

## Thiocarbohydrazide-Modified Chitosan as Anticorrosion and Metal Ion Adsorbent

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**ABSTRACT:** To explore the application of chitosan (CS) derivatives in anticorrosion and adsorption, thiocarbohydrazide-modified chitosan (TCHECS) derivative was synthesized and characterized. The preliminary electrochemical measurements of the behaviors of 304 steel and Cu sheets in 2% HAc (v/v) containing TCHECS, chitosan (CS), and hydrazine cross-linked epoxy-*N*-phthaloylchitosan (HECS) had been performed. The short-term electrochemical tests show that the new compound can act as a mixed-type metal anticorrosion inhibitor; its inhibition efficiency is 88% when the concentration was 30 mg/L. The preliminary adsorption studies for sorbents TCHECS and HECS on a metal ion mixture aqueous solution were also performed. The results show that TCHECS can absorb As (V), Ni (II), Cu (II), Cd (II), and Pb (II) efficiently at pH 9; the removal of the As (V), Ni (II), Cu (II), Cd (II), and Pb (II) are around 55.6–99.9%. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40671.

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### INTRODUCTION

Chitosan (CS) which is partially deacetylated derivatives obtained from chitin has advantages of nontoxic, biocompatible, and biodegradable.<sup>1,2</sup> The present fundamental studies brought forth abundant modification methods and applications of CS, such as antibacterial<sup>3</sup> and antimicrobial activities,<sup>4</sup> and anticoagulant<sup>5</sup> and potential carriers for gene transfection.<sup>6,7</sup> In the field of tissue engineering, CS presents excellent biocompatibility<sup>8</sup> and enhances the biological performance of a biomaterial.<sup>9</sup> CS and their derivatives may be expansively utilized in many more fields.<sup>10,11</sup> Furthermore, the presence of a considerable percentage of free amine and hydroxyl groups on this natural polymer endows it anticorrosion properties<sup>12</sup> and good capability of complexation with metal ions.<sup>13–17</sup> To amplify its application capability, modification procedures for CS were often handled at the two chemical active sites: hydroxy group at 6-site and amino group at 2-site, and new derivatives containing novel functional groups in CS structure await to be synthesized efficiently.<sup>18</sup>

Recently, the development of inhibitors or adsorbents has been the subject of great interest especially from the point of view of their efficiency and applications.<sup>19,20</sup> Compounds containing heteroatom in the conjugated system have been particularly reported as efficient corrosion inhibitors,<sup>20,21</sup> and these kinds of compounds can be used as chelate sorbents in dealing with waste water.<sup>22</sup> Aminothiourea was a useful compound contain-

ing heteroatom conjugated structure. They were widely used in pharmaceutical and materials science as chemical intermediate.<sup>23–25</sup> Their derivatives were also employed as corrosion inhibitor and metal ion adsorbents in treated with heavy metal pollutants.<sup>26–29</sup> Literature has reported that chitosan derivatives modified with Thiocarbohydrazide (TC) could stabilize silver and copper nanoparticles in their matrix.<sup>30,31</sup> By the methods of using formaldehyde as linkages, adsorbents containing aminothiourea groups were synthesized,<sup>32</sup> and water soluble CS derivatives could be synthesized smoothly.<sup>33</sup>

On the basis of the analysis above, we attempted to synthesize new CS derivative containing TC groups to match specific applications such as anticorrosion and heavy metal sorbents. In this work, the introduction of oxirane ring by conjugating with epichlorohydrin at 6-hydroxyl groups of CS is designed as a precursor to crosslink with hydrazine hydrate. And then, formaldehyde was chosen as linkages to react with TC to get target compound. The preliminary tests of anticorrosion, and heavy metal adsorption were also investigated.

### EXPERIMENTAL

#### Materials

All compounds were analytical grade and used as received. Chitosan (CS) and phthalic anhydride were purchased from Sino-pharm Chemical Reagents (Shanghai, China). The deacetylation

degree of CS was 90%. Hydrazine aqueous solution (80%) was purchased from Tianli Chemical Reagent (Tianjin, China). Thiocarbonylhydrazide (TC) was purchased from Solarbio Sci. & Tech (Beijing, China). Formaldehyde solution (37–40%) was purchased from Xilong Chem. (Chengdu, China). Deionized (DI) water (Milli-Q, Millipore, Bedford, MA) was used to prepare aqueous solutions. A heavy metal mixture solution contained As (V) (2.0 mg/L), Ni (II) (2.0 mg/L), Cu (II) (1.6 mg/L), Cd (II) (0.8 mg/L), Zn (II) (0.8 mg/L), and Pb (II) (8.0 mg/L) was prepared by diluting the standard stock solution purchased from Sigma-Aldrich (St. Louis, MO).

### Synthesis of Hydrazine Crosslinking Epoxy-*N*-Phthaloylchitosan

The synthesis of epoxy-*N*-phthaloylchitosan (ECS) was followed as the method reported before.<sup>34</sup> In shortly, Chitosan was firstly reacted with phthalic anhydride (3 mol equivalent to pyranose ring) at 120°C under nitrogen for 6 h to prepare *N*-protected CS. The reactants were precipitated into DI water and filtrated. After being washed with methanol several times, the *N*-protected CS was dried under vacuum. Afterwards, the obtained product was treated with epichlorohydrin (10 mol equivalent to pyranose ring) at 60°C for 12 h and purified as above method to give product ECS. Then, compound ECS was dissolved in hydrazine aqueous solution (10 mol equivalents to pyranose ring) at 60°C for 6 h to give gel-like product. After being concentrated and precipitated in DI water, it was filtrated and washed with DI water and methanol several times, and dried under vacuum to give hydrazinolysis product (HECS).

### Synthesis of Thiocarbonylhydrazide Grafts Chitosan

HECS (0.45 g) was mixed with TC (0.5 mol equivalent to pyranose ring) in 40 mL 5% (v/v) HAc and stirred thoroughly. After about 45 min, formaldehyde (2 mL) was added and stirred thoroughly for 12 h at room temperature to get gel-like mixture. The obtained product TCHECS was neutralized with NaOH aqueous solution to form precipitates. The precipitates were filtrated and washed with DI water and Methanol several times, and then dried under vacuum to give TCHECS as pale powder.

### Characterization

The Fourier transform infrared spectra (FTIR) of CS, HECS, and TCHECS were recorded in powder form by using a Nicolet 5700 instrument (Thermo Company, USA) over the wave number range of 4000–400 cm<sup>-1</sup> in KBr discs. Software OPUS viewer from Bruker Optics was used to analyze the spectra. The elemental analysis (C, H, N, and S) was performed on a Thermo Scientific FLASH 2000 organic elemental analyzer (Thermo Fisher, Italy). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a TGA/DSC1 analyzer (Mettler, Switzerland) between 20 and 500°C with a 10°C/min heating rate under a nitrogen flow rate of 20.0 mL/min. The sample TCHECS was put into aluminum cup and sealed. An empty pan was used as reference in the test.

### Surface Morphology

Images of the surface morphology of the product TCHECS and CS were observed using an S-4800 (Hitachi, Japan) field emission scanning electron microscope (SEM) method. Samples were sputter-coated with gold and were imaged.

### Electrochemical Tests

The electrochemical measurements were employed for the preliminary tests of anticorrosion. The electrochemical measurements were performed in a typical three-compartment glass cell consisted of a working electrode (WE), a platinum wire as the counter electrode (PE), and a saturated calomel electrode (SCE) as the reference electrode (RE). The electrochemical tests were performed using a CH1660 electrochemical station (CH instrument, Shanghai, China). For potentiodynamic polarization experiments, the potential was scanned from -0.7 to 0.6 V with scan rate of 1.0 mV s<sup>-1</sup>. Totally, 304 steel sheets and Cu sheets as working electrodes for electrochemical measurements were prepared from olefin sealed metal sheets with an exposed total area of 1 cm<sup>2</sup> and were immersed into a stagnant acetic acid (HAc) solution containing the different samples. Prior to the experiments, the exposed metal surfaces were abraded smoothly with a series of emery papers of different grades (1200–2000), degreased with AR-grade ethanol and acetone, rinsed with DI water, and then dried in air.<sup>12</sup> Acetic acid solutions (2%, v/v, pH 3) were prepared by dilution of analytical grade ice acetic acid with DI water. Electrochemical parameters include corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $i_{\text{corr}}$ ) were determined by extrapolation of the Tafel curves to the open circuit corrosion potentials (OCP). The inhibition efficiency (%IE) of each sample was then calculated by using the equation as follows:

$$\text{IE} (\%) = \frac{i_{\text{corr}} - i_{\text{inh}}}{i_{\text{corr}}} \times 100 \quad (1)$$

where  $i_{\text{corr}}$  and  $i_{\text{inh}}$  are the corrosion current densities without and with different inhibitors, respectively.<sup>35</sup>

### Batch Adsorption Studies

Batch adsorption experiments were conducted to examine the properties of samples TCHECS and HECS in removing heavy metal ions from aqueous solutions. In a typical experiment, 50 mg of sample was added to a plastic centrifuge tube containing 10 mL of heavy metal ion mixture solution diluted from a standard stock solution. The pH of the solution was then adjusted with 0.1 mol/L or 0.01 mol/L HNO<sub>3</sub> and NaOH; the test tube was kept standing for 36 h at room temperature. At the end of the experiment, sample was filtrated through a 0.10- $\mu\text{m}$  membrane filter and concentration of heavy metal ions in the filtrate was analyzed with ICP-MS (Agilent 7700, Agilent Tech., US). The heavy metal ion removal by adsorption of the sample was calculated by mass balance as of the concentration of heavy metal ion before and after adsorption. Adsorption percentages for each metal ion in the sample were established by using the equation as follows:

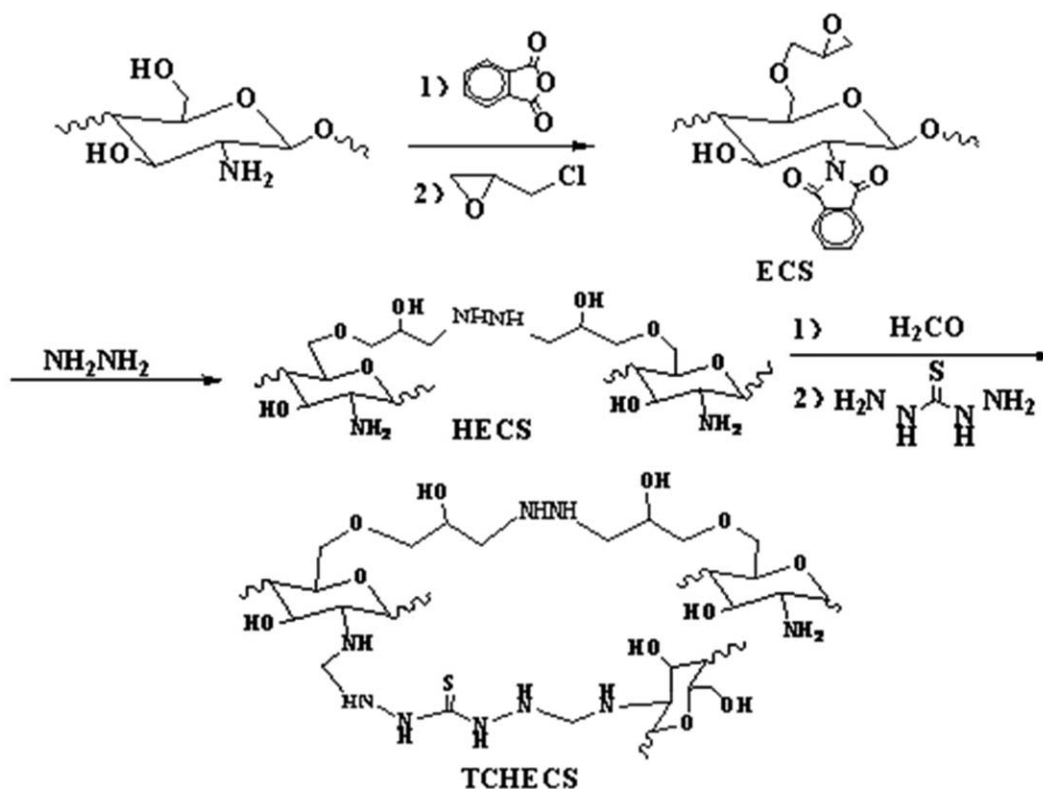
$$A(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

in which,  $C_0$  and  $C_e$  are the initial and equilibrium concentrations (mg/L) for each metal cation in solution, respectively.<sup>36</sup>

## RESULTS AND DISCUSSION

### Synthesis and Characterization

The synthesis of TCHECS was outlined as Scheme 1. The whole reactions include two times cross-linking procedures and both



Scheme 1. Synthesis of HECS and TCHECS.

of them aimed at introducing more nitrogen atoms on CS structure. According to method available in literature,<sup>34</sup> the first crosslinking was conducted by an epoxy-hydrazinolysis reaction. The introducing of TC caused another crosslinking and the reaction was performed in acid aqueous solution, since both raw materials were easily dissolved in HAc solution. Schiff's base intermediates were produced by free amino groups of aminoglucose units of deacetyl CS with formaldehyde, and readily underwent addition reaction with the amino groups of TC.<sup>32</sup> Since two amino groups locating on both ends of TC could sep-

arately react with two different intermediates of Schiff's bases on CS, a crosslinking structure of TCHECS would be formed. This phenomenon could be observed at the end of the reaction. At this time, the reactants changed from viscous solution to gel.

The FTIR of ECS, HECS, and product TCHECS are shown in Figure 1. The IR curve of ECS shows characteristic peaks of phthalimido groups at  $1770\text{ cm}^{-1}$  and  $1715\text{ cm}^{-1}$ , and epoxy rings at about  $907\text{ cm}^{-1}$ . The IR figure of HECS shows phthalimido groups and oxirane rings' peaks disappear, which implies the successful deprotection and oxirane rings' opening. TCHECS shows all characteristic peaks of CS along with two new peaks. The new peak appears at about  $1545\text{ cm}^{-1}$  is attributed to thiourea group.<sup>37</sup> The peak appears at about  $1250\text{ cm}^{-1}$  should be attributed to C=S bonds' stretching vibration.<sup>38</sup> The formation of TCHECS was further confirmed by elemental analysis and the results were listed in Table I. As shown in Table I, the changing trends of the C/N values which represented the different degree of substitution of CS accorded with the different chemical structure of products. On the basis of the C/N

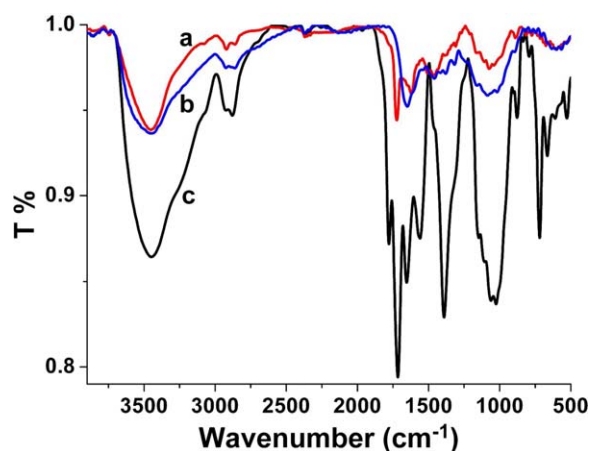
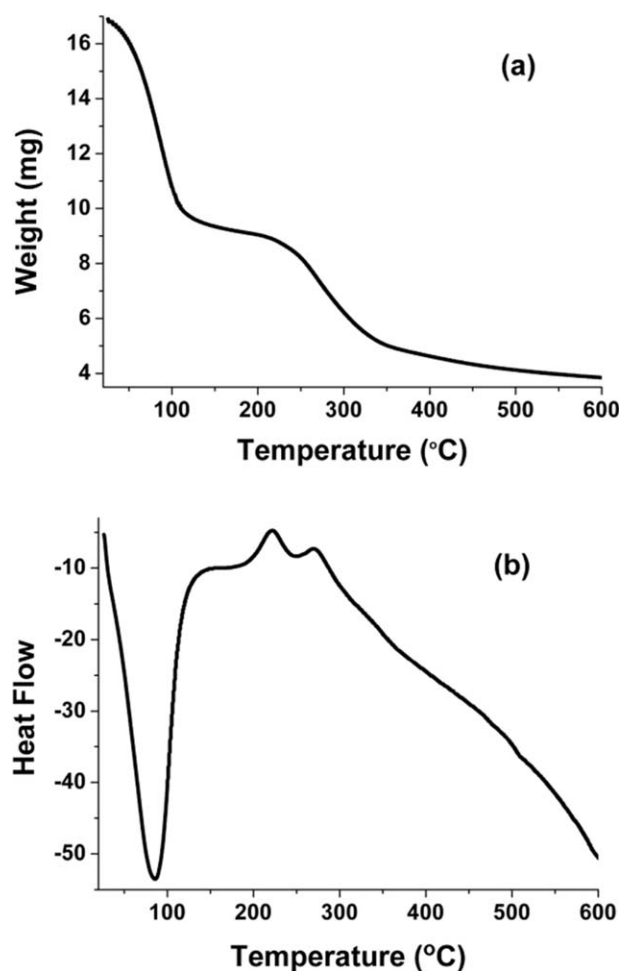


Figure 1. Comparative FTIR spectra of (a) HECS, (b) TCHECS, and (c) ECS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Elemental Analysis Results of HECS, TCHECS, and CS

Sample	Elemental analysis (%)				
	C	H	N	S	C/N
HECS	36.88	6.22	9.12		4.04
TCHECS	35.64	5.85	10.66	0.78	3.34
CS	44.98	6.79	8.52	-	5.28



**Figure 2.** (a) TGA thermograph for TCHECS and (b) DSC curve for TCHECS.

values, the degree of substitution (DS) of HECS and TCHECS could be calculated as 69% and 23%, respectively. Moreover, the results showed that S element was detected in the product, and this implied the formation of product.

TGA curve of TCHECS is presented in Figure 2(a). The TGA curve shows two different stages of weight loss. The first weight

loss at about 86°C is mainly due to the evaporation of water and moisture content in the structure of TCHECS. The second stage of weight loss at about 290°C for TCHECS is might due to the decomposition of the graft polymer. DSC thermogram of TCHECS is shown in Figure 2(b). The curve shows two endothermic peaks at 75°C ( $T_g$ ) and 185°C ( $T_m$ ) and two exothermic peaks at 208°C and 287°C. On the basis of the DSC and TGA analysis, TCHECS shows high thermal stability and can be utilized at a large temperature range.

Moreover, the swelling studies were also performed. Both TCHECS and HECS were insoluble in pure water but could dissolve in acidic solution. In the pH controlled (pH = 6) DI water at about 30°C, the swelling ratios of the sample TCHECS and HECS were 3.2 and 2.1 (g/g, 24 h), respectively.

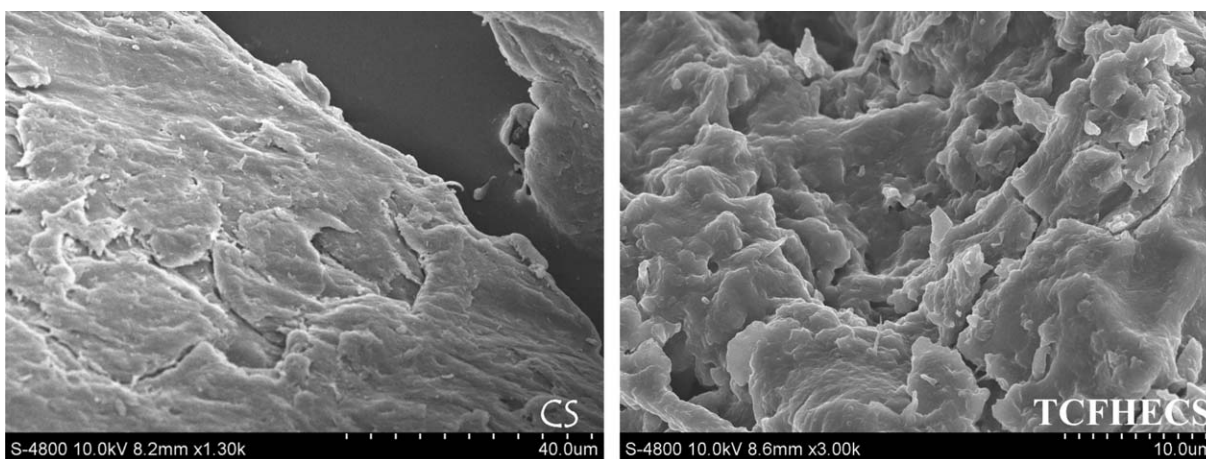
### Surface Morphology

The SEM images showed different surfaces of CS and TCHECS in Figure 3. CS had a nonporous and flat lamellar phase surface, while TCHECS had a complicated three dimensional highly porous structures. This might imply that the target product TCHECS was prepared successfully and the various cross-linking degree caused the different morphologies. Moreover, the highly porous structure of the product can supply more active sites for the adsorption of metal ions.

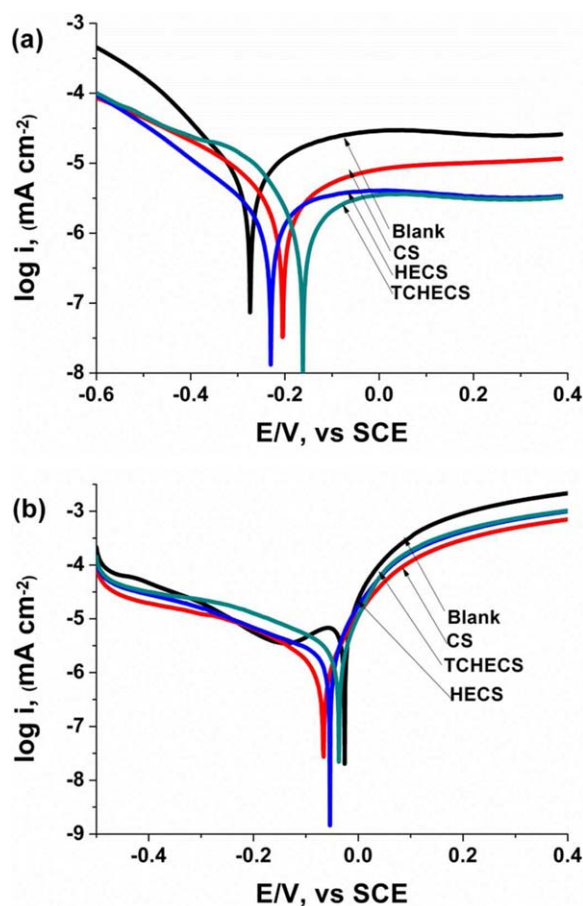
### Electrochemical Measurements

Previous studies have reported that CS can be used as a copper corrosion inhibitor in acid medium.<sup>12</sup> Hence, CS was employed as reference to evaluate the short-term anticorrosion capability of the prepared products. The Tafel curves of inhibitors CS, HECS, and TCHECS by using 304 steel and Cu sheets as WE were exhibited in Figure 4(a,b), respectively. Electrochemical parameters include  $E_{corr}$  and  $i_{corr}$  are summarized as Table II.

Figure 4(a) presents the cathodic and anodic polarization curves of various inhibitors (CS, HECS and TCHECS, 30 mg/L) by using 304 steel as WE, in which a decrease in both cathodic and anodic currents appeared. The values of the corrosion potentials shifted to more positive values from HECS to CS to TCHECS. These phenomena indicate that the inhibitor TCHECS has a stronger influence on the steel dissolution or hydrogen evolution reaction than CS and HECS. The results of IE values



**Figure 3.** SEM micrographs of (a) CS and (b) TCHECS.



**Figure 4.** Potentiodynamic polarization curves of (a) 304 steel and (b) Cu sheet in the absence and presence of different inhibitors (30 mg/L) in 2% HAc (v/v) at  $32 \pm 2^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

revealed that CS, HECS, and TCHECS can be used as inhibitors for 304 steel in acidic medium, and TCHECS was more effective (Table II). Figure 4(b) presents the cathodic and anodic polarization curves of various inhibitors by using Cu sheets as WE. The corrosion currents decreased in the presence of various inhibitors. IE values revealed that CS, HECS, and TCHECS could be used as inhibitors for Cu material in acidic medium, and TCHECS was more effective (Table II). The corrosion potentials values shifted to more negative values from TCHECS to HECS to CS which indicated that all the inhibitors had a stronger influence on the oxygen cathodic reduction than on the copper oxidation. Moreover, the results of the electrochemical measurements meant that these inhibitors might be classified as mixed inhibitors and the target compound TCHECS could be used as corrosion inhibitor preferably on the cathodic site of Cu and anodic site of steel.<sup>35,39,40</sup> The TGA and swelling tests revealed water adsorption in TCHECS structure, which might affect less to the tests results when the samples were dissolved in acidic medium, but would cause the new corrosion when coated on WE. The stability of the coatings is not known and further tests are needed in order to assess the corrosion inhibition properties of the coatings.

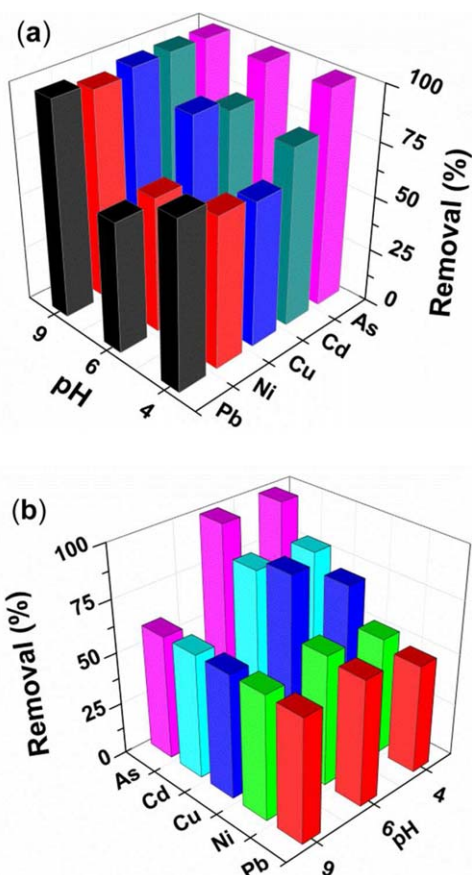
### Batch Adsorption Studies

The preliminary batch adsorption experiments were conducted to examine the adsorption properties of samples TCHECS and HECS. To the target adsorbent TCHECS, the main functional groups are amino at 2-sites of CS and aminothiurea group of TC. The pH of solution was known as one of the most important variables affecting the adsorption amount of heavy metal ions. It could influence the protonation of the functional groups on the adsorbents as well as the solution chemistry of the heavy metal ions. In the preliminary tests, the adsorption characteristics at different pH were carried out. Adsorption histograms of As (V), Ni (II), Cu (II), Cd (II), and Pb (II) on the samples TCHECS and HECS at pH 4.0, 6.0, and 9.0 are shown in Figure 5. As shown in Figure 5, it is evident that both TCHECS and HECS cannot adsorb Zn (II) ion; the removal of the As (V), Ni (II), Cu (II), Cd (II), and Pb (II) are around 55.6–99.9%, and 52.5–99.9% for the two adsorbents TCHECS and HECS, respectively. For the adsorbent TCHECS, the removal of the As (V), Ni (II), Cu (II), Cd (II), and Pb (II) at pH 9 is more effective than that at pH 4 and 6 [Figure 5(a)]. But for the adsorbent HECS, the removal of the As (V), Ni (II), Cu (II), Cd (II), and Pb (II) at pH 4 and 6 is more effective than that at pH 9 [Figure 5(b)]. Moreover, both adsorbents are more effective for the removal of As (V), Cu (II), and Cd (II) than other ions and TCHECS is more effective. These results partially accorded with conclusions available in literature.<sup>41,42</sup> In the literature, the best pH range for the removal of ions was between 4.5 and 5.5. To the sorbent TCHECS, As (V) removal was almost found to be the same as pH variations between pH 4 and 9. These phenomena might be caused by the introduction of active groups TC in CS structures,<sup>36</sup> and the removal mainly achieved through hydrogen bonds effect, which could have been strengthened by thiourea groups.

In general, it seemed that the adsorption of TCHECS for metal ions was effective in some extent. This might can be explained by the fact that the ion adsorption strongly depends on the structures of the adsorbents since the samples TCHECS have many thiourea and amino groups contained in the structures. As a result, the adsorption of As (V) and Cd (II) might be fulfilled by stronger hydrogen bonds strengthened by aminothiourea groups. To claim the adsorption mechanism and adsorption capacity, the further study needed to be conducted.

**Table II.** Corrosion Parameters Calculated from Polarization Measurements in Presence of Different Inhibitor (30 mg/L) in 2% HAc (v/v) Solution at  $30 \pm 2^\circ\text{C}$  for (a) 304 steel and (b) Cu

WE	Inhibitors	$E_{\text{corr}}/\text{mV}$	$J_{\text{corr}}/(\mu\text{A}/\text{cm}^2)$	IE/%
<b>a</b>	Blank	-274	5.824	-
	CS	-205	2.930	50
	HECS	-230	2.457	58
	TCHECS	-162	1.746	70
<b>b</b>	Blank	-27	12.08	-
	CS	-66	1.685	86
	HECS	-54	3.662	70
	TCHECS	-37	1.467	88



**Figure 5.** The heavy metal ion adsorption at different pH by (a) TCHECS and (b) HECS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## CONCLUSIONS

The synthesis of thiocarbohydrazide-modified CS derivatives has been developed. By using this approach, target compound TCHECS was synthesized and characterized. The preliminary electrochemical tests showed the target product possesses short-term corrosion inhibition properties but no conclusions can be drawn about long-term stability and inhibition. The adsorption studies revealed this CS derivative can also act as heavy metal ion adsorbent. All the results imply the product TCHECS might be having potential applications in anticorrosion and treatment of heavy metal ion contamination.

## ACKNOWLEDGMENTS

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