Easy separated 3D hierarchical coral-like magnetic polyaniline adsorbent with enhanced performance in adsorption and reduction of Cr(VI) and immobilization of Cr(III)

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HIGHLIGHTS

- 3D hierarchical PANI was used as an efficient adsorbent for Cr(VI) removal.
- Two types of magnetic CL-PANI adsorbents were prepared and compared.
- Fe₃O₄@CL-PANI was found to exhibit extra active sites for immobilizing Cr(III).
- Fe₃O₄@CL-PANI showed a better removal performance of Cr(VI) than CL-PANI@Fe₃O₄.

GRAPHICAL ABSTRACT

We present an easy separated 3D hierarchical coral-like magnetic PANI adsorbent with enhanced performance in adsorption and reduction of Cr(VI) and immobilization of Cr(III).

ABSTRACT

A coral-like hierarchical micro/nano-structural polyaniline consisting of short nanowires (CL-PANI) was synthesized via a simple chemical oxidation method and firstly used as an adsorbent for removal toxic Cr(VI) ions. Two types of magnetic CL-PANI nanocomposites, i.e., CL-PANI shell coated by Fe₃O₄ nanoparticles (CL-PANI@Fe₃O₄) and Fe₃O₄ nanoparticles protected by CL-PANI (Fe₃O₄@CL-PANI), were further prepared for the easy separation purpose in the practical application. As-prepared adsorbents were well characterized and their performance for the removal of Cr(VI) were systemically investigated and compared. Adsorption results showed that the adsorption of Cr(VI) ions was dependent on solution pH and temperature for all three adsorbents. The fitted data revealed that the adsorption process followed the pseudo-second-order kinetic model and Langmuir isotherm model. CL-PANI exhibited an enhanced adsorption performance due to its well-defined and accessible mesoporous and plenty surface active sites compared with common synthesized irregular nanorod PANI. Moreover, modified with Fe₃O₄ nanoparticles endowed CL-PANI with a slight decreased adsorption capacity, but provided more active sites for immobilizing the reduced Cr(III) ions. Besides, compared with CL-PANI@Fe₃O₄, Fe₃O₄@CL-PANI was found to be more promising in the practical treatment of Cr(VI)-containing wastewater.

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1. Introduction

In recent decades, tremendous increase of industries ranging from battery manufacturing, cement ceramics, electroplating and mining to production of plastics worldwide have led to the release of various heavy metals (Cr, Sb, Cu, Ni, Cu, Pb,...) [1–3]. The removal of these inorganic pollutants has been attracted considerable attention due to their non-biodegradable and potential carcinogenicity which greatly threat human health and ecological environment [4,5]. Among these heavy metals, hexavalent chromium (Cr(VI)) has been considered as a serious pollutant which is high migration, toxic, carcinogenic and mutagenic to living organism. And the maximum allowable concentration for Cr(VI) in inland surface waters and drinking water are 0.1 mg L$^{-1}$ and 0.05 mg L$^{-1}$, respectively, according to US Environmental Protection Agency (US-EPA) [6]. Unlike Cr(VI), Cr(III) is less toxic and a vital micronutrient needed for the metabolic process in living organism [7,8]. Therefore, different techniques such as chemical precipitation, oxidation-reduction, membrane separation, ion exchange, and adsorption have been developed to remove or reduce Cr(VI) ions to Cr(III) ions from wastewater [9–15]. Among these techniques, adsorption has been considered as a versatile and economic technique without large amount of reagents, difficult operation technology, high-cost materials such as membrane, which has received particular attentions in recent years [16–18].

Conducting polymers (CPs) such as polyaniline (PANI) and polypyrrole (PPy) have been extensively applied in heavy metal ions’ removal owing to their good environmental stability, low preparation cost and functional amine or imine groups [19,20]. The attracted interest also stems from the fact that their reversible acid/base doping/dedoping chemical property and unique redox electrochemical property endow the adsorbents with excellent reusability and reduction capacity [21,22]. As of late, nanostructured CPs have been demonstrated to show enhanced adsorption performance compared with their conventional bulk counterparts because of their increased surface area, more accessible active sites and shorter diffusion length. PANI nanoparticles and 1D nanostructures prepared via a sono-assisted chemical oxidation method showed efficient adsorption for Cr(VI) [23]. Guo et al. [21] prepared 1D PANI nanowire/tube with rough surface using a simple chemical oxidation method and this kind of PANI nanostructure could remove Cr(VI) rapidly and effectively by reducing Cr(VI) to Cr(III) and adsorbing the reduced Cr(III) simultaneously. Li et al. [24] reported that bamboo-like PPy nanotubes exhibited much higher adsorption capacity than traditional PPy nanoparticles. Different strategies including changing the component of CPs, preparation of 3D hierarchical structures, introducing other functional material into CPs and forming nanocomposites have also been developed to further improve the adsorption capacity. For example, Madhumita et al. [25] prepared PPy-PANI 1D nanofibers by a chemical oxidative synthesis using FeCl₃ as the oxidant. The PPy-PANI nanofibers exhibited an enhanced adsorption capacity of 227 mg g$^{-1}$ for Cr(VI) at pH 2 compared with the PPy homopolymer nanospheres. Das et al. [26] adopted folic acid to prepare a porous 3D folic acid-PANI hybrid gel with a high BET surface area of 236 m$^{2}$ g$^{-1}$, which presented an excellent adsorption capacity of 168.3 mg g$^{-1}$ and large amount of Cr(VI) was reduced to Cr(III) due to the presence of folic acid during the adsorption process. Qiu et al. [27] fabricated a recyclable 3D flowerlike nanocomposite of MoS$_2$@hybrid acid-doped PANI immobilized on porous polycrylonitrile nanofibers (MoS$_2$@PANI/PAN), which showed the advantages of a fast equilibrium rate of 30 min, a high removal capacity of 6.57 mmol g$^{-1}$ and a good recyclability. However, the relative complex preparation process and low adsorption capacity make them not perfect for practical applications and it is always desirable to find a low-cost nanostructured CPs-based absorbent with an excellent removal performance.

3D hierarchical micro/nanostructures consisting of one dimensional nanorods, nanowires and other nanostructures have the merits of well-defined and accessible mesoporous, plenty active sites, large surface area, and enhanced structural stability and so on [28]. They have been demonstrated to show improved performance in energy storage area like supercapacitor [29,30] and lithium battery [31]. However, there exists no quantitative study evaluating the adsorption performance of 3D hierarchical micro/nanostructured adsorbents for the removal of toxic Cr(VI) from water. Moreover, so far, 3D PANI micro/nanostructures have been synthesized with the aid of soft template or specific structure-directing agents or under extreme condition like frozen and high acid concentration [32,33]. The reported methods adopting expensive specific structure-directing dopants or extreme conditions restricted them for large scale applications. Here, in this paper, we developed a simple and low-cost way to scalable synthesize 3D coral-like hierarchical micro/nanostructured PANI and clarified its adsorption properties for Cr(VI).

From a practical standpoint, nanostructured PANI is hard to be settled, separated and recovered due to the nature of small colloidal size and low mass density. One of the effective strategies to solve this problem is preparing adsorbents in magnetite composite form [34]. Meanwhile, spineltype ferrite based nanomaterials have been found to show relative good performance towards heavy metal ions [35]. Therefore, the adsorbent combining 3D hierarchical micro/nanostructured CP with magnetic particles is expected to exhibit excellent adsorption and easy separation performance. Normally, magnetite composites are fabricated in two ways, i.e., coating magnetic nanoparticles directly on the substance or modifying magnetic nanoparticles with protective shell [5,36]. To the best of our knowledge, few reports were extensively carried out to study the difference in performances including the separation, adsorption behavior and mechanism, reusability of these two type magnetite composites, especially for magnetic CPs.

Therefore, in this study, we prepared a novel PANI-based adsorbent with 3D hierarchical coral-like nanostructures (CL-PANI) by a simple one-step chemical polymerization method. Two different 3D CL-PANI based magnetite adsorbents, i.e., CL-PANI coated by Fe$_3$O$_4$ nanoparticles (CL-PANI@Fe$_3$O$_4$) and Fe$_3$O$_4$ nanoparticles protected with CL-PANI shell (Fe$_3$O$_4$@CL-PANI) were further synthesized to solve the tough separation problem of CL-PANI. The synthesized CL-PANI and two CL-PANI-based magnetic composites were well characterized by various technologies. Their adsorption and reduction performances of Cr(VI) from aqueous solution were systemically evaluated. Moreover, the differences in separation, adsorption and reusability performances of two type magnetite composites were firstly compared. The possible mechanism of Cr(VI) removal on these adsorbents were finally proposed based on adsorption studies and instrumental analyses.

2. Experimental

2.1. Chemicals

All chemicals, including aniline (C$_6$H$_5$NH$_2$), ammonium peroxysulfate ((NH$_4$)$_2$S$_2$O$_8$, APS), FeCl$_3$4H$_2$O, FeCl$_3$6H$_2$O, K$_2$Cr$_2$O$_7$, NH$_3$H$_2$O (25%), and HCl in this study were purchased from Sinopharm group chemical reagent Co. Ltd. They were of analytical grade and used as received. The deionized water was produced by EPEDE-40TF Superpure Water System (EPED, China) and used throughout the experiments.

2.2. Synthesis of 3D coral-like hierarchical micro/nanostructured PANI (CL-PANI)

The 3D PANI hierarchical micro/nanostructures were synthesized using in situ conventional chemical oxidative polymerization method by adjusting the charging sequence. In a typical process, aniline (4.0 mL) was added into 200 mL deionized water under magnetic stirring at 0°C for 10 min. HCl (5 M, 10 mL) was then added to the dispersion, followed by the addition of an aqueous solution of APS (14.8 g) dissolved in HCl.
After mechanical stirring for 12 h, the obtained precipitate was filtered and washed with deionized water and acetone to remove oligomers. The obtained dark green product was dried at 50 °C for 24 h and labeled as CL-PANI. For comparison, a control experiment was carried out using the same polymerization method but under room temperature and the gained product was labeled as R-PANI.

2.3. Syntheses of CL-PANI based magnetic composites

2.3.1. CL-PANI core – Fe₃O₄ shell (CL-PANI@Fe₃O₄)

0.688 g FeCl₂·4H₂O and 2.204 g FeCl₃·6H₂O were added into a baker containing 16 mL deionized water. After sonication for 10 min, the dissolved solution was added into the baker containing 2 g as-synthesized CL-PANI dispersed in 16 mL deionized water. The mixture was then magnetic stirred at a constant temperature of 80 °C for 30 min followed by adding 4 mL NH₃·H₂O (22%). After reacting for 1 h, the solid was separated via a magnet and washed with deionized water until neutral pH was achieved. The obtained product was then dried in the vacuum oven at 50 °C for 24 h and labeled as CL-PANI@Fe₃O₄.

2.3.2. Fe₃O₄ core – CL-PANI shell (Fe₃O₄@CL-PANI)

Another CL-PANI based magnetic composite was synthesized as the one for CL-PANI but using 200 mL deionized water containing 2 g fresh Fe₃O₄ nanoparticles as the solution of aniline. The fresh Fe₃O₄ nanoparticles were prepared via a reported co-precipitation method [37]. The obtained product was named as Fe₃O₄@CL-PANI.

2.4. Characterisation

The morphology and element distribution of samples were characterized by scanning electron microscopy (SEM, Gemini SEM 500) equipped with energy-dispersive x-ray spectroscopy (EDS) and transmission electron microscopy (TEM, JEM-F200). X-ray diffraction (XRD) patterns of adsorbents were recorded on a Rigaku DMAX-RA with a scan rate of 4 deg min⁻¹. Fourier transform infrared (FT-IR) spectra of adsorbents were obtained on a Bruker, TENSOR37 infrared spectrometer, with KBr pellets in the range of 400–4000 cm⁻¹. The thermogravimetric analyses (TGA) experiment were kept at a heating rate of 10 °C min⁻¹ over a temperature within 30–800 °C in N₂ flow and carried out on the SHIMADZU TA-60WS Thermal Analyzer. Magnetic properties were studied on a vibrating sample magnetometer (735 VSM Thermomagnetometer). Nitrogen adsorption-desorption isotherm was tested on a Builder SSA-4200 instrument adopting the Barrett-Joyner-Halenda (BJH) method. NanoBrook 90Plus zeta Analyzer was used to measure the zeta potential of adsorbents at different pH value. X-ray photoelectron spectroscopy (XPS) measurements were performed on an AXIS Ultradifl Spectrometer with C1s signal at 284.8 eV as the reference. Electrical impedance spectroscopy (EIS) were measured on the CHI 660D electrochemical workstation using a conventional three electrode cell in 1.0 M H₂SO₄ electrolyte solution, where Pt foil and Ag/Ag⁺ were counter electrode and reference electrode, respectively. The working electrodes were different adsorbents-modified carbon paste electrodes (CPE). In a typical preparation process, high purity graphite powder, paraffin and adsorbent were thoroughly mixed and packed into a glass tube with Φ = 3 × 1 mm with a fixed copper wire contacting the external circuit. The EIS measurements were investigated under the frequency ranging from 1 Hz to 10⁶ Hz at open circuit voltage with ac perturbation of 10 mV and the obtained data were fitted with R(QR) equivalent circuit.

2.5. Adsorption experiment

The adsorption experiments were carried out by shaking the mixture of Cr(VI) solution with the as-prepared adsorbents at various conditions like adsorbent dosage (0.5 g L⁻¹–2 g L⁻¹), pH (2–8) (adjusted with 0.1 M HCl or 0.1 M NaOH), initial concentration (100 mg L⁻¹–1000 mg L⁻¹) and temperature (298 K–318 K). The suspensions obtained from pure PANI and magnetic composites were collected by centrifugation and magnet, respectively and then filtered through 0.45 µm filter membrane. The Cr(VI) concentration in the solution was measured at 540 nm using a UV–Vis spectrophotometer (UV-2600, Shimadzu) by the diphenylcarbazide method. The amounts of total chromium (total Cr) were determined by inductively coupled plasma (ICP) emission spectroscopy (ICPE-9000, Shimadzu, Japan). And the concentration of released Cr(III) was calculated as the difference between total Cr and Cr(VI) concentration, i.e. Cr(III) = total Cr – Cr(VI). The adsorption capacity of adsorbents Qₑ (mg g⁻¹) at time t (min) and the adsorption rate R(%) were calculated by the following Eqs. (1) and (2), respectively:

\[
Qₑ(\text{mg g}^{-1}) = \frac{C_o - C_t}{M} \times V
\]

\[
R(\%) = \frac{C_o - C_t}{C_o} \times 100
\]

where \(C_o\), \(C_t\), and \(V\) are the initial Cr(VI) concentration (mg L⁻¹), concentration of Cr ions in the solution in time t, the mass of the used adsorbent (g) and solution volume (L), respectively.

3. Results and discussion

3.1. Morphology and structure of the as-prepared samples

3.1.1. Morphology

The morphologies of the as-prepared P-Fe₃O₄, CL-PANI, CL-PANI@Fe₃O₄ and Fe₃O₄@CL-PANI measured by SEM, TEM and HRTEM are shown in Fig. 1. It can be observed that R-PANI prepared at room temperature exhibited unordered short rods structures (Fig. 1a), while CL-PANI obtained at 0 °C showed 3D hierarchical micro/nanostructures consisting of the well-defined nanofibers with an average diameter of ca. 20 nm (Fig. 1b). Depressed reaction kinetics for heterogeneous nucleation caused by low temperature was speculated to be the possible reason for the direction growth of nanofibers [38]. Coating with Au nanoparticles could prevent CL-PANI from deforming under the high energy of electron beam irradiation and the obtained SEM image shown in Fig. 1c indicated that the CL-PANI presented highly quality 3D coral-like hierarchical structures (Fig. 1c inset). Plenty mesoporous structures were generated between the interconnected nanofibers, which was expected to provide more active paths and sites for adsorbates (See the following textural properties analysis).

The SEM and TEM images of CL-PANI@Fe₃O₄ shown in Fig. 1d and e suggested that the surface of CL-PANI was successfully coated by magnetite nanoparticles with ca.10 nm in diameter. HRTEM image in Fig. 1f clearly demonstrated the lattice fingers with an inter-planar distance of 0.3 nm corresponding to (2 2 0) plane of the magnetite phase [39]. And the corresponding energy EDX elemental mapping of C, O, Fe and N given in Fig. 1g showed the uniformly distribution of Fe₃O₄ nanomaterials. Comparably, the SEM and TEM images of Fe₃O₄@CL-PANI shown in Fig. 1h and i illustrated that Fe₃O₄@CL-PANI kept the 3D coral-like structures of CL-PANI and no obviously magnetite particles could be seen in the surface. However, the lattice fingers with an inter-planar distance of 0.3 nm could still be observed in its HRTEM image (Fig. 1i), indicating that Fe₃O₄ nanoparticles existed inside the Fe₃O₄@CL-PANI sample. Moreover, the EDS elemental mapping presented in Fig. 1k further confirmed the uniformly distribution of Fe₃O₄ nanoparticles for Fe₃O₄@CL-PANI sample. In short, CL-PANI@Fe₃O₄ and Fe₃O₄@CL-PANI, i.e., two different composite modes, were successfully prepared here.

3.1.2. Structure and textural analysis

The molecular structures of as-prepared samples were then
characterized by powder XRD and FT-IR spectra. Fig. 2a shows the powder XRD pattern of these samples. The main peaks located at 2θ values of 14.7, 20.2 and 25.5° together with two shoulder peaks around 26.8 and 29.5°, which are assigned to the (0 1 0), (1 0 0), (1 1 0), (1 1 1) and (0 2 0) reflections of PANI [40], respectively, were observed for both CL-PANI and R-PANI samples. It indicated that both CL-PANI and R-PANI were in the form of highly doped emeraldine salt (ES) and had good crystallinity [41]. In the powder XRD pattern of CL-PANI@Fe3O4, the characteristic reflections of PANI could not be recognized due to the coverage of plenty Fe3O4 nanoparticles on its surface and main peaks at 30.05°, 35.55°, 43.08°, 53.89°, 57.26°, and 62.86°, which are corresponded to the (2 2 0), (3 1 1), (4 0 0), (5 1 1), (4 4 0) and (6 2 0) reflections of Fe3O4, respectively, were observed. These peaks were well in agreement with the standard XRD pattern (JCPDS no. 65-3107). Comparably, both characteristic reflections of PANI and Fe3O4 could be noted in the powder XRD pattern of Fe3O4@CL-PANI, indicating a different combination way of two components from CL-PANI@Fe3O4. The obtained results were in accordance with the electron microscopy analyses.

From Fig. 2b, it can be seen that CL-PANI and R-PANI presented the
similar FT-IR spectrum, with main characteristic stretching vibrations locating at 1571 cm\(^{-1}\) (\(\nu_{c=c}\) for quinoid rings), 1491 cm\(^{-1}\) (\(\nu_{c=c}\) for benzeniod rings), 1302 cm\(^{-1}\) (\(\pi\)-electron delocalization), 1245 cm\(^{-1}\) (\(\nu_{c-N}+\cdot\) and 1138 cm\(^{-1}\) (\(\nu_{\text{NH}^+}\)), respectively. These characteristic peaks are typical for PANI in ES state\[^{42}\]. Compared with the spectrum of CL-PANI, two new peaks around 3445 cm\(^{-1}\) and 624 cm\(^{-1}\) appeared in both composites, which are corresponding to the O–H stretching vibration and Fe-O lattice vibration of Fe\(_3\)O\(_4\) \[^{43}\]. Notably, the red-shift (ca. 25 cm\(^{-1}\)) of O–H characteristic peak in the composites compared with the one in the pure Fe\(_3\)O\(_4\) demonstrated the successful combination of Fe\(_3\)O\(_4\) and PANI and rather than the simple mix of the two components\[^{44}\]. Meanwhile, the relatively low intensity of the band at 624 cm\(^{-1}\) in both composites suggested the low content of Fe\(_3\)O\(_4\), which could be further verified by the following TGA analysis.

As shown in Fig. 2c, there are five steps of weight loss for the synthesized CL-PANI. The first step below 135 °C could be attributed to the release of unbound water, the second step occurring between around 210 °C and 320 °C may represent the loss of unbound HCl, the third weight loss step over 320–440 °C could be for HCl acting as the primary dopant, the fourth step occurring within 440–610 °C was referred to the degradation of PANI main chains and the final step at around 610–800 °C may be due to the final carbonization of intermediate chemicals \[^{45,46}\]. Both CL-PANI@Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)@CL-PANI composite showed the similar decomposition of Fe\(_3\)O\(_4\) and PANI and rather than the simple mix of the two components. A vibrating sample magnetometer was then used to study the magnetic properties of these two composites. As illustrated in Fig. 3, the saturated magnetization value of as-synthesized Fe\(_3\)O\(_4\) nanoparticles was 28.60 emu g\(^{-1}\), and the values of CL-PANI@Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)@CL-PANI composite were measured to be 10.44 emu g\(^{-1}\) and 7.75 emu g\(^{-1}\), respectively. The superparamagnetic nature of composites could endow them with easy separation feature under an external magnetic field, as photo images, which were taken within 30 s after separation, shown in the inset of Fig. 3a. The better separation performance of CL-PANI@Fe\(_3\)O\(_4\) could be resulted from its higher content of Fe\(_3\)O\(_4\) decorating on the exterior surface.

It is well known that the adsorption performance is well related with the textural properties of adsorbents. Therefore, N\(_2\) adsorption-desorption study was then investigated to estimate the Brunauer-Emmett-Teller (BET) specific surface area (\(S_{\text{BET}}\)), total pore volume (\(V_p\)), and micropore volume (\(V_{\text{Micro}}\)) of as-prepared samples. As shown in Fig. 4, the nitrogen adsorption isotherm of CL-PANI showed a Type-III curve obtained by the stronger adsorbate-adsorbate interaction than adsorbent-adsorbate interaction according to the IUPAC classification \[^{47}\]. A H3 hysteric loop locating at relative pressure \(P/P_0\) > 0.7 was observed, indicating that CL-PANI exhibited mesoporous and macroporous structures \[^{48–51}\]. And the pore size distribution calculated from Barrett-Joyner-Halenda (BJH) shown in the inset revealed a bimodal distribution centered around 2.1 nm and 15.7 nm in the mesopore region. These smaller mesopores were generated by the intercross of Y-shaped or V-shaped nanofibers units of 3D hierarchical structure according to the SEM analysis. The calculated \(S_{\text{BET}}\) of CL-PANI was...
24.48 m² g⁻¹, which is similar as the one obtained from other 3D urchin-like PANI [52] but lower than that of R-PANI (Fig. S1). A likely reason is that more micropores existing in the R-PANI with a value of 0.01736 cm³ g⁻¹ attributed to its higher surface area. In other words, more mesoporous existed in CL-PANI because both samples exhibited the similar total pore volume (Table 1). This further supported the generation of plenty unique mesoporous structures between the interconnected nano fibers in CL-PANI, which would provide more active paths and sites for adsorbates.

Compared with CL-PANI, the surface areas of both composites increased due to the combination of Fe₃O₄ nanoparticles that had a larger S_BET value of 59.69 m² g⁻¹ (Fig. S1). The different textural properties of these samples may have a great impact on their adsorption behaviors for Cr(VI).

### 3.2. Batch adsorption studies

#### 3.2.1. Effects on the adsorption capacity

The effect of adsorbent dosage on the adsorption for Cr(VI) was firstly studied to determine the optimal dosage of these samples in the successive batch adsorption studies. As shown in Figs. 5 and S2, the adsorption efficiency increased consequently with the increase of dosage for all samples, where the adsorption efficiency reached equilibrium when the dosage was 1.5 g L⁻¹ for CL-PANI and Fe₃O₄@CL-PANI and 2.0 g L⁻¹ for CL-PANI@Fe₃O₄. The decreased adsorption capacity may be resulted from the unsaturation of adsorption site and particle interactions in the high adsorbent dose [53]. Given the cost effectiveness of adsorbents and comparable performance of the prepared adsorbents, the dosage of 1.5 g L⁻¹ was chosen in this study.

Moreover, the removal efficiencies of total Cr ions on all samples were lower than that of Cr(VI), suggesting that Cr(VI) ions were partially reduced to Cr(III) and released to solution. Besides, as the dosage amount increased, the amount of released Cr(III), i.e., the difference between the adsorption rate of Cr(III) and total Cr ions, was kept almost same on CL-PANI@Fe₃O₄, while those on CL-PANI, R-PANI and Fe₃O₄@CL-PANI increased. This indicated that coating CL-PANI shell on Fe₃O₄ core endowed magnetic composite with similar adsorption and reduction performance as pure PANI. The possible reason for the difference between two magnetic composites will be illustrated in the below mechanism section.

### Table 1

<table>
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<th></th>
<th>S_BET/m² g⁻¹</th>
<th>V₁/cm³ g⁻¹</th>
<th>V_Micro/cm³ g⁻¹</th>
<th>D/nm</th>
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<td>0.01736</td>
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<tr>
<td>CL-PANI</td>
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<td>28.38</td>
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<td>0.01525</td>
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<tr>
<td>Fe₃O₄@CL-PANI</td>
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<td>0.01231</td>
<td>24.80</td>
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<tr>
<td>Fe₃O₄</td>
<td>59.69</td>
<td>0.1413</td>
<td>0.02556</td>
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Fig. 5. Effect of adsorbent dosage on the adsorption of Cr(VI) and total Cr ions on the as-synthesized samples and corresponding photo images of the treated wastewater after adsorption. Conditions: C₀ = 330.0 mg L⁻¹, pH = 2, contact time = 24 h, T = 298 K.

Fig. 4. N₂ adsorption – desorption isotherms of CL-PANI and Fe₃O₄ with inset showing the pore size distribution of R-PANI, CL-PANI, CL-PANI@Fe₃O₄, Fe₃O₄@CL-PANI and Fe₃O₄.

Fig. 6. Effect of initial solution pH on adsorption capacities of Cr(VI) and released Cr(III) at different values (inset) of as-prepared samples (adjusted by 0.1 mol L⁻¹ HCl or 0.1 mol L⁻¹ NaOH aqueous). Conditions: C₀ = 330.0 mg L⁻¹, dosage = 1.5 g L⁻¹, contact time = 24 h, T = 298 K.

7.06, 6.09 and 7.20, respectively for R-PANI, CL-PANI, CL-PANI@Fe3O4 and Fe3O4@CL-PANI, allowing the anionic HCrO4− and CrO42− being easily adsorbed by the electrostatic interaction. Secondly, it is well known that the pronation degree of PANI increases with the decrease in pH value [54]. Therefore, more imine groups were protonated at the lower pH value and more counter ions (i.e. Cl− ions) existed to keep the balance of charge, which provided more active sites for HCrO4− ions, which were the main specie in the pH of 2.0–6.0 [55], to replace Cl− ions by ions exchange and form electrostatic interaction with pronated N+. Therefore, the adsorbents showed better adsorption performances in the acid condition. Thirdly, in the strong acidic solution of Cr(VI) (at pH 2), the Cr(VI) removal process was accompanied by a chemical reduction process [20]. From Fig. 6 inset, it can be observed that the amount of released Cr(III) decreased for all samples with the increase in pH value. This may be another possible reason for the better removal performance of adsorbents at lower pH values. Compared with R-PANI, the enhanced uptake in the weak acid (pH = 4–6) and neutral condition of CL-PANI suggested that the unique ordered 3D hierarchical structure was benefitting for Cr(VI) adsorption. Besides, the effect of initial solution pH on adsorption capacities of Cr(VI) with a lower concentration (182.0 mg L−1) can be seen in the Fig. S4. By comparing two magnetic PANI composites, Fe3O4@CL-PANI exhibited a similar trend with pure PANI, while CL-PANI@Fe3O4 showed a poor adsorption performance which was similar to Fe3O4 nanoparticles at pH of 4–6 (Fig. S4). Nevertheless, given the best removal rate of Cr(VI), the pH of 2.0 was selected for samples in the following study.

3.2.2. Adsorption kinetics

Adsorption kinetic data obtained with different initial concentrations (102.0 mg L−1, 206.0 mg L−1 and 307.0 mg L−1) of Cr(VI) were simulated with pseudo-first-order, pseudo-second-order and Elovich models to investigate the rate of the adsorption process and potential rate-controlling step of PANI and its magnetic composites, as presented by the following Eqs. (3)–(5) [56], respectively:

\[ Q_t = Q_e (1 - e^{-Kt}) \]  
\[ Q_t = \frac{KtQ_e^2}{1 + KtQ_e t} \]  
\[ Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \]

where \( Q_e \) (mg g−1) is the adsorption capacity for the Cr(VI) at equilibrium; \( K_1 \) (min−1) and \( K_2 \) (g mg−1 min−1) are the equilibrium rate constant of the pseudo-first-order and pseudo-second-order models, respectively; \( \alpha \) (mg g−1 min−1) and \( \beta \) (g mg−1) are the initial Cr(VI) adsorption rate and constant of the Elovich model, respectively.

The fitting curves and the determined values of the kinetics parameters based on these models are shown in Fig. 7 and Table S1. On the one hand, the adsorption equilibrium of Cr(VI) on CL-PANI and R-PANI could be achieved within 30 min for the Cr(VI) with concentration of 102.0 mg L−1, where 90% of adsorption efficiency could be attained at the first 5 min. After combined with magnetic particles which showed a slow adsorption rate (Fig. S5), 45 min and 20 min were found for both CL-PANI@Fe3O4 and Fe3O4@CL-PANI to achieve adsorption equilibrium and 90% of adsorption efficiency respectively. For the higher
concentration (206.0 mg L\(^{-1}\)), the equilibrium needed to be established within 390 min and 210 min for CL-PANI@Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4@\)CL-PANI, respectively. Nevertheless, the obtained results suggested that Fe\(_3\)O\(_4@\)CL-PANI was more promising than CL-PANI@Fe\(_3\)O\(_4\) in terms of equilibrium time. Notably, Fe\(_3\)O\(_4\) and CL-PANI@Fe\(_3\)O\(_4\) presented larger SBET values than Fe\(_3\)O\(_4@\)CL-PANI. The superior kinetic adsorption performance should be attributed to the outer coated PANI that showed an equilibrium time of 150 min. On the other hand, among three kinetic models, the calculated \(Q_e\) and correlation coefficients \(R^2\) values from the pseudo-second-order fitted well with the experimental data for these four samples at different initial concentrations. This suggested that chemisorption between the PANI-based adsorbents and Cr(VI) was the rate controlling step [57].

### 3.2.3. Adsorption isotherms

Adsorption isotherms of Cr(VI) at different temperature (298 K, 308 K and 318 K) were gained through shaking the mixture of different concentrations of Cr(VI) with 1.5 g L\(^{-1}\) of as-synthesized adsorbents for 24 h. Two frequently employed isotherm models, i.e., Langmuir and Freundlich, were adopted to further study the interaction between adsorbate and adsorbent and the adsorption capacities of adsorbents, which are described in the Eqs. (6) and (7) [34], respectively:

\[
Q_e = \frac{Q_{\text{max}} K_L C_e}{1 + K_L C_e} \tag{6}
\]

\[
Q_e = K_F C_e^{1/n} \tag{7}
\]

where \(Q_{\text{max}}\) (mg g\(^{-1}\)) and \(C_e\) (mg L\(^{-1}\)) are the maximum adsorption capacity and equilibrium concentration of Cr(VI) in the solution, respectively; \(K_L\) (L mg\(^{-1}\)) and \(K_F\) (mg g\(^{-1}\) (mg L\(^{-1}\))\(^{-n}\)) are the Langmuir isotherm constant related to the adsorption heat and Freundlich isotherm constant describing the adsorption density and \(n\) is the adsorption intensity, respectively.

Fig. 8 shows the fitted plots and Table S2 displays the corresponding isotherm constants calculated from these plots. Although two models gave good fit to the data gained at 298 K for R-PANI, CL-PANI and Fe\(_3\)O\(_4@\)CL-PANI, Langmuir is the better one describing adsorption of Cr (VI) as it gave a higher \(R^2\) value at the higher temperature, i.e., 308 K and 318 K. And the data of CL-PANI@Fe\(_3\)O\(_4\) were well correlated by Langmuir isotherm model at all three temperatures compared with Freundlich model. And the maximum adsorption capacity of Cr(VI)
onto R-PANI, CL-PANI, CL-PANI@Fe3O4, Fe3O4@CL-PANI derived from the Langmuir model at 318 K was 462.7 mg g\(^{-1}\), 489.3 mg g\(^{-1}\), 358.8 mg g\(^{-1}\), and 416.6 mg g\(^{-1}\), respectively. It revealed that the unique 3D hierarchical structure could endow PANI with more active sites and make CL-PANI a more promising adsorbent for Cr(VI) removal compared with R-PANI. Coating CL-PANI on the Fe3O4 particles endowed the composite with a higher adsorption capacity when compared with the one with Fe3O4 particles shell exhibiting a lower adsorption capacity (Fig. S6). Moreover, the as-synthesized adsorbents also showed highly effective adsorption capacities for Cr(VI) with low concentration (Fig. S7). For comparative study, the adsorption capacities of other nanostructured conducting polymer based composites are listed in Table 2, from which it is clearly showed that the synthesized CL-PANI and its magnetic composites exhibited superior adsorption performance.

3.2.4. Cr(VI) adsorption mechanism

In order to uncover the possible adsorption mechanism, CL-PANI and two magnetic composites obtained before and after Cr(VI) ions adsorption were characterized by FT-IR. It is well known that the intensity ratio of peaks at 1571 cm\(^{-1}\) (\(\nu_{\text{C=O}}\) for quinoid rings) and 1491 cm\(^{-1}\) (\(\nu_{\text{C-N}}\) for benzenoid rings) \(I_{\text{Q}}/I_{\text{B}}\) is related to the oxidation state of PANI. Generally, for PANI in oxidized pernigraniline base (PB) state, the value of \(I_{\text{Q}}/I_{\text{B}}\) is higher than that of PANI in ES state owing to the transformation of quinoid structure from benzenoid structure during the oxidation process of PANI in ES state. As shown in Fig. 9, after treating Cr(VI) ions, the \(I_{\text{Q}}/I_{\text{B}}\) values of all three adsorbents increased, indicating the occurrence of oxidation of PANI (ES) and the reduction of Cr(VI) ions during the adsorption process. Notably, for the both magnetic adsorbents, the peak located at 3445 cm\(^{-1}\) was red shifted, suggesting a possible molecular interaction between OH derived from Fe3O4 (Fe-O-H) and Cr ions such as the electrostatic interaction (Fe-OH\(_2^+\)-HCrO\(_4^−\)) and the formation of Fe-Cr(OH)\(_3^+\) complex [61].

The conductivity and electrical resistivity of PANI is also related with its oxidation states. Electrical impedance spectra (EIS) of adsorbents-modified carbon paste electrodes (CPE) were therefore carried out to study the electrical properties of the adsorbents obtained before and after Cr(VI) removal and the results are shown in Fig. S8 and Table S3. It can be observed that Nyquist plots of all electrodes presented semicircle shapes, illustrating that resistive (R) and capacitive (C) features existed in a parallel mode. And for all adsorbents after treating toxic ions, the modified CPEs had the higher value of charge transfer resistance \(R_\text{ct}\) and lower value of constant phase element, indicating that these adsorbents had the lower conductivity and higher resistance. This result further verified that PANI (ES) was partially oxidized by Cr (VI). Besides, it can be seen that Fe3O4@CL-PANI modified CPE had a lower \(R_\text{ct}\) than CL-PANI@Fe3O4, demonstrating that the different combination modes played different roles in changing electrochemical property of CL-PANI, where coating CL-PANI outside could improve CL-PANI’s conductivity at some extent. Meanwhile, it can be found that the \(R_\text{ct}\) difference \((\Delta R_\text{ct})\) of Fe3O4@CL-PANI-Cr modified-CPE and Fe3O4@CL-PANI-Cr modified-CPE was the largest among three adsorbents, suggesting that the Fe3O4@CL-PANI exhibited an enhanced reduction capacity than CL-PANI and CL-PANI@Fe3O4 had a slight weaker reduction capacity.

To investigate the possible adsorption mechanism, the adsorbents were further characterized by XPS. Firstly, the appearance of Cr information in the full-range XPS spectra of all three samples after Cr(VI) adsorption showed the successful uptake of Cr onto the surface of the adsorbents (Fig. S9). As the Cr 2p core-level spectra shown in Fig. 10a-c, Cr 2p\(_{3/2}\) peak and Cr 2p\(_{1/2}\) peak in all three adsorbents were deconvoluted to two components at around 576 eV, 578 eV and 586 eV, 587 eV, which were attributed to Cr(VI) 2p\(_{3/2}\), Cr(III) 2p\(_{3/2}\) and Cr(VI) 2p\(_{1/2}\), Cr(III) 2p\(_{1/2}\), respectively [4]. This result demonstrated that Cr (VI) and partially reduced Cr(III) ions were immobilized on these adsorbents. Fig. 10d summarizes the solid-solution distribution of Cr \((C_0 = 228.0 \text{ mg L}^{-1})\) after treatment with three adsorbents. It can be calculated that the total percent of reduced Cr(III) ions obtained in CL-PANI, CL-PANI@Fe3O4 and Fe3O4@CL-PANI was 65.5%, 48.5%, and 67.7%, respectively, which was in accordance with the result gained from the above EIS analysis. Interestingly, more Cr(III) ions (51.4%) were found to be immobilized on Fe3O4@CL-PANI than that on CL-PANI (42.9%), indicating that Fe3O4 provided extra active sites such as functional hydroxyl group for attracting Cr(III) ions by chelation effect [62]. In the Fe 2p core-level spectra of magnetic composite (Fig. 10e), two peaks located at 710.5 eV and 724.0 eV, corresponding to Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\), were observed, which are typical characteristics of Fe3O4 [63]. However, no significant change in peak position after adsorbing Cr(VI) ions was observed, indicating that Fe3O4 nanoparticles did not involve in the reduction process. In Fig. 10f-h, the N 1s core-level spectra of three adsorbents were curve-fitted into three peak components, i.e. quinoid imine \((-\text{NH}−\text{N})\sim\text{HCrO}_4^−\), benzoinoid \((-\text{NH}−\text{N})\sim\text{HCrO}_4^−\) and positively charged nitrogen \((-\text{NH}^-\text{N})\sim\text{HCrO}_4^−\sim\text{HCrO}_4^−\sim 400.5 \text{ eV}) [64]. It can be noted that the percentage of \(-\text{NH}^-\text{N}^+\) increased for all samples after adsorption, indicating the existence of PANI (PB) state and the occurrence of redox between PANI(ES) and Cr (VI). And the generated \(-\text{N}^-\text{N}^+\) functional groups could be served as new active sites for adsorbing Cr(III) by forming complexes [55].

Besides, it is desirable to reveal the relationships between the adsorption of Cr(VI), reduction of Cr(VI) and immobilization of Cr(III) ions on these adsorbents. As the concentrations of total Cr, Cr(VI), and Cr(III) in the solution upon different adsorption times shown in Fig. 11, different change trends of total Cr and Cr(III) concentrations as a function of adsorption time were observed for CL-PANI and its magnetic adsorbents. For CL-PANI, only a few amounts (less than 5 mg L\(^{-1}\)) of Cr (III) could be measured at the very beginning of adsorption. With the adsorption went on, the amount of released Cr(III) increased, even when the adsorption of Cr(VI) was over around 210 min. It indicated
Fig. 10. Cr 2p XPS spectra of CL-PANI (a), CL-PANI@Fe₃O₄ (b) and Fe₃O₄@CL-PANI (c) before and after equilibrium adsorption of Cr(VI) ions with initial concentration of 228.0 mg L⁻¹; chromium distribution of three adsorbents after equilibrium adsorption (d); Fe 2p XPS spectra of CL-PANI@Fe₃O₄ (e) before and after equilibrium adsorption; N 1s 2p XPS spectra of CL-PANI (f), CL-PANI@Fe₃O₄ (g) and Fe₃O₄@CL-PANI (h) before and after equilibrium adsorption.
that Cr(VI) was absorbed on the CL-PANI firstly and then reduced to the Cr(III). Comparably, large amount of released Cr(III) could be detected for CL-PANI@Fe_3O_4 (∼30 mg L^{-1}) and Fe_3O_4@CL-PANI (∼110 mg L^{-1}) after adsorption for 1 min and the concentration of total Cr did not change obviously at this time. Moreover, the amount of released Cr(VI) decreased with the increase in adsorption time during the adsorption equilibrium period, i.e., after 250 min, suggesting that Cr(VI) was reduced to Cr(III) firstly on the surface of magnetic adsorbents and then the released Cr(III) was immobilized. Compared two magnetic adsorbents, they showed different reduction capacities, which were in accordance with the previous EIS and XPS analyses. In short, we can deduce that the adsorption process occurred firstly for pure CL-PANI, while reduction process happened firstly for magnetic adsorbents. The possible explanation for this interesting phenomenon is under investigated.

Therefore, combined pH effect, FT-IR, EIS and XPS analyses, possible adsorption and reduction mechanisms of Cr(VI) together with Cr (III) sequestration by CL-PANI and its magnetic adsorbents could be proposed. An adduced scheme on CL-PANI@Fe_3O_4 is shown in Fig. 12. At the optimum pH of 2.0, HCrO_4^{-} specie was the main Cr(VI) anions, which were attracted by plenty amount of pronated amino groups (−NH_3^{+}−) and imine groups (−N═N−) in the CL-PANI (ES) and functional pronated (−OH_2^{+}) groups in the Fe_3O_4 via electrostatic interactions. Due to the high redox potential value of HCrO_4^{-} (+1.35 V at the standard condition), the adsorbed HCrO_4^{-} ions were then partially reduced into Cr^{3+} which was the dominate species for Cr(III) when pH below 4, by CL-PANI in ES state. Except for the functional imine groups in CL-PANI (PB) served as active sites for chelating Cr^{3+} ions, the functional OH group in the Fe_3O_4 could also immobilize Cr^{3+} by forming Cr(OH)_3^{+} complex [61], which was the possible reason for the more active sites existed in the magnetic composite, as observed above.

**3.2.5. Effects of coexisting ions and reusability**

The competitive influence of coexisting ions was further investigated since more than one ion exist in the wastewater and the existence of these ions may affect the adsorption performance of Cr(VI) onto the adsorbents. Coexisting ions including Cl^{-}, NO_3^{-}, SO_4^{2−}, H_2PO_4^{-} and ARG^{-} were chosen to study their effects on Cr(VI) adsorption. As shown in Fig. S10, the effects of these coexisting ions on the adsorption of Cr(VI) were insignificant, suggesting that they did not compete for the active sites for adsorbing Cr(VI). Similar results were reported in other studies [65]. This result indicated that all of the adsorbents showed a selective adoption on Cr(VI).

The stability and regeneration performance of as-synthesized adsorbents by ten adsorption-desorption cycles were finally evaluated, which is indispensable for the practical application. The Cr ions-loaded adsorbents were eluted by 0.1 M NaOH solution for 0.5 h. As shown in Fig. S11, after 10 cycles, CL-PANI and R-PANI still retained high
adsorption capacity of 95%, while 80% of adsorption capacity was observed for both magnetic composites. Meanwhile, the concentrations of Fe leaching in the treated water were examined and shown in Fig. S12. Less than 0.37 mg L⁻¹ and 0.29 mg L⁻¹ of Fe ions were detected in the solution treated with CL-PANI@Fe₃O₄ and Fe₃O₄@CL-PANI, respectively in the previous 7 adsorption-desorption cycles, and no Fe leaching was observed in the next 3 cycles, indicating the structural stability of magnetic composites. The less Fe leaching amount compared with other studies may result from the fact that the pronation of CL-PANI (EB) consumed amount of H⁺, therefore protecting Fe₃O₄ from corrosion in some way [66]. Moreover, the less amount of Fe leaching detected from Fe₃O₄@CL-PANI than CL-PANI@Fe₃O₄ suggested that coating PANI shell to the magnetic cores could further inhibit the corrosion of Fe₃O₄ particles.

4. Conclusion

In this study, 3D hierarchical coral-like PANI and the corresponding magnetic nanocomposites were successfully prepared. The obtained absorbents exhibited highly effective adsorption capacities for Cr(VI) ions mainly through electrostatic interaction and redox reaction, with the maximum capacities achieved at pH 2.0, 318 K. Mechanism studies showed that the magnetic particles provide extra complexing sites for binding the reduced Cr(III) in Fe₃O₄@CL-PANI. Moreover, compared with CL-PANI@Fe₃O₄, Fe₃O₄@CL-PANI exhibited the shorter adsorption-equilibrium time, higher adsorption and reduction capacity and less Fe leakage. Therefore, combined with its easy separation property and good reusability, Fe₃O₄@CL-PANI was an excellent adsorbent for the treatment of Cr(VI)-containing wastewater.

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Appendix A. Supplementary data

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