{0.5} + C \]  

...(10)

\[ -\ln\left(1 - \frac{q_t}{q_e}\right) = K_{id}t \]  

...(11)

where \( q_t \) and \( q_e \) (mmol/g) are the amount of adsorbate adsorbed at time \( t \) (min) and at equilibrium, respectively, \( K_{id} \) is the diffusion rate constant, and \( C \) indicates the thickness of the boundary layer.

According to the Weber–Morris model, if \( q_t \) versus \( t^{1/2} \) is a straight line passing through the origin, the rate of the sorption process can be considered as an intraparticle diffusion-limiting process.\(^{63,85}\) However, if the plots are multilinear, then the sorption process is controlled by two or more steps. Figure 15 shows that \( q_t \) versus \( t^{1/2} \) has two distinct regions which suggests that the adsorption process includes two stages. The first steep portion of the curve is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intraparticle diffusion is the rate-limiting step. As can be seen from Table 5, the model coefficient \( K_{id1} \) (= 0.187) is greater than the model coefficient \( K_{id2} \) (= 0.043), which indicates that the diffusion speed in liquid film is faster than that in the particle.

The Boyd model assumes that the adsorption resistances are all concentrated at the boundary of adsorbent particles, that is,
the external diffusion is the rate-limiting step. Accordingly, the plot will yield a straight line passing through the origin if the adsorption is governed by intraparticle diffusion. Otherwise, the process is controlled by film diffusion.86,87 As can be seen from Figure 16, the Boyd plot of \( \ln(1 - q_t/q_e) \) versus \( t \) does not pass through the origin. Moreover, the correlation coefficients are not satisfactory for the Boyd model fitting of Cr(VI) ions adsorbed on the Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)\(_-\)P4VP NTs (Table 6), which indicates that the boundary layer diffusion is not the sole rate-controlling step. Therefore, both intraparticle diffusion and external film diffusion affect the adsorption of Cr(VI) ions on the Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)\(_-\)P4VP NTs.

3. CONCLUSIONS

A magnetic Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)\(_-\)P4VP NT adsorbent has been successfully prepared by partial reduction and ATRP. The Cr(VI) adsorption capacity of the resultant Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)\(_-\)P4VP NTs is up to 104.26 mg/g which is about 16 times higher than that of Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\) NTs. The reduction and grafting of P4VP does not change the bulk structure of Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\) NTs. The presence of a P4VP polymer brush grafting of P4VP does not change the bulk structure of Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\) NTs. Both the intraparticle and liquid film diffusion affects the adsorption of Cr(VI) NTs better for the Cr(VI) adsorption on magnetic Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)\(_-\)P4VP. (Table 5). The deionized water used in the following experiments was purified using an ultrapure reverse osmosis system (Chengdu Ultrapure Technology Co. China).

4. MATERIALS AND METHODS

4.1. Materials. Triethylamine, K\(_2\)Cr\(_2\)O\(_7\), NaBH\(_4\), methylbenzene, and ethanol were analytical grade and purchased from Kelong Co., Ltd. (Chengdu, China). CuCl, CuCl\(_2\), CTS (99%), and 4VP (>98%) were purchased from Aladdin Industrial Co. (Shanghai, China). Tris(2-dimethylaminooethyl) amine (Me6TREN, 99%) was purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Other reagents used were analytical grade. All chemical reagents and solvents are used without further purification. The deionized water used in the following experiments was purified using an ultrapure reverse osmosis system (Chengdu Ultrapure Technology Co. China).

4.2. Synthesis of Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)\(_-\)P4VP NTs. Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)\(_-\)P4VP NTs were prepared in four steps (Figure 17). First, Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\) NTs were prepared by a hydrothermal method according to the literature.88 Second, Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\) NTs were partially reduced by hydrothermal treatment with aqueous sodium borohydride to endow magnetism. Approximately 0.4 g of Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\) NTs were dispersed in a mixture of 100 mL of deionized water and 3.0 g of sodium borohydride, and then the mixture was sealed in a PPL-sealed autoclave for hydrothermal treatment at 180 °C for 10 h. The partially reduced Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\) NTs were rinsed several times with ethanol and deionized water alternately and dried for 24 h at 60 °C in a vacuum oven. Third, surface silylanization of the Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\) NTs with CTS was performed. Approximately 0.2 g of Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\) NTs was dispersed in a mixture of 15 mL of methylbenzene, 0.3 mL of TEA, and 0.1 mL of CTS, and the mixture was refluxed for 24 h at 25 °C. The Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)Cl NTs were rinsed several times with ethanol and deionized water alternately and dried for 12 h at 40 °C in a vacuum oven.

Table 5. Correlation Coefficients of Multi-Segment Linear Fitting Curve of Weber–Morris

| Parameter | intraparticle diffusion (1) | intraparticle diffusion (2) |
|-----------|-----------------------------|-----------------------------|
| \( K_{sl} \) (mmol·g\(^{-1}\)·min\(^{-1/2}\)) | 0.187 | 0.043 |
| \( C_1 \) (mg·g\(^{-1}\)) | 0.058 | 0.697 |
| \( R^2 \) | 0.957 | 0.811 |

Table 6. Boyd Model Fitting Parameters of Cr(VI) Adsorption on Magnetic Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)\(_-\)P4VP

| Parameter | \( K_0 \) (min\(^{-1}\)) | \( C \) (mmol·g\(^{-1}\)) | \( R^2 \) |
|-----------|-----------------------------|-----------------------------|-----------|
| \( K_0 \) (min\(^{-1}\)) | 0.017 | 0.508 | 0.950 |

Figure 15. Weber–Morris model fitting Cr(VI) adsorption curve of the magnetic Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)\(_-\)P4VP.

Figure 16. Boyd model fitting Cr(VI) adsorption curve on magnetic Ni\(_3\)Si\(_2\)O\(_5\)(OH)\(_4\)\(_-\)P4VP.
Fourth, the immobilization of P4VP on the formed Ni3Si2O5(OH)4-Cl NTs was achieved through the surface initiated-ATRP described in our previous study. Briefly, 0.2 g of Ni3Si2O5(OH)4-Cl NTs was dispersed in 4 mL of 4VP solution of isopropanol under N2 atmosphere; then CuCl2, Me6TREN, and CuCl were added in turn (n[4VP]/n[Me6TREN]/n[CuCl]/n[CuCl2] = 50:1.0:1.0:0.1) and reacted at 50 °C for 24 h. Finally, the obtained products were rinsed several times with ethanol and deionized water alternately to remove the oligomers and residual copper, and then dried at 40 °C for 12 h.

4.3. Characterization of the Ni3Si2O5(OH)4-g-P4VP NTs. The morphologies of the resultant Ni3Si2O5(OH)4-g-P4VP NTs were observed under a Tecnai G2 F20 S-TWIN field emission TEM (FEI, USA) equipped with an energy dispersive X-ray (JEOL, Japan). The FTIR spectra were recorded in a Frontier FTIR spectrometer (PerkinElmer, USA) with KBr disks in the wave number range of 600–4000 cm⁻¹. The XPS measurements were conducted on a Kratos AXIS Ultra DLD spectrometer (Kratos Analytical, UK) under monochromatized Al Kα X-ray radiation (1486.6 eV). The organic loading in Ni3Si2O5(OH)4-g-P4VP NTs was measured by thermogravimetric analysis (TGA) performed with a TGA/DSC2 thermogravimetric analyzer (Mettler Toledo, Switzerland) at a heating rate of 20 °C/min from 30 to 700 °C under nitrogen atmosphere. The paramagnetic properties of the magnetic particles were verified by the magnetization curve measured by vibrating sample magnetometry. The content of chromium was determined by atomic absorption spectrometer (Varian AA 320, Varian Inc. Palo Alto, CA).

4.4. Batch Adsorption Experiments. 4.4.1. Effect of Solution pH. The effect of pH on Cr(VI) adsorption was studied after adding 50 mg of Ni3Si2O5(OH)4-g-P4VP NTs into 100 mL of Cr(VI) solution (0.96 mmol·L⁻¹) at a pH range of 1.0–8.0. These flasks were shaken in a thermostatic shaker at 298 K and 150 rpm for 240 min. The Cr(VI) concentrations of each sample before and after adsorption were determined by an atomic absorption spectrophotometer (Varian AA 320, Varian Inc. Palo Alto, CA).

\[ q_e = \frac{(c_0 - c_e) \times V}{m} \]  

where \( q_e \) (mg·g⁻¹) is the amount of Cr(VI) adsorbed per gram of Ni3Si2O5(OH)4-g-P4VP NTs at equilibrium, \( c_0 \) is the initial Cr(VI) concentration (mg·L⁻¹), \( c_e \) is the residual Cr(VI) concentration (mg·L⁻¹), \( V \) stands for the volume of the solution (L), and \( m \) is the mass of the adsorbent (g).

4.4.2. Adsorption Kinetics. The kinetics adsorption experiments were carried out in 100 mL of 0.96 mmol·L⁻¹ Cr(VI) solution with 50 mg of Ni3Si2O5(OH)4-g-P4VP NTs. The pH of the solutions was adjusted to 3.0, and the adsorption process was conducted at 298 K and 150 rpm. The Cr(VI) solution was sampled at a regular interval during the adsorption process and analyzed by atomic absorption spectrometer.

4.4.3. Adsorption Isotherms. Isotherm adsorption experiments were conducted in 100 mL of the Cr(VI) solution, where the initial concentrations of Cr(VI) ranged from 0.96 to 2.31 mmol·L⁻¹, and the dose of Ni3Si2O5(OH)4-g-P4VP NTs was 50 mg. The pH of the solutions was adjusted to 3.0, and the adsorption process was kept at 298 K and 150 rpm successively for 240 min. The adsorption capacity at equilibrium was calculated according to eq 13.

\[ q_e = \frac{(c_0 - c_e) \times V}{m} \]  

4.4.4. Regeneration of the Ni3Si2O5(OH)4-g-P4VP NTs. For the examination of the adsorbent’s desorption properties, 50 mg of Ni3Si2O5(OH)4-g-P4VP NTs was added into 100 mL of the Cr(VI) solution with initial concentration and pH of 0.96 mmol·L⁻¹ and 3.0, respectively. The mixtures were then placed in a shaking bath at 298 K and 150 rpm for 240 min. The adsorbent was separated from the solution under the action of an external magnetic field, washed with distilled water, and used in the desorption tests. For the regeneration tests, the saturated adsorbent was stirred in 40 mL of KOH solution (0.1 mol·L⁻¹) at 298 K and 150 rpm for 60 min. Then, the adsorbents were washed with distilled water and dried in an oven before the re-adsorption tests.

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#### Notes

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