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Stable hierarchical microspheres of 1D Fe–gallic acid MOFs for fast and efficient Cr(vi) elimination by a combination of reduction, metal substitution and coprecipitation†

Hongyun Niu,^a Yang Zheng,^{ab} Saihua Wang,^{ab} Sijing He^{ab} and Yaqi Cai^{abc}

One-dimensional Fe–gallic acid MOFs were assembled into stable hierarchical microspheres in DMF solvent taking advantage of DMF decomposition by heat. The rapid electron transfer ability and high accessibility of the multiple reaction sites on Fe–gallic acid microspheres ensure fast and complete elimination of Cr(vi) from water samples.

Discharges of heavy-metal-containing wastewaters from various industries (such as electroplating, dyeing, mining, and tanning) have led to serious impacts on the environment worldwide.¹ In particular, hexavalent chromium species are well known for their high toxicity and can cause various symptoms.^{1–3} It is imperative to remove excess Cr(vi) from wastewater before it is discharged into the environment.

Several methods such as adsorption, biosorption, reduction, and filtration reverse osmosis, ion-exchange, foam flotation, electrolysis, and surface adsorption have been reported for chromium removal. Adsorption/reduction is considered as the most attractive way to treat Cr(vi)-laden wastewater due to its high feasibility, high efficiency and low-cost. Since Cr(III) species are less toxic and hydroxide precipitants have low solubility in water,^{2,3} *in situ* reduction combined with adsorption of reduced Cr(III) through metal ion coprecipitation can achieve a nearly complete removal of chromium from water. Hybrid polymeric materials,^{4–9} metal or metal oxide-based materials,^{10–13} carbon materials^{14–19} and bioadsorbents^{20–23} are reported to have the ability to simultaneously reduce Cr(vi) and adsorb the produced Cr(III) from water. However, these adsorbents still have some shortcomings for Cr(vi) elimination. For example, biosorbents and metal/metal oxides often have small surface areas and

relatively low adsorption capacity for Cr(vi)/Cr(III). These drawbacks have hindered their applications for Cr(vi) removal from wastewater. The development of new materials with good water stability, strong reduction ability and high adsorption capacity for Cr(vi)/Cr(III) is urgent.

Metal–organic frameworks (MOFs) have drawn the attention of scientists due to their ultrahigh surface areas and pore volumes, multiple reaction sites, and diverse and easily tailored structures. Recently, the adsorption performance of MOFs or MOF hybrids in Cr(vi) removal has been tested.^{24–27} But these MOF-type adsorbents have not shown obvious advantage for the removal of Cr(vi) over metal oxides, metal nanoparticles, or polymer composites with low surface areas and small pore volume. This might result from the micropores of MOFs that restrain the diffusion of target molecules into the inner adsorptive sites.²⁸ Recent studies suggest that low-dimensional MOFs (1D and 2D MOFs) have higher electrical conductivity and more accessible active sites,^{28,29} which accelerates interactions with targets in water. Until now, there are very few studies on the preparation of 1D MOFs.^{30,31} Most of the reported 1D-MOF compounds occur within bulk crystal structures of 3D MOF. Their separation or attainment into self-standing nano-objects or small collections of nano-objects is still a challenge.³⁰

Iron–gallic acid hybrids (Fe–GA) have been known since antiquity and used as inks and dyes.^{32,33} Fe–GA is a classic example of a 1D MOF, containing infinite chains of *trans*-corner-sharing MO6 octahedra.³² Normally, Fe–GA is synthesized in hot water *via* a hydrothermal method. The produced hybrid shows a nanoscaled rod-like morphology.^{32,34} Due to their high surface activity, Fe–GA nanorods tend to aggregate in solvent by weak interactions among nanorods and between nanorods and solvent molecules. Herein, we employed *N,N*-dimethylformamide (DMF) as solvent, which can be decomposed to dimethylamine in the presence of water at temperatures above 110 °C and thus promote the deprotonation of carboxylic ligands.³⁵ Since both the precursors of Fe salt and gallic acid contain crystal water, decomposition of DMF might reasonably occur at *T* > 100 °C with dissolved water in DMF.

^aState Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: caiyaqi@rcees.ac.cn; Tel: +86-10-6284-9239

^bUniversity of Chinese Academy of Sciences, Beijing, 100049, China

^cInstitute of Environment and Health, Jiangnan University, Wuhan 430056, China

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Desorption of DMF sorbed on the Fe-GA nanorod surface would lead to disassembly of the aggregated nanorods, which may change the morphology of Fe-GA hybrids. We examined the effect of temperature on Fe-GA hybrid shapes. As shown in Fig. S1,[†] the Fe-GA hybrids showed a nonporous block and a compact spherical morphology when the reaction temperature was 80 and 100 °C, respectively. At $T \geq 120$ °C, the Fe-GA hybrids became much fluffier and looser. But a lot of microspheres were destroyed to form smaller spheres and nanorods at 150 °C due to the increased decomposition percentage of DMF adsorbed on Fe-GA. If water, ethanol or methanol was adopted as the solvent, the Fe-GA hybrids were heavily aggregated, proving that DMF decomposition controlled the hierarchical structure of Fe-GA.

The Fe-GA nanorods (abbreviated as Fe-GA(D)) obtained at 120 °C were microspheres with a diameter of 2–3 μm (Fig. 1A and C). The magnified FESEM and HRTEM images clearly exhibit that the Fe-GA(D) microspheres were constructed by randomly self-assembled nanorods (Fig. 1B and D), which induced the desirable interconnected meso- and macropores.

The properties of the hierarchical Fe-GA(D) hybrids were investigated *via* FTIR, XRD and XPS analysis. The Bragg peaks in the XRD pattern of the Fe-GA(D) microsphere (Fig. 2A) were consistent with the published XRD pattern of GA/Fe^{III} MOFs.³⁴ The FTIR spectrum of Fe-GA(D) (Fig. 2B) was similar to that of Fe-GA in the literature³³ except for the presence of a sharp peak at 1640–1670 cm^{-1} related to the $\text{V}_{\text{C}=\text{O}}$ of amide from DMF. The Fe2p XPS line of Fe-GA(D) indicates that the iron cations existed as mixed Fe(II) and Fe(III) (Fe(II)/Fe(III) = 1/1), suggesting that redox reactions occurred in the DMF solvent (Fig. 2C and S2A[†]). The Fe-GA complex could be stored for a long time without loss of Fe(II) species in the absence of the protection of inert gases (such as N_2), reflecting the perfect stability of the complex.

The measured BET surface area and pore volume of Fe-GA(D) hybrids were 297.8 $\text{m}^2 \text{g}^{-1}$ and 1.0 $\text{m}^3 \text{g}^{-1}$, respectively. In the pore size distribution plot of Fe-GA(D) obtained from the nitrogen adsorption data, there were four peaks located at 2, 23, 50, and 86 nm, respectively. This result suggested that the Fe-GA(D) was composed of micropores, mesopores and macropores (Fig. S3A[†]). The determined pHPzc value of Fe-GA(D) was 2.3 (Fig. S3B[†]), and thus Fe-GA(D) was negatively charged in

Fig. 1 SEM images (A and B) and TEM images (C and D) of hierarchical Fe-GA(D) hybrids. The scale bar in (A) and (C) is 1 μm , and in (B) and (D) is 100 nm.

Fig. 2 XRD pattern of Fe-GA(D) (A) and FTIR spectra (B), and XPS spectra of Fe2p (C) and Cr2p (D) of Fe-GA(D) before and after interaction with Cr(VI). The red lines in (A) represent the simulated XRD pattern of GA/Fe^{III} MOFs reported in ref. 34.

water at pH > 2.3, which favored the adsorption of metal cations.

We utilized the hierarchical Fe-GA(D) hybrids to eliminate Cr(VI) from water. The removal efficiency for Cr(VI) and total Cr (including Cr(VI) and the resulting Cr(III)) was in the range of 85–100% and 82–97%, respectively, in the presence of 1 g L^{-1} of Fe-GA(D) as the initial concentration of Cr(VI) changed from 100 to 2000 mg L^{-1} (Fig. 3A). The suspension turned from yellow to colorless when the initial concentration of Cr(VI) was 100–600 mg L^{-1} . The adsorption of Cr(VI) and total Cr on Fe-GA could be described by the Freundlich adsorption model (Table S1[†]), indicating the multilayer adsorption of Cr(VI) onto the Fe-GA(D) surface. The Langmuir maximum adsorption capacity (Q_m) of Fe-GA(D) for Cr(VI) and total Cr was 1709.2 and 1666.7 mg g^{-1} , respectively (Table S1[†]), which were significantly higher than those obtained with other materials, such as

Fig. 3 Adsorption amount and the corresponding equilibrium concentration of Cr(VI) and total Cr at different Cr(VI) initial concentrations (A), and effect of reaction time (B), solution pH (C) and coexisting cations (D) on Cr(VI)/Cr(III) elimination.

bioadsorbents (40–333 mg g⁻¹), metal/metal oxide-based materials (4–473 mg g⁻¹), carbon or graphene oxide materials (23–581 mg g⁻¹) and hybrid polymeric materials (90–377 mg g⁻¹) (see Table S2†). The adsorption ability of Cr(vi) on Fe-GA(D) was more than 10–95 times higher than those on 3D MOFs.^{24–27}

The interaction between Cr(vi) and Fe-GA(D) and the removal of total Cr reached equilibrium within 10 min and 72 h, respectively (Fig. 3B). A pseudo-second-order model perfectly described the adsorption kinetics of total Cr ($R^2 = 0.9994$) (Table S3†), suggesting a chemisorption process.¹⁰ The 1D structure of Fe-GA nanorods benefits electron transfer, which contributes to fast interaction kinetics towards Cr(vi).

Fe-GA(D) exhibited excellent stability in acidic (pH 2) and alkaline (pH 11) solutions, in which the crystalline and pore size of the material were generally not changed and leaching of Fe atoms was not detected (Fig. S4†). The effect of solution pH on Cr(vi) removal was studied. The removal efficiency for Cr(vi) was 100% in the pH range of 3.0–9.0, and decreased to 85% at the initial pH of 10.0 (Fig. 3C). The reduction of Cr(vi) in water solution consumes H⁺; therefore a higher solution pH disfavored Cr(vi) reduction. Compared to most of the reported adsorbents, the removal of Cr(vi) by Fe-GA(D) was less pH-dependent (see Table S2†). In the presence of Cr(vi), we detected released Fe atoms at pH 3, possibly resulting from ion exchange between the produced Cr(III) and Fe cations in Fe-GA(D). Since the pHpzc of Fe-GA(D) is pH 2.3, the released Fe cations and produced Cr(III) should adsorb onto the surface of negatively charged Fe-GA(D) at pH > 2.3. Hydroxylation of Fe(III) on the surface of Fe-GA(D) might take place at pH ≥ 4.0, which causes coprecipitation of Cr(III) on the Fe-GA(D) surface. The hydroxylation of Fe and Cr cations decreased the solution pH, and thus promoted the reduction of Cr(vi) and the removal of total Cr in turn, which contributed to the excellent resistance of Cr(vi) reduction by Fe-GA(D) to pHs. The elimination of total Cr increased as the pH increased from 3.0 to 4.0, and levelled off until pH 5.0, suggesting the important role of Fe hydroxylation in Cr(III) removal. Further increase of the solution pH decreased the removal of total Cr. This may be contributed by the fact that the precipitation of mixed chromium(III)/iron(III) hydroxides blocked exchange between Cr(III) and Fe on Fe-GA,¹⁰ leading to decreased adsorption of Cr(III). The possible reaction mechanisms between Fe-GA and Cr(vi) are listed below:

To prove the reaction mechanisms, Fe-GA(D) after treatment of Cr(vi) at pH 4 and pH 8 was collected and analyzed by FTIR

and XPS. In the FTIR spectrum of Fe-GA(D) (Fig. 3B), the intensity of V_{O-H} of water at 3400 cm⁻¹ increased after interaction with Cr(vi). A new peak present at 1500 cm⁻¹ was related to the surface metal hydroxyl groups.³⁶ The adsorption band at 1100 cm⁻¹ strengthened remarkably, resulting from the formation of Fe(OH)₃ and Cr(OH)₃ on the Fe-GA(D) surface.³⁷ These results proved the deposition of metal hydroxides on the Fe-GA(D) surface.

After interaction with Cr(vi), the binding energies of C1s shifted to high values, suggesting the oxidation of the GA ligand in the reaction process (Fig. S5†). The Fe2p core-level lines of Fe-GA(D) (Fig. 3C) were characteristic of Fe(III) species, suggesting the oxidation of Fe(II) species into Fe(III). Compared with the as-prepared Fe-GA(D), a new species at 530.3 eV appeared in the O1s spectra of Fe-GA(D) after treating with Cr(vi) at pH 4 and pH 8 (Fig. S6B and C†), which was associated with the surface metal hydroxides. The content of OH⁻ species on the Fe-GA(D) surface was 17.7 and 19.2% after treatment of Cr(vi) at pH 4 and pH 8, respectively. In Fig. 3D, the Cr2p spectra showed that Cr(vi) ions were completely reduced to Cr(III) cations. The Cr2p line of Cr adsorbed on the Fe-GA(D) consisted of chelated Cr (BE = 576.8 eV) and Cr(OH)₃ (BE = 577.6 eV)³⁸ with the ratio of about 1.1 : 1 at both pH 4 and pH 8 (Fig. S2B and C†). This result implied that exchange between produced Cr(III) and Fe cations in Fe-GA(D) and formation of surface metal hydroxides played important roles in total Cr elimination. Metal cation substitution controlled the adsorption kinetics of total Cr, which was the main reason for the much slower elimination rate of total Cr than that of Cr(vi) (Fig. 3B). After reduction/adsorption of Cr(vi), the O content increased and C content decreased obviously compared to the as-synthesized Fe-GA(D) due to the formation of metal hydroxides. The ratio of Cr/Fe at pH 4 and pH 8 was 0.47 and 0.40, respectively (Table S4†). These results confirmed the strong reduction/adsorption ability of Fe-GA(D) towards Cr(vi) in both weak acid and alkaline solutions.

The selective adsorption ability of Fe-GA(D) towards Cr(vi)/Cr(III) was investigated in the presence of several interfering anions (Cl⁻, PO₄³⁻, SO₄²⁻ or NO₃⁻) and metal ions (Cu²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Ba²⁺, and Mn²⁺). The result showed that Cr(vi) removal by Fe-GA(D) hybrids was nearly not or slightly affected by the coexisting anions (Fig. S7†). The removal efficiency of Fe-GA(D) for Cr(III) was 6–22 times higher than for other metal cations (Fig. 3D). Parajuli³⁹ found that trivalent metal cations (Fe³⁺ and Al³⁺) had a higher complexation ability to catechol modified lignin than divalent cations (such as Ni²⁺, Zn²⁺, Cd²⁺, and Co²⁺). Therefore, the ion exchange ability of metal cations with Fe atoms on Fe-GA(D) hybrids determined the selectivity of Fe-GA(D) hybrids toward Cr(III).

After reaction with Cr(vi), the morphologies of Fe-GA(D) hybrids were retained, and the Fe-GA nanorods and Fe or Cr hydroxides (nanosheets) can be observed in TEM and SEM images (Fig. S8†). The EDX analysis together with elemental mapping indicated that Cr atoms were homogeneously distributed throughout the whole Fe-GA(D) hybrids (Fig. S9†), which proved the availability of all the adsorptive sites on Fe-GA(D) for the targets. The used Fe-GA(D) could be partly regenerated by soaking in diluted HCl solution (pH = 2) to

remove the adsorbed $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$, and then immersing in 30 mM $\text{Fe}(\text{II})$ solution at pH 3.0 for 12 h to exchange $\text{Cr}(\text{III})$ ions complexed with GA by $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ ions. The regenerated Fe-GA(D) could remove 90% of $\text{Cr}(\text{VI})$ from 100 mg L^{-1} of $\text{Cr}(\text{VI})$ solution. Although Fe-GA(D) could not be totally recycled, the ultrahigh adsorption/reduction ability and strong interactions between Fe-GA and $\text{Cr}(\text{VI})/\text{Cr}(\text{III})$ ions avoid the leaching of sorbed Cr ions into water and ensure a long and effective treatment ability of Fe-GA(D) to $\text{Cr}(\text{VI})$ -laden wastewater and thus reduce the cost of water treatment.

To test the performance of Fe-GA(D) for $\text{Cr}(\text{VI})$ elimination in wastewater, electroplate liquids sampled directly from electroplating baths were treated with Fe-GA(D) (see the ESI†). After adjusting the solution pH to 5.0, the concentration of $\text{Cr}(\text{VI})$ in two electroplate liquid samples was 172122.2 and 18305.5 mg L^{-1} , respectively. As the dosage of Fe-GA(D) was in the range of 2–10 g L^{-1} , $\text{Cr}(\text{VI})$ removal efficiency increased from 15.9 to 52.6%, and 10.9 to 46.0% in the two samples, respectively. After reaction, green $\text{Cr}(\text{OH})_3$ precipitates can be observed obviously in the cuvette, indicating the reduction of $\text{Cr}(\text{VI})$ by Fe-GA(D) . If electroplate liquid samples were treated with 10 g L^{-1} of Fe-GA(D) three times, the removal efficiency for $\text{Cr}(\text{VI})$ attained was 90% and 85%, respectively. It's worth mentioning that the electroplate liquids contain a high concentration of Fe element. After treatment with Fe-GA(D) , the concentration of Fe atoms was not changed, suggesting the good stability of Fe-GA(D) in the reaction process. If 10 g L^{-1} of activated carbon was used as the adsorbent, 19.0 and 17.3% of $\text{Cr}(\text{VI})$ could be removed from the two samples without the formation of $\text{Cr}(\text{OH})_3$, and the total removal efficiency for $\text{Cr}(\text{VI})$ was less than 30% after treatment with 10 g L^{-1} of activated carbon three times (Table S5†). These results indicated that Fe-GA(D) could be regarded as a powerful adsorbent for $\text{Cr}(\text{VI})$ elimination from wastewater samples.

In summary, Fe-GA(D) hybrids possess various interaction sites for $\text{Cr}(\text{VI})$ and provide multiple interaction mechanisms for $\text{Cr}(\text{VI})$. The advantages of hierarchical Fe-GA(D) hybrids over other inorganic–organic hybrids include the following: cheapness and natural abundance of gallic acid and Fe salts, simpleness of the synthesis method, availability of the majority of the adsorptive sites, strong reduction ability and fast interaction kinetics towards harmful $\text{Cr}(\text{VI})$ anions.

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