Bacteria cell templated porous polyaniline facilitated detoxification and recovery of hexavalent chromium†

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In this study, bacteria cells served as a novel green pore-forming agent and template to fabricate porous polyaniline (Bac@PANI) by in situ oxidative polymerization. The achieved specific surface area of 51.2 m² g⁻¹ for Bac@PANI at a bacteria dosage of OD₆₀₀ = 0.536 was far higher than that of the pristine PANI (27.5 m² g⁻¹). The Bac@PANI presented an emeraldine form, hydrophilicity and decreased isoelectric point (4.2) after being modified by bacteria. All these properties contributed to an enhanced removal performance of hexavalent chromium (Cr(VI)), with a high removal rate of 0.5 mg (min g⁻¹) and capacity of 835.06 mg g⁻¹ of Bac@PANI. Efficient removal was achieved in both acidic and neutral solutions due to its high H⁺ storage capacity. More than 90% of Cr(vi) can be reduced to trivalent chromium (Cr(III)) by oxidation of amide groups in both acidic and neutral solutions. These Cr(III) ions can be adsorbed by Bac@PANI simultaneously, resulting from the reversal of negative surface charge after treatment of Cr(vi); then Bac@PANI can be easily recovered in an acidic solution.

1. Introduction

Cr(vi) is classified as one of the most toxic heavy metals for human health. Its existing anion forms in aqueous environment, e.g., Cr₂O₇²⁻, CrO₄²⁻ and HCrO₄⁻, lead to its strong mobility. Reducing Cr(vi) anions to Cr(III) ions is recommended as an efficient protocol for purifying Cr(vi) contaminants. Cr(III) has low toxicity, exists as Cr³⁺ ions in a solution, and can be easily immobilized. This reduction can be achieved by both biological processes and chemical reactions.⁸⁻¹²

Among the increasingly studied functional materials for rapid reduction of Cr(vi), PANI, as a conductive polymer containing both reductive amine groups (–NH–) and oxidative imine groups (–N=) simultaneously, has attracted considerable interests for reducing Cr(vi).⁶,⁷ PANI has three oxidation states based on the –NH–/–N= ratio: emeraldine (EB), pernigraniline (PB) and leucoemeraldine (LB).⁸ Electrons can be donated when PANI is transferred from LB or EB state to PB state.⁹ This remarkable electron donation ability is the most important reason for its application in Cr(vi) remediation. Cr(vi) wastewater of 1 mg L⁻¹ can be completely removed within 15 minutes by PANI.¹⁰ In addition, PANI has a high resistance against acidic conditions, which coincides with the fact that the Cr(vi) is easily reduced in acidic conditions.¹⁰⁻¹⁸ All these findings imply that PANI is a good candidate for the remediation of Cr(vi) contamination.

PANI in the powder/film morphology has been widely synthesized by the chemical oxidation polymerization method.¹⁹,²⁰ However, these PANI samples had low removal capacity for Cr(vi) despite its rapid kinetics. For example, ~15 and 35 mg Cr(vi) was reduced by 1 g PANI and cellulose modified PANI, respectively.⁸ The poor porosity of PANI in such forms was found to be responsible for this low capacity.¹¹ Thus, increasing its porosity seems to be important, which can increase the accessibility of the –NH– groups in PANI for Cr(vi) reduction.

Cr(vi) is easily reduced in acidic conditions (pH < 3) than in the basic or neutral solutions, as H⁺ is an important reactant participating in the Cr(vi) reduction reaction.²²,²³ Thus, adjusting the solution pH to acidic is always needed in order to achieve a fast reaction, which limits the application of many synthesized materials on treating Cr(vi)-containing wastewater. Fortunately, the polar –N= groups in PANI can be easily protonated by H⁺, forming acid doped PANI.²⁴ Therefore, PANI is supposed to have the ability to capture H⁺ ions from the solution and store them on the polymer chains. These doped chains can provide H⁺ required for Cr(vi) reduction, thus facilitating the Cr(vi) reduction in versatile conditions, which may widen the applications of PANI based materials.
As documented, the surface of PANI is positively charged when pH < 10.\textsuperscript{25} Moreover, Cr(vi) is present as negatively charged anions, which can be easily adsorbed onto positively charged PANI. However, after the reaction, the obtained reduction product Cr(m) (Cr\textsuperscript{3+}) is positively charged. Thus, this electrical charge transition of chromium in the reduction process prevented further adsorption of Cr\textsuperscript{3+} due to the repulsion between PANI and Cr\textsuperscript{3+}. For decreasing the isoelectric point (pI), PANI has been modified with many materials, such as magnetite (Fe\textsubscript{3}O\textsubscript{4}) nanoparticles,\textsuperscript{26,27} sawdust,\textsuperscript{28} fibers,\textsuperscript{29} biomass\textsuperscript{a} and carbon materials.\textsuperscript{30} However, these modifications cannot meet the requirements of low pI, high porosity and acid doping simultaneously. Thus, a new method is needed to synthesize PANI that is much more suitable for Cr(vi) remediation.

To achieve this goal, bacterial cells appear to be a good candidate to modify PANI. A bacterial cell is composed of a cell wall and an aqueous cytoplasm within the cell wall. The cell wall mainly contains abundant –NH\textsubscript{2} and –OH groups,\textsuperscript{27} which can serve as active sites for PANI growth. Furthermore, bacterial cells can be easily broken, and cytoplasm will leak when the cell wall and an aqueous cytoplasm within the cell wall. The cell wall serves as active sites for PANI growth. Furthermore, bacterial cells can be easily broken, and cytoplasm will leak when the cell is dried, which causes the formation of a porous PANI.\textsuperscript{30} Additionally, lower pI of the bacterial cell (pH = ~3)\textsuperscript{14} could decrease overall pI of the as-synthesized porous Bac@PANI.

In this study, a bacterial cell was used as a green porous template to prepare porous PANI by surface initiated polymerization. This paper aims at elucidating the effects of bacteria on the properties of porous PANI, such as porosity, pI, and capacity of H\textsuperscript{+} capture and storage. Performance of the porous PANI for Cr(vi) reduction and further adsorption were also evaluated. Moreover, the mechanisms of enhanced performance by bacteria templated PANI were discussed.

2. Materials and methods

2.1 Materials

Simulated contaminants of potassium dichromate (K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}) and chromogenic agent 1,5-diphenylcarbazide were purchased from Beijing Chemical Works, China for batch assays of Cr(vi) removal. Aniline monomers, p-toluene sulfonic acid (C\textsubscript{7}H\textsubscript{8}O\textsubscript{3}S), ammonium persulfate (APS) and acetone were purchased from Xiya Chemical Company Limited, China for PANI synthesis. All reagents were used as received. Bacterial strain used in this study was isolated from activated sludge in our lab and exhibited a spherical shape. It was incubated in a nutrient solution at 35 °C for 24 h. The solution was centrifuged and washed by normal saline 3 times to remove the nutrients. Bacteria cells were suspended in water to obtain an OD at 1.362 (OD is the optical density value of bacteria solution measured at 600 nm, which represents the amount of cells in the solution). This bacteria solution was used as stock solution for the synthesis of porous PANI.

2.2 Fabrication of porous PANI

Porous PANI was fabricated using a novel template method combined with the reported surface oxidation polymerization.\textsuperscript{3} Specifically, aniline (3.2 mL) was dispersed in 200 mL bacteria solution with a desired OD and was cooled to 0–3 °C under stirring at 600 rpm for 30 minutes. The OD value of bacteria solution was adjusted by diluting the stock bacteria solution. Then, a precooled 100 mL solution of 36.0 mM APS and 15.0 mM PTSA was added dropwise to the aniline-bacteria solution at one milliliter per minute in an ice bath for polymerization. The obtained deep dark green product was washed with acetone and deionized water, in sequence, to remove any oligomers and for further cleaning. Finally, the Bac@PANI composites were dried at 80 °C for 12 h and preserved until application. As porous PANI was synthesized under acidic and strongly oxidative conditions, the bacteria cells were destroyed and lost their activity. Thus, the bacteria template is safe for further synthesis of porous PANI.

2.3 Cr(vi) removal and Cr(m) recovery

As the key influential factors for Cr(vi) removal performance of Bac@PANI composites, the kinetics, pH and initial concentration, were studied by batch assays. Briefly, for a kinetic study, 10.0 mg porous Bac@PANI was employed to remove 5.0 mg L\textsuperscript{−1} Cr(vi) from wastewater (25.0 mL) for different removal time intervals at room temperature. pH investigation was conducted at different pH values (1.0–11.0) adjusted with hydrochloric acid and sodium hydroxide for 30 minutes (based on kinetic experiment). For studying the effect of initial concentration of Cr(vi) while maintaining other parameters constant, the concentration was adjusted from 1.0 to 150.0 mg L\textsuperscript{−1}.

For removal performance analysis, the concentration of Cr(vi) was measured using a spectrophotometric method.\textsuperscript{16} Removal percentage (R\%) and removal capacity (Q, mg g\textsuperscript{−1}) of Cr(vi) were obtained by eqn (1) and (2), respectively:

\[
R\% = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)
\]

\[
Q = \frac{(C_0 - C_e)V}{m} \quad (2)
\]

where C\textsubscript{0} and C\textsubscript{e} (mg L\textsuperscript{−1}) represent initial and equilibrium concentration (mg L\textsuperscript{−1}), respectively; V (L) and m (g) are volume of the solvent solution and dry mass of the Bac@PANI, respectively.

For the recovery of Cr(m), the used Bac@PANI was transferred to acidic solutions with pH ranging from 1 to 5. Then, the mixtures were stirred at 600 rpm for 12 hours to fully release Cr(m) ions. The concentration of Cr(m) ions released to the acidic solution was measured using inductively coupled plasma mass spectrometry.

2.4 Characterizations of Bac@PANI

Micromorphology image of Bac@PANI was obtained using a scanning electron microscope (JEOL, JSM-6301F). Fourier transform infra-red (FT-IR) spectra were recorded using a FTIR spectrometer (Bruker, Vertex-70 with an ATR accessory). Pore structure and specific surface area (S\textsubscript{BET}) were recorded by a specific surface and micropore analyzer (Builder, SSA-7000).
Pore distribution was measured using the current international BJH method. Elemental species of Bac@PANI and chromium were detected by X-ray photoelectron spectroscopy (XPS) (ESCALAB, 250Xi) with an Al Kz and Mg/Al dual anode light source. Isoelectric points of pristine polyaniline and Bac@PANI were detected by a Malvern zeta potentiometer (Malvern, Zetasizer Nano ZEN2600). Total chromium concentration in each batch assay was analyzed using inductively coupled plasma mass spectrometry (ICP-MS, Agilent, 7900). Cr(III) concentration was calculated as the difference between total Cr and Cr(VI) concentrations.

3. Results and discussion

3.1 Hexavalent chromium removal

A rapid removal process was achieved by the bacteria-templated porous PANI (Fig. 1A). In total, 1000 µg L⁻¹ Cr(VI) was removed by Bac@PANI (dosage of 500 mg L⁻¹) in 10 minutes, which was much faster than raw PANI without using bacteria template (1 h). This result indicates that the bacteria template significantly enhanced Cr(VI) removal by PANI. It was noted that a faster removal was achieved by Bac@PANI using bacteria template with a dosage at OD₆₀₀ = 0.536. Thus, OD₆₀₀ = 0.536 of bacteria template was demonstrated as the optimized dosage for synthesizing porous PANI, which was suitable for remediation of chromium pollution. Moreover, increased initial concentration of Cr(VI) would enhance the removal capacity of porous PANI (Fig. 1B). Nevertheless, exorbitant initial concentrations (>1200 mg L⁻¹) have almost no impact on the removal capacity.

Accordingly, 835.06 mg g⁻¹ was calculated to be the maximum removal capacity of porous PANI, indicating a 3.5-fold increase as compared with that of pristine PANI doped with hydrochloric acid (~180 mg g⁻¹). Moreover, compared with PANI modified with other substrates (Table 1), Bac@PANI synthesized in this study has a higher removal capacity.

3.2 Characterization of Bac@PANI

The used bacterial templates exhibit a spherical form with a particle size of about 50 nm (Fig. S1A†). As shown in Fig. 2A, aniline was attached evenly on the surface of bacterial cell, and then polymerized and grown around the spherical bacteria due to surface energy of the cells, thus forming small core–shell bacteria@PANI. Then, the small PANI pellets were stacked into a large sphere during further polymerization of aniline. Following this, the bacterial cell was broken and cytoplasmic substances were released out of the cell when the composite was dried, forming the porous structure of PANI. Bac@PANI also presents as spherical particles with an average diameter of ~400 nm (Fig. 2B and C), which was different from the pristine PANI nanofibers (Fig. S1B†). Spherical shape and protein-rich environment of the bacteria contributed to the spherical morphology and the surface roughness of the as-synthesized PANI, respectively.

BET surface area (S_BET) and pore structure were influenced by the bacterial template. In detail, S_BET initially increased with increase in dosage of bacterial template, and then decreased when the bacteria dosage became higher than OD₆₀₀ = 0.536 (Fig. 3A). A maximum S_BET of ~51 m² g⁻¹ was obtained when

![Fig. 1](A) Cr(VI) removal rate of porous PANIs using different template dosages, and (B) Cr(VI) removal capacity of porous PANI.

<table>
<thead>
<tr>
<th>Materials</th>
<th>pH</th>
<th>Removal capacity (mg g⁻¹)</th>
<th>Modified substance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl/PANI</td>
<td>4.0</td>
<td>180.0</td>
<td>Hydrochloric acid (HCl)</td>
<td>43</td>
</tr>
<tr>
<td>DI/PANI</td>
<td>4.0</td>
<td>92.0</td>
<td>Deionized water (DI)</td>
<td>43</td>
</tr>
<tr>
<td>PAN/PANI</td>
<td>2.0</td>
<td>33.4</td>
<td>Polyacrylonitrile (PAN)</td>
<td>38</td>
</tr>
<tr>
<td>H-TNB/PANI</td>
<td>2.0</td>
<td>156.9</td>
<td>Hydrogen-titanate (H-TNB)</td>
<td>44</td>
</tr>
<tr>
<td>MC/PANI</td>
<td>2.0</td>
<td>172.33</td>
<td>Magnetic porous carbon (MC)</td>
<td>45</td>
</tr>
<tr>
<td>MnO₂/PANI</td>
<td>2.0</td>
<td>263.2</td>
<td>MnO₂</td>
<td>46</td>
</tr>
<tr>
<td>PTSA/PANI</td>
<td>1.0</td>
<td>184.0</td>
<td>P-Toluene sulfonic acid (PTSA)</td>
<td>This study</td>
</tr>
<tr>
<td>Bac/PANI</td>
<td>1.0</td>
<td>835.06</td>
<td>Bacterial (Bac)</td>
<td>This study</td>
</tr>
</tbody>
</table>
the bacteria dosage was OD$_{600} = 0.536$. This is about two times higher than $S_{BET}$ of pristine PANI (27.5 m$^2$ g$^{-1}$). Moreover, the pore diameter increased when the bacteria dosage was higher than OD$_{600}$ of 0.536 (Fig. S2†). During polymerization, the bacteria cell was damaged, releasing gelatinous cytoplasm, which formed the porous structure of Bac@PANI upon drying. However, excess cytoplasm blocked the pores of PANI, leading to a decrease in $S_{BET}$. The porous structure exposes more amine groups, thus increasing the available active sites for Cr(VI) reduction (Fig. 3B), which determined the rapid Cr(VI) and high removal capacity of the Bac@PANI synthesized with suitable dosage of bacteria templates (Fig. 1A).

Hydrophilic property of PANI is important for the mass transfer between solution and solid PANI. Pristine PANI presented a hydrophilic surface with a contact angle of 68.6° (Fig. 4A). Bacteria cell mainly contains protein, which is a hydrophobic substance. Hence, the hydrophilicity of PANI decreased with an increase in the dosage of bacterial templates. However, the bacterial templates with low dosage (OD$_{600} < 0.536$) have no significant impact on the hydrophilicity of porous PANI. Identical result was obtained as the removal rate of Cr(VI) decreased significantly for the porous PANI with a template dosage higher than OD$_{600} = 0.536$ (Fig. 1A). Thus, OD$_{600} = 0.536$ was determined as the optimal bacteria template dosage for fabrication of Bac@PANI. As shown in Fig. 4B, upon

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Fig. 2 (A) Proposed synthesis pathway of porous PANI using bacteria as the template, SEM images of porous PANIs with template dosages of (B) OD$_{600} = 0.276$ and (C) OD$_{600} = 0.833$.

Fig. 3 (A) BET surface area of porous PANI using different dosages of bacteria templates; (B) schematic diagram of the exposed amino groups in porous PANI.
increasing the solution pH, the surface charge of both pristine and bacteria-templated porous PANI (template dosage of OD$_{600}$ = 0.536) gradually decreased. pI of the bacteria-templated porous PANI was observed at pH = ~4.2, which was reduced by half compared to that of pristine PANI (pI = 8.0). Bacterial cells have a low pI at pH ~3; thus, residual bacteria material contributed to the significantly decreased pI of the as-synthesized porous PANI. Bac@PANI tends to attract negative substances in acidic solutions (pH < 4.2). In addition, the hydrophilic and positively charged properties facilitate fast Cr(VI) anion adsorption on the porous PANI surface, which is a vital step before Cr(VI) reduction.

FTIR spectrum of Bac@PANI (Fig. 4C) indicated the appearance of N=Q=N (1566 cm$^{-1}$) and N–B–N (1483 cm$^{-1}$), where Q and B were quinoid ring and benzenoid ring, respectively. The pristine and bacteria-templated porous PANI have almost the same characteristic peaks, while the characteristic peaks of the porous PANI shifted to higher wave-numbers compared to those of the pristine PANI. This indicated that functional groups of bacterial cells participated in the polymerization reaction. The peaks at 1566 and 1483 cm$^{-1}$ represent the amine (-NH-) and imine (-N=) groups in PANI, respectively, while their intensity ratio indicated the presence of EB form in both pristine PANI and bacteria-templated PANI. The -NH- group has high electron donating ability, and is considered as a good electron donor for Cr(VI) reduction. The abundant -NH- groups (electron donor) and large surface area determined the rapid reduction and high Cr(VI) removal capacity of the bacteria-templated porous PANI.

3.3 Wide pH range

As documented, H$^+$ plays a vital role in this reduction (eqn (3)–(6)). Fig. 5A shows removal performance of Cr(VI) by the bacteria-templated porous PANI at different initial pH values from 1.0 to 13.0. It is noteworthy that although Cr(VI) reduction is highly pH dependent, more than 90% Cr(VI) can also be reduced by porous PANI at initial pH as high as 9. For pristine PANI, 90% of removal percentage could be achieved only when the pH was lower than 3 (Fig. 4A). This indicated that the bacteria templates widened the application of PANI for Cr(VI) reduction. This as-synthesized porous PANI can reduce Cr(VI) under a wider pH range than a traditional modification by other substrates (1.0 to 3.0), such as Fe$_3$O$_4$, cellulose, and carbon fiber.

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- & \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \\
\text{CrO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- & \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O} \\
\text{H}_2\text{CrO}_4 + 6\text{H}^+ + 3\text{e}^- & \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O} \\
\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}^- & \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}
\end{align*}
\]
forming an acidic micro-environment for Cr(VI) reduction. H⁺ storage capacity increased significantly with an increase in dosage of bacteria cells, which indicated the capture of H⁺ by the PANI from the solution and storage of H⁺ on its chains due to the electronegativity of –N and –NH. It must also be mentioned that both the maximum adsorption rate and H⁺ storage capacity were obtained when the dosage of bacteria templates was controlled at OD600 = 0.536 (Fig. S3†). Four peaks observed in the N 1s XPS spectrum (Fig. 5C) were ascribed to –N (399.0 eV), –NH (399.6 eV) and N⁺ in doped imine and amine group (400.3 and 401.4 eV, respectively).39,40 This indicated that H⁺ was captured and stored on the porous PANI (Fig. 5D). The H⁺ stored on the –N in PANI can provide an acidic microenvironment for Cr(VI) reduction. Moreover, stored H⁺ can also release into the environment (Fig. S4†), which makes it available for Cr(VI) reduction. As reported, chromic ions primarily exist in the form of HCrO₄⁻ and H₂CrO₄ in acidic solutions (pH < 6.8). Moreover, HCrO₄⁻ holds a higher redox potential (1.33 eV),41 which will contribute to easier reduction.

3.4 Removal mechanisms of Cr(vi)

Bacteria-templated porous PANI has been proved as a promised material for chromium removal due to its high porosity and abundant –NH groups. The removal mechanisms of Cr(vi) were revealed using FT-IR and XPS techniques. Fig. S5† shows that the intensity ratio of imine group (1580 cm⁻¹) to amine group (1482 cm⁻¹) slightly increased after treatment of Cr(vi), indicating that a fraction of –NH groups in the composite have been oxidized to –N=,32 XPS spectra of the porous PANI (Fig. SSB†) show the binding energy peak positions at 576.0 and 585.2 eV, ascribed to the trivalent chromium (Cr(III)).42 Moreover, no Cr(vi) was detected on the porous PANI, implying that all the adsorbed Cr(vi) was completely reduced. The significantly increased ratio of peak intensities of –N= (397.6 eV) and –NH– (399.0 eV) in N 1s spectra (Fig. S5C†) of the treated porous PANI also confirmed the reductive effect of –NH in PANI in the removal of Cr(vi). Thus, the removal mechanism for Cr(vi) was proposed, as shown in Scheme 1. First, due to availability of a large number of binding sites (–N=) in the porous structure, the H⁺ in the solution was captured and stored on the porous PANI (Fig. 5D). The H⁺ stored on the –N= in PANI can provide an acidic microenvironment for Cr(vi) reduction. Moreover, stored H⁺ can also release into the environment (Fig. S4†), which makes it available for Cr(vi) reduction. As reported, chromic ions primarily exist in the form of HCrO₄⁻ and H₂CrO₄ in acidic solutions (pH < 6.8). Moreover, HCrO₄⁻ holds a higher redox potential (1.33 eV),41 which will contribute to easier reduction.

3.5 Cr(III) recovery

As discussed above, Cr(vi) anions were completely reduced to Cr³⁺. The further removal of Cr³⁺ was often difficult by PANI due to the charge transition of chromium. As shown in Fig. 6A, only half of Cr³⁺ was adsorbed by porous PANI, indicating that ~50% of chromium has not been safely disposed when the solution pH is 1.0. The electrostatic repulsion between PANI and Cr³⁺ was reduced on increasing the pH, as evidenced by the
significantly decreased Cr\(^{3+}\) concentration. More than 90% of Cr\(^{3+}\) can be removed by the porous PANI at pH 3.0, while only ∼40% of Cr\(^{3+}\) was removed by the pristine PANI at pH 5.0 (Fig. 6B). It was demonstrated that the bacteria-templated porous PANI better adsorbs Cr\(^{3+}\) compared to pristine PANI. Cr\(^{3+}\) exists as positively charged ions in the acidic solution, and electrostatic repulsion between bacteria-templated porous PANI and Cr\(^{3+}\) led to high Cr\(^{3+}\) aqueous concentration. Moreover, when the initial solution pH was 3.0, the final pH reached ∼4.5 after the reaction due to the consumption of H\(^+\) during Cr\(^{6+}\) reduction. When the pH of the wastewater exceeded pl of Bac@PANI (pH = 4.2), its surface charge was reversed to negative. This property was consistent with the charge reversal of chromium (from Cr\(^{6+}\) anions to Cr\(^{3+}\). Thus, the surface charge of Bac@PANI facilitated the adsorption of Cr\(^{6+}\) anions, assuring their reduction and further Cr\(^{3+}\) ions removal after the reduction reaction by the electrostatic attraction (Scheme 1). Then, the adsorbed Cr\(^{3+}\) on the surface of bacteria-templateed porous PANI can be desorbed easily in an acidic solution (pH ≤ 3) (Fig. 6B), regenerating the Bac@PANI. Recovery efficiency increased with the decrease in pH, and almost 99% Cr\(^{3+}\) was recovered when the solution pH was maintained at 1.

4. Conclusions

A bacteria cell induced porous structured PANI was synthesized using a chemical polymerization method. The porous PANI exhibits a 2-fold increase in \(S_{\text{BET}}\) compared to the pristine PANI. The porous PANI synthesized with the bacteria cell as templates demonstrated excellent Cr\(^{6+}\) removal performance with a fast removal rate of 0.5 mg (min\(^{-1}\) g\(^{-1}\)) and maximum removal capacity of 835.06 mg g\(^{-1}\). The formed porous structure, decreased pl, and increased H\(^+\) storage capacity were responsible for the enhanced chromium removal performance. Cr\(^{6+}\) reduction and adsorption of Cr\(^{3+}\) can be achieved.
simultaneously by the bacteria templated PANI. Moreover, the adsorbed Cr(III) can be easily recovered in an acidic solution. Thus, porous PANI was demonstrated as an efficient material for Cr(VI) remediation and Cr(III) recovery. Furthermore, with unique electrical conductivity, low density and high specific surface area, these PANI nanostructures can have other potential applications, such as those in sensors, anticorrosion coatings, multifunctional materials, and energy storage.47–51

Conflicts of interest
There are no conflicts to declare.

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References