Combination of electroreduction with biosorption for enhancement for removal of hexavalent chromium

Yining Hou a, Huijuan Liu a,*, Xu Zhao a, Jiuhui Qu a, J. Paul Chen b,∗

a State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China
b Department of Civil and Environmental Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore

1. Introduction

Chromium and its compounds are extensively used in industry, with the most usual and important sources coming from the alloy reparation, metal cleaning and processing, leather tanning, wood preservation, ore processing, and petroleum refining processes [1,2]. In the effluents from these industries, chromium is present primarily as hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Cr(VI) is more toxic and mobile than Cr(III), and acts as carcinogen and mutagen in biological systems [3–5]. Research on Cr(VI) decontamination has always attracted wide attention [6–10].

Various physicochemical technologies used for Cr(VI) removal include chemical reduction and precipitation, reverse osmosis, ion exchange, and adsorption on activated carbon. However, these conventional methods have severe constraints, such as ineffective metal removal at low concentrations, high reagent requirements, high operating and maintenance costs, and secondary environmental problems from waste disposal [6]. This has led to the development of alternative technologies for the removal of chromium species from wastewaters.

Biosorption is considered as a promising technology for toxic metal elimination, thanks to the low-cost and easily available biosorbents and the high eliminating efficiency for a variety of heavy metals. Among numerous biosorbents, brown seaweeds are known as one of the most promising biosorbents because of their enormous abundance in worldwide coastal areas and relative ease in collection [11,12].

It has been reported that brown seaweeds are capable of removing Cr(VI) from aqueous phase [2,7,9,10,13]. In the biosorption process, Cr(VI) can be bound onto the surface of brown seaweeds through anionic adsorption, and/or can be converted to Cr(III) via the abiotic reduction [9]. However, it has also been found that the adsorption of Cr(VI) onto brown seaweeds is a rather slow process, with the time required for reaching sorption equilibrium being 24–72 h or even hundreds of hours [2,10,13–15]. On the other hand, brown seaweeds are recognized to offer much faster adsorption kinetics for cationic metal ions, and the biosorption equilibrium can generally be achieved in several hours [10,16,17]. Hexavalent chromium usually occurs in aqueous phases as oxyanions like CrO4 2−, HCrO4 −, and Cr2O7 2−, while trivalent chromium is primarily present as cations like Cr3+, Cr(OH)2+, and Cr(OH)4− [10,18]. It is natural to expect that, if a more rapid and more efficient procedure for reducing Cr(VI) into Cr(III) is introduced into the biosorption process, the removal of both Cr(VI) and Cr(III) by brown seaweeds would be greatly enhanced due to the brown seaweeds’ excellent kinetics and capacity for cationic metal adsorption.

Among various technologies, electrochemical reduction is more attractive because it is environment-friendly, highly efficient and selective, convenient to implement, and easy to realize automatic...
operation. In this study, we designed to combine electrochemical reduction and biosorption to create a process of electrochemically assisted biosorption (ECAB) in which the electroreduction of Cr(VI) and the biosorption of Cr(III) were coordinated to accomplish a simultaneous removal of Cr(VI) and Cr(III). Brown seaweed Sargassum sp. was selected and employed after chemically modification as the biosorbent. A palladium (Pd) film electrode was prepared and used as the cathode because Pd was reported to exhibit high catalytic or electrocatalytic activity in many reductive reactions [19–21]. Experiments were designed to fully elucidate the coupled mechanisms for the simultaneous removal of Cr(VI) and Cr(III) in the ECAB process.

2. Materials and methods

2.1. Materials

The raw biomass of Sargassum sp. was collected from the coasts of Singapore. The modified seaweed (MSW) was prepared according to Chen and Yang [16]. The particle size of MSW ranged from 500 to 800 μm. Na₂Cr₂O₇·2H₂O, Na₂SO₄, NaOH, and H₂SO₄ of analytical-reagent grade were all purchased from China National Medicines Corporation Ltd. All solutions were prepared with deionized water.

2.2. Electrochemically assisted biosorption

All the ECAB experiments were carried out in a batch reactor of two compartments. The cathode cell (45 mm × 30 mm × 75 mm) and anode cell (45 mm × 12 mm × 75 mm) were separated by a cation-exchange membrane (Nafion 117, Dupont). The homemade Pd film electrode (30 mm × 40 mm) was used as working electrode (cathode), a saturated calomel electrode (SCE) was selected as the reference electrode, and platinum (Pt) wire, 72 mm in length with a diameter of 1.5 mm, was positioned in the anode compartment as a counter electrode. The background electrolyte was Na₂SO₄, adjusting pH value with diluted H₂SO₄ and NaOH solution. Our previous studies showed that the optimal biosorption was achieved around pH 2.0 [10]. Typically, the waste effluents laden with Cr(VI) from industrial sources has pH < 3. Hence, the initial pH of tested solutions was selected at pH 2.0. Cr(VI) and MSW were added into the cathode cell. The cathodic solution was stirred magnetically to keep MSW in suspension. The power source was an EG&G model 263A potentiostat (Princeton Applied Research, USA).

The experiments for biosorption-alone and electrochemical reduction (ECR)-alone were both carried out in the same reactor under the same conditions. The biosorption-alone study was conducted in the absence of electrodes, while the ECR-alone study was carried out without the addition of MSW.

2.3. Analysis and characterization

The concentration of total chromium ions consisting of Cr(III) and Cr(VI) was measured by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, OPTIMA 2000, PerkinElmer, USA). The concentration of Cr(VI) was determined by measuring the absorbance at 540 nm after complexation with 1,5-diphenylcarbazide [10], using a UV–vis spectrophotometer (Hitachi U-3010, Japan). When only Cr(III) was initially present in the solution, its concentration was analyzed by the ICP-OES.

Fourier transformed infrared spectroscopy (FTIR) was employed to determine the changes in vibration frequency in the functional groups on biosorbents used in different processes. The spectra were collected by a Thermo-Nicolet 5700 FTIR spectrometer (Thermo Co., USA) within the wavenumber range of 650–4000 cm⁻¹. Specimens of various biosorbents were mixed with KBr and ground in an agate mortar at an approximate ratio of 1/100 for the preparation of pellets. The resulting mixture was pressed at 14 tons for 3 min. The spectral resolution was set to 4 cm⁻¹ and 32 scans were collected in each spectrum. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. All spectra were plotted using the same scale on the absorbance axis.

The chemical analysis on the surfaces of selected biosorbents was conducted by X-ray Photoelectron Spectroscopy (Kratos AXIS Ultra, UK). The XPS spectra were obtained by applying monochromatic Al Kα X-ray energy source (1486.7 eV) working at 15 kV and 10 mA. The vacuum in the analysis chamber was always better than 3 × 10⁻⁸ Torr. High-resolution scans for the element Cr were performed over the 568–600 eV ranges, with the pass energy of 40 eV. The XPS results were collected in binding energy forms and fit using the software of CasaXPS (2.3.12Dev7). The spectral deconvolution was performed using the curve-fitting program with the subtraction of Shirley background.

3. Results and discussion

3.1. Enhanced chromium removal by ECAB

The removal efficiencies of both Cr(VI) and total Cr by ECAB were tested and compared with those by biosorption-alone and ECR-alone. As shown in Fig. 1a, 99.9% of Cr(VI) were reduced and
15.7% of total Cr were removed by 360 min in ECR process. This is expected as the electrochemical reduction of Cr(VI) can lead to the formation of Cr(III), which is the most stable chromium species.

The presence of Cr(III) species had led to the formation of its precipitation after the adjustment of the pH in the above solution using NaOH. White precipitate was observed around pH 7.0, indicating the presence of Cr(III) and the formation of the Cr(OH)3 precipitate [22].

The high efficiency for Cr(VI) reduction in ECR process demonstrates that the prepared Pd film electrode provides a satisfying performance in reducing Cr(VI) to Cr(III). The Cr(VI) removal is significantly enhanced by the introduction of electrochemical reduction into biosorption, based on the comparison of the removal efficiency for Cr(VI) between the ECAB with that of biosorption-alone. In the ECAB, 99.1% of Cr(VI) was removed within 360 min, whereas only 51% of Cr(VI) was removed by biosorption-alone after the same duration.

Theoretically speaking, besides the electrochemical reduction of Cr(VI), the Cr(VI) removal could also be attributed to the adsorption of Cr(VI) by MSW and the reduction of Cr(VI) by MSW in the ECAB process. The role of the adsorption of Cr(VI) by MSW will be discussed later in the following sections.

As for the reduction of Cr(VI) by MSW, several experiments were carried out to investigate the effect of MSW dose on the removal efficiency for Cr(VI) in the ECAB. Comparing the Cr(VI) removal at an MSW dose of 0 (i.e., ECR), 1.5 and 3.0 g/L, it is found that the removal efficiency of Cr(VI) is decelerated to a degree as the MSW dosage is increased. This finding indicates that the reduction of Cr(VI) by MSW plays a less important role in the ECAB. The decrease in the reduction of Cr(VI) with the increase of MSW dosage could be ascribed to that the addition of MSW may affect the conductivity of the reaction solution to some extent. Nevertheless, a satisfying removal of Cr(VI) (>99.0%) could still be accomplished after 360 min in the presence of MSW biosorbent with the dosage of 1.5 g/L or 3.0 g/L.

The removal of total Cr is much higher in the ECAB system than that in biosorption-alone system as shown in Fig. 1b. By contrast with the 35.7% removal of total Cr in biosorption, a much efficient depletion of the chromium-bearing solution is obtained in the ECAB and the concentration of total Cr is decreased by 87.0% after 360 min.

Combining the results for the removal of Cr(VI) and total Cr in these two processes demonstrates that the reduction efficiency of Cr(VI) could exert a direct influence on the removal of total Cr. During the ECAB process, Cr(VI) is reduced efficiently into Cr(III) on the Pd film cathode. The resulted Cr(III) is rapidly and effectively adsorbed onto the MSW solution, leading to the high efficiency of removal of total Cr. Yang and Chen [10] had reported that the reduction of Cr(VI) by the biosorbent essentially controlled the overall biosorption process since the sorption of cations (Cr(III)) that was formed via the reduction of hexavalent chromium ion) onto the seaweed-based biosorbents was a fast process. In the ECAB system, the barrier of Cr(VI) reduction can be easily overcome by the electrochemical reduction, thus leading to the substantial improvement in total Cr removal. In contrast, in the course of biosorption-alone, the reduction of Cr(VI) on MSW proceeds slowly and the Cr(VI) anions have a limited adsorption kinetics onto MSW. Thus, the removal of total Cr is much poorer.

The above results clearly demonstrate that the reduction of Cr(VI) can be enhanced by introducing an electrochemical process. In order to check whether the adsorption of Cr(III) onto MSW could be improved by the electrochemical process, a solution containing Cr(III) (1 mmol/L) instead of Cr(VI) was used for a series of experiments, namely ECAB (pHinit. 2.0), ECR (pHinit. 2.0), biosorption (pHinit. 2.0), ECAB (pHconst. 2.0), ECR (pHconst. 2.0), and biosorption (pHconst. 2.0). The former three processes were conducted with initial pH of 2.0 and without adjusting pH afterward; the latter three processes were performed at constant pH controlled at 2.0 during the whole reaction.

As shown in Fig. 2, no notable removal of Cr(III) is observed in ECR (pHconst. 2.0), while a weak removal of Cr(III) is obtained in ECR (pHinit. 2.0), achieving 7.3% removal at 360 min. As the cathodic evolution of hydrogen (H2) consumes hydrogen ion (H+), the solution pH increases gradually as the electrochemical reaction goes. The final pH increases to 2.3 at 360 min. The solution pH on/near the surface of Pd cathode would be even higher than that of the bulk solution due to the diffusion lag of protons. Under such a situation, a small amount of Cr(III) is prone to deposit on the surface of Pd cathode as Cr(OH)3 with a large quantity of free Cr(III) ions existing in the solution, which accounts for the slight removal of Cr(III). This also explains the small removal of total Cr in ECR process starting with 1 mmol/L Cr(VI) shown in Fig. 1b.

The pH values were found to increase to 2.5 in ECAB (pHinit. 2.0) and to 2.3 in biosorption (pHinit. 2.0) at 360 min, and these three processes showed better removal of Cr(III) than ECAB (pHconst. 2.0) and biosorption (pHconst. 2.0). This observation can be expected as the adsorption capacity of Cr(III) by MSW is increased with the pH elevation [7]. The removal rate of Cr(III) in ECAB (pHconst. 2.0) is almost parallel to that in biosorption (pHconst. 2.0), whereas the removal efficiency of Cr(III) by ECR (pHinit. 2.0) is higher than that by biosorption (pHinit. 2.0), for example, about 11.5% higher at 360 min. The above results indicate that the enhancement of the Cr(III) removal by electrochemical process is mostly due to the elevation in solution pH, and partly to the formation of Cr(OH)3 deposition.

3.2. Effect of cathodic potential on chromium removal by ECAB

The estimated potential for H2 evolution is ~0.6 V on the Pd film electrode. The peak corresponding to the reduction of Cr(VI) into Cr(III) on the Pd film is observed at ~0.25 V (voltammogram shown in Fig. S4). When a bias more positive than ~0.6 V is applied on the cathode, the evolution of H2 does not significantly occur on the Pd film surface generating only quite a small amount of H2. It is reported that Pd is able to chemisorb the generated H2 and then decompose H2 into atomic H, a highly activated intermediate hydrogen radical [19,20,23]. Cr(VI) may also gain electrons (e−) directly on Pd cathode surface and be reduced to Cr(III). The reduc-
tion of Cr(VI) likely involves two processes: direct electroreduction and indirect electroreduction by atomic H\(^+\). When the cathodic bias is more negative than \(-0.6\) V, the evolution of H\(_2\) will become much more dramatical with lowering the bias, and hence an increasing amount of H\(_2\) will be chemisorbed on the Pd cathode surface boosting production of atomic H\(^+\). As a result, the contribution from the indirect electroreduction by atomic H\(^+\) turns increasingly more important in the reduction of Cr(VI).

The reaction between Cr(VI) and atomic H\(^+\) can be expressed as follows, where Cr(VI) exists dominantly as HCrO\(_4\) and Cr\(_2\)O\(_2\)\(^{2-}\) around pH 2.0.

\[
\text{HCrO}_4^- + 3\text{H}^+ + 4\text{H}^+ \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O} \quad (1)
\]

\[
\text{Cr}_2\text{O}_2^{2-} + 6\text{H}^+ + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad (2)
\]

The effect of cathodic bias on the efficiency of Cr removal by ECAB was studied with the results demonstrated in Fig. 3. The Cr(VI) removal is accelerated as the cathodic bias is decreased from \(-0.5\) to \(-1.5\) V. The Cr(VI) removal raises from 94.9% to 99.1% between \(-0.5\) V and \(-1.0\) V after 360 min.

At \(-1.5\) V, 99.3% of Cr(VI) is removed after 120 min. At \(-0.5\) V bias that is less than the onset potential for H\(_2\) evolution on the Pd film cathode (\(-0.6\) V), direct electroreduction and indirect electroreduction by atomic H\(^+\) both account for the reduction of Cr(VI). At \(-1.0\) V and \(-1.5\) V bias, as the quantity of atomic H\(^+\) is notably enlarged on the Pd film surface at the potential more negative than \(-0.6\) V, the indirect electroreduction by atomic H\(^+\) starts to play a greater role in the reduction of Cr(VI). As the generation of atomic H\(^+\) is much weaker at \(-0.5\) V than that at \(-1.0\) V, and the direct electroreduction of Cr(VI) is also limited at \(-0.5\) V, a higher efficiency for Cr(VI) removal is obtained at \(-1.0\) V. Compared with that at \(-1.0\) V, a larger amount of atomic H\(^+\) is generated at \(-1.5\) V, leading to more efficient Cr(VI) removal. However, when the bias is lowered to \(-2.0\) V, 90.9% of Cr(VI) is removed by 120 min, less than 99.3% at \(-1.5\) V. A higher evolution of H\(_2\) is expected at \(-2.0\) V than at \(-1.5\) V. Nevertheless, not all the generated H\(_2\) could be chemisorbed onto the Pd film surface and subsequently decomposed into atomic H\(^+\). A higher production of H\(_2\) would also make more excessive hydrogen bubbles accumulating on the Pd film surface, which then hinders the contact between the Pd cathode and the target pollutant, that is, Cr(VI), resulting in the decrease in the removal efficiency for Cr(VI) [23–25].

The removal efficiency for total Cr follows the order \(-0.5\) V < \(-1.0\) V < \(-2.0\) V < \(-1.5\) V, which is coincident with that of the removal efficiency for Cr(VI). Except at \(-0.5\) V, the differences among the removal efficiencies of total Cr at \(-1.0\) V, \(-1.5\) V, and \(-2.0\) V are less than those among the removal efficiencies of Cr(VI) at these three cathodic potentials. Especially by 360 min, a close removal percentage of total Cr is observed at \(-1.0\), \(-1.5\), and \(-2.0\) V, that is, 87.0%, 84.2%, and 86.4%, respectively. Despite the different rates for Cr(VI) reduction, a reaction time of 360 min is sufficient for achieving an effective reduction of Cr(VI), further leading to an effective removal of total Cr at the three biases.

### 3.3. Effect of Na\(_2\)SO\(_4\) concentration on ECAB

Fig. 4 shows the removal efficiencies for Cr(VI) and total Cr in the ECAB at different concentrations of Na\(_2\)SO\(_4\) electrolyte. When enlarging Na\(_2\)SO\(_4\) concentration from 5 to 10 mmol/L, the efficiency for Cr(VI) removal is enhanced. At 10 mmol/L Na\(_2\)SO\(_4\), 99.0% of Cr(VI) is eliminated after 120 min, whereas 99.1% removal is achieved until 360 min at 5 mmol/L Na\(_2\)SO\(_4\).

When Na\(_2\)SO\(_4\) concentration is further raised to 25 and 50 mmol/L, the efficiency for Cr(VI) removal does not further increase and decreases to some extent. The removal efficiencies, however, are still higher than at 5 mmol/L Na\(_2\)SO\(_4\). At 25 and 50 mmol/L Na\(_2\)SO\(_4\), 99.4% and 99.5% removal of Cr(VI) is reached after 240 min, which is more than 120 min for the same removal at 10 mmol/L Na\(_2\)SO\(_4\).

Anionic Cr(VI) is adsorbed onto MSW mainly through the binding of Cr(VI) to the positively-charged groups present on the MSW surface [9]. SO\(_4^{2-}\), as an anion with a similar structure, would compete the adsorptive sites with the MSW surface with Cr(VI) [26]. If the adsorption of Cr(VI) by MSW was a predominant process in the ECAB, the removal efficiency of Cr(VI) would decrease with enlarging the concentration of SO\(_4^{2-}\). The obtained results, however, do not support this hypothesis.

Nonetheless, it is acceptable that the electrochemical reduction of Cr(VI) is the dominant process in the ECAB. Increasing the concentration of Na\(_2\)SO\(_4\) electrolyte would promote the conductivity of the reaction solution, then leading to greater cathodic current under the same cathodic bias (\(-1.0\) V). Stronger evolution of H\(_2\) is expected at greater cathodic current, accordingly generating more atomic H\(^+\). This explains the enhanced efficiency for Cr(VI) removal at 10 mmol/L Na\(_2\)SO\(_4\) than that at 5 mmol/L Na\(_2\)SO\(_4\). At 25 and 50 mmol/L Na\(_2\)SO\(_4\), overly high production of H\(_2\) is accompanied by excessive accumulation of hydrogen bubbles on the Pd film surface, forming an impediment to the contact between the Pd film and Cr(VI), then retarding the reduction of Cr(VI) by atomic H\(^+\) and obtaining lower efficiencies for Cr(VI) removal than that at 10 mmol/L Na\(_2\)SO\(_4\).

The removal percentages of total Cr are 87.0%, 70.1%, 55.9%, and 49.5% after 360 min at 5, 10, 25, and 50 mmol/L Na\(_2\)SO\(_4\), respectively, indicating that a decrease in the removal for total Cr as an increase in Na\(_2\)SO\(_4\) concentration. This phenomenon can be ex-
explained by the behavior of the adsorption of Cr(III) by MSW. An effective reduction of Cr(VI) is accomplished during the reaction at the various concentrations of Na₂SO₄, and especially at the later reaction stage when the total Cr is mainly composed of Cr(III).

At pH 2.0, Cr³⁺ and Cr(OH)₂⁺ exist as the predominant species of Cr(III) [18], and the adsorption of Cr(III) cations by MSW is able to be achieved through ion exchange besides the complexation of Cr(III) with the surface functional groups of MSW [10,18]. On the other hand, sodium ion as a cation may compete with Cr³⁺ and Cr(OH)₂⁺ for active sites on the MSW surface. The competitive effect (Cr(III) vs. Na⁺) becomes stronger at higher Na⁺ concentration (Na₂SO₄ concentration), which lowers the adsorption of Cr(III).

3.4. Mechanism for chromium removal by ECAB

Extra experiments were conducted (C₀, Cr(VI) = 2 mmol/L, MSW dose = 3 g/L, initial pH = 2.0, anolyte: 5 (10, 25, 50) mmol/L Na₂SO₄, catholyte: 5 (10, 25, 50) mmol/L Na₂SO₄, cathodic potential = −1.0 V).

Fig. 4. Effect of Na₂SO₄ concentration on the efficiency for chromium removal. (a) Cr(VI) removal efficiency. (b) Total Cr removal efficiency. C₀, Cr(VI) = 1 mmol/L, MSW dose = 3 g/L, initial pH = 2.0, anolyte: 5 (10, 25, 50) mmol/L Na₂SO₄, catholyte: 5 (10, 25, 50) mmol/L Na₂SO₄, cathodic potential = −1.0 V.

Fig. 5. FTIR spectra of: (A) MSW after use in the ECAB, denoted as MSW-E. (B) MSW after use in the biosorption, denoted as MSW-B. (C) Protonated MSW, denoted as MSW-H.

Fig. 6. XPS spectra of Cr 2p₁/₂: (a) MSW after use in the ECAB, denoted as MSW-E. (b) MSW after use in the biosorption, denoted as MSW-B.
where M denotes to metal cations [16]. Accordingly, surface carboxylic groups would exist preferentially in the form of $\text{COO}^{-}$ instead of that of $\text{COOH}$, which is reflected by a decrease in the $\text{COOH}$ intensity and an increase in the $\text{COO}^{-}$ intensity in the MSW-E and MSW-B spectra.

Moreover, the MSW-E spectrum exhibits a much greater proportion of the $\text{COO}^{-}$ intensity to the $\text{COOH}$ intensity, compared with the proportion between the two peaks’ intensities in the MSW-B spectrum. This indicates that much more chromium is absorbed on the MSW-E than on the MSW-B because the change in $\text{COO}^{-}$ and $\text{COOH}$ intensity is enhanced with an increment in the adsorption of Cr(III) on MSW by forming more $\text{COO}^{-}\text{Cr(III)}$.

The peak corresponding to the C=O stretching of $\text{COO}^{-}/\text{CO}$ is found to be higher in the MSW-E spectrum than in the MSW-B spectrum, which is supported by the experimental observation of adsorption of more chromium onto the MSW-E.

The peak at 1058 cm$^{-1}$ decreases in the MSW-B spectrum compared with that in the MSW-E and MSW-H. This indicates that the alcoholic hydroxyl groups on the MSW-B surface are lost to some extent, likely because Cr(VI) is able to oxidize alcoholic hydroxyl groups on the MSW-B into aldehyde, ketone, or even carboxyl groups in biosorption-alone. Nonetheless, in the ECAB, Cr(VI) experiences quite efficient electroreduction leaving less opportunity for Cr(VI) to oxidize the MSW-E, resulting in no decrease in the peak of alcoholic hydroxyl groups. The peaks assigned to $\text{NH}$ or $\text{NH}_2$ and $\text{SO}_3$ groups are weakened after the chromium sorption onto MSW. They become even more in the MSW-E spectrum than in the MSW-B spectrum, demonstrating a greater uptake of chromium on the MSW-E.

XPS was applied to examine the oxidation state of the chromium bound to MSW. Binding energy (BE) profiles of chromium atom (Cr 2p3/2) in the MSW-E and MSW-B are shown in Fig. 6.

The BE values of chromium in Cr, Cr$_2$O$_3$, and K$_2$Cr$_2$O$_7$ (or K$_2$CrO$_4$) are 574.1 eV, 576.6 eV, and 579.1–579.3 eV, representing Cr(0), Cr(III), and Cr(VI), respectively [31]. The peaks at 577.2 eV and 579.1 eV can be assigned to Cr(III) and Cr(VI). The chromium bound to the MSW-E surface is predominant in the Cr(III) form with a slight part of Cr(VI), and the ratio of Cr(VI)/Cr(III) calculated by peak areas is 0.065. In contrast, the corresponding ratio of Cr(VI)/Cr(III) becomes 1.22, indicating the presence of a large number of Cr(VI) species on the MSW-B.

The XPS data further support the conclusion drawn from the above results in Section 3.1. In the ECAB, the reduction of Cr(VI) is predominantly accomplished by the electrochemical process on the Pd film cathode, and the converted Cr(III) is subsequently sorbed on the MSW-E.

Table 1

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>MSW-E</th>
<th>MSW-B</th>
<th>MSW-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1736.3</td>
<td>1736.4</td>
<td>1737.4</td>
<td></td>
</tr>
<tr>
<td>1643.8</td>
<td>1647.4</td>
<td>1654.5</td>
<td></td>
</tr>
<tr>
<td>1420.9</td>
<td>1409.3</td>
<td>1420.1</td>
<td></td>
</tr>
<tr>
<td>1543.0</td>
<td>1541.3</td>
<td>1541.2</td>
<td></td>
</tr>
<tr>
<td>883.1</td>
<td>879.4</td>
<td>878.5</td>
<td></td>
</tr>
<tr>
<td>1384.2</td>
<td>1384.1</td>
<td>1374.7</td>
<td></td>
</tr>
<tr>
<td>1058.4</td>
<td>1058.3</td>
<td>1058.8</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Functional groups of MSW-E, MSW-B, and MSW-H and the corresponding FTIR absorption wavenumbers.

The peak at 1058 cm$^{-1}$ decreases in the MSW-B spectrum compared with that in the MSW-E and MSW-H. This indicates that the alcoholic hydroxyl groups on the MSW-B surface are lost to some extent, likely because Cr(VI) is able to oxidize alcoholic hydroxyl groups on the MSW-B into aldehyde, ketone, or even carboxyl groups in biosorption-alone. Nonetheless, in the ECAB, Cr(VI) experiences quite efficient electroreduction leaving less opportunity for Cr(VI) to oxidize the MSW-E, resulting in no decrease in the peak of alcoholic hydroxyl groups. The peaks assigned to $\text{NH}$ or $\text{NH}_2$ and $\text{SO}_3$ groups are weakened after the chromium sorption onto MSW. They become even more in the MSW-E spectrum than in the MSW-B spectrum, demonstrating a greater uptake of chromium on the MSW-E.

XPS was applied to examine the oxidation state of the chromium bound to MSW. Binding energy (BE) profiles of chromium atom (Cr 2p3/2) in the MSW-E and MSW-B are shown in Fig. 6.

The BE values of chromium in Cr, Cr$_2$O$_3$, and K$_2$Cr$_2$O$_7$ (or K$_2$CrO$_4$) are 574.1 eV, 576.6 eV, and 579.1–579.3 eV, representing Cr(0), Cr(III), and Cr(VI), respectively [31]. The peaks at 577.2 eV and 579.1 eV can be assigned to Cr(III) and Cr(VI). The chromium bound to the MSW-E surface is predominant in the Cr(III) form with a slight part of Cr(VI), and the ratio of Cr(VI)/Cr(III) calculated by peak areas is 0.065. In contrast, the corresponding ratio of Cr(VI)/Cr(III) becomes 1.22, indicating the presence of a large number of Cr(VI) species on the MSW-B.

The XPS data further support the conclusion drawn from the above results in Section 3.1. In the ECAB, the reduction of Cr(VI) is predominantly accomplished by the electrochemical process on the Pd film cathode, and the converted Cr(III) is subsequently sorbed on the MSW-E.
On the other hand, in the biosorption-alone, Cr(VI) is firstly sorbed onto the MSW-B and then a part of Cr(VI) is reduced to Cr(III) by surface reductive groups. The produced Cr(III) might be still sorbed on the MSW-B or release into the bulk solution. Additionally, the possibility that the reduction of Cr(VI) to Cr(III) is achieved by a quick contact of Cr(VI) with the MSW-B surface cannot be excluded.

Fig. 7 presents the conceptual pathways for the removal of Cr(VI) and Cr(III) by the ECAB:

1. Indirect electroreduction of Cr(VI) by atomic H\(^2\): H\(_2\) is generated on the cathode surface from the reduction of H\(^+\). A large amount of generated H\(_2\) is chemisorbed on the Pd film surface and then decomposed into atomic H\(^+\). Atomic H\(^+\) serves as a highly active reductant for converting Cr(VI) into Cr(III).
2. Direct electroreduction of Cr(VI): Cr(VI) could also gain electrons directly on the cathode surface and is reduced to Cr(III).
3. Adsorption of Cr(III) by MSW: The produced Cr(III) is favorably adsorbed onto MSW via ion exchange and complexation.
4. Reduction of Cr(VI) by MSW: Cr(VI) is capable of being reduced into Cr(III) by the abiotic reduction of MSW.
5. Adsorption of Cr(VI) by MSW: Cr(VI) is also able to be bound on MSW through the interaction with the positively-charged groups.

Pathways (1), (2), and (3) are proved to be the predominant processes. On the other hand, Pathways (4) and (5) are minor processes.

4. Conclusions

The removal efficiencies of both Cr(VI) and total Cr were remarkably enhanced in the ECAB compared with those in biosorption-alone. In the ECAB, Cr(VI) underwent efficient electroreduction on the Pd film cathode. The converted Cr(III) was favorably adsorbed onto MSW; the adsorption was facilitated by the pH elevation due to the cathodic H\(_2\) evolution. The slow kinetics for Cr(VI) reduction by MSW was a barrier to the efficient removal of Cr(VI) and total Cr through biosorption; however, this barrier was overcome with the assistance of electrochemical reduction leading to the notable enhancement in chromium elimination in the ECAB. The experiments at different MSW dosages and Na\(_2\)SO\(_4\) concentrations provided a clear evidence that the reduction and adsorption of Cr(VI) by MSW was a minor process in the ECAB.

The electrochemical reduction of Cr(VI) involved direct electroreduction and indirect electroreduction by atomic H\(^+\), and the contribution of indirect electroreduction became increasingly important with lowering the bias. FTIR study confirmed that larger amount of chromium was sorbed on the MSW-E than on the MSW-B, and showed that the alcoholic hydroxyl groups were oxidized by Cr(VI) in biosorption-alone. XPS results demonstrated that in the ECAB the chromium adsorbed onto the MSW-E was predominantly in the Cr(III) form whereas MSW-B adsorbed both Cr(VI) and Cr(III) in biosorption-alone.

Acknowledgments

This project was supported by Fund for the Creative Research groups of China (50921064) and National Science Foundation of China (Grant No. 50728806). Ms. L. Wang from National University of Singapore had contributed some experimental work to this study. The authors would like to express their appreciation to Agency for Science, Technology and Research of Singapore (Grant Nos. 0 921 010 059 and R-288-000-066-305) for financial support of this study for the instrumental analysis.

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.jcis.2012.05.056.

References