Synthesis and Characterization of Two-Dimensional Transition Metal Dichalcogenide Magnetic MoS$_2$@Fe$_3$O$_4$ Nanoparticles for Adsorption of Cr(VI)/Cr(III)

A. Santhana Krishna Kumar,† Shiuh-Jen Jiang,*†,‡ and Jolanta Karolina Warchoł§

†Department of Chemistry, National Sun Yat-sen University, Kaohsiung 80424, Taiwan
‡Department of Medical Laboratory Science and Biotechnology, Kaohsiung Medical University, Kaohsiung 80708, Taiwan
§Department of Water Purification and Protection, Rzeszow University of Technology, 12 Powstanców Warszawy Str., 35-959 Rzeszów, Poland

ABSTRACT: Recently, two-dimensional transition metal dichalcogenides (TMDs) have received tremendous attention in many fields including environmental remediation. Magnetic nanoparticles (Fe$_3$O$_4$NPs) decorated with MoS$_2$ (MoS$_2$@Fe$_3$O$_4$NPs) have been synthesized via a new one-step synthesis route and utilized as an efficient adsorbent for removal of Cr(VI)/Cr(III) from aqueous solutions. The obtained MoS$_2$@Fe$_3$O$_4$NPs with numerous surface hydroxyl groups show uniform size and shape, excellent water-dispersibility, and superior magnetic property to enhance the adsorption. The physicochemical properties of the adsorbent prior to and after adsorption of Cr(VI)/Cr(III) were extensively characterized using several advanced instrumental techniques. The adsorption of Cr(VI)/Cr(III) on MoS$_2$@Fe$_3$O$_4$NPs was performed under batch conditions aiming at identification of optimal contact time, pH value of chromium solution, and influence of the presence of competitive ions. This study was supported by modeling of adsorption equilibrium and kinetics by using empirical equations.

1. INTRODUCTION

The tremendous increase in the usage of heavy metals in diverse industrial applications has caused in an increased amount of “chromium pollution” into the water bodies. The global awareness of their underlying detrimental effects has received great attention in the past decade. The chromium oxidation states vary from −2 to +6, whereas the most stable oxidation states are +3 and +6. Between the last two, Cr(VI) compounds cause more concerns due to their high water solubility and mobility.$^{1−3}$ The permitted levels for Cr(III) and Cr(VI) in wastewater are 2 and 0.05 mg L$^{-1}$, respectively.$^{5,5}$ To meet the required levels, several treatment technologies have been developed, among which adsorption-based processes are primarily preferred due to their removal efficiency and cost efficiency.$^{5}$ Current research focuses on development of selectivity toward sorbent chromium ions, which when dispersed in water, can be easily captured to be then regenerated and reused.

Fe$_3$O$_4$ nanoparticles (NPs) represent an alternative group of materials in which application for water cleanup started to be developed several years ago.$^{6}$ The undisputed advantage of the Fe$_3$O$_4$NP over other sorbents, membranes, or filter materials is their high adsorption capacity and selectivity for a broad range of hydrocarbons and toxic anions such as As(III/V) and Cr(III/V) VI).$^{1−4,7}$ On the other hand, Fe$_3$O$_4$NPs is highly susceptible to oxidation, which can be exposed to the atmosphere which then can affect particle storage and save transport.$^{9}$ Furthermore, they are challenging to use in continuous-flow systems due to their small particle size and variability. To overcome these difficulties, several researchers have prepared magnetic Fe$_3$O$_4$NP cross-linked by transition metal dichalcogenide (TMD) materials.$^{9,10}$ The TMDs have a widespread formula MX$_2$, where M can denote molybdenum (Mo), and X can denote chalcogens, like sulfur (S). Every Mo is coordinated in a trigonal prismatic geometry to six S atoms.$^{11,12}$ Such a modification not only stabilizes the nanoparticles and ultimately inhibits their oxidation but also ensures large surface area and high porosity of synthesis product.$^{13}$

In practical applications, Fe$_3$O$_4$NP can be synthesized to exhibit unique properties$^{4−7}$ such as chemical stability,$^{9,10}$ water solubility,$^{9,12}$ biocompatibility,$^{7}$ uniform particle size$^{17}$ and good dispersion in an aqueous medium.$^{9,10}$ For example, co-assembly of Ag and Fe$_3$O$_4$ NPs on MoS$_2$ nanosheets has recently emerged as promising high-perform-
Song et al. have developed NPs by dispersion of MoS2 in ethanol/water solution and further dissolution in FeCl3·6H2O and FeCl2·4H2O. The obtained material exhibits excellent performance for dye removal (such as congo red, methylene blue, methylene green, rhodamine B, etc.). An additionally, two-step hydrothermal synthesis of MoS2@Fe3O4NPs was proposed by Yu et al. First, polyethylene glycol was dissolved into H24Mo7N6O24·4H2O followed by addition of thioacetamide. Then the obtained polyethylene glycol-coated MoS2 was mixed with FeCl3 and ascorbic acid. It leads to material possessing magnetically targeted photothermal therapy guided by magnetic resonance imaging. Undoubtedly, the combination of MoS2 nanosheets and magnetic properties (Fe3O4NPs) can generate a new class of materials with great potential application of environmental remediation. Therefore, it would be important to develop a simple synthesis route to reduce the production cost.

Table 1. Cr(VI) Adsorption Capacity of Various Adsorption Materials Reported in the Literature

| adsorption material | pH  | uptake (mg g\(^{-1}\)) | reference |
|---------------------|-----|------------------------|-----------|
| Fe3O4 magnetic particles | 3.0 | 12.30 | 1 |
| core–shell Fe@Fe3O4 nanowires | 6.28 | 177 | 2 |
| cobalt ferrite nanoparticles | 2.0 | 16.73 | 3 |
| magnetic chitosan–iron(III) hydrogel | 3.0 | 144.9 | 4 |
| ionic liquid functionalized multiwalled carbon nanotubes | 2.5–4.0 | 85.83 | 5 |
| layered double hydroxide intercalated with MoS2\(^{2-}\) | 4–10 | 130 | 7 |
| MoS2-coated Mg/Al layered double hydroxide composite | 5.0 | 76.3 | 24 |
| polyaniline-modified 3D-flower-like MoS2 composite | 3.0 | 526.3 | 25 |
| tetraethylenepentamine functionalized nanosized magnetic polymer adsorbents | 2.0 | 370.4 | 29 |
| Fe2O3NPs decorated with MoS2 (MoS2@Fe3O4NPs) | 5.0 | 218.18 | present study |

Figure 1. Raman spectra of Fe3O4NPs (A), bulk MoS2 (B), and MoS2@Fe3O4NPs (C).

Figure 2. XRD spectra of Fe3O4NPs (A), bulk MoS2 (B,C), and MoS2@Fe3O4NPs (D).

Until now, there are no reports on the study of application of magnetic MoS2@Fe3O4NPs for chromium uptake (Table 1). Its use for chromium uptake from real water streams requires estimation of optimal process conditions. As one can expect, chromium adsorption is controlled by the initial pH of the solution, which defines both Cr(III) and Cr(VI) hydrolysis products and availability of functional groups of new adsorbents. In acidic condition, the surface-active groups of Fe\(^{2+}\) and quaternary ammonium cation functionalized MoS2@Fe3O4NPs will be protonated and positively charged, which favors the uptake of negatively charged Cr(VI) species. Whereas in alkaline pH, deprotonation of adsorbed surface facilitates interaction with positively charged Cr(III) species. It is especially important in real wastewater treatment where the presence of Fe(II) and Mn(II) can reduce Cr(VI) to Cr(III), while other heavy metals could form tetrahalo complexes (e.g., HgCl4\(^{2-}\), NiCl4\(^{2-}\), PdCl4\(^{2-}\)), which, similarly to competitive...
anions (e.g., sulfate, nitrite), could also compete with Cr(VI) for sorption efficiency.18

The aims of the present work were to provide a one-step synthesis route of magnetic nanoparticles (Fe3O4NPs) decorated with MoS2. We determined capability of obtained material to adsorb Cr(VI)/Cr(III) from binary and multi-component solutions as well as from real wastewaters. Finally, we checked the material’s ability for regeneration and reuse.

2. RESULTS AND DISCUSSION

2.1. Raman Spectra and Powder XRD. The chemical composition of the Fe3O4NPs, MoS2, and MoS2@Fe3O4NPs was confirmed by Raman spectra, which are measured at 532 nm excitation. A well-resolved Raman peak was observed at 217, 282, 395, and 596 cm−1, which is attributed to the A1g vibration mode of bare Fe3O4NPs (Figure 1A).19,23 For the bulk MoS2 sample, two characteristic Raman peaks are attributed to 390 and 416 cm−1, which correspond to the A1g and E2g vibration modes (Figure 1B).11,15,20 Related peak frequency difference is Δk = 26 cm−1. However, as-synthesized MoS2@Fe3O4NPs peaks were slightly shifted to 392 and 417 cm−1, which correspond to the A1g and E2g vibration modes (Figure 1C). In this case, a peak frequency difference was Δk = 25 cm−1. This result is in line with the results obtained by Liu et al.20

The XRD spectra of Fe3O4NPs, MoS2, and MoS2@Fe3O4NPs are depicted in Figure 2. Diffraction peaks at 2θ = 30.3, 35.7, 43.2, 53.3, and 56.9° could be indexed to (220), (311), (400), (422), and (511) planes of the magnetite structure (JCPDS no. 019-0629) of the cubic lattice of Fe3O4NPs, respectively (Figure 2A).9,19,21 The bulk MoS2 diffraction peaks of 2θ = 14.4, 29.6, 39.5, 49.8, and 58.4° correspond to the reflections (002), (100), (103), (105), and (110) indexed by JCPDS no. 037-1492, respectively (Figure 2B,C). The visible dominant peak reflects the (002) plane, which strongly confirms the nature of the MoS2 nanosheets.11,15,24 Moreover, the very sharp peak of high intensity and strong peak of XRD spectra further confirm a well-stacked crystalline structure.11,15,24 Apparently, MoS2@Fe3O4NPs exhibited peaks at 2θ = 29.2, 30.3, 32.9, 33.7, 35.7, 39.8, 44.4, 50.0, 57.2, and 58.5° (Figure 2D). Two new weak diffraction peaks emerge from the low-angle region, where 32° corresponds to the (100) plane of the pristine 2H-MoS2, indicating the formation of MoS2@Fe3O4NPs.9,20,21

2.2. Brunauer—Emmett—Teller (BET) Surface Area. Both Fe3O4NPs and MoS2@Fe3O4NPs have type IV isotherms and type H3 hysteresis loops, which indicate mesoporous structures of the as-prepared samples (Figure 3).22,23 Yet decoration of Fe3O4NPs with MoS2 results in increase of the surface area (74.6 m2 g−1) in comparison with pure Fe3O4NPs (65 m2 g−1). Furthermore, the Barrett—Joyner—Halenda (BJH) pore size distribution curve obtained for the MoS2@Fe3O4NPs reveals a pore size of 14.5 nm and maximum pore volume of 0.27 cm3 g−1 (Table 2). Thus, the high surface area of the one-step synthesized material is associated with its mesoporous features, beneficial for chromium ion adsorption.

2.3. TEM Analysis of Fe3O4 and MoS2@Fe3O4 NPs. The high-resolution transmission electron microscopy (HR-TEM) images of the as-synthesized Fe3O4NPs show highly crystalline nature of the material, which was confirmed by clearly visible diffraction rings on the selected area electron diffraction (SAED) pattern (figures not shown here) indexed to (111), (220), (311), (400), (422), and (511), which are in line with our previous studies.19,23 Moreover, the measured distance between two adjacent lattice fringes is 0.47 nm and corresponds to the lattice spacing of (111) planes of a cubic lattice of Fe3O4NPs.7,19,24 The HR-TEM histograms of as-synthesized Fe3O4NPs decorated with MoS2 via chemical reaction have the lattice fringe spacings of 0.25 and 0.31 nm (Figure 4C). The (311) and (004) planes of cubic lattice of both Fe3O4NPs and MoS2 nanosheets are determined, which indicate uniform distribution of Fe3O4NPs on the MoS2 surface. Comparable dark cloudy patterns are visible on HR-TEM images of MoS2@Fe3O4NPs (Figure 4A) and pristine MoS2 (Figure 4B).9,10,16,17 Two diffraction rings visible on the SAED pattern of MoS2@Fe3O4NPs (Figure 4D) correspond to the hexagonal MoS2 crystalline structure indexed by JCPDS no. 37-1492. High-resolution magnification of Fe3O4NPs decorated on the surface of MoS2 nanosheets allowed us to measure an average size of Fe3O4NPs, which was around 27 nm (particle size distribution bar chart shown in Figure 4F).

2.4. Scanning Electron Microscopy (SEM). Detailed observation of the nanoparticles’ morphology and size distribution is obtained by SEM analysis. SEM image of both Fe3O4NPs and MoS2@Fe3O4NPs reveal morphology features, which are in good agreement with the TEM results. The clumpy tiny particles correspond to Fe3O4NPs, which are decorated on the surface of MoS2 nanosheets. The average size of the Fe3O4 is around several micrometers.9,10 The SEM

![Figure 3. BET N2 adsorption isotherm of Fe3O4NPs (A) and MoS2@Fe3O4NPs (B).](Image)

**Table 2. BET and Pore Diameters of the Different Samples**

| sample no. | material     | BET surface area (m² g⁻¹) | BJH pore volume (cm³ g⁻¹) | pore diameter (nm) |
|------------|--------------|---------------------------|--------------------------|-------------------|
| 1          | Fe3O4NPs     | 65.1                      | 0.18                     | 11.1              |
| 2          | MoS2@Fe3O4NPs| 74.6                      | 0.27                     | 14.5              |
images of bulk MoS₂ nanosheets, Fe₃O₄NPs, and MoS₂@Fe₃O₄NPs as well as their images after Cr(VI) adsorption are illustrated in Figure 5. As shown in Figure 5A,B, two-dimensional ultrathin uniform sheet-like structures of MoS₂ nanosheets were successfully functionalized with Fe₃O₄NPs, which provides large surface area. However, bulk MoS₂ and Fe₃O₄ clearly show that the thickness of bulk MoS₂ was around several micrometers with Fe₃O₄ diameters ranging from 1 to 5 μm. These particles tended to be aggregated together, as can be seen from Figure 5D,E, whereas Fe₃O₄NPs were successfully distributed on the surface of MoS₂ nanosheets. In other words, the MoS₂ nanosheet structure was not destroyed after being introduced with Fe₃O₄NPs during the synthesis. All the above data proved that Fe₃O₄NPs were effectively decorated onto the surface of MoS₂ nanosheets.

2.5. Energy-Dispersive X-ray Spectrometry (EDX). The results of EDX analysis of the MoS₂@Fe₃O₄NPs (shown in Figure 6A–C) identified the presence of Mo, S, Fe, and O. After adsorption of Cr(VI), an additional peak in the 0–6 keV region appeared (Figure 6D).³⁻⁵,⁷⁻¹²,²⁴,²⁵ The spectra of MoS₂ reveal a peak at 528 cm⁻¹ assigned to the stretching vibrations of the Mo–S bond.²⁶ Furthermore, the peak at 595 cm⁻¹ and the tiny peak at 587 cm⁻¹ in the spectra of MoS₂ reflect the terminal vibration ν(S–S) and bridging S₂⁻ ligands, respectively (Figure 8B,C). The peak at 1089 cm⁻¹ indicates the terminal stretch vibration of (MoVI–O) groups.²⁷ Nevertheless, the observed peaks below 700 cm⁻¹ reflect the ν(Mo–O)’s deformation mode, which can result from the sulfidation vibrations observed between 750 and 1000 cm⁻¹, giving the most conclusive information on Mo–O coordination. It could confirm successful decoration of Fe₃O₄NPs on the MoS₂ surface (Figure 8D). The chromium adsorption is confirmed by two new peaks around 839 and 819 cm⁻¹ characteristic for Cr=O and Cr–O (Figure 8E,F).¹⁻⁵,¹⁸

2.8. Thermogravimetric (TGA) Analysis. The TGA curve showed about 3.1% weight loss of naked Fe₃O₄NPs over 600 °C (Figure 9, curve A), which is related to the loss of residual water molecules. The sharp decrease at 500 °C could be explained by elimination of more stable functional groups. The lower range of magnetization (emu g⁻¹) for the MoS₂@Fe₃O₄NPs indicates the decrease of Fe₃O₄ content in MoS₂@Fe₃O₄NPs.⁸⁻¹² When comparing Figure 7C,D, it is evident that homogeneous black MoS₂@Fe₃O₄NP suspension can be easily separated from solution under magnet influence.

2.7. Fourier Transform Infrared (FT-IR) Spectra. FT-IR spectra of MoS₂, Fe₃O₄NPs, and MoS₂@Fe₃O₄NPs (before and after adsorption of Cr(VI)) are depicted on Figure 8. The peak at 582–626 cm⁻¹ could reflect the vibration of Fe–O groups, and the peak at 3417 cm⁻¹ is attributed to the stretching frequencies of Fe–OH groups (Figure 8A).⁹⁻¹⁵ The spectra of MoS₂ reveal a peak at 528 cm⁻¹ assigned to the stretching vibrations of the Mo–S bond.²⁶ Furthermore, the peak at 595 cm⁻¹ and the tiny peak at 587 cm⁻¹ in the spectra of MoS₂ reflect the terminal vibration ν(S–S) and bridging S₂⁻ ligands, respectively (Figure 8B,C). The peak at 1089 cm⁻¹ indicates the terminal stretch vibration of (MoVI–O) groups.²⁷ Nevertheless, the observed peaks below 700 cm⁻¹ reflect the ν(Mo–O)’s deformation mode, which can result from the sulfidation vibrations observed between 750 and 1000 cm⁻¹, giving the most conclusive information on Mo–O coordination. It could confirm successful decoration of Fe₃O₄NPs on the MoS₂ surface (Figure 8D). The chromium adsorption is confirmed by two new peaks around 839 and 819 cm⁻¹ characteristic for Cr=O and Cr–O (Figure 8E,F).¹⁻⁵,¹⁸

Figure 4. HR-TEM images of MoS₂@Fe₃O₄ NPs (A–F), pristine MoS₂ (B), SAED pattern of MoS₂@Fe₃O₄NPs (D), and MoS₂@Fe₃O₄NP particle size distributions (F).

Figure 5. FE-SEM images of bulk MoS₂ (A,B), pure Fe₃O₄NPs (C), MoS₂@Fe₃O₄ NPs (D,E), and MoS₂@Fe₃O₄NPs after chromium adsorption (F).
total weight loss of MoS$_2$ was 8.0 wt % at 620 °C. It is close to the theoretical value of SO$_2$ (10 wt %), meaning that during the heating process MoS$_2$ could transform to molybdenum oxide and SO$_2$ (Figure 9B). The TGA curvature of MoS$_2$ and Fe$_3$O$_4$NPs shows a decrease of weight by 5.1% at 620 °C. Relatively low weight loss of the MoS$_2$@Fe$_3$O$_4$NPs up to around 500 °C indicates its better thermal stability compared to that of MoS$_2$.26

2.9. X-ray Photoelectron Spectroscopy (XPS). Consequent XPS analysis gives further details about the chemical state of the MoS$_2$@Fe$_3$O$_4$NPs (Figure 10A–E). The values of characteristics depicted in Table 3 identified the presence of the following ions: Mo$^{4+}$, Mo$^{6+}$, SO$_4^{2-}$, S$^{2-}$, Fe$^{2+}$, and Fe$^{3+}$. It is in accordance with results of similar material analysis performed by other researchers and suggests the existence of Fe–S and Fe–O bonds, with the lattice oxygen of Fe$_3$O$_4$NPs and the hydroxyl group originating from the surface modification, respectively.11,15–17,24–28

The results of XPS analysis of the MoS$_2$@Fe$_3$O$_4$NPs after chromium adsorption are depicted in Figure 10F. The high resolution of the Cr 2p region identified Cr 2p$_{1/2}$ and Cr 2p$_{3/2}$.
line peaks located at 583.8 and 573.6 eV, respectively.\textsuperscript{29–32} The broad peak of Cr 2p\textsubscript{3/2} could be fitted into two peaks at binding energies of 574.5 and 573.4 eV, which are characteristic for Cr(VI) and Cr(III), respectively. It identifies coexistence of both Cr(VI) and Cr(III) on the MoS\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}NPs surface. According to Fang's observation, Fe\textsubscript{3}O\textsubscript{4}NPs in MoS\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}NPs favor the Cr(VI) reduction to Cr(III).\textsuperscript{33} The splitting of the Cr 2p\textsubscript{3/2} line peak into two peaks indicated precipitation of Cr\textsubscript{2}O\textsubscript{3} or Cr(OH)\textsubscript{3} during the adsorption.\textsuperscript{34}

2.10. Batch Adsorption Study. The adsorption experiments were conducted under batch studies at an ambient temperature using the optimum conditions of pertinent factors such as chromium concentration (from 40 to 400 mg L\textsuperscript{-1}), solution pH (2–10), and solid–liquid contact time (form 2 to 10 min). The subsequent adsorption experiments were carried out only with optimized parameters: pH = 5.5, a contact time of 10 min for equilibrium study; C\textsubscript{init} = 40 and 50 mg L\textsuperscript{-1} for kinetics study of Cr(VI) and Cr(III), respectively. The experiments were performed in individual batches containing a mixture of 0.02 g of MoS\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}NPs and 0.01 L of Cr(VI)/Cr(III) solution at constant pH values.\textsuperscript{1–3} At the designed time, the adsorbent was separated from the solution using by simple magnetic process.\textsuperscript{9,10} The supernatant was analyzed by an inductively coupled plasma mass spectrometry (ICP-MS) with a PerkinElmer, Sciex-Elan-6100 DRC PLUS. The quantity of adsorbed chromium per unit mass of the adsorbent (mg g\textsuperscript{-1}) was calculated as follows:

\[
q = \frac{(C_{\text{init}} - C_{\text{final}})}{M} W
\]  

where C\textsubscript{init} and C\textsubscript{final} are the initial and final chromium concentration in liquid phase (mg L\textsuperscript{-1}), respectively, and C\textsubscript{final} relates either to C\textsubscript{e} (equilibrium experiment) or to C\textsubscript{t} (kinetics experiment); V and W represent the volume of the solution (L) and the weight of the adsorbent (g), respectively. The chromium adsorption efficiency was calculated as

\[
\%AE = 100 \frac{(C_{\text{init}} - C_{\text{final}})}{C_{\text{init}}}
\]  

2.11. Point of Zero Charge (pHpzc), Effect of pH, and Adsorption Mechanism. The MoS\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}NPs was synthesized through a one-step chemical reaction of Fe\textsuperscript{3+} and Fe\textsuperscript{2+} with cetyltrimethylammonium bromide (CTAB)-coated MoS\textsubscript{2} in the presence of NH\textsubscript{4}OH.\textsuperscript{9,10} Addition of 0.1% (w/v) CTAB to MoS\textsubscript{2} solution caused electrostatic repulsion between the MoS\textsubscript{2} surfaces and prevented them from aggregating in aqueous solution. This is due to the fact that positively charged CTAB exhibits a strong electrostatic attraction toward negatively charged MoS\textsubscript{2} nanosheets.

The point of zero charge (pHpzc) of MoS\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}NPs was determined from the plot of \(\Delta pH\) \(pH_{\text{initial}} - pH_{\text{final}}\) versus \(pH_{\text{init}}\) (Figure 11A). The pH\textsubscript{pzc} was found to be 6.9. Below this value, the material surface is positively charged and
favorable for Cr(VI) oxyanion adsorption. As pH increases, the surface of MoS$_2$@Fe$_3$O$_4$NPs becomes less positively charged and the interaction between MoS$_2$@Fe$_3$O$_4$NPs and Cr(VI) decreases and changes to a repulsive force at pH >6.9, resulting in significant decrease of Cr(VI) uptake.  

The isoelectric point (IEP) of Fe$_3$O$_4$NPs and MoS$_2$@Fe$_3$O$_4$NPs was found to be 6.68 and 6.15 (see Figure 11B,C). The IEP values obtained are slightly bigger than the value reported in literature, which could be ascribed to the different suppliers and purity of CTAB and molybdenum disulfide (MoS$_2$). At pH values lower than the IEP, the hydrated surface of the MoS$_2$@Fe$_3$O$_4$NPs is protonated and therefore acquires positive charge:

$$\text{MoS}_2@\text{Fe(OH)}^+ + \text{H}^+ = \text{MoS}_2@\text{Fe(OH)}_2^+$$  \hspace{1cm} (3)

Opposite, at pH values higher than the IEP, the surface is deprotonated and acquires a negative charge:

$$\text{MoS}_2@\text{Fe(OH)}^- + \text{OH}^- = \text{MoS}_2@\text{Fe(OH)}_2^- + \text{H}_2\text{O}$$  \hspace{1cm} (4)

Additionally, Cr(VI) oxyanions interacting with the neutral surface via a ligand exchange mechanism cannot be excluded either:

$$\text{MoS}_2@\text{Fe(OH)}^- + \text{CrO}_4^{2-} = \text{MoS}_2@\text{Fe(OH)}_2^- + \text{CrO}_4^{2-} + \text{OH}^-$$  \hspace{1cm} (5)

At pH below the IEP, the Cr(VI) adsorption onto MoS$_2$@Fe$_3$O$_4$NPs can occur through electrostatic attraction or surface

| element              | peak splitting | peak positions (eV) | references |
|----------------------|----------------|---------------------|------------|
| molybdenum (Mo)      | Mo 3d$_{5/2}$ (Mo$^{4+}$) | 229.7 | 11, 15, 17, 21, 22, 24, 25 |
|                     | Mo 3d$_{3/2}$ (Mo$^{4+}$) | 230.2 |
|                     | Mo 3d$_{5/2}$ (Mo$^{6+}$) | 233.1 |
| sulfur (S)           | S 2p$_{3/2}$ | 165.8 | 11, 15, 17, 21, 22, 24, 25 |
| iron (Fe$^{2+}$ and Fe$^{3+}$) | Fe 2p$_{3/2}$ | 711.4 | 2, 7, 15, 17, 19 |
| oxygen (O)           | O 1s           | 527.7 | 2, 7, 15, 17 |
| chromium (Cr)        | Cr 2p$_{3/2}$  | 574.5 | 2, 5, 24, 25, 33, 34 |
|                      | Cr 2p$_{1/2}$  | 573.4 |
|                      | Cr 2p$_{3/2}$  | 583.8 |

Figure 10. XPS spectra of total survey (A), Mo 3d spectra (B), S 2p spectra (C), Fe 2p spectra (D), O 1s spectra (E), and Cr 2p spectra (F).
complexation. The association between the positively charged surface of MoS2@Fe3O4NPs and HCrO4− can occur as follows:

\[
\text{MoS}_2@\text{FeOH} + \text{HCrO}_4^- \rightarrow \text{MoS}_2@\text{FeO}^- + \text{Cr}^{3+} + 4\text{H}_2\text{O}
\]

(6)

The acidic environment promotes the Cr(VI) reduction to Cr(III): 1,5,24,25

\[
\text{Cr(OH)}_2^+ + \text{H}_2\text{O} \rightarrow \text{Cr}^{3+} + 2\text{OH}^-
\]

(7)

As depicted in Figure 11D,E, the increasing of initial pH increases the efficiency of chromium removal. The maximum uptake (99%) was obtained at pH between 4 and 7 when the surface of the adsorbent is highly protonated and positively charged. At pH >7, the removal efficiency drops gradually, and further increase of alkalinity enhances ionization of the −OH groups on the sorbent surface and production of negatively charged (Fe−O−), which attracts Cr3+. Its uptake can occur via ion exchange mechanism according to Scheme 1. At high alkali environment, the deprotonated surface hydroxyl groups of the adsorbent act as an electron donor facilitating electrostatic interactions with chromium oxyions: Cr(OH)2+ and Cr(OH)+ (Figure 12).

2.12. Adsorption Equilibrium. The saturation curves for Cr(VI) and Cr(III) adsorption are shown in Figure 13 as a function of the amount of chromium adsorbed onto the adsorbent at equilibrium versus the chromium concentration in aqueous solution. As can be seen, the experimentally obtained data for both Cr(VI) and Cr(III) follow L type adsorption isotherms, providing initially a sharp increase of adsorbed chromium and tending to approach a maximum adsorption capacity equal 218 and 119 mg g−1, respectively. Table 4 gives a comparison between the adsorption capacity obtained for the materials investigated during this work and those of other sorbents found in the literature. The Cr(VI) uptake values determined in this work were significantly higher than almost all of those reported in the literature. The effective electrostatic interactions between the chromium oxyions and the MoS2@Fe3O4NPs are evident from the ascending portion of the curve and relatively flat terrains at higher C_e values, which indicate the saturation of the fixed number of adsorption sites. The most commonly used equilibrium models, the Langmuir and the Freundlich, were used to explain the observed phenomena. The Langmuir model assumes a homogeneous adsorption on limited amounts of sites of equal energies and the same percentage to desorption of each adsorbate, thus relating to a physical adsorption:
where \( q_e \) (mg g\(^{-1}\)) and \( C_e \) (mg L\(^{-1}\)) are the equilibrium chromium concentrations in solid and liquid phase, respectively, \( q_{\text{max}} \) (mg g\(^{-1}\)) is the maximum adsorption capacity, and \( K_L \) represents the energy of adsorption.

Contrary to the Langmuir model, the Freundlich one does not reach a limited sorption capacity and can deal with both homo- and heterogenous adsorption, which can be physical or chemical:\(^{37,38}\)

\[
q_e = K_F C_e^{1/n_F} \quad (9)
\]

where \( K_F \) represents a unit capacity coefficient and \( n_F \) is a parameter related to the degree of system heterogeneity.

Modeling calculations were conducted using the Maple program by means of a nonlinear regression method based on the Levenberg–Marquardt algorithm. The model’s parameters were determined by minimizing the sum of the squares of the error (SSE) function across the concentration range studied:

\[
\sum_{i=1}^{n} (q_{e,\text{exp}} - q_{e,\text{calc}})^2 \quad (10)
\]
The parameters obtained along with the Fisher Test (FT), mean error (ME), and the approximation (σ) are listed in Table 4. The comparison of the data obtained indicated that the isotherm data are not represented appropriately by the Freundlich model in the concentration range studied. Opposite, the Langmuir model correlated quite well with the experimental data. The estimated \( q_{\text{max}} \) value for Cr(III) (119.38 mg g\(^{-1}\)) is very close to the experimentally obtained maximum adsorption capacity. As can be seen in Figure 13, the Langmuir curve obtained for Cr(VI) overlapping the experimental points in linear range (origin of the plot \( q_e \) versus \( C_e \)) is less convex than the one obtained for Cr(III) and tends to increase in the equilibrium plateau range (\( q_{\text{max}} \)). As a consequence, the Langmuir model overestimates the \( q_{\text{max}} \) value for Cr(VI).

### 2.13. Adsorption Kinetics

Figure 14 shows a plot of the experimental data points for the adsorption of chromium by the MoS\(_2@Fe_3O_4\) NPs as a function of time. These data correspond to chromium adsorption efficiency (AE, eq 2) higher than 85% and exhibits almost horizontal distribution of experimental points, when \( q_e \) gets close to its equilibrium value. Most of both Cr(VI) and Cr(III) were removed within the first 1–2 min. Then the efficiency of chromium removal shows only a gradual increasing trend. Both Cr(VI)-NP and Cr(III)-NP systems needed 10 min to attain the equilibrium, which is quite faster than that in the earlier reported research.\(^{2-5}\) It suggests that the active sites on the adsorbent surface are equally available for both chromium species adsorption. The kinetics data were modeled by the solid phase adsorption pseudo-first-order model and the pseudo-second-order kinetics model. The first-order rate expression of Lagergren\(^{39}\) can be expressed mathematically as

\[
q_t = q_e (1 - e^{-kt})
\]

(11)

where \( q_t \) is the amount of adsorbed chromium, \( q_e \) its value at equilibrium, \( k_1 \) is the pseudo-first-order constant, and \( t \) is the time. A pseudo-second-order reaction model\(^{40}\) utilized in the study of adsorption can be expressed mathematically as

\[
q_t = \frac{q_e^2 k_{2e} t}{1 + q_e k_{2e} t}
\]

(12)

in which \( k_2 \) is the pseudo-second-order constant. Similarly to modeling of adsorption equilibrium, the Maple program based on the Levenberg–Marquardt algorithm was used to regress the values of \( k_1 \) and \( k_2 \). For both sets of experimental points, better results for the pseudo-second-order reaction model were confirmed by the higher values of the FT and lower value of both the ME and the approximation \( \sigma \) (Table 5). It is quite common that this model gives better approximation if the experimental data (\( q_t \)) are located very close to the equilibrium (\( q_e \)) and do not cover fast initial rise range.\(^{41}\) Nevertheless, the discrepancy between modeling curves (Figure 14) and the first experimental point (which is underestimated) identifies that neither of the rate equations described the kinetics of both Cr(VI) and Cr(III) on the MoS\(_2@Fe_3O_4\) NPs well. However, it does not exclude that a fast initial uptake limited by diffusion in the external layer is followed by a slower second step limited by adsorption reaction.\(^{1-5,24,25}\)

### 2.14. Thermodynamics of Adsorption

The thermodynamic parameters, standard free energy (\( \Delta G^0 \)), standard enthalpy (\( \Delta H^0 \)), and standard entropy (\( \Delta S^0 \)) depicted in Table 6 were calculated by using the following equations.\(^{5}\)

\[
\Delta G^0 = -RT \ln K
\]

(13)

\[
\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]

(14)

Table 6. Thermodynamic Parameters

| temperature (K) | \( E_a \) (kJ mol\(^{-1}\)) | \( \Delta H^0 \) (kJ mol\(^{-1}\)) | \( \Delta S^0 \) (J mol\(^{-1}\) K\(^{-1}\)) | \( \Delta G^0 \) (kJ mol\(^{-1}\)) |
|-----------------|-------------------------------|---------------------------------|---------------------------------|-------------------------------|
| 298             | -63.49                        | -8.61                           | -175.67                         | -61.01                        |
| 308             | -66.66                        | -6.52                           |                                 |                               |
| 318             | -63.74                        | -5.46                           |                                 |                               |
| 328             | -63.82                        | -3.14                           |                                 |                               |

where \( R \) is the gas constant (J K\(^{-1}\) mol\(^{-1}\)), \( T \) is the temperature (in Kelvin), and \( K \) is obtained from the ratio of the concentration of Cr(VI) in the solid and liquid phases, respectively. \( \Delta H^0 \) and \( \Delta S^0 \) were obtained from the slope and intercept of the van’t Hoff plot of \( \ln K \) against 1/\( T \) (Figure 14C). The obtained positive slope as well as the fact that the equilibrium constants decrease with increase of temperature indicates an exothermic reaction.\(^{42}\) The adsorption of Cr(VI) gradually decreases at higher temperature, indicating that low temperature is more favorable to the adsorption process, and the following electrostatic interactions HCrO\(_4^–\)…OH\(_2^+\), Fe–OH\(_2^+\)…Cr\(_2\)O\(_7^{2–}\), and Fe–OH\(_2^+\)…CrO\(_2^{2–}\) result in compactness which randomly decreases at the solid–solution interface.

Furthermore, the enthalpy change (\( \Delta H^0 \)) and the value of \( E_a \) were found to be negative, confirming the exothermic nature of adsorption. The magnitude of \( \Delta H^0 \) gives information about the adsorption mechanism.\(^{1-5}\) For physical adsorption, \( \Delta H^0 \) is generally less than \(-20 \text{ kJ mol}^{-1}\), which was the case for Cr(VI) adsorption (\( \Delta H^0 = -61.01 \text{ kJ mol}^{-1}\)). The negative value of entropy (\( \Delta S^0 = -175.67 \text{ J mol}^{-1} \text{ K}^{-1}\)) also indicates favorable adsorption of HCrO\(_4^–\) and CrO\(_2^{2–}\) ions onto the adsorbent surface (Table 6). At acidic pH, functional groups (Fe–OH\(_2^+\)) of the adsorbent are protonated, resulting in positively charged surface which attracts the negatively charged Cr(VI) oxyions. This attraction is more efficient at lower temperature because the obtained \( \Delta G^0 \) values increase along with temperature (Table 6). The negative free energy (\( \Delta G^0 \)) values further confirm the effectiveness of the electrostatic interaction between HCrO\(_4^–\), CrO\(_2^{2–}\), and adsorbent surface.\(^{1-5}\)

### 2.15. Effect of Competitive Ions on the Cr(VI) Adsorption

The study of competitive adsorption was performed to investigate the effect of commonly present ions in aqueous solutions on the Cr(VI) uptake. Briefly, 1 g of MoS\(_2@Fe_3O_4\) NPs was contacted for 10 min with 100 mL sample volumes containing 10 mg L\(^{-1}\) of Cr(VI) and along with a foreign anion (F\(^–\), Cl\(^–\), NO\(_3^–\), SO\(_4^{2–}\), HCO\(_3^–\), and HPO\(_4^{2–}\)) with a concentration of 500 mg L\(^{-1}\). The initial pH of the solutions depended on the competitive anions used and
varied between pH = 4.0 and 7.0. The final concentration of anions was analyzed by using ICP-MS on a PerkinElmer, Sciex-Elan-6100 DRC PLUS. The data obtained (Figure 15A)

![Figure 15A](image)

identify that the presence of competitive anions leads to a drop in the Cr(VI) adsorption. Similarly to Cr(VI) ions, other anions could form stable ion pairs with protonated Fe−OH groups on the adsorbent surface and compete with the bichromate for active sites. The sulfate and nitrate ions can also interfere by reducing hexavalent chromium to the trivalent one.18,42

The effect of cations on the Cr(VI) uptake was studied by addition of foreign cations V5+, As5+, Se4+, Mn2+, Pb2+, Cd2+, Zn2+, Ni2+, and Hg2+ with concentrations of 100 and 250 mg L−1 to the Cr(VI) solution (50 mg L−1, ICP-MS standard solution). The final concentration of cations was analyzed by using ICP-MS in a PerkinElmer, Sciex-Elan-6100 DRC PLUS. The data obtained (Figure 15B) identified that Cr(VI) adsorption was not influenced by Mn2+, Hg2+, Cd2+, Co2+, Zn2+, Ni2+, and Pb2+ at their lower concentration (100 mg L−1) (data not shown). However, at higher concentration (250 mg L−1), the relaxation of the diffusion barrier leads to the competing ability of cations such as Pd2+, Hg2+, Zn2+, Co2+, Cd2+, and Ni2+ by forming their respective chloro complexes.18,29 It causes a decrease in Cr(VI) uptake (Figure 15B). Much stronger negative influence on Cr(VI) uptake is observed in the presence of V5+, As5+, and Se4+. It results from the fact that at acidic pH all of them exist in various negatively charged oxion forms (i.e., SeO2−4, HSeO3−, H2AsO4−, HAsO4−2, VO2(OH)2−5, VO3(OH)−2) which compete with Cr(VI) for the same active sites on the MoS2@Fe3O4NP surface.18,19,29

2.16. Application of Synthesized MoS2@Fe3O4NPs for Wastewater Treatment. 2.16.1. Chromium Uptake from Electronics Industry Wastewater. The wastewater was collected from a local electronics manufacturer in Kaohsuing, Taiwan. The samples were filtered by 0.45 μm pore size membranes to remove the suspended particles. The removal efficiency experiments were performed using a standard addition method by spiking the real electronic industrial wastewater (pH 6.5) with the total Cr standards at three concentration levels (2.0, 5.0, and 10.0 μg L−1) and analyzing three replicates for each concentration. A minimum adsorbent dose of 0.1 g removed about 93.5%–97.5% of the total Cr(VI) from 10 mL of wastewater sample containing 7.4 μg L−1 of Cr(VI) in the presence of other ions; pH was adjusted to pH 5.5. The adsorbent was separated from the solution using a simple magnetic process, and the supernatant was analyzed by ICP-MS. The data depicted in Table 7 identify effective chromium uptake up to 97.5% from electronic wastewaters by adsorption onto MoS2@Fe3O4NPs.

![Figure 15](image)

**Figure 15. Efficiency of Cr(VI) adsorption by MoS2@Fe3O4NPs in the presence of competitive anions (A) and cations (B).**

2.16.2. Chromium Uptake from Eyeshadow Samples. Four eyeshadow samples of two different brands and colors were acquired from a local market in Kaohsuing, Taiwan. The sample pretreatment was done according to method D335-85a of the American Society for Testing Materials (ASTM).43 Brieﬂy, an adsorbent dose of 0.3 g of MoS2@Fe3O4NPs was contacted for 10 min with 10 mL of appropriate diluted eyeshadow sample containing Cr(VI) in the presence of multiple ions (cations and anions); pH was adjusted to pH 5.5. The adsorbent was able to remove 90.2%–98.2% of total Cr(VI) from the diluted eyeshadow sample (concentration = 140–700 μg L−1). Analytical results along with the removal efficiency are given in Table 8. Furthermore, the adsorbent exhausted with chromium ions was entirely generated by 0.5 M NaOH.

![Table 7](image)

**Table 7. Total Chromium Determinations in Spiked Sample Solutions (Volume = 10 mL, Mean ± SD, n = 3)**

| sample name                  | spiked value (μg L−1) | before adsorption (μg L−1) | after adsorption (μg L−1) | % removal |
|------------------------------|----------------------|---------------------------|--------------------------|-----------|
| electronic industrial wastewater | 2.0                  | 7.4 ± 5                   | 6.95 ± 3                 | 93.5      |
|                              | 5.0                  | 8.9 ± 7                   | 8.1 ± 8                  | 91.0      |
|                              | 10.0                 | 12.9 ± 3                  | 12.3 ± 9                 | 95.3      |

![Table 8](image)

**Table 8. Eyeshadow Samples Pretreatment and after Treatment with MoS2@Fe3O4NPs**

| sample no. | sample name | before adsorption (μg L−1) | after adsorption (μg L−1) | % removal |
|------------|-------------|---------------------------|--------------------------|-----------|
| 1          | eyeshadow A | 147 ± 2                   | 143.3 ± 1                | 97.4      |
| 2          | eyeshadow B | 498 ± 5                   | 465.0 ± 1                | 93.3      |
| 3          | eyeshadow C | 711 ± 6                   | 646 ± 6                  | 90.8      |
| 4          | eyeshadow D | 464 ± 8                   | 45.6 ± 6                 | 98.2      |

2.17. Adsorbent Regeneration. From the perspective of practical application of the obtained MoS2@Fe3O4NPs, it is important to investigate its regeneration possibility toward multiple adsorption/desorption cycles. Hence, the following reagents (sodium sulfite, sodium nitrite, l-ascorbic acid, sodium hydroxide and ammonium hydroxide at concentration of 1.0 M) were used to elute Cr(VI) from the adsorbent by its reduction to Cr(III) as well as to the corresponding chromate salt.5,18,29 During the experiment, we followed two strategies in order to avoid the direct disposal of Cr(VI) into the laboratory sink. The hexavalent chromium was desorbed from the
3. CONCLUSIONS

Novel adsorbent for Cr(VI)/Cr(III) removal was obtained by synthesis of Fe3O4NPs and its decoration with MoS2. The HR-TEM images, BET surface area, Raman, XRD, XPS, and FT-IR analyses identified that the MoS2@Fe3O4NP synthesis process is controllable toward the size and morphology, and a new adsorbent has cubic lattice structure and exhibits good dispersibility in polar solvents. Its superparamagnetic properties with zero coercivity and remanence for Fe3O4NPs and MoS2@Fe3O4NPs enable easy separation from aqueous solution by an external magnetic field.

The efficiency of chromium removal was shown to be strongly affected by the pH of the solution, which defines the chromium hydrolysis products and influences the surface charge of the MoS2@Fe3O4NPs. The optimum pH of chromium adsorption was found to vary in the range of 4.0–7.5 for Cr(VI) and 5.63–10 for Cr(III). The adsorption efficiency is more affected by the presence of other anions than cations in the solution. The adsorption of Cr(VI) and Cr(III) correlated well with Langmuir isotherms. The kinetics data exhibit a fast initial rise that cannot be represented correctly by either rate law equations.

Regeneration of the adsorbent by using NaOH does not significantly reduce the efficiency of chromium uptake up to two repetitive adsorption/desorption cycles. This indicates substantial potential of the MoS2@Fe3O4NPs application in practice.

4. MATERIALS AND METHODS

4.1. Chemicals. The starting material of molybdenum disulfide (MoS2) was purchased from Alfa-Aesar, and cetyltrimethylammonium bromide (CTAB) was purchased from Merck; FeCl3 and FeCl2 were obtained from Showa Chemicals. Stock solutions of 1000 mg L−1 Cr(VI) and Cr(III) as well as ICP-MS standard were purchased from Merck. Working solutions were prepared by appropriate dilution with Milli-Q water.

4.2. Synthesis of Fe3O4NPs and Its Decoration with MoS2. MoS2 (0.5 g) was dispersed in 100 mL of dimethylformamide (DMF) and ultrasonicated for 10 h at room temperature. For purification, the obtained solution was centrifuged at 6000 rpm twice, and the supernatant was collected to remove unexfoliated MoS2 and also excess DMF solution. Again, the solid was dispersed in water and centrifuged at 2000 rpm; the obtained product was used for further functionalization with CTAB (20 mL 0.1% v/v) at ambient temperature by magnetically stirring for 2 h. The CTAB-coated MoS2 was mixed with FeCl3·6H2O (2.16 g) and FeCl2·4H2O (0.8 g). The resulting solution was deoxygenated by bubbling with nitrogen gas for 10 min, followed by being heated to 80 °C for 10 min. The NH4OH (10 mL, 8 M) was slowly added drop by drop to the heated solution, which was left to stir for 1 h. After being cooled to an ambient temperature, the formed MoS2@Fe3O4NPs were magnetically collected, washed two times with deionized water (100 mL), and stored at 4 °C. The concentration of MoS2@Fe3O4NPs was estimated to be 15.1 mg mL−1. For comparison purposes, the pure Fe3O4NPs were also synthesized under the same experimental conditions without having added the MoS2. The adsorbent Fe3O4NPs and MoS2@Fe3O4NPs could be used for further comprehensive characterization studies using various physicochemical techniques to confirm the presence of the adsorbents.

4.3. Instruments and Characterizations. The pH of the adsorbent MoS2@Fe3O4NPs was measured at 25 °C by taking 0.1 g of adsorbent in 50 mL of 0.1 mol L−1 potassium chloride electrolyte solution. The initial pH was adjusted using 0.1 mol L−1 of HCl or NaOH with constant orbital shaking at 250 rpm followed by a time period of 24 h, and the final pH was measured. Raman spectra were recorded on a WITec Confocal Raman microscope Alpha 300R using a 532 nm He–Ne laser at 5 mW. The TEM analysis was carried out using a PHILIPS CM-200 TWIN instrument under an operating voltage of 200 kV. A drop of DMF solution to the sample was

Figure 16. Regeneration of the adsorbent (A) and adsorbent regeneration cycles (B).
dispersed and deposited on a carbon-coated copper grid. Nitrogen adsorption–desorption isotherms were measured with a Micromeritics ASAP 2010 instrument, before measurement of adsorbent samples were outgassed for 10 h under vacuum at 200 °C. The BET method was used to calculate the surface areas and pore size distributions, whereas pore volume was derived from the adsorption branches of the BJH method. Magnetometry was performed with a superconducting quantum interference device (Quantum Design, San Diego, CA). The XPS (Kratos Axis Ultra) instrument was used to record samples, X-ray sources: 500 mm Rowland circle monochromator Al–Mg/Al acromatic source 450 W max power. The spectra were recorded using a monochromatic Al Kα X-ray source (15 mA, 14 kV). All obtained spectra were calibrated to a C 1s peak at 284.6 eV and fitted with a mixed Gaussian–Lorentzian function by XPSPEAK (a freeware). The pressure in the analyzer chamber was 1 × 10−8 Torr. High-resolution spectra were collected using 40 eV pass energy, the spot size of 300 μm, and 0.05 eV step size. The FT-IR spectrometer (spectrum100) was used to characterize the spot size of 300 μm. Resolution spectra were collected using 40 eV pass energy, the spot size of 300 μm, and 0.05 eV step size. The spectra were recorded using a monochromatic Al Kα X-ray source (15 mA, 14 kV). All obtained spectra were calibrated to a C 1s peak at 284.6 eV and fitted with a mixed Gaussian–Lorentzian function by XPSPEAK (a freeware). The pressure in the analyzer chamber was 1 × 10−8 Torr. High-resolution spectra were collected using 40 eV pass energy, the spot size of 300 μm, and 0.05 eV step size. The FT-IR spectrometer (spectrum100) was used to characterize the functional groups of the material (in the range of 400–4000 cm−1) by mixing 0.01 g of the material with 0.1 g of KBr (spectroscopy grade). X-ray diffraction (powder XRD) was carried out on a D8 Discover X-ray diffractometer with Cu Ka radiation (k = 0.1541 nm, Bruker, Germany) and utilized to record the characteristic changes in the diffraction pattern of the adsorbent material. The TGA analysis was done by using a PerkinElmer (TGA-4000) thermal analyzer, where the samples were heated between 30 and 700 °C at a rate of 10 °C min−1 under a nitrogen atmosphere. The pH adjustments of the aqueous solutions were done using the METTLER TOLEDO pH meter S20. The concentration of chromium in the aqueous solution was measured using inductively coupled plasma mass spectrometry (PerkinElmer, Sciex-Elan DRC Plus software and used Elan-6100 DRC PLUS).

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