

Kinetics and Molecular Mechanism of Chromate Uptake by Dithiocarbamate Functionalized Starch

Rumei Cheng,¹ Shengju Ou,³ Yijiu Li,² Bo Xiang²

¹*Institute of Advanced Materials for Nano-Bio Applications, Biomedical Engineering Academy, School of Ophthalmology and Optometry, Wenzhou Medical College, Wenzhou, Zhejiang 325027, China*

²*Department of Chemistry, Tongji University, Shanghai 200092, China*

³*Shichuang Energy Co. Ltd., Hangzhou 310000, China*

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ABSTRACT: Heavy-metal fixation by the chelating polymers is of great importance in environmental applications. In this work, the molecular mechanism of chromate uptake by dithiocarbamate modified starch (DTCS) was investigated. It was found that the DTCS can achieve a maximum adsorption capacity at pH value of 5.0. In such solution, the adsorption kinetics showed two stages, which involved in different molecular mechanisms. The first was a fast stage. It lasted for about 60 min. In the stage, over 80% of maximum adsorption occurred and a Cr(VI)-DTC

ester formed. The ester was stable in the first hour, and then the Cr(VI) reduction took place in the second stage. The reduction of Cr(VI) was coupled with the oxidation of DTC, producing elemental sulfur and sulfonate. The formed Cr(III) still fixed in the oxidized DTCS without lost of adsorption capacity. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2930–2936, 2012

Key words: dithiocarbamate; starch; chromate; adsorption; molecular mechanism

INTRODUCTION

Water pollution due to toxic heavy metals has caused serious environmental and public problems.¹ The removal of heavy metals from river water, lake water, and wastewater is a crucial issue of concern to health.² Adsorption process is generally preferred for the removal of heavy metal ions because of its high efficiency, ease of handling, and availability of a wide range of adsorbents.^{3,4} Heavy-metal removal by using the chelating polymers would be of great importance in environmental applications.^{5,6} The functional group, dithiocarbamate (DTC), has attracted much attention due to strong chelating ability for heavy metals.^{7,8} The synthesis of DTC functionalized materials is of particularly interest still today.^{9–11} However, the DTC modified starch (DTCS) was not well studied.^{12,13}

Starch is an abundant, inexpensive, and renewable natural raw material. Usually, crosslinking reaction is applied to acquire stable modified starch.¹⁴ Furthermore, functional group (such as phosphate carbamate, carboxylate, and so on) is grafted onto the crosslinked starch (CS), which enhances affinity with metals.^{15,16} In this article, the DTC was decorated on

corn starch, and the chromium(VI) uptake was investigated.

Hexavalent chromium are common ions existing in water because it is widely used in various industries including metallurgy, leather tanning, and electroplating.¹⁷ It exists in water as oxyanions such as chromate (HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$). Its speciation is dependent on the pH. Such ions can be a major pollutant of the wastewater discharged by these industries causing serious environmental problems.¹⁸ Removal of Cr(VI) by using adsorption procedure is promising. Several sorbents have been used for the removal of hexavalent chromium. These sorbents can be biomaterials from agriculture such as lignocellulosic substrate extracted from wheat bran,¹⁹ natural material such as chitosan²⁰; or synthesized polymers such as 4-vinyl pyridine grafted poly(ethyleneterephthalate) fibers.²¹ However, the interaction of chromium(VI) with DTC functionalized polymer (DTC-polymer) was not well studied. The most important factors controlling the adsorption of the Cr(VI) onto various adsorbents are the type of active adsorption sites and the driven force. The adsorption mechanism may be electrostatic attraction, hydrogen bonding, van der Waals force, chelation, redox, and so on. It is crucial to clarify whether the Cr(VI) forms a strong complex with DTC-polymer or just adsorbs onto DTC-polymer via a physical attraction. In this article, the kinetics of hexavalent chromium(VI) adsorption onto DTCS

Correspondence to: R. Cheng (rumeicheng@yahoo.com).

was investigated. Several spectroscopic methods were used to make clear the molecular mechanism.

EXPERIMENTAL

Materials and equipments

Commercial corn starch, of food-grade quality, was used in this research. The potassium chromate and other routine reagents were of analytical grade. The elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. The total chromium contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on POEMS-2. Fourier transform infrared spectra (FT-IR) were recorded on a PE Spectrum One spectrometer with KBr pellets in the 4000–450 cm^{-1} region. Ultraviolet-visible spectra were measured with a Perkin-Elmer Lambda 35 spectrometer. X-ray photoelectron spectra (XPS) were measured on ESCALB MK-II spectrometer. The binding energies were corrected on the basis of the standard value of C1s from contaminants at 284.6 eV. Narrow scanned spectra were used to obtain the chemical state information for sulfur and chromium. X-band electron spin resonance (ESR) spectrum was measured on an EMX spectrometer.

Preparation of DTCS

The DTCS was first synthesized by a modified procedure reported previously.²² To a dilute NaOH solution (0.10 mol L^{-1}), 100g starch and 10.0 mL epichlorohydrin (ECH) were added. After stirring for 20 h, the pH of the solution was adjusted to 6–7 and the precipitation CS was separated out. Then the intermediate, 3-chloro-2-hydroxypropyl CS (CHCS) was prepared from dried CS with ECH in the presence of 60% HClO_4 . The dried CHCS further reacted with ethylenediamine to produce ethylenediamine modified CS cross-linked ethylenediamine modified starch (CAS) in basic solution under 60°C for 12 h. The CAS was further mixed with 15 mL CS_2 in alkaline medium. The mixture was warmed up to 40°C. After 12h, the precipitation was separated and washed with deionized water, dilute HCl solution, dilute NaOH solution, and acetone in sequence. The acquired DTCS was kept in a vacuum oven for 1 day and stored in desiccators. Elemental analysis: C 33.16, H 8.75, N 2.87, S 3.06%.

Sorption experiments

Sorption studies were performed by the batch technique. The temperature of all experiments was maintained at $25 \pm 1^\circ\text{C}$. For all adsorption tests, blank experiments were performed and the same experimental procedure was carried out to check the extent of adsorption by the glass flasks and the

membrane filters. The amount of DTCS used in each flask is 0.100 g. The pH of the solution was monitored and kept constant. The effect of pH was observed by studying the adsorption of chromate over a pH range of 2–7. For these experiments, a series of 100 mL conical flasks were used. Each flask was filled with 50 mL of chromate solution having a chromium concentration of 25 mg L^{-1} at varying pH. The flasks were shaken for 12 h to reach equilibrium in the thermostatic shaker bath. After filtration, the total soluble chromium in the supernatant were determined by ICP-AES and the Cr(VI) was assayed by the 1,5-diphenylcarbazide method.²³ The adsorption kinetics was studied with the initial concentration of chromium 25 mg L^{-1} and the volume of solution was 50 mL. The solution pH was monitored and kept at 5.0. The concentration of chromium was measured at different time intervals up to equilibrium. Each data point was obtained from an individual flask; therefore, no correction due to withdrawn sampling volume was necessary. The amount of chromium adsorbed at time t , q_t (mg g^{-1}), was deduced from the mass balance between initial concentration and concentration at time t in solution.²⁴ Experiments were carried out twice, and results were averaged; experimental errors were below 5%.

Kinetics model

To evaluate the effectiveness of the adsorbate and sorption mechanism, studies on kinetics of adsorption processes are necessary. A simple kinetic analysis of adsorption is the pseudofirst-order equation in the form²⁵

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

A pseudosecond-order equation was also tested on the experimental data.²⁶ the kinetic rate equation is given as follows:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

where q_t is the amount of chromium on the sorbent (mg g^{-1}) at any time t (min), q_e is the amount of chromium absorbed at equilibrium (mg g^{-1}), k_1 is the rate constant of pseudofirst-order adsorption (min^{-1}), and k_2 is the rate constant of pseudosecond-order adsorption ($\text{g mg}^{-1} \cdot \text{min}^{-1}$).

RESULTS AND DISCUSSION

Synthesis of DTCS

Four steps reactions were used to prepare DTCS. The syntheses were simple and mild although the

course seemed complex. Compared with other modified or unmodified polysaccharides (i.e., chitosan and the schiff base type starch), the DTCS exhibited higher particle stability, fast adsorption, and strong ability for cation metal fixation as previous reports.^{27–29} It is a promising adsorbent for wastewater treatment.

Influence of pH

The influence of pH on chromium sorption can be observed in Figure 1. The maximum capacity of DTCS for chromium was obtained at the pH value of 5. The adsorption of chromium decreased at pH < 5.0 as well as at pH > 5.0. The effect of pH on the adsorption of chromium onto DTCS can be interpreted in terms of the speciation of chromium and reduction of Cr(VI). Many researchers have plotted the diagram for the distribution of Cr(VI) species as a function of pH.³⁰ According to this diagram, Cr(VI) can predominantly form four different soluble species, including neutral species (H_2CrO_4), and anionic species (CrO_4^{2-} , HCrO_4^- , and $\text{Cr}_2\text{O}_7^{2-}$). It is well-known that, at pH values of 1.0–5.0, the principal Cr(VI) species mainly exists in the HCrO_4^- form.^{31–33} Thus, the HCrO_4^- can adsorb to the protonated DTCS. However, the increase of H^+ ions in the solution led to a decrease of uptake of chromium ions due to reduction of Cr(VI). At lower pH (< 4), the Cr(VI) is with redox potential about 1.33V.³⁴ The fact means that the Cr(VI) is much easier to be reduced to Cr(III). The formed Cr(III) ions do not effectively adsorb to DTCS at lower pHs because of an increasing competition between protons and trivalent chromium toward surface sites. It results in the decrease of capacity for total chromium. With an increase in pH from 6.0 to 7.0, the protonated DTC can dissociate and be converted to $-\text{NCS}_2^-$ anion, which induces the decrease in removal efficiency at higher pH values. The presence of anionic surface

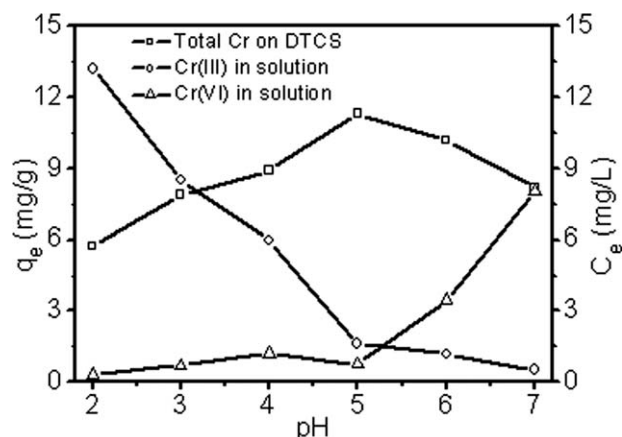


Figure 1 Influence of pH on chromium uptake by DTCS.

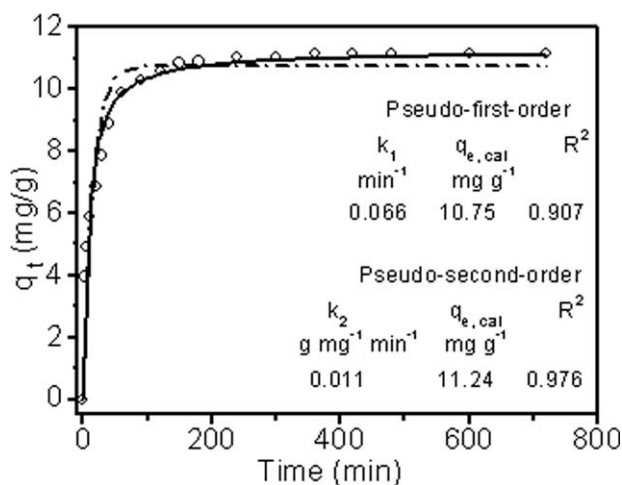


Figure 2 Kinetics of chromium adsorption onto DTCS for an initial Cr(VI) concentration of 25 mg L^{-1} at pH 5.0. The real line represents modeled result using the pseudosecond-order equation, and the dash dot line represents modeled result using the pseudofirst-order equation.

sites on DTCS weakened the interaction between chromate ions and DTCS. Thus more chromium remains in solution. The maximum adsorption at pH 5.0 indicates that the predominant HCrO_4^- species of Cr(VI) adsorbed preferentially on the DTCS surface. In many cases, the HCrO_4^- ion plays an important role in interaction with various materials such as polyaniline³⁵ and some clays.³⁶

Adsorption kinetics and mechanism

To make clear mechanistic aspects of the chromium(VI) adsorption on DTCS, sorption kinetics was investigated. The kinetics obtained by batch contact time studies is showed in Figure 2. The plot represents the total chromium adsorbed q_t versus time. As can be seen from the figure, the chromium uptake has two stages. The first is a fast increase stage which lasts for about 60 min, where most of chromium removal occurs. A slower stage follows the first stage and extends to 3 h achieving equilibrium. Compared with pseudofirst-order equation, there is a higher match between pseudosecond-order equation and experimental results. This indicates chemisorption for uptake of chromium by DTCS. It has been clearly found that the pseudosecond-order equation, which agrees with chemisorption as the rate controlling mechanism, was able to better describe the adsorption of metal ions on chitosan³⁷ and peat.³⁸ The concentrations of Cr(VI) and Cr(III) in solution also changed with time (Fig. 3). The decrease of free Cr(VI) concentration with time is normal. However, the Cr(III) concentration in solution increases with time in accordance with the two kinetic stages. The concentration of aqueous Cr(III) is very close to zero within the first hour, whereas it

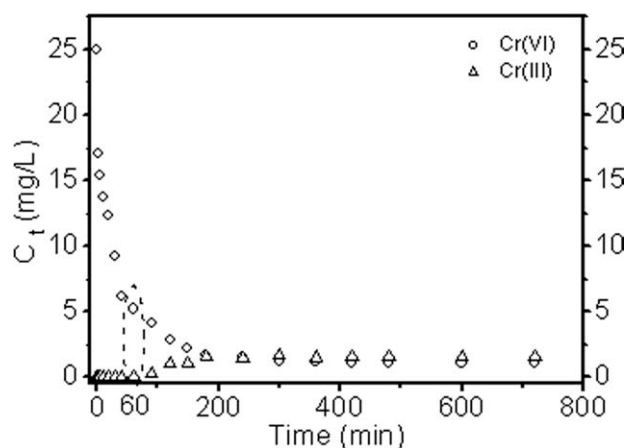


Figure 3 Changes of Cr(VI) and Cr(III) concentrations with time in aqueous solution at pH 5.0.

increases significantly after 90 min. Such facts demonstrate that the two kinetic stages are controlled by different mechanism. The adsorption occurs within 1 h is the first stage and probably determined by electrostatic attraction or another force. The followed second stage might be governed by reduction course.

Spectroscopic investigation and molecular mechanism

To clarify the sorption mechanism, the DTCS samples after exposure to Cr(VI) solution for 1 and 3 h were separated out and investigated by spectroscopic methods. The two samples are denoted as DTCSr1 and DTCSr2, respectively. Usually, the infrared spectra can provide meaningful information to find out functional groups responsible for the sorption processes. It can be seen from Figure 4 that the DTCS shows a broad vibration of $\delta\text{H}_2\text{O}$ and $\delta\text{N}-\text{H}$ at 1642 cm^{-1} .³⁹ The peaks at 1461 and 1336 cm^{-1}

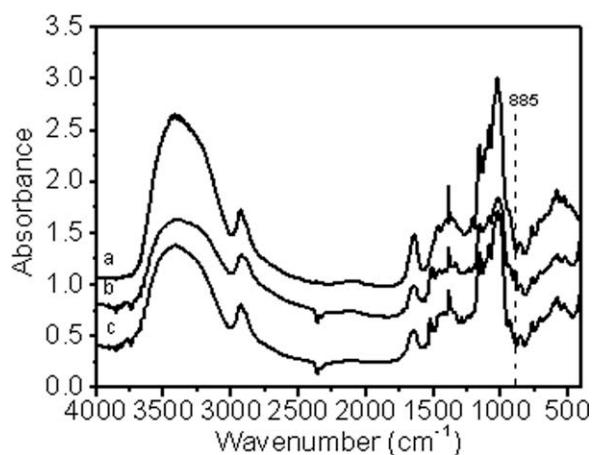


Figure 4 FT-IR spectra of DTCS(a), DTCSr1(b), and DTCSr2(c).

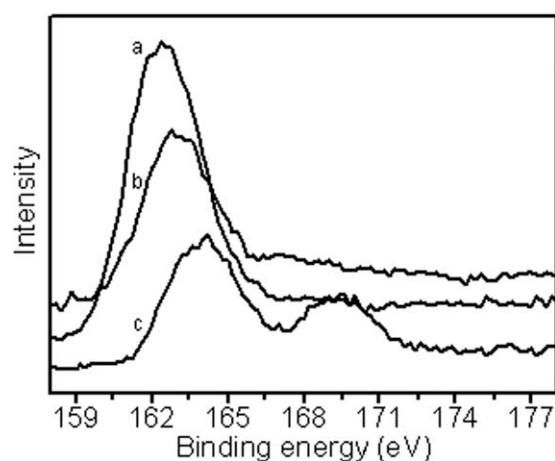


Figure 5 S2p XPS spectra of DTCS(a), DTCSr1(b), and DTCSr2(c).

cm^{-1} are the $\nu(\text{S}-\text{C}\cdots\text{N})$ and $\nu(\text{S}\cdots\text{C}-\text{N})$ vibrations, respectively.^{40,41} Another important bands of $\nu_{\text{as}}\text{CS}_2$ and $\nu_{\text{s}}\text{CS}_2$ vibrations separately appeared at 1204 and 1111 cm^{-1} .⁴² After adsorption of hexavalent chromium in acidic solution, a new peak appeared at 1507 cm^{-1} attributed to the δNH_2^+ vibration.⁴³ Thus, the ionic interaction between protonated DTCS and the HCrO_4^- (the predominant species at pH 5) can occur. However, the changes of DTC group were different in DTCSr1 and DTCSr2. In DTCSr1, the $\nu(\text{S}\cdots\text{C}-\text{N})$ vibration shifted to 1328 cm^{-1} and the $\nu_{\text{as}}\text{CS}_2$ vibration shifted to 1231 cm^{-1} . It indicated interactions between the HCrO_4^- and the DTC group. A new sharp peak at 885 cm^{-1} demonstrated the presence of chromate ions.⁴⁴ Therefore, the HCrO_4^- bound to DTC group in the first hour of contact. While in the DTCSr2, the characteristic peaks of DTC almost vanished. Also, the sharp peak of chromate ion is hard to identify. A typical $\nu_{\text{as}}\text{SO}_2$ vibration at 1287 cm^{-1} appeared. Such observations indicated the fact that a reduction course had took place in DTCSr2 during stage 2.

The changes of chemical states of chromium and sulfur atoms can be further determined by XPS spectra. Figure 5 shows the S2p XPS spectra of the DTCS without or with the adsorption of chromium species, respectively. The S2p spectrum of the DTCS without the adsorption of chromium species can be assigned to the peak at the binding energy of 162.3 eV , which is in agreement with other DTC compounds.^{45,46} After the DTCS contacted with chromium(VI) for 1 h, the signal of sulfur shifted to 162.8 eV . The slight change of binding energy indicated that the $-\text{NCS}_2$ was not oxidized. It is well-known that the occurrence of S2p peaks above 164 eV can be attributed to the presence of some type of oxidized sulfur (such as elemental S, sulfonate and so on). The compounds containing "reduced" sulfur (i.e., $-\text{C}-\text{S}-$ or $\text{C}=\text{S}$) will not exhibit S2p binding energies much above

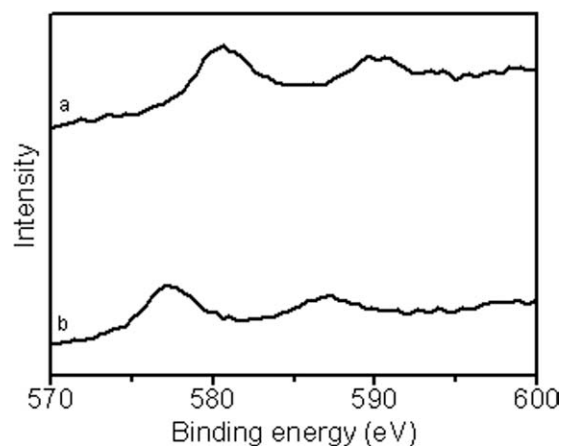


Figure 6 Cr2p XPS spectra of DTCSr1(a) and DTCSr2(b).

164 eV.⁴⁷ However, the coordination of metal ions often induces the peak of S2p moving to a higher position. The + 0.5 eV upper binding energy suggests the $-NCS_2$ chelates the chromium. Interestingly, the Cr(VI) forms are observed and characterized by binding energies 580.5 and 590.1 eV (Fig. 6).⁴⁸ The former corresponds to Cr2p_{3/2} orbitals, the latter to Cr2p_{1/2} orbitals. In this analysis we took into consideration the fact that the formation of chromium(VI) thio esters with DTC occurred. Many reports have mentioned the Cr(VI)-thio ester formation as an intermediate step in Cr(VI) reduction by penicillamine, cysteine, and glutathione.⁴⁹ The chromium(VI) thio esters are much stable than chromium(VI) oxy esters.⁵⁰ Some chromium(VI) thio esters are stable in aqueous solution for about 1 h, whereas they can exist over 2 h in nonaqueous solution.^{51,52} Followed the chromium(VI) thio ester course, reduction takes place by an inner-sphere mechanism.⁵³ Significant bands of Cr(III) appear at binding energies of 577–578 and 587–588 eV, and the peaks of Cr(VI) fade away.⁵⁴ The reduction of Cr(VI) resulted in the oxidation of DTC. The peaks of S2p shifted to 164.2 and 169.5 eV, which can be assigned to oxidation of $-NCS_2$ groups producing elemental sulfur and sulfonates.⁵⁵ To further confirm the oxidation number of chromium after reduction, the ESR spectrometry was used. The signal of DTCSr1 is silent, whereas the DTCSr2 shows typical Cr(III) peaks with g values of 5.502 and 1.970 (Fig. 7). The broad positive lobe around $g = 5.5$ is characteristic peak of mononuclear Cr(III) in octahedron field.^{56,57} It has long been recognized that chromium can exist in several chemical forms displaying oxidation numbers from 0 to 6. Only two of them, trivalent and hexavalent Cr, are stable enough to occur in the environment. Cr(IV) and Cr(V) can exist in restricted biosystems.⁵⁸ Cr(II) species are stable only in the absence of any oxidant.

According to the above facts, the uptake of Cr(VI) oxyanions (predominant in the form $HCrO_4^-$ at pH 5) by DTCS proceeds by the formation of a Cr(VI)-DTC ester. A mechanism proposed for the adsorption of Cr(VI) by DTCS is illustrated in Figure 8. The first stage involves the electrostatic attraction and the formation of a chromium(VI)-DTC ester. In the stage, more than 80% of the ultimate adsorption occurs within the first hour of contact. The second stage involves either an intramolecular electron transfer of the chromium(VI)-DTC complex or the reaction of the ester with a second Cr(VI) oxyanion. The latter favored the increase of capacity in the second stage. Large amount of Cr(III) produced and the DTC was oxidized, producing sulfonate and elemental sulfur. The formed Cr(III) ions chelated to sulfonates, amines, and hydroxyls on the oxidized DTCS without loss of capacity. The reduction course took place slower than the electrostatic attraction and the formation of thioester.

CONCLUSIONS

In summary, this work demonstrated the molecular mechanism of aqueous Cr(VI) adsorption by DTCS. The adsorption kinetics showed two stages and involved in different molecular mechanisms. There is a higher match between pseudosecond-order equation and experimental results. The chromate adsorption efficiency was largely related to the DTC groups available on the DTCS and solution pH. At the optimum pH value of 5.0, the predominant chromium species $HCrO_4^-$ adsorbed to the polymer by electrostatic attraction and the formation of Cr(VI)-DTC ester in the first hour. Then Cr(VI) reduction took place, producing Cr(III). Elemental sulfur and sulfonate are the main stable products during DTC oxidation by Cr(VI). During the reduction course, the total chromium on polymer was not lost. Such

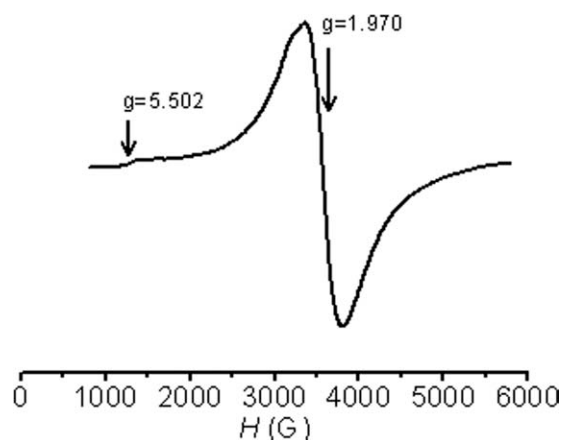


Figure 7 ESR spectrum of DTCSr2 at room temperature.

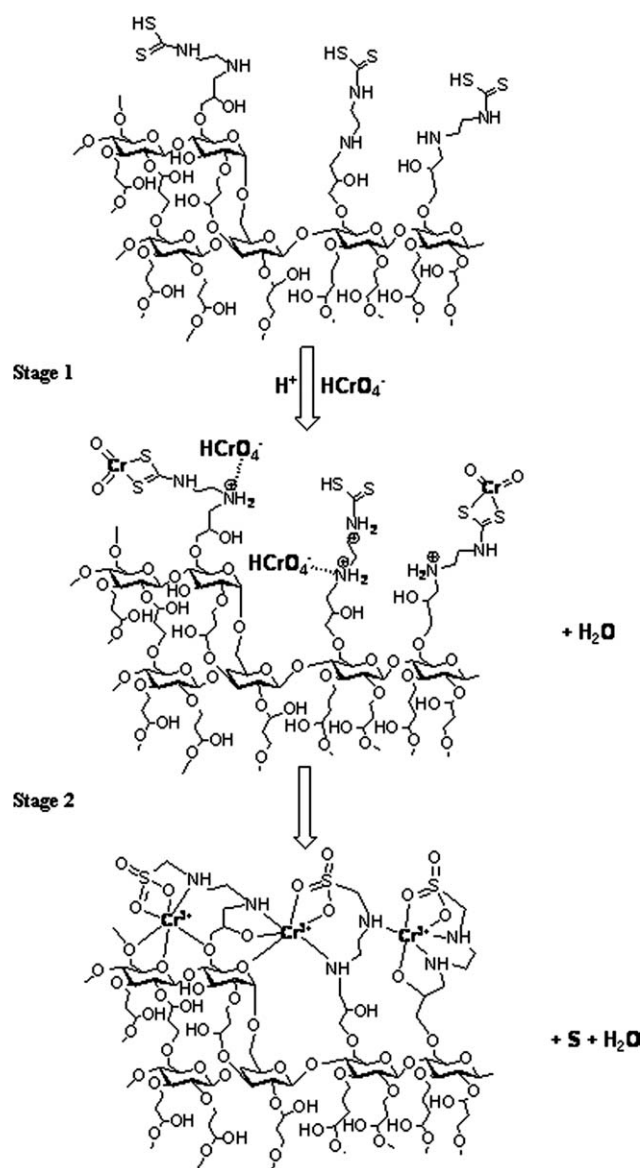


Figure 8 Proposed mechanism of Cr(VI) uptake by DTCS.

understanding provides insights as how to optimize the use of DTC-based polymers for the remediation of chromate-contaminated water and to assess the system performance.

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