



Combination of cathodic reduction with adsorption for accelerated removal of Cr(VI) through reticulated vitreous carbon electrodes modified with sulfuric acid–glycine co-doped polyaniline

Xi Mo^{a,b}, Zhao-hui Yang^{a,b,*}, Hai-yin Xu^{a,b}, Guang-ming Zeng^{a,b}, Jing Huang^{a,b}, Xia Yang^{a,b}, Pei-pei Song^{a,b}, Li-ke Wang^{a,b}

^a College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China

^b Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China

HIGHLIGHTS

- RVC/PANI-SA-GLY electrode was applied as a novel electrode material for accelerated removal of Cr(VI).
- Faster reduction kinetics of Cr(VI) was observed by RVC/PANI-SA-GLY electrode when compared with RVC/PANI-SA and RVC electrode.
- Cr(VI) removal experienced an adsorption–reduction system built by RVC/PANI-SA-GLY electrode.
- The stability of RVC/PANI-SA-GLY electrode was relatively satisfactory.

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ABSTRACT

Improving the reduction kinetics is crucial in the electroreduction process of Cr(VI). In this study, we developed a novel adsorption–electroreduction system for accelerated removal of Cr(VI) by employing reticulated vitreous carbon electrode modified with sulfuric acid–glycine co-doped polyaniline (RVC/PANI-SA-GLY). Firstly, response surface methodology confirmed the optimum polymerization condition of co-doped polyaniline for modifying electrodes (Aniline, sulfuric acid and glycine, respectively, of 0.2 mol/L, 0.85 mol/L, 0.93 mol/L) when untraditional dopant glycine was added. Subsequently, RVC/PANI-SA-GLY showed higher Cr(VI) removal percentages in electroreduction experiments over RVC electrode modified with sulfuric acid doped polyaniline (RVC/PANI-SA) and bare RVC electrode. In contrast to RVC/PANI-SA, the improvement by RVC/PANI-SA-GLY was more significant and especially obvious at more negative potential, lower initial Cr(VI) concentration, relatively less acidic solution and higher current densities, best achieving 7.84% higher removal efficiency with entire Cr(VI) eliminated after 900 s. Current efficiencies were likewise enhanced by RVC/PANI-SA-GLY under quite negative potentials. Fourier transform infrared (FTIR) and energy dispersive spectrometer (EDS) analysis revealed a possible adsorption–reduction mechanism of RVC/PANI-SA-GLY, which greatly contributed to the faster reduction kinetics and was probably relative to the absorption between protonated amine groups of glycine and HCrO_4^- . Eventually, the stability of RVC/PANI-SA-GLY was proven relatively satisfactory.

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1. Introduction

Nowadays, water pollution is prevalent in majority countries and threatens the environment, the health of humans and wildlife. Chromium has long been considered as one of the priority pol-

lutants [1], generally existing in water with two stable oxidation forms: Cr(VI) and Cr(III) [2,3]. Cr(VI) possesses carcinogenicity, mutagenicity, toxicity and a wider range of applications in industries, whereas Cr(III) is less toxic and can be readily precipitated out from wastewater in the form of $\text{Cr}(\text{OH})_3$ [2,4,5]. Consequently, it is imperative to remedy Cr(VI) contamination, and meanwhile the reduction of Cr(VI) to Cr(III) is deemed as a key process [6–8]. Common treatment strategies include chemical reduction, biological reduction and electroreduction. During the chemical reduction process, the typical procedure is reduction of Cr(VI) to Cr(III) by adding

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China. Tel.: +86 15717484818; fax: +86 0731 88822829

E-mail address: yzh@hnu.edu.cn (Z.-h. Yang).

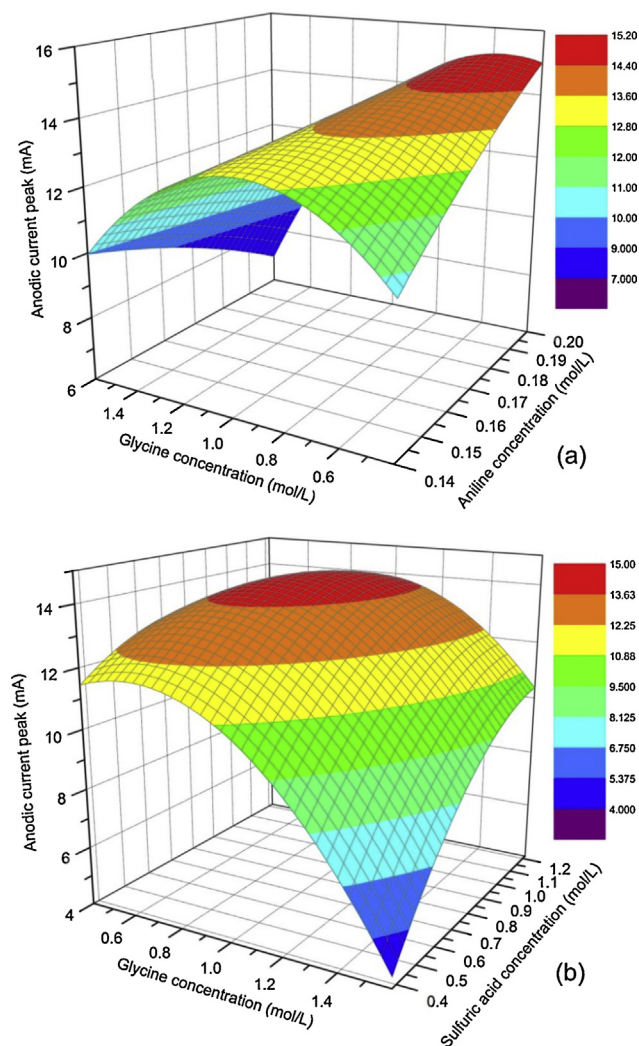


Fig. 1. Surface graphs of anodic current peak showing the effect of variables: (a) aniline and glycine concentration (b) sulfuric acid and glycine concentration.

reducing agents, followed by its precipitation as Cr(III) hydroxide [9–11]. Biological reduction primarily involves three stages: (1) binding of Cr(VI) onto the cell surface, (2) translocation of Cr(VI) into the cell, and (3) reduction of Cr(VI) to Cr(III) [12,13]. Electrore-

duction, a process merely depending on the electron gain and loss of electrodes to reduce Cr(VI), is commonly considered preferable due to its less impact on environment, owing to no reagents addition and the cleaner process with less sludge production [14,15]. However, suffering from slow kinetics, low current efficiency and large energy consumption, its applications are limited [16,17]. Fortunately, there are some available approaches to improve above problems, which mainly focus on the following aspects:

(1) Increase the surface-to-volume ratio of electrode material. Applications with three-dimensional electrodes are typical measures, which can be obtained in a number of ways, including rotating electrode [18], fluidized bed [19] and packed bed [20]. Additionally, porous materials provide alternatives, such as reticulated vitreous carbon electrode (RVC) and fibrous carbon electrode, which possess high surface-to-volume ratio that facilitates electron transfer and have been reported to achieve faster kinetics and require less time for the reduction of Cr(VI) [14,21–23].

(2) Electrode modification. In recent decades, conductive polymers, playing a major role as frequently-used modified films on the surface of electrodes, exhibit fast catalytic properties for optimizing Cr(VI) reduction [17,24,25]. Among them, polyaniline (PANI) appears to be one of the most widely-studied polymers since its fastest reaction rate and favorable stability under closed circuit conditions [26,27]. Electrodes modified with PANI films have served as spontaneous electron donors for the removal of Cr(VI) [27–31], leading to not only improving the electrical conductivity of electrodes but also inducing the faster site to site electron hopping transfer from PANI film to Cr(VI), which diminishes the energy consumption and expedites the reduction process.

(3) Combine with adsorption at the cathode. Severe hydrogen production competes with Cr(VI) reduction for electrons, generating alkaline environment near the cathode. Negatively charged cathode (quite negative potentials and high cathodic currents are usually applied) and rich OH^- hamper Cr(VI) anions transport and decrease reduction kinetics. For improvement, a potentiodynamic process for faster Cr(VI) reduction has been proposed, tactfully promoting anions capture at positive potentials through electro-adsorption and then reducing captured Cr(VI) at negative potentials [17]. Besides, some authors have developed a technology of combining electroreduction with biosorption for the enhancement removal of Cr(VI) in cathode cell [32]. Consequently, it seems feasible to accelerate Cr(VI) reduction through providing adsorption at the cathode, which virtually increases the opportunities for Cr(VI) anions to contact with cathode, whereas few related researches were reported.

Coincidentally, except the applications in electrochemical modified electrodes, PANI doped with a variety of dopants have also acted as adsorbents of Cr(VI) [33–35]. Due to the particular doping mechanism of PANI, the dopant species and the ratio of co-dopants have great impacts on its properties including cycling stability, conductivity and adsorption capacity etc. [36,37]. Therefore, PANI films doped with particular dopants offering excellent adsorption performance for Cr(VI), theoretically could closely associate electroreduction process of Cr(VI) with adsorption when loaded on cathode surface as modified films, but no literature has utilized yet.

In this study, we attempted to improve the reduction kinetics of Cr(VI) from aforementioned three aspects. RVC electrode acted as substrate material and then was covered with PANI film as modification measure. More importantly, to increase the positively charged adsorption sites on the cathode surface then benefit anions capture, an uncommonly used dopant, i.e., glycine, which has been proven to have good adsorption for Cr(VI) due to its protonated amine group ($-\text{NH}_3^+$) [38,39], was added in traditional sulfuric acid solution to prepare RVC electrode modified with sulfuric acid–glycine co-doped PANI (RVC/PANI-SA-GLY).

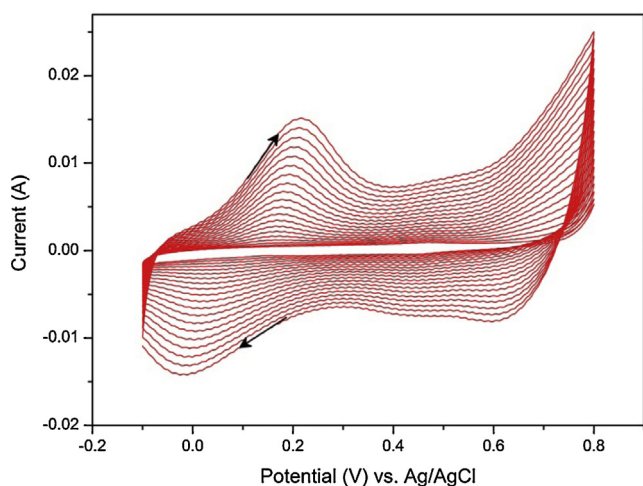


Fig. 2. Cyclic voltammogram of electrochemical synthesis of PANI-SA-GLY on RVC.

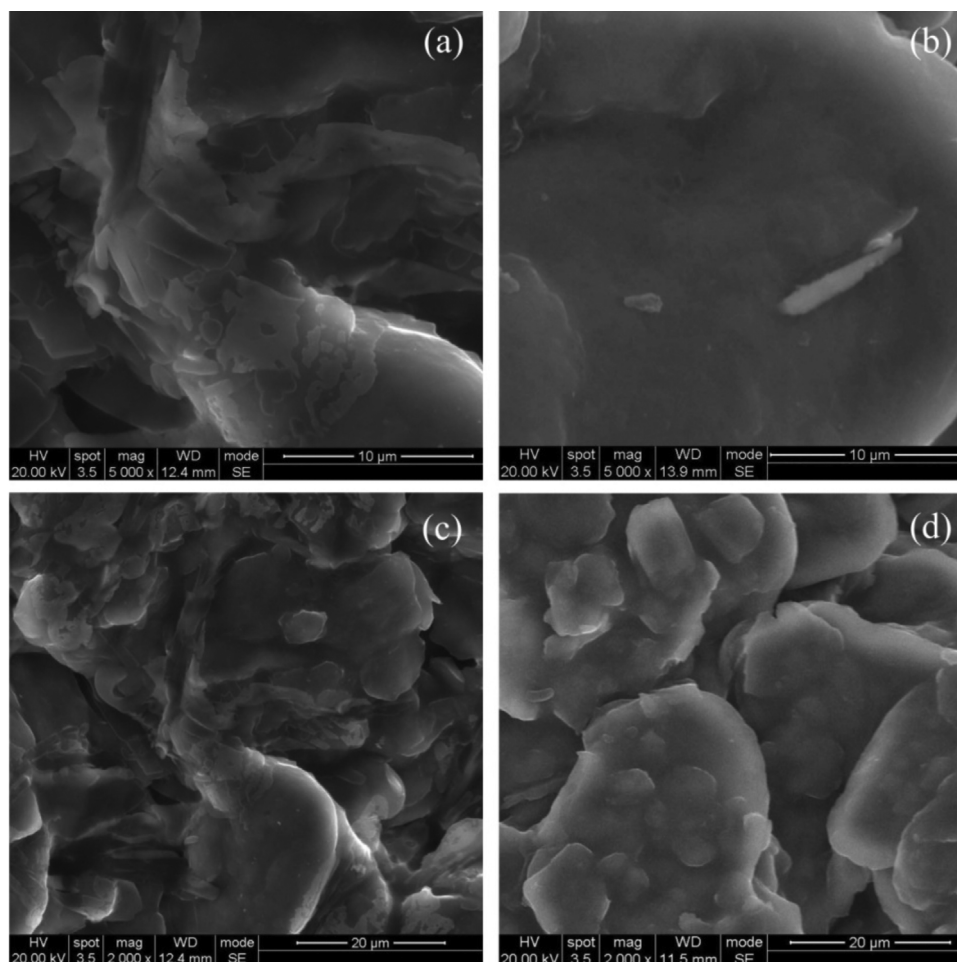


Fig. 3. ESEM images of RVC/PANI-SA-GLY. Current peak: (a) 10 mA, 5000 $\times$ (b) 30 mA, 5000 $\times$ (c) 10 mA, 2000 $\times$ (d) 30 mA, 2000 $\times$.

Firstly, response surface methodology (RSM) was selected for the optimum polymerization condition of co-doped PANI synthesis since uncommonly used glycine served as one of dopants. Next, studies were further focused on Cr(VI) electroreduction process, during which the influences of potential, initial concentration of Cr(VI), initial pH and current density on the reduction of Cr(VI) by RVC/PANI-SA-GLY were investigated, based on a comparison with RVC electrode modified with sulfuric acid doped PANI (RVC/PANI-SA) and bare RVC electrode. Following these investigations, a potential adsorption–reduction mechanism of RVC/PANI-SA-GLY to Cr(VI) was verified and elucidated. Finally, the stability of RVC/PANI-SA-GLY electrode was assessed.

2. Materials and methods

2.1. Materials

Aniline (AN, Tianjin Guangfukeji Ltd., China) was previously distilled under vacuum. The stock solution containing 100 mg/L Cr(VI) was prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) in distilled water. This stock solution was diluted as required to obtain working solutions containing 5–100 mg/L Cr(VI). The solution pH was adjusted in the range of 1.0–5.0 by adding H_2SO_4 or NaOH. Subsequently, Na_2SO_4 was added to the Cr(VI) solution as background electrolyte to adjust the solution conductivity to unified 3 mS/cm. All chemicals were of analytical reagent grade. A 50 pores per inch (ppi) RVC 3D mesh (1.0 cm $\times$ 1.0 cm $\times$ 3.0 cm, specific surface area 3200 m 2 m $^{-3}$,

Advanced Graphite Materials, China) was used as substrate material of working electrode/cathode and rinsed under ultrasound in alcohol followed distilled water prior to polymerization experiment. A platinum electrode and an Ag/AgCl electrode worked respectively as counter electrode/anode and reference electrode.

2.2. Preparation of working electrodes and Cr(VI) electroreduction conditions

The co-doped PANI was potentiodynamically polymerized as a thin film on the RVC substrate by electrochemical method in electrolyte composed of aniline, sulfuric acid and glycine (designed concentrations by CCD). Cyclic voltammetry was employed within the potential range of -0.1 to 0.8 V at a sweep rate of 50 mV/s. The first anodic current peak in the synthesis voltammograms (at approximately 0.2 V) was regarded as a criteria to indirectly control the thickness of PANI film. The preparation of RVC/PANI-SA was similar to that of RVC/PANI-SA-GLY except for the addition of glycine in electrolyte.

RVC/PANI-SA-GLY and RVC/PANI-SA were prepared for the electroreduction of 90 mL Cr(VI) solution under potentiostatic or galvanostatic conditions, bare RVC was also employed to reduce Cr(VI) as another comparison. Four factors including potential vs. Ag/AgCl (0.2, -0.2 , -0.4 , -0.6 , -0.8 V), initial concentration of Cr(VI) (5, 10, 25, 50, 100 mg/L), initial pH (1–5) and current density (0.012, 0.022, 0.032, 0.042, 0.052 mA/cm 2) were explored to compare their effects on three electrodes. A magnetic stirrer with stirring rate of 180 rpm was applied during electroreduction pro-

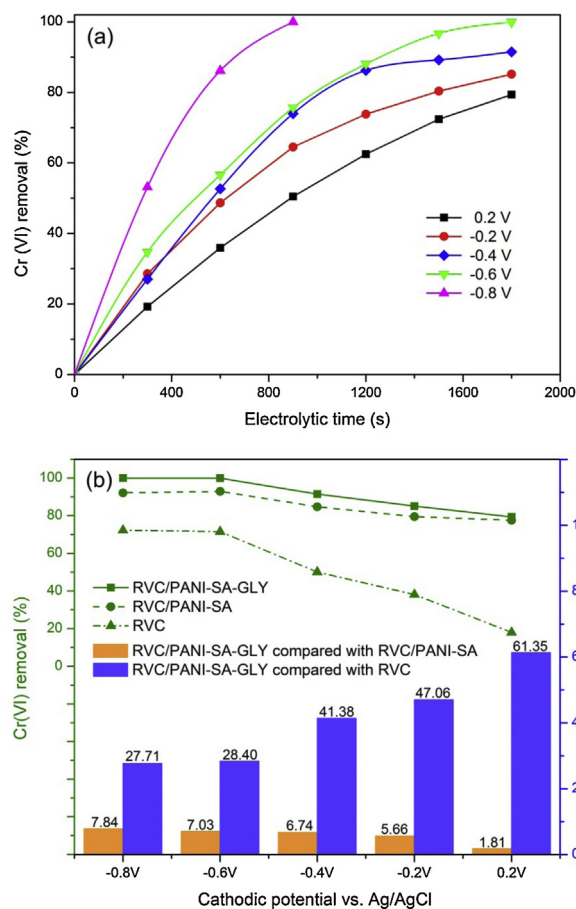


Fig. 4. Cr(VI) removal efficiencies (a) vs. time curves under RVC/PANI-SA-GLY, (b) correspondingly gained by RVC/PANI-SA, RVC when best removals were gained by RVC/PANI-SA-GLY and comparisons of three electrodes at different cathodic potentials (vs. Ag/AgCl); electrolyte stirring rate = 180 rpm, pH 2, $C_0 = 10$ mg/L.

cess to ensure adequate mixing. The electrochemical responses of electrodes were recorded in 0.5 mol/L H_2SO_4 at a sweep rate of 50 mV/s before and after the reaction with Cr(VI), acting as an evaluation of polymer stability. All the electrochemical measurements were performed on an electrochemical workstation CHI760E (Shanghai, China). All potentials in the text were measured versus Ag/AgCl reference electrode.

Environmental scanning electron microscope (ESEM) (Quanta 200 FEG, FEI, US) was used to observe the degree of surface coverage on RVC by PANI film. Fourier transform infrared (FTIR) spectra of electrodes were recorded by fourier transform-infrared spectrometer (FTIR-8400S, IRprestige-21) using KBr pellets in the range of 400–4000 cm^{-1} . The elemental composition analyses of electrodes after contacted with Cr(VI) were performed with energy dispersive spectrometer (EDS) (Quanta 200 FEG, FEI, US).

2.3. Central composite design (CCD)

CCD was applied to select the optimum polymerization condition. In the experimental design model, concentrations of aniline (x_1 : 0.12–0.22 mol/L), sulfuric acid (x_2 : 0.1–1.5 mol/L) and glycine (x_3 : 0–2 mol/L) were taken as factors. The first anodic current peak (y) in the synthesis voltammograms after 20 circles was response variable, which was fitted by a second-order model as described specifically in Supplementary Data. Response surface was generated using Design Expert Software Version 8.0.6 (STAT-EASE Inc., Minneapolis, USA).

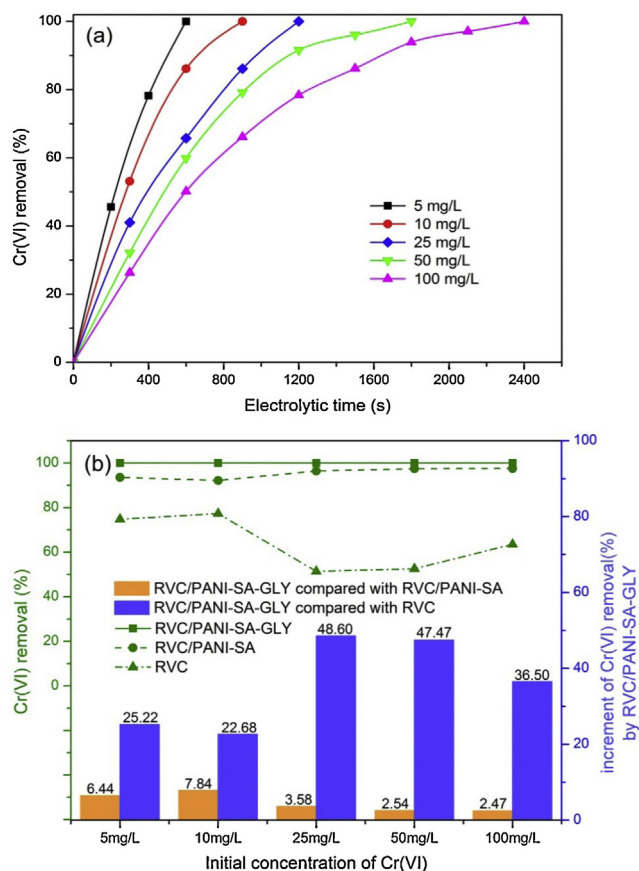


Fig. 5. Cr(VI) removal efficiencies (a) vs. time curves under RVC/PANI-SA-GLY, (b) correspondingly gained by RVC/PANI-SA, RVC when complete eliminations were gained by RVC/PANI-SA-GLY and comparisons of three electrodes at different C_0 ; electrolyte stirring rate = 180 rpm, pH 2, $E = -0.8$ V.

2.4. Analysis and calculations

The measurement method of Cr(VI) concentration, the calculations of Cr(VI) removal efficiency and current efficiency were detailed in Supplementary Data.

3. Results and discussion

3.1. Response surface methodology for polymerization conditions

Due to the adding of untraditional dopant, i.e., glycine in electrolyte, the influences it has on the synthesis of co-doped PANI and interrelations with other factors remained unknown. Therefore, to obtain a best proportion of aniline and two dopants which could promote the synthesis of PANI and maximize the effective function of NH_3^+ of glycine to Cr(VI) removal, CCD was employed for the optimization of polymerization conditions. Tables S1 and S2 and Fig. S1, respectively, showed the response variables of anodic current peak acquired from 20 groups of experiments, the analysis of variance (ANOVA) results of the quadratic model and the synergistic effect graph of aniline and sulfuric acid on the polymerization rate of PANI, and their details were discussed in Supplementary Data.

Fig. 1(a) displayed anodic current peak with the variation of aniline and glycine concentration. Corresponding to each level of aniline concentration, there was an optimum glycine dosage making the reaction keep the fastest rate, meaning appropriate glycine could promote the synthesis of PANI, which was probably related to the property of glycine and the best adjustment of H^+ concen-

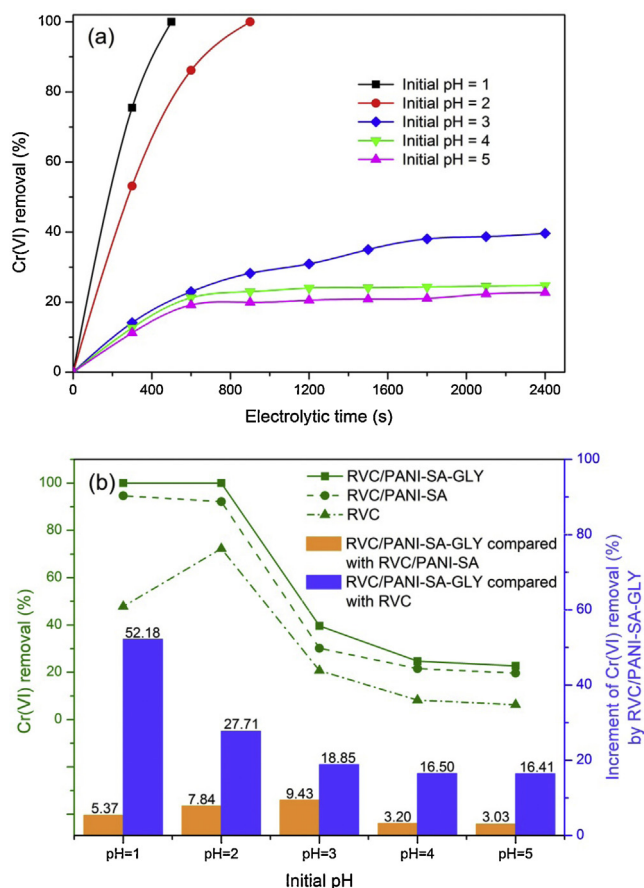


Fig. 6. Cr(VI) removal efficiencies (a) vs. time curves under RVC/PANI-SA-GLY, (b) correspondingly gained by RVC/PANI-SA, RVC when best removals were gained by RVC/PANI-SA-GLY and comparisons of three electrodes at different initial pHs; electrolyte stirring rate = 180 rpm, $C_0 = 10$ mg/L, $E = -0.8$ V.

tration by glycine. Besides, as Fig. 1(b) exhibited clearly, there was indeed a best ratio of sulfuric acid and glycine making the synthesis of co-doped PANI stay at high-point when aniline amount was fixed to the central value 0.17 mol/L.

According to RSM, the optimum polymerization conditions calculated from the regression equations were acquired. From 39 solutions provided, one (x_1 : 0.2 mol/L, x_2 : 0.85 mol/L, x_3 : 0.93 mol/L) was selected, under which not only glycine theoretically had more opportunities to exist in electrolyte as zwitter ion $^-OOC-CH_2-NH_3^+$ then doped in PANI but also where after the best Cr(VI) removal efficiency was actually obtained.

Fig. 2 showed the cyclic voltammogram of electrochemical synthesis of PANI-SA-GLY under the optimum polymerization condition. The characteristic peak shapes and positions similar to those gained in other literature [29,31] indicated PANI was deposited on RVC successfully. However, the peak shapes were not so sharp as

that of single sulfuric acid doping possibly due to the incorporation of $^-OOC-CH_2-NH_3^+$. The existence of SO_4^{2-} and $^-OOC-CH_2-NH_3^+$ in PANI would be discussed in Section 3.7. The practically reached anodic current peak was quite close to the predicted value. Hence, RVC/PANI-SA-GLY was prepared under aforesaid condition for subsequent experiments.

3.2. The thickness of PANI-SA-GLY

Ruotolo et al. [31] have proved that the electroreduction of Cr(VI) reacted at PANI/solution boundary, meaning PANI thickness will not influence the reaction rate when whole RVC surface was covered by the polymer. Since the current peak was regarded as a criteria to control the PANI thickness in this work, therefore, we actually expected to find a current peak, which could ensure the substrate surface was already totally covered by PANI-SA-GLY once the current peak was reached during the electrochemical synthesis process.

The degree of surface coverage on substrate was observed by ESEM images. When the synthesis was performed for current peak to 10 mA, the substrate surface was not totally covered and some portions of the substrate still can be observed in Fig. 3(a) and (c). However, when PANI-SA-GLY synthesis was carried out up to current peak value of 30 mA, no more substrate was observed in Fig. 3(b) and (d). A polymer film synthesized up to current peak of 40 mA was also prepared to verify the influence of PANI-SA-GLY thickness on the adsorption–reduction process of Cr(VI). Electroreduction experiments under RVC/PANI-SA-GLY obtained at 30 mA and 40 mA achieved close Cr(VI) removal efficiencies, demonstrating that effective adsorption sites also worked at PANI-SA-GLY/solution boundary or nearby it rather than pertained to PANI-SA-GLY thickness.

Consequently, synthesis of PANI-SA-GLY was discontinued when the current peak reached 30 mA. The same current peak was chosen for the synthesis of PANI-SA to ensure the total coverage of substrate, which was beneficial to compare the function of glycine during Cr(VI) electroreduction.

3.3. Influence of potential

Fig. 4(a) showed the variation of Cr(VI) removal efficiency with time under RVC/PANI-SA-GLY working electrode for different applied potentials: 0.2, -0.2 , -0.4 , -0.6 , and -0.8 V. It's observed that whereas 79.37%, 85.17%, 91.51%, 100% of Cr(VI) initially present was transformed respectively at 0.2, -0.2 , -0.4 , -0.6 V in 1800s, essentially 100% was transformed at -0.8 V in a much shorter period of 900s. The more negative the potential was, the faster reduction kinetics of Cr(VI) was gained, which was ascribed to the stronger reducing capacity and reducing environment provided by the more negative potential. In addition, the reduction rate with time (slope of each curve) weakened with the decreased Cr(VI) concentration, which suggested the first-order kinetics, as reported in other literature earlier [14,20].

Table 1

Current efficiencies for the reduction of Cr(VI) at different cathodic 50 mV/s potentials under three electrodes.

Electrolysis time (s)	Cathodic potential (V vs. Ag/AgCl)	Current efficiency (%)		
		RVC/PANI-SA-GLY	RVC/PANI-SA	RVC
900	-0.8	78	72	70
1800	-0.6	79	69	64
1800	-0.4	81	83	69
1800	-0.2	94	97	88
1800	0.2	98	99	142

For better parallel with other two electrodes and displaying the superiority of RVC/PANI-SA-GLY, at the moment RVC/PANI-SA-GLY obtained the best Cr(VI) removal efficiency during 1800s, the corresponding removal efficiencies by RVC/PANI-SA and RVC were plotted as lines in Fig. 4(b), meanwhile the absolute increments of Cr(VI) removal efficiency improved by RVC/PANI-SA-GLY were plotted intuitively as columns. We observed that RVC/PANI-SA-GLY achieved higher removal percentage in all cases but merely a difference of degree. In the case of the contrast with RVC/PANI-SA, the increments of Cr(VI) removal efficiency increased with the potential shift to the negative direction. When the potential was -0.8 V, Cr(VI) removal efficiency by RVC/PANI-SA-GLY was 7.84% higher than that by RVC/PANI-SA. This may be imputed to the opposite charges of NH_3^+ attached on RVC/PANI-SA-GLY due to the doping of glycine as zwitter ions, which played a role of electrostatic adsorption for Cr(VI) anions as expected, making Cr(VI) anions prefer to approach the electrode and be captured easily. Under more negative potential, the stronger repulsive interaction of electrode field to Cr(VI) anions [17] highlighted the function of NH_3^+ adsorption sites, thus the advantage of RVC/PANI-SA-GLY was naturally more obvious. Interestingly, the case of the contrast with RVC behaved oppositely, the increments were higher under more positive potentials. This was caused by their tremendous differences on electron transfer ability of these two electrodes, weakening the strength of adsorption. When electron transfer was harder to occur under a more positive potential, the gap between RVC/PANI-SA-GLY and RVC was widened owing to the faster site to site electron hopping transfer from polymer film to Cr(VI) [40].

Table 1 showed the effect of potentials on current efficiency. In all the three cases, when applied potential decreased from 0.2 to -0.6 V but with same electrolysis time, current efficiency decreased owing to the intensifying hydrogen evolution at more negative potentials. Nevertheless, at potentials of -0.8 V and -0.6 V prone to hydrogen evolution but providing stronger reducing capacity, current efficiencies were drastically improved by RVC/PANI-SA-GLY. Faster transport of Cr(VI) anions from bulk solution to PANI-SA-GLY/solution interface was obtained due to the positive traction provided by RVC/PANI-SA-GLY, consequently making electron transfer greatly focus on Cr(VI) and hydrogen production be inhibited effectively. Moreover, current efficiencies more than 100% were observed at the potential of 0.2 V, perhaps resulting from the electric absorption process of positive electrode field to Cr(VI) anions [17].

3.4. Influence of initial concentration of Cr(VI)

To investigate the suitability of RVC/PANI-SA-GLY for treating wastewater containing different levels of Cr(VI), we tested the following initial concentrations, $C_0 = 5, 10, 25, 50$, and 100 mg/L. Fig. 5(a) showed the percent of Cr(VI) reduction as a function of C_0 . With $C_0 = 5, 10$ mg/L, we obtained reduction percentages of virtually 100%, respectively, at $t = 600$ s and $t = 900$ s, whereas when C_0 was 100 mg/L, only 66.15% of Cr(VI) got reduced at $t = 900$ s. However, complete elimination under various C_0 can all be achieved by extending treatment time as Fig. 5(a) showed. Although it's apparent that lower C_0 needed shorter treatment time, but Cr(VI) with a high C_0 was discovered relatively easier to remove by comparing the ratios of C_0 to corresponding treatment time that needed to gain 100% removal.

Fig. 5(b) represented corresponding removal efficiencies by RVC/PANI-SA and RVC at the moment RVC/PANI-SA-GLY obtained complete elimination of Cr(VI) at different C_0 . It's evident that RVC/PANI-SA-GLY accelerated the reduction of Cr(VI) regularly. When compared with RVC/PANI-SA, the increments of Cr(VI) removal efficiency increased with the decreasing C_0 . With high C_0 (25, 50, 100 mg/L), Cr(VI) removal efficiencies were only improved

by approximately 3%, whereas when C_0 was at low values (5, 10 mg/L), we gained reduction percentages improved by 6%–8% under RVC/PANI-SA-GLY. Relatively high C_0 can ensure Cr(VI) anions distributed densely in solution, which originally provided plenty of opportunities for them to approach cathode with much ease; to the contrary, reactions occurred at relatively low C_0 were limited for the sparse distribution of Cr(VI) anions in solution, just giving chance to RVC/PANI-SA-GLY to offer positive attraction and promote anion transport as a result that faster reduction response generated. By this token, RVC/PANI-SA-GLY seemed to have more advantages on dealing with wastewater containing low concentration of Cr(VI), such as micro-pollution ground water and surface water etc. Inversely, when compared with RVC, relatively higher increments were obtained at high C_0 (25, 50, 100 mg/L). At this point, the electron transfer ability rather than additional absorption of electrodes played a dominate role in causing the difference on reduction rate. The increase of Cr(VI) removal efficiencies by RVC/PANI-SA-GLY mainly depended on the faster electron transfer from polymer to Cr(VI). Therefore, the higher the C_0 was, the greater the proportion of electron transfer happening through PANI film to Cr(VI) anions was, making the gap between RVC/PANI-SA-GLY and RVC on reduction rate more apparent.

3.5. Influence of initial pH

Fig. 6(a) showed the percentage of Cr(VI) reduction as a function of initial pH under RVC/PANI-SA-GLY. Complete reduction of Cr(VI) was achieved at pH 1–2 with dramatic reduction kinetics, yet the Cr(VI) removal percentage rapidly decreased as soon as the pH became greater than 3. Similar regularities were discovered in other literature [14,27]. This decrease of reduction ability was potentially due to: (i) when $\text{pH} \geq 3$, the standard potential for the reduction of Cr(VI) became less positive with pH where after the Gibbs free energy gradient (ΔG) became less negative [41]; (ii) although the overall pH of solution was low, quite high pH could appear in the vicinity of cathode, thus generating OH^- promoted the forming of insoluble $\text{Cr}(\text{OH})_3$ on cathode surface, which greatly hindered electron transfer [42].

Although unsatisfactory removal efficiencies were obtained when $\text{pH} \geq 3$, but RVC/PANI-SA-GLY still exhibited improvements as Fig. 6(b) showed. In the comparison with RVC/PANI-SA, the increments of Cr(VI) removal efficiency increased with the advance of pH in the range 1–3, removal efficiency was highest improved by 9.43% despite only 39.62% of Cr(VI) was finally reduced at initial pH 3. This may be attributed to the more effective adsorption of RVC/PANI-SA-GLY to Cr(VI) anions with pH shift to alkaline direction. However, there was small difference on reduction ability between these two electrodes when $\text{pH} > 3$. Firstly, less negative ΔG under less acidic solution (pH 4 and 5) made it hard for captured Cr(VI) through adsorption to be reduced timely, thus the adsorption sites of RVC/PANI-SA-GLY was limited, which interrupted the process of promoting anion transport through adsorption; secondly, quite high pH near the cathode was not neutralized effectively under relatively high solution pH, which may deprive the adsorption of RVC/PANI-SA-GLY by deprotonating $-\text{NH}_3^+$ of glycine to $-\text{NH}_2$. When compared with RVC, the increments by RVC/PANI-SA-GLY negatively correlated with pH. The great differences on Cr(VI) reduction of these two electrodes under strongly acidic conditions may be engendered by their different abilities to prevent hydrogen production, which was favored when there were greatly excess hydrogen ions in solution [27].

3.6. Influence of current density

The curves of Cr(VI) conversion percentage with time under RVC/PANI-SA-GLY for different current densities can be compared

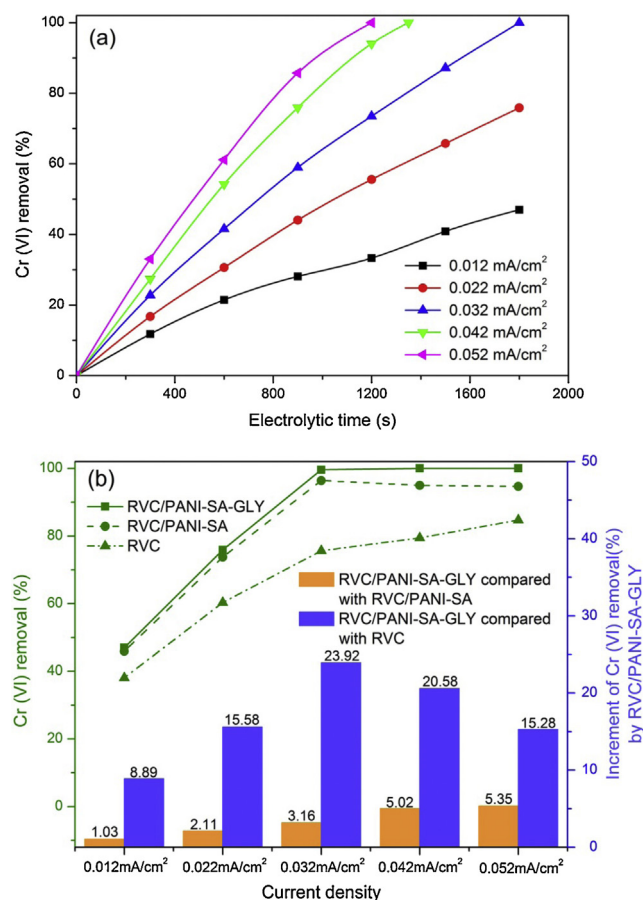


Fig. 7. Cr(VI) removal efficiencies (a) vs. time curves under RVC/PANI-SA-GLY, (b) correspondingly gained by RVC/PANI-SA, RVC when best removals were gained by RVC/PANI-SA-GLY and comparisons of three electrodes at different current densities; electrolyte stirring rate = 180 rpm, pH 2, $C_0 = 10$ mg/L.

in Fig. 7(a). We observed that virtually 100% reduction was achieved at 0.052 mA/cm² in 1200 s, during which merely 33.31%, 55.57%, 73.50%, 94.02% of Cr(VI) initially present were converted respectively at 0.012, 0.022, 0.032, 0.042 mA/cm², indicating that the reaction rate increased gradually with the increasing current density, which resulted from more electrons provided [27,28].

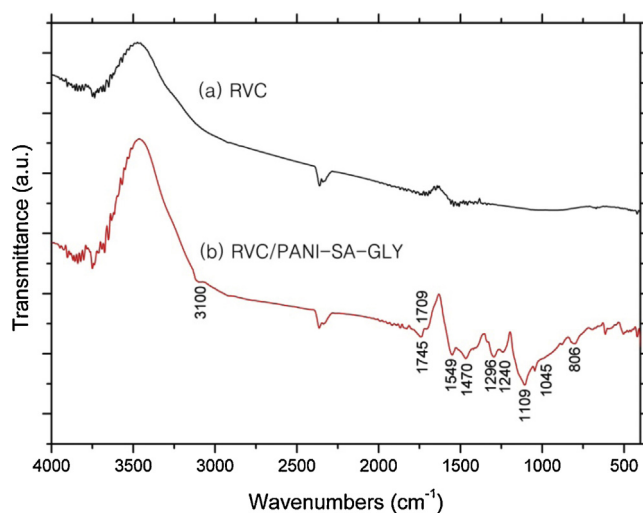


Fig. 8. FTIR spectra of (a) RVC and (b) RVC/PANI-SA-GLY.

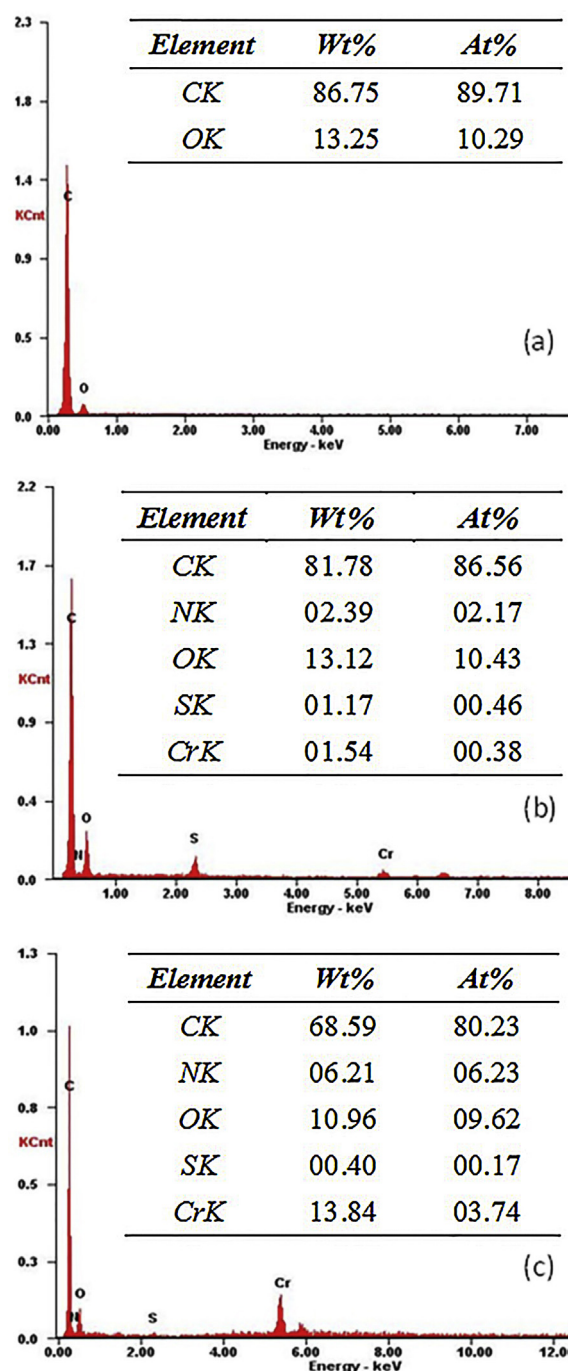


Fig. 9. EDS spectra of (a) RVC, (b) RVC/PANI-SA and (c) RVC/PANI-SA-GLY after contacted with Cr(VI).

The comparisons of RVC/PANI-SA-GLY with RVC/PANI-SA and RVC at the moment RVC/PANI-SA-GLY obtained the best Cr(VI) removal efficiency under different current densities during 1800s were displayed in Fig. 7(b). In contrast to RVC/PANI-SA, the increments of Cr(VI) removal efficiency by RVC/PANI-SA-GLY increased with the increase of current density. While the current density increased to 0.052 mA/cm², RVC/PANI-SA-GLY gained 5.35% higher Cr(VI) removal efficiency than RVC/PANI-SA. Likewise, it was probably ascribed to the electrostatic adsorption of RVC/PANI-SA-GLY for Cr(VI) anions, which readily captured more Cr(VI) anions on cathode surface. Under higher current density, the more abundant electrons offered enlarged the chance for captured Cr(VI) anions to receive electrons for reduction, making the process of promoting

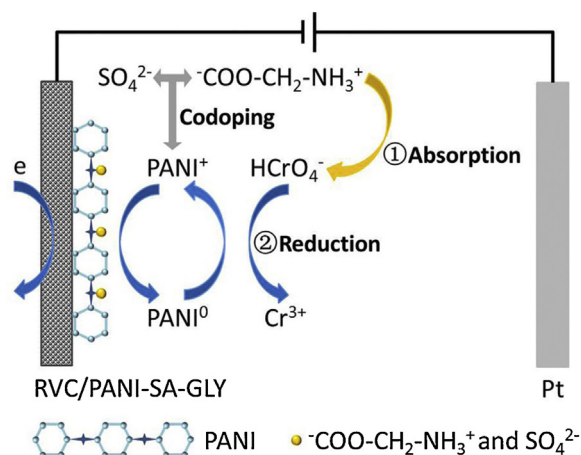


Fig. 10. Possible reaction schematic of Cr(VI) on RVC/PANI-SA-GLY.

anion transport through adsorption keep rapid and continuous due to the timely emptied adsorption sites, which greatly contributed for the higher increments. In contrast to RVC, with the advance of current density, the increments increased first and then decreased. When relatively fewer electrons were supplied under relatively lower current density, the function of faster site to site electron hopping transfer from polymer film to Cr(VI) of RVC/PANI-SA-GLY was highly embodied. However, when current density changed to much lower levels, more scarce electrons even made it hard for the preferable electron transfer ability of RVC/PANI-SA-GLY to work, thus the gap between these two electrodes was automatically narrowed.

3.7. Possible adsorption-reduction mechanism of RVC/PANI-SA-GLY

Under the optimum polymerization condition, PANI carried positive charges on the N atoms when protons in electrolyte entered the polymer chain. Meanwhile, part of glycine existed in a zwitter ionic form $^-OOC-CH_2-NH_3^+$, whose amount increased with the increasing pH during electrochemical synthesis process, benefiting more $^-OOC-CH_2-NH_3^+$ being incorporated into the polymer as counterions together with SO_4^{2-} anion to neutralize the positive charges on the N atoms. In this way, co-doped PANI-SA-GLY on RVC was formed.

Fig. 8 displayed the FTIR spectras of RVC and RVC/PANI-SA-GLY. Since the potentiodynamically deposited PANI-SA-GLY film combined closely with substrate electrode, FTIR spectrum of RVC/PANI-SA-GLY was obtained by grinding the whole electrode. There were obvious changes of spectrum characteristics before and after the deposit of PANI-SA-GLY on RVC, despite the intensity of absorption peaks in Fig. 8(b) was not as high as expected due to the relatively high content of RVC powder in the sample. The bands at 1549, 1470, 1296, 1240, 1109 and 806 cm^{-1} were due to the stretching vibrations of C=C of quinoid ring, C=C and C-N of benzenoid ring, C-N⁺ in proton acid doped PANI, C=N in quinoid ring and the bending vibration of C-H out of the plane of para-substituted aromatic ring, respectively. These bands agreed well with the bands of PANI reported by others [43,44], suggesting PANI prepared in this work was mostly in the form of emeraldine salt. Additionally, PANI-SA-GLY presented bands at 1045 cm^{-1} , which may be assigned to S=O stretching in sulfate counterions [34,43]. The presence of zwitter ion $^-OOC-CH_2-NH_3^+$ in PANI-SA-GLY structure was indicated by the appearance of the peaks in 1745, 1709, 3100 cm^{-1} , assigned, respectively, to the vibration of carboxyl groups, C=O and asymmetric stretching of NH_3^+ group of zwitter ionic glycine [38,45,46].

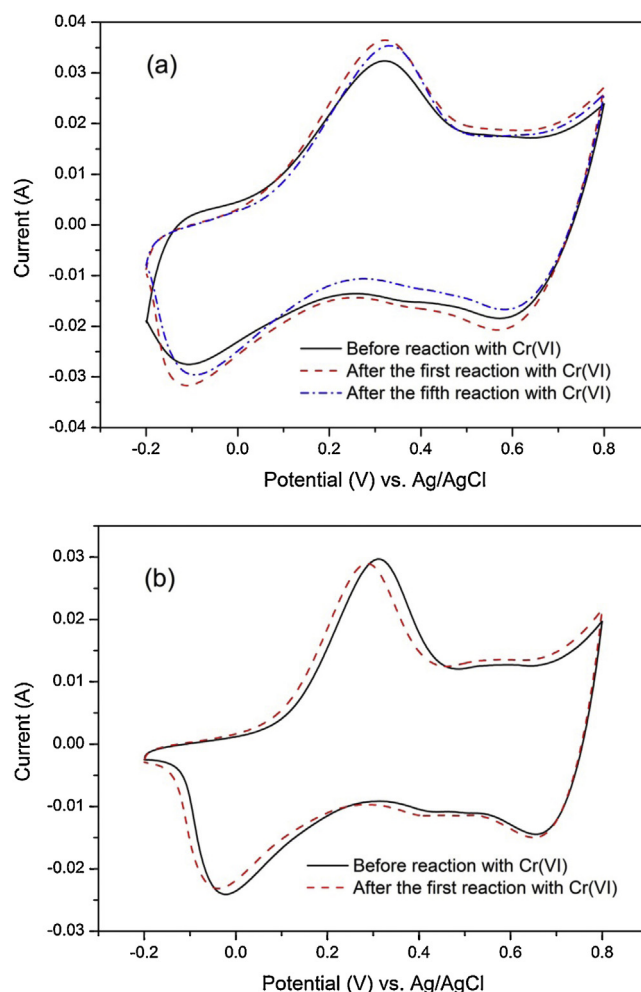


Fig. 11. Electrochemical responses of (a) RVC/PANI-SA-GLY and (b) RVC/PANI-SA before and after reaction with Cr(VI) at $E = -0.8$ V. Sweep rate: 50 mV/s.

Therefore, sulfuric acid-glycine co-doped PANI film was proved to be successfully loaded on RVC electrode.

EDS was used to analyze the elemental composition of three electrodes after contacted with Cr(VI), which could provide direct evidences for their different adsorption ability of Cr(VI) anions. Obviously, RVC/PANI-SA-GLY showed much stronger signal value of Cr peak than other electrodes in Fig. 9, probably resulting from the increase of adsorption sites especially the intense adsorption of $^-OOC-CH_2-NH_3^+$ [38,39]. Thus, EDS analysis gave puissant supports to previous experimental results.

According to the results of FTIR and EDS, we supposed that the faster reduction kinetics of Cr(VI) by RVC/PANI-SA-GLY may be attributed to an adsorption-reduction mechanism. Cr(VI) anions reduced on the surface of RVC/PANI-SA-GLY probably experienced the following process as Fig. 10 showed: (1) zwitter ions doped into oxidized PANI ($PANI^+$) can promote the ion transport rate of Cr(VI) anions and capture more Cr(VI) on cathode surface due to

Table 2
The results of cycle experiments by RVC/PANI-SA-GLY.

Cycle times of RVC/PANI-SA-GLY	Cr(VI) removal efficiency (%)
The first cycle	100.00
The second cycle	99.48
The third cycle	99.26
The fourth cycle	98.43
The fifth cycle	97.74

the electrostatic adsorption of NH_3^+ ; (2) when a negative potential was applied, PANI^+ was firstly transformed to its reduced state (PANI^0) via receiving electrons offered by substrate electrode and then immediately transported the electrons to captured Cr(VI) ions, accompanied by itself turning back to PANI^+ and simultaneously incorporating $^-\text{OOC-CH}_2\text{-NH}_3^+$ and SO_4^{2-} still in the vicinity of cathode surface, making the adsorption–reduction process recyclable. In this way, RVC/PANI-SA-GLY played an important role as adsorption and electrocatalytic media in improving the reduction rate of Cr(VI) .

3.8. The stability of RVC/PANI-SA-GLY

Electrochemical response of PANI-SA-GLY film was recorded within the potential range of -0.2 to 0.8 V, which was also done to RVC/PANI-SA to form comparison. Comparing voltammograms before and after the first reaction with Cr(VI) in Fig. 11, no significant losses in electrochemical activity were observed in both cases, implying the films all remained stable. Interestingly, slight increase in current peak was observed in the case of PANI-SA-GLY, which perhaps was connected with the loss of zwitter ions during electroreduction process and its being replaced by sulfate anions with better electrical conductivity [47]. Experiments in which a same RVC/PANI-SA-GLY was used for five successive Cr(VI) reduction cycles ($E = -0.8$ V, $C_0 = 10$ mg/L, pH 2, $t = 900$ s) were carried out. The results (Table 2) showed that there was still a removal efficiency of almost 98% in the fifth cycle and the fifth electrochemical response of RVC/PANI-SA-GLY changed little as Fig. 11(a) displayed, collectively indicating that the loss of glycine was a relatively slight and slow process and the absorption of RVC/PANI-SA-GLY can work continuously for several cycles with little change in accelerating Cr(VI) reduction rate.

4. Conclusions

Our research explored the optimum polymerization condition of co-doped PANI when glycine served as one of dopants. The optimal adding of glycine not only made the synthesis of co-doped PANI stay at high-point, but also maximized the adsorption of glycine theoretically and practically leading to the improvement of Cr(VI) removal. The PANI-SA-GLY thickness did not influence the adsorption–reduction rate, but complete coverage of substrate surface must be guaranteed.

Electroreduction experiments revealed that RVC/PANI-SA-GLY can be successfully applied to remove Cr(VI) , during which faster reduction kinetics response than RVC/PANI-SA and bare RVC was observed. The effect of doped glycine was significantly highlighted in the contrast of RVC/PANI-SA-GLY and RVC/PANI-SA, where the improvement of Cr(VI) removal was particularly obvious at more negative potentials, lower initial concentrations of Cr(VI) (5 mg/L, 10 mg/L), relatively less acidic solution (initial pH 2 and 3) and higher current densities, best obtaining 7.84% higher removal efficiency with entire Cr(VI) transformed ($E = -0.8$ V, $C_0 = 10$ mg/L, pH 2, $t = 900$ s). Additionally, under extremely negative potentials (-0.6 V, -0.8 V) benefitting for hydrogen evolution but providing stronger capacity for reduction, current efficiencies were improved by RVC/PANI-SA-GLY, which resulted from its inhibition effect on hydrogen production, adsorption for Cr(VI) and faster electron transfer.

Based on the results of FTIR and EDS, a possible adsorption–reduction mechanism of RVC/PANI-SA-GLY was proposed, suggesting that the intense adsorption of RVC/PANI-SA-GLY for Cr(VI) anions made great contributions to the faster reduction kinetics and higher current efficiency. The stability of PANI-SA-GLY film was relatively satisfactory, whereas it's necessary to consider the recovery of zwitter ions back to PANI film in further study.

In conclusion, PANI-SA-GLY modified electrode could be a promising alternative for the electroreduction of low concentration Cr(VI) with favorable advantages of less processing time and higher current efficiency.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2015.01.002>.

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