Inclusion of bimetallic Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC MOFs into Alginate-MoO\(_3\)/GO as a novel nanohybrid for adsorptive removal of hexavalent chromium from water

Mohamed E. Mahmoud, Mohamed F. Amira, Mayar M. H. M. Azab & Amir M. Abdelfattah

Metal–organic frameworks (MOFs) as porous materials have recently attracted research works in removal of toxic pollutants from water. Cr(VI) is well-known as one of the most toxic forms of chromium and the selection of efficient and effective Cr(VI)-remediation technology must be focused on a number of important parameters. Therefore, the objective of this work is to fabricate a novel nanohybrid adsorbent for removal of Cr(VI) by using assembled bimetallic MOFs (Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC)-bound-Alginate-MoO\(_3\)/Graphene oxide (Alg-MoO\(_3\)/GO) via simple solvothermal process. The aimed Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO nanohybrid was confirmed by FTIR, SEM, TEM, XRD and TGA. Adsorptive extraction of Cr(VI) from aqueous solution was aimed by various optimized experimental parameters providing optimum pH = 3, dosage = 5–10 mg, starting concentration of Cr(VI) = 5–15 mg L\(^{-1}\), shaking time = 5–10 min. The point of zero charge \((pH_{\text{pzc}})\) was 3.8. For Cr(VI) removal by Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO, four isotherm models were estimated: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) with calculated correlation coefficient \((R^2 = 0.9934)\) for Langmuir model which was higher than others. The collected results from the kinetic study clarified that pseudo-second order model is the most convenient one for describing the adsorption behavior of Cr(VI) and therefore, the adsorption process was suggested to rely on a chemisorption mechanism. Thermodynamic parameters referred that the adsorption mechanism is based on a spontaneous and exothermic process. Finally, the emerged Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO nanohybrid was confirmed as an effective adsorbent for extraction of hexavalent chromium from real water specimens (tap, sea water and wastewater) with percentage recovery values > 98%.

The disposal of toxic materials from water has shown a great challenge for scientists to save the environment and human health from these hazardous substances. The discharged undesirable substances, in the aquatic environment are categorized as either organic contaminants viz. dyes, pesticides and antibiotics or inorganic contaminants as toxic heavy metals\(^1\). Heavy metals are toxic species that threaten humanity especially due to their impacts as carcinogenic and nonbiodegradable therefore, their pollution control has become one of the most concerns worldwide\(^2\). Industrial activities are representing the major source of pollution with toxic heavy metals including painting, mining, electroplating and others\(^3\). Hexavalent chromium (Cr (VI)) is an example of highly mobile, toxic, and non-biodegradable heavy metal ion with acceptable concentration limit in drinking water of 0.05 mg L\(^{-1}\) according to the World Health Organization (WHO)\(^4\).

Effective remediation methods of water containing toxic metal ions as Cr(VI) are needed and up till now, there are several investigated and reported methodologies as coagulation, photocatalytic reduction, membrane filtration, biodegradation and adsorption\(^5\). The adsorption method is highly recommended owing to its effectiveness, simplicity, and availability of a wide range of adsorbent materials\(^6\). Nowadays, a great number of materials...
were identified to exhibit good affinity to Cr(VI) and thus were effectively applied to eliminate it from water including metal oxides, biocars and carbonaceous nanoparticles. One of the drawbacks of the adsorption method is the long time that is needed to reach the equilibrium conditions and obtain the maximum recovery percentage. Consequently, the synthesis of new classes of adsorbents with large surface area is generally aimed and required to save time and energy.

Metal–organic Frameworks (MOFs) are excellent porous network structure materials that consist of metal ion and bridging organic ligands (connectors). These materials have been recently applied in various fields as water remediation, drug delivery, gas storage and catalysis owing to their large specific surface area, ordered structure, facile modification, tunable porosity between microporous and mesoporous scale, possibility of preparing different interesting structures and the presence of various functional groups that are helpful for selective adsorption. Based on such outlined promising features, MOFs have been reported as favorable adsorbents in the removal of contaminants from water. For example, Cu-based MOF was used in the removal of organic (methylene blue and levofloxacin drug) and inorganic (Cr (VI)) contaminants from water. The adsorption and the catalytic performance of MOFs were also found to improve by changing organic ligands, grafting more active groups, introducing additional metal centers to pristine MOFs, and making composites with other convenient materials. One of the most appropriate materials to prepare MOFs composites is carbon–based substances as graphene oxide (GO). Graphene oxide possesses numerous functional oxygen-containing groups with a two-dimensional structure by which graphene oxide can be introduced as a substrate for MOFs. The structure of pure MOFs has free voids and spaces. Because of weak dispersion forces between their nanocrystals and based on their combination with GO fewer inter-void MOFs are obtained. Also, GO increases the stability of MOFs in water via binding between functional groups of GO with metal ions in the MOFs structure and therefore, enhances the dispersive force with the MOFs by prevention of their aggregation and improving removal efficiency. Moreover, the ability of graphene oxide to control the morphology and size of MOFs during the synthesis was also investigated and reported for removal of organic pollutants by GO-MOFs composites.

Sodium alginate (Alg) is a natural biologically polysaccharide polymer that contains active functional groups (–OH and –COOH) and it has β–D-M (mannuronic acid) and α–L-G (guluronic acid). Alg is known to exhibit strong binding capabilities, renewability, and hydrophilic properties, so it is regarded as an excellent adsorbent for extraction of heavy metals and other pollutants from water. Furthermore, nanometal oxides have been known for their effectiveness in water treatment, photocatalysis and supercapacitors owing to their high thermal and mechanical stability. Herein, the nanometal oxide used is molybdenum trioxide (nano MoO₃) due to its physiochemical properties and thermodynamic stability and its effectiveness in the removal of water pollutants based on the previous research. The stability of molybdenum-based materials can be improved by its dispersion onto carbon support material as graphene oxide.

The presence of multi-functional groups in bimetallic MOFs as well as the related unique properties of some oxides as GO and MoO₃ have directed our attention to combine these three materials with sodium alginate as a biodegradable material, for the first time, to fabricate a novel chemical network structure of Fe₀.₇₅C₀.₂₅−BDC@Alg-MoO₃/GO as a novel nanocomposite. The assembled nanocomposite characterized by the presence of reactive multifunctional groups with strong affinity and capability for binding and extraction of the toxic Cr(VI) from matrices. In addition, the assembled Fe₀.₇₅C₀.₂₅−BDC@Alg-MoO₃/GO nanocomposite was prepared by a green chemical method via simple solvothermal process and microwave-assisted synthesis technique. The applicability of the assembled nanocomposite was aimed to investigate and evaluate its performance in removal of Cr(VI), as an example of highly toxic heavy metal, from aqueous solution under the influence and impact of various experimental parameters as initial pH, shaking time, dosage, concentration, temperature and ionic strength.

Materials and analytical methods

Chemicals and instrumentations. The specifications of all chemicals and instruments are listed and compiled in Table 1. The employed chemicals were all of analytical grades and used without further purifications.

Experimental. Microwave synthesis of Alg-MoO₃/GO. GO was first prepared by oxidation of graphite powder by KMnO₄ in the presence of sulfuric acid. In a brief, 5 g of graphite were mixed with 15 mL of concentrated H₂SO₄ and 25 mL of 0.5 M KMnO₄, and then the mixture was heated in the microwave oven for 5 min at 80 °C allowing the oxidation process to proceed. The step of adding KMnO₄ was repeated 4 times to the point of black precipitation of GO. This was collected and washed with DW till neutrality and finally, it was dried at the oven (65 °C).

Alg-MoO₃ was synthesized by adding 20 mL of DW in a mixture containing 2 g sodium alginate and 2 g molybdenum trioxide. This mixture was exposed to microwave irradiation for 5 min at 80 °C. The step of adding DW was repeated 4 times to ensure the complete binding process of Alg with MoO₃.

Alg/GO was synthesized by adding 20 mL of DW in a mixture of sodium alginate and GO with a ratio 1:1 (w/w). This mixture was heated by microwave irradiation for 5 min and the step of adding DW was repeated 4 times to ensure the complete binding process of Alg with GO.

Synthesis of Alg-MoO₃/GO was accomplished by mixing 20 mL of glutaraldehyde as a crosslinker with a mixture of Alg-MoO₃ and Alg/GO in a 1:1 (w/w) ratio. This resultant mixture was then exposed and heated by microwave irradiation at 80 oC for 5 min and the obtained black precipitate of Alg-MoO₃/GO was collected and dried at 65 °C in an oven overnight.

Synthesis of bimetallic MOFs (Fe₀.₇₅C₀.₂₅−BDC). The bimetallic MOFs (Fe₀.₇₅C₀.₂₅−BDC) were prepared by using a solvothermal method. In this process, FeCl₃·6H₂O (7.5 mmol) was added to Cu(NO₃)₂·3H₂O (2.5 mmol) in 30 mL DMF. This was then poured into a solution of H₂BDC (5 mmol) that had already been dissolved in
30 mL DMF and exposed to magnetic stirring for 30 min at room temperature to form a clear solution. The above mixture was placed into a Teflon-lined autoclave with a volume of 100 mL and allowed to react for 36 h at 120 °C. After completion of the reaction, the obtained MOFs precipitate (Fe0.75Cu0.25-BDC) was washed with DMF and DW and then dried in a 70 °C oven overnight.

Synthesis of Fe0.75Cu0.25-BDC@Alg-MoO3/GO nanohybrid. Fe0.75Cu0.25-BDC was introduced to Alg-MoO3/GO by a simple solvothermal process. The dried Alg-MoO3/GO was used as a platform for the growth of Fe0.75Cu0.25-BDC MOFs on its surface. Typically, 0.25 g of Alg-MoO3/GO in 20 mL DMF was stirred for 1 h, then 1 g of H2BDC was well dissolved in 35 mL DMF and poured into Alg-MoO3/GO for 30 min stirring. The suspension was then stirred for 1 h at room temperature with dissolved 2.5 g FeCl3.6H2O and 0.74 g Cu(NO3)2.3H2O in 30 mL DMF. Finally, the attained mixture was placed into a Teflon-lined autoclave with a volume of 100 mL and allowed to react for 36 h at 120 °C. The Fe0.75Cu0.25-BDC@Alg-MoO3/GO nanohybrid was separated by filtration then washed with DMF and DW and dried in a 65 °C oven.

Adsorption behavior of Fe0.75Cu0.25-BDC@Alg-MoO3/GO nanohybrid. The adsorption behavior of hexavalent chromium ion onto Fe0.75Cu0.25-BDC@Alg-MoO3/GO nanohybrid was optimized by the batch operation at different factors. The source of Cr(VI) ion was potassium dichromate and the required concentration (5, 10 and 15 mg L⁻¹) was prepared via dilution of the stock solution (1000 mg L⁻¹). The maximum wavelength of Cr(VI) is 540 nm that was detected in presence of 1,5 diphenylcarbazide. In this study, Fe0.75Cu0.25-BDC@Alg-MoO3/GO nanohybrid was added to 10 mL of hexavalent chromium ion solution. After 30 min of shaking time, the mixture was filtered and the concentration of filtrate was estimated by spectrophotometric determination at λmax 540 nm. The removal percentage was evaluated from Eq. (1).

\[
\% E = \frac{C_0 - C}{C_0} \times 100
\]

The initial and residual concentrations of chromium ion is represented by C0 and C (mol L⁻¹) respectively.

Table 1. Chemicals and instrumentations.

| Chemicals                  | Chemical formula | Company              | Molar mass (g/mol) | Assay       |
|----------------------------|------------------|----------------------|-------------------|-------------|
| Graphite powder            | C                | NICE CHEMICALS       | 12.01             |             |
| Potassium permanganate     | KMnO4            | BDH Chemicals Ltd    | 158.03            | ≥ 99.0%     |
| Terephthalic acid (H2BDC)  | C6H4O4           | Merck                | 166.13            | ≥ 98.0%     |
| N,N Dimethylformamide (DMF)| C3H7NO           | SDFCL fine-chem      | 73.09             | 99.0%       |
| Iron(III) chloride hexahydrate | FeCl3.6H2O      | Alpha chemika        | 270.3             | 99.0%       |
| Copper nitrate tribrate    | Cu(NO3)2.3H2O    | Merck                | 241.60            | 99.5%       |
| Sodium alginate            | C2H3O2Na         | Alfa Aesar, UK       | 216.12            | ≥ 99.0%     |
| Molybdenum trioxide        | MoO3             | VEB laborschene Apelda | 143.94         | 99.5%       |
| Glutaldehyde               | C2H4O2           | BDH chemicals Ltd.   | 100.11            | ≥ 95.0%     |
| 1,5-Diphenylcarbazide      | C12H8N2O         | Sigma-Aldrich        | 242.28            | ≥ 99.0%     |
| Sulfuric acid              | H2SO4            | Sigma-Aldrich, USA   | 98.07             | 98.0%       |
| Sodium hydroxide           | NaOH             | Riedel de Haen, Germany | 40.00          | ≥ 99.0%     |
| Hydrochloric acid (HCl)    | HCl              | Sigma Aldrich, USA   | 36.46             | 37.0% (w/w |
| Sodium chloride            | NaCl             | VWR international Ltd | 58.44           | 99.5%       |

Measurements

The model of the instrument

- UV-Vis spectrophotometer: Unico UV-Vis-7200
- pH values: Adwa pH-meter
- microwave oven: KOG-1BSH, Korea, 1400 W and 2.45 GHZ
- Fourier transform infrared (FT-IR): BRUKER Tensor 70
- Scanning electron microscope (SEM): JEOL-JSM-5300
- High Resolution Transmission Electron Microscope (HR-TEM): JEOL- JSM
- X-ray diffraction (XRD): JED-2300T model
- Thermal gravimetric analysis (TGA): Linseis STA PT1000
20.0 mg of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid was mixed with 10 mL of the selected concentration of Cr(VI) ion solution then a batch operation was allowed for 30 min. The mixture was filtered and the residual chromium ion in the filtrate was estimated at $\lambda_{\text{max}}$ 540 nm. Finally, the removal percentages (%E) were computed from Eq. (1).

Furthermore, the point of zero charge (PZC) of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid was performed by addition of 0.1 mol L$^{-1}$ sodium chloride with definite volume to 100 mg of the prepared nanohybrid, then the pH was adjusted from 2 to 11, while the batch operation was applied for 4 h. The final pH was estimated after 24 h.

The influence of reaction time on removal of Cr(VI) ion by Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid was studied using time intervals 5–80 min. 20.0 mg of nanohybrid was mixed with 10 mL of the selected concentration of chromium ion (5, 10 and 15 mg L$^{-1}$) at pH 3 (optimum pH) at room temperature. From the data of this factor, the kinetic models were investigated to elucidate the extraction mechanism(s) of Cr(VI) by Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid.

The dosage influence of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid on the removal of hexavalent chromium ion was also investigated utilizing different masses 5–70 mg. The chosen mass was mixed with 10 mL of the selected concentration of chromium ion (5, 10 and 15 mg L$^{-1}$) at pH 3 for 30 min.

The influence of the initial concentration of the solution of chromium ion was studied with various concentrations from 5 to 100 mg L$^{-1}$ in which 20.0 mg of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid was mixed with 10 mL of chromium solution and each prepared concentration was adjusted at pH 3. The removal percentage was estimated from Eq. (1). The data collected from this factor were used to investigate the isotherm study and to understand the mechanism of adsorption of the contaminant.

The influence of temperature on the extraction of Cr(VI) was also studied utilizing distinct values of temperature (298, 307, 316, 323 and 328 K). 20.0 mg of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid was added to 10 mL of the selected concentration of chromium solution (5, 10 and 15 mg L$^{-1}$) at pH 3. This factor was also employed to study the thermodynamics parameters of Cr(VI) ion removal onto Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid.

The influence of ionic strength using various masses (5–100 mg) of sodium chloride electrolyte was also studied. The chosen mass of the electrolyte was mixed with 20.0 mg of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid in 10 mL of Cr(VI) ion solution (5, 10 and 15 mg L$^{-1}$) that was adjusted at pH 3 and shaken for 30 min. The Cr(VI) ion removal percentage was estimated as before from Eq. (1).

The recycling capability of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO was also investigated by applying 0.05 mol L$^{-1}$ HCl as the regeneration reagent to activate the loaded Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid with hexavalent chromium ion. 100 mg Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid was mixed with 10 mL of hexavalent chromium solution at pH 3 and shaken for 30 min. The loaded nanohybrid was then washed with HCl and DW and dried to be ready for the recycling operation.

Finally, the potential applicability of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid for removal of hexavalent chromium ion from real water specimens (tap, seawater and industrial wastewater) was also investigated in this study. This study was carried out at optimum conditions using three concentrations of spiked Cr(VI) ion solution (5, 10 and 15 mg L$^{-1}$). 70.0 mg of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO was mixed with 10 mL of spiked solution at pH 3. Water specimens used in this factor were drinking water from the tap, seawater from the Mediterranean Sea and eventually collected wastewater from Elmahmodya canal, Alexandria, Egypt.
Results and discussions

Characterization. Fourier transform-infrared (FT-IR) study. The FT-IR spectra of Fe_{0.75}Cu_{0.25}-BDC MOFs, GO, Alg-GO, Alg-MoO_3/GO and Fe_{0.75}Cu_{0.25}-BDC@Alg-MoO_3/GO were acquired to confirm their structures. The chemical structure of Fe_{0.75}Cu_{0.25}-BDC MOFs is represented by the illustrated FTIR spectrum in Fig. 2. There is no broad peak found at 3400 cm\(^{-1}\) which proves the absence of O–H stretching vibration. The characteristic absorption bands at 1686, 1537, 1421 and 1289 cm\(^{-1}\) are assigned to the vibration of the carboxylate groups which coordinated with Cu\(^{2+}\) and Fe\(^{3+}\) in Fe_{0.75}Cu_{0.25}-BDC MOFs\(^3\). The sharp band that appeared at 736 cm\(^{-1}\) is attributed to the C–H bending vibration of the benzene ring, while the band at 566 cm\(^{-1}\) refers to the Fe–O stretching vibration\(^3\). The result of FT-IR analysis confirms the presence of a metal-oxo bond between the C = O of terephthalic acid and metal ions (Cu\(^{2+}\) and Fe\(^{3+}\)) to refer to the successful formation of bimetallic Fe_{0.75}Cu_{0.25}-BDC MOFs. The FT-IR spectrum of microwave-synthesized graphene oxide was also studied. The presence of a peak at 3411 cm\(^{-1}\) is assigned to the stretching vibrations of the O–H bond to prove the successful oxidation of graphite\(^3\). The peak at 1724 cm\(^{-1}\) is attributed to the C = O stretching vibrations of the carboxylic acid in GO. There are also some C = C bonds of sp\(^2\) carbons in the 1619 cm\(^{-1}\) region. The presence of a peak at 571 cm\(^{-1}\) in GO may be attributed to the presence of traces of Mn–O as the employed oxidizing agent\(^3\). The displayed peaks at 3176 cm\(^{-1}\) and 2920 cm\(^{-1}\) in the Alg-GO spectrum denote to the O–H and CH\(_2\)
stretching vibrations from graphene oxide and/or alginate, while the bands at 1088 and 1031 cm⁻¹ are attributed to glucuronic and mannuronic units, respectively. The observed bands at 1580 and 1413 cm⁻¹ are evident in the symmetric stretching frequency and the asymmetric one of the carboxylic acid group of alginates. In the FT-IR spectrum of Alg-MoO₃/GO, a broad peak was found at 3432 cm⁻¹ that corresponds to the O–H stretching vibrations in GO and/or alginate, while the peak at 2937 cm⁻¹ is assigned to C–H bond vibration. The characteristic peaks of MoO₃ are identified at 944 and 620 cm⁻¹ which are attributed to Mo = O bonds, Mo–O–Mo vibrations of Mo⁶⁺ and Mo–O–Mo, respectively. The peaks of epoxy group of graphene oxide are located at 1035 and 1130 cm⁻¹ in Alg-MoO₃/GO and therefore, the epoxy-functional groups may be attached to molybdenum trioxide. The peak at 3308 cm⁻¹ in Fe₀.₇₅Cu₀.₂₅-BDC@Alg-MoO₃/GO, corresponds to stretching vibrations of O–H of GO. The peaks at 1657 cm⁻¹, 1537 cm⁻¹ and 1390 cm⁻¹ are evident to carbonyl group (COOH) asymmetric and symmetric vibrations and sp² C = C bond. The peaks at 1104 cm⁻¹ and 1016 cm⁻¹ correspond to stretching vibrations of C–O bond in COO⁻ and C–O–H. The peaks resulting in stretching vibrations of metal-O bonds are confirmed by their presence at 851 cm⁻¹, 750 cm⁻¹ and 542 cm⁻¹ respectively.

Scanning and transmission electron microscopic analysis. SEM characterization refers to the surface morphology of Fe₀.₇₅Cu₀.₂₅-BDC@Alg-MoO₃/GO at magnification order ×35,000 as illustrated in Fig. 3. The SEM image shows that the particles of Fe₀.₇₅Cu₀.₂₅-BDC@Alg-MoO₃/GO nanohybrid are spherical in shape and homogeneously distributed with no aggregation. Furthermore, the average particle size in the assembled Fe₀.₇₅Cu₀.₂₅-BDC@Alg-MoO₃/GO nanohybrid material was characterized as 20.52 nm. This fact proves the successful preparation of Fe₀.₇₅Cu₀.₂₅-BDC@Alg-MoO₃/GO at nanoscale range thus providing good adsorption of Cr(VI) ions. The morphology of Fe₀.₇₅Cu₀.₂₅-BDC@Alg-MoO₃/GO nanohybrid was further proved by the TEM imaging Fig. 4. which elucidates that the prepared nanohybrid was spherical in shape with accurate particle size distribution in the range from 4.19 nm to 8.33 nm. The image also shows the good distribution of nanosized Fe₀.₇₅Cu₀.₂₅-BDC@Alg-MoO₃/GO.

X-Ray diffraction. XRD is a significant non-destructive method to determine the crystallinity of a material. Herein, the XRD pattern of Fe₀.₇₅Cu₀.₂₅-BDC MOFs, Alg-MoO₃/GO and Fe₀.₇₅Cu₀.₂₅-BDC@Alg-MoO₃/GO was performed as illustrated in Fig. 5. The XRD pattern of Fe₀.₇₅Cu₀.₂₅-BDC MOFs shows some characteristic peaks at 2θ = 12.11° 16.80° 20.06° 23.61° and 32.5° which prove the successful incorporation of copper in Fe₀.₇₅Cu₀.₂₅-BDC MOFs. The XRD curve of Alg-MoO₃/GO indicates the crystalline structure with a broad reflection around 11.62° as a characteristic peak for alginate. Furthermore, the diffraction peaks at 2θ = 9.32°, 12.93° and 25.95° correspond to the graphene oxide and molybdenum trioxide which consistent with the standard graphite JCPDS file no. 75-2078 and ICDD sheet no. 00-021-0569 respectively. Finally, the XRD pattern of Fe₀.₇₅Cu₀.₂₅-BDC@Alg-MoO₃/GO nanohybrid is quite different and shows several diffraction peaks at 2θ = 9.01° 12.38° 17.93° and 24.75° which clearly illustrate the increase in the crystallinity of the final nanohybrid as well as its successful preparation.

Thermal analysis. The thermal stability Fe₀.₇₅Cu₀.₂₅-BDC MOFs, Alg-MoO₃/GO and Fe₀.₇₅Cu₀.₂₅-BDC@Alg-MoO₃/GO nanohybrid was studied by TGA analysis. The stages of weight loss are illustrated in the TGA diagram (Fig. 6). Firstly, Fe₀.₇₅Cu₀.₂₅-BDC MOFs exhibited only one degradation stage with 25.29% mass loss that could be due to the decomposition of volatile compounds and no more mass loss above 377 °C to refer to the good thermal stability of the prepared bimetallic MOF. There are three degradation stages of Alg-MoO₃/GO. The first step is evident with a mass loss 16.17% due to the evaporation of water molecules adsorbed on the surface.
The second step is evident with a mass loss of 29.31% as sodium alginate began to decompose and the degradation of oxygen-containing functional groups in GO, while the third one with 53.60% loss due to further cracking of sodium alginate and decomposition of GO into CO and CO$_2$. Finally, the thermogram of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid elucidates two decomposition steps with a total mass loss of 76.77% due to the above-mentioned degradation steps.

**Adsorption optimization. Impact of initial pH values.** The initial pH of the solution is a significant factor as it affects the charge on the surface of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid and its ionized forms as well as metal species. Figure 7a. depicts the removal of Cr(VI) onto Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid under pH range values from 2 to 7 using three different concentrations of Cr(VI) ions (5, 10 and 15 mg L$^{-1}$). It’s evident that the removal percentages of the three chromium ion concentrations were decreased with increasing pH values. The optimum removal percentages were achieved at pH 3 as 92.27%, 93.27 and 85.32% by 5, 10 and 15 mg L$^{-1}$ respectively. Hexavalent chromium is favorably adsorbed at low pH onto Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid owing to the protonation of the functional groups at the surface of nanohybrid at low pHs. Thus, the binding and electrostatic attraction between the surface and anionic chromium at pH 3 dominated the adsorption process. Furthermore, the removal percentage values were decreased at higher pH values because of the repulsion force between the negatively charged surface of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid and anionic hexavalent chromium to favor less available active sites on the surface$^{49}$.

The point of zero charge of the prepared Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid was also studied for further confirmation of the effect of pH on the adsorption mechanism. The PZC is determined when the surface of the nanohybrid becomes neutral. Figure 7b represents the plot between $\Delta$pH ($pH_{\text{final}} - pH_{\text{initial}}$) versus $pH_{\text{initial}}$ from which the value of PZC was obtained at $pH_{\text{PZC}} = 3.8$. At $pH < pH_{\text{PZC}}$, the surface is positively charged and therefore, it is favorable to adsorb anions by electrostatic attraction force$^{50}$.

**Impact of time and kinetic studies.** The influence of time using batch operation between Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO and hexavalent chromium ion is necessary for studying the mechanism(s) of adsorption. The...
time range was adjusted from 5 to 80 min utilizing 20 mg of Fe\textsubscript{0.75}Cu\textsubscript{0.25}-BDC@Alg-MoO\textsubscript{3}/GO nanohybrid with 10 mL of hexavalent chromium ion (5, 10 and 15 mg L\textsuperscript{-1}) at room temperature and pH 3 and the collected results are shown in Fig. 8a. It's obvious that the removal of Cr(VI) almost remained constant as the shaking time increases. The removal percentages reached equilibrium after only five minutes for 5 mg L\textsuperscript{-1} and 10 mg L\textsuperscript{-1}, while 10 min for 15 mg L\textsuperscript{-1} concentrations. The characterized maximum removal percentages were 92.28%,
Figure 7. (a) Impact of initial pH on the removal of Cr(VI) by Fe_{0.75}Cu_{0.25}-BDC@Alg-MoO_3/GO (b) PZC plot.

Figure 8. (a) Impact of time on Cr(VI) ions removal by Fe_{0.75}Cu_{0.25}-BDC@Alg-MoO_3/GO and (b) Pseudo-second order model for removal of Cr(VI) ions.
94.08% and 85.07% for 5, 10 and 15 mg L\(^{-1}\) respectively. This proves the efficient binding between the active sites of Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO nanohybrid with Cr(VI) as it reached full saturation very fast\(^{51}\).

Kinetic study is very significant as it elucidates the rate of adsorption of adsorbate at solid/liquid interface. The mechanism of adsorption of hexavalent chromium ion onto Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO nanohybrid was studied by using four various kinetic techniques; pseudo-first order, pseudo-second order, intra-particle diffusion and Elovich kinetic models. The first studied model for adsorption of Cr(VI) onto Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO nanohybrid is the pseudo-first order and its related parameters are computed from Eq. (2).

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

where the adsorption capacities at equilibrium and at any time t can be denoted by \(q_e\) and \(q_t\) respectively. The \(k_1\) describes the value of rate constant (min\(^{-1}\)). The \(R^2\) values for pseudo-first order model were very low (\(R^2 = 0.166, 0.3770\) and 0.1727). Therefore, this model is inappropriate to describe this adsorption mechanism of hexavalent chromium ion onto Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO nanohybrid. Similarly, the pseudo-second order kinetic parameters are calculated from Eq. (3).

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

where, the rate constant for pseudo-second order is denoted by \(k_2\) (g/mg.min). This model was examined by plotting \(t/q_t\) vs t (Fig. 8b). The correlation coefficients for this model were 1.000, 0.9998 and 0.9993 for 5, 10 and 15 mg L\(^{-1}\) chromium ion concentrations, respectively. Furthermore, the \(q_t\) was nearly equal to \(q_t\) as predicted. So, the adsorption behavior obviously fit this model to illustrate that the adsorption reaction of hexavalent chromium ion via multi active sites on the nanohybrid surface. The intra-particle diffusion and Elovich models were both studied from equations Eqs. (4) and (5), respectively. It was found that these two models were inconvenient to elucidate adsorption behavior of Cr(VI) onto Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO nanohybrid based on the computed \(R^2\) values\(^{52}\).

\[
q_t = k_1t^{1/2} + C
\]

\[
q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t
\]

Finally, the collected results from the kinetic study clarify that pseudo-second order model is the most convenient one to depict the adsorption behavior of hexavalent chromium ion onto Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO nanohybrid and therefore, the adsorption behavior is suggested to rely on a chemisorption mechanism (chemically rate control mechanism)\(^{53}\).

**Impact of Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO dosage.** The selected mass of Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO nanohybrid is known to affect the uptake of various adsorbates as Cr(VI). Figure 9 depicts the relationship between Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO dosages (5–70 mg) with the Cr (VI) removal percentages by using three concentrations of hexavalent chromium ion (5, 10 and 15 mg L\(^{-1}\)). It can be outlined that the removal percentages of hexavalent chromium were initially increased with the increase of Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO dosage and then reached to the maximum value at 30 mg. The removal percentages increased from 84.68%, 78.86% and 65.77% to 94.81%, 95.45% and 93.28% by using 5, 10 and 15 mg L\(^{-1}\), respectively. This may be attribute to the structure of Fe\(_{0.75}\)Cu\(_{0.25}\)-BDC@Alg-MoO\(_3\)/GO nanohybrid which provides a great number of functional groups at the surface to enable efficient adsorption of the contaminant\(^{54}\).
Impact of initial Cr(VI) concentration and adsorption isotherms. Various concentrations of hexavalent chromium are known to affect its removal and uptake values by Fe0.75Cu0.25-BDC@Alg-MoO3/GO nanohybrid. It has been confirmed that the removal percentages was declined from 92.41% to 45.56% when the initial concentration was raised from 5 to 100 mg L−1 as illustrated in Fig. 10a. This declining order is due to the decrease in the number of nanohybrid particles compared to Cr(VI) ratio. However, as the concentration of Cr(VI) increased, while maintaining the active sites of Fe0.75Cu0.25-BDC@Alg-MoO3/GO nanohybrid constant, a great number of chromium ion were left unadsorbed. So, the deficiency of active sites at higher concentrations of the contaminant led to a decrease in the removal efficiency for Cr(VI)55.

Herein, four adsorption isotherm models (Langmuir, Freundlich, Dubinin-Radushkevich and Temkin) were studied to understand the reaction adsorption mechanism(s) of Cr(VI) onto Fe0.75Cu0.25-BDC@Alg-MoO3/GO surface and the parameters of these four models are listed in Table 2. In Langmuir model, the behavior of adsorption mainly depends on a unimolecular chemical reversible process. It is obvious that the adsorption of Cr(VI) onto Fe0.75Cu0.25-BDC@Alg-MoO3/GO surface was most convenient to Langmuir model owing to the larger value of correlation coefficient (R² 0.9934) as represented in Fig. 10b. This proves that the adsorption reaction was dependent on the formation of a homogeneous monolayer of loaded Cr(VI) onto Fe0.75Cu0.25-BDC@Alg-MoO3/GO nanohybrid in which all active sites possess equivalent attraction forces for adsorption of hexavalent chromium. The R² value indicates whether the adsorption process is favorable or not. Herein, this was

| Isotherm Model | Langmuir | Freundlich | D-R | Temkin |
|---------------|----------|------------|-----|--------|
| Equation      | $\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}}$ | $\ln q_e = \ln K_F + \frac{1}{2} \ln C_e$ | $\ln q_e = \ln q_{max} + (K_{des}^{2})^{1/2}$ | $q_e = \frac{q_{max}}{1 + \frac{C_e}{K_L}}$ |
| Plot          | $C_e/q_e$ vs. $C_e$ | $\ln q_e$ vs.$\ln C_e$ | $\ln q_e$ vs.$\epsilon^{2}$ |
| Parameters    | $q_{max}$ | b | $R^2$ | n | $K_F$ | $R^2$ | $q_{max}$ | $K_{ad}$ | $R^2$ | E | a | b | $R^2$ |
| Units         | mg g⁻¹ | L mg⁻¹ | - | - | L mg⁻¹ | - | mg g⁻¹ | mol²J⁻² | - | kJ/mol | 1/mg | J/mol | - |
| Cr(VI)        | 24.81 | 0.1669 | 0.9934 | 0.05654-0.5451 | 2.182 | 4.154 | 0.9862 | 14.09 | 20.47 | 0.7211 | 0.2210 | 2.871 | 657.52 | 0.9704 |

Table 2. Adsorption isotherm models for Cr(VI) using 20 mg Fe0.75Cu0.25-BDC@Alg-MoO3/GO and shaking time = 30 min at pH 3. Significant values are in bold.
fraction values (0.05654–0.5451) to prove that the reaction between Cr(VI) and Fe_{0.75}Cu_{0.25}-BDC@Alg-MoO_{3}/GO nanohybrid is a favorable adsorption process. Freundlich isotherm model postulated that the adsorption process could be established onto heterogeneous surface of the sorbent with unequal available active sites with the formation of multilayer adsorption. The characterized $R^2$ value was 0.9862 which is not as good as Langmuir model. This result states that the adsorption of Cr(VI) onto Fe_{0.75}Cu_{0.25}-BDC@Alg-MoO_{3}/GO didn't proceed on a heterogeneous surface. The $n$-value equal 2.182 to indicate a favorable adsorption process since $n$-value is greater than one. The adsorption mechanism by Dubinin-Radushkevich model depends on pore filling and postulates a multilayer character via physical process. The characterized $R^2$ value from the D-R model was 0.7211. Temkin model states that the reaction between the adsorbent and the adsorption depends on temperature with neglecting the concentration and also assumes that as the surface coverage increases the heat of adsorption declines linearly. The $R^2$ value of this model was identified as 0.9701. The $R^2$ values, D-R model and Temkin models referred to the inapplicability of these models to depict the mechanism for adsorption of Cr(VI) onto Fe_{0.75}Cu_{0.25}-BDC@Alg-MoO_{3}/GO nanohybrid.

Impact of temperature and thermodynamics studies. The adsorption behavior of Fe_{0.75}Cu_{0.25}-BDC@Alg-MoO_{3}/GO nanohybrid towards hexavalent chromium was studied at various temperatures (293–328 K). This study showed that as the temperature increased from 293 to 328 K, the removal percentage decreased from 95.57% to 86.08%, 96.78% to 78.50% and 90.50% to 74.03% by using 5, 10 and 15 mg L^{-1} chromium ion concentrations, respectively. The decline in the adsorption at high temperatures may be attributed to the high mobility and solubility of hexavalent chromium in aqueous solution at higher temperatures. As illustrated in Fig. 11a, the plot between ln $K_D$ versus 1000/T gives a slope ($\Delta H^\circ/R$) and an intercept ($\Delta S^\circ/R$) from which the ($\Delta H^\circ$) and ($\Delta S^\circ$) values are evaluated using Van’t Hoff equation Fig. 11b. The calculated values of $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ from equations Eqs. 6–8 are compiled in Table 3. The negative values of Gibbs free energy displayed that the adsorption process Cr(VI) onto Fe_{0.75}Cu_{0.25}-BDC@Alg-MoO_{3}/GO is spontaneous process. The values of enthalpy change are negative to confirm that the adsorption of Cr(VI) onto Fe_{0.75}Cu_{0.25}-BDC@Alg-MoO_{3}/GO was an exothermic process. The values of entropy change were negative to prove that the adsorption process is an ordered process.

\[
\Delta G^\circ = -RT\ln K_D
\]  
\[
K_D = \frac{q_e}{C_e}
\]  
\[
\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}
\]
Eventually, the evaluated parameters from the thermodynamic study prove that the adsorption behavior for adsorption of Cr(VI) onto Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid was exothermic spontaneous ordered process.

Impact of ionic strength. The presence of an electrolyte may affect the electrostatic attractions and binding mechanism between adsorbate (Cr(VI)) and adsorbent (Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO). Figure 12 illustrates the effect of ionic strength by the addition of various doses of sodium chloride from 5 to 100 mg. It was found that the presence of NaCl slightly enhanced the removal percentage of Cr(VI) with percentages 95.44%, 96.01% and 90.85% by using 5, 10 and 15 mg L$^{-1}$, respectively. This behavior may be based on the fact that under acidic conditions (pH 3) the surface of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO carries a positive charge and the presence of NaCl electrolyte increased the loaded positive charges on the surface to favor higher removal efficiency$^{61}$.

Reusability test of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO. The recycling capability of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO is a significant operation that must be studied to investigate the applicability of the prepared nanohybrid. Herein, the regeneration reagent was 0.05 mol L$^{-1}$ HCl to activate and desorb the loaded Cr(VI) from the surface of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid. In this study, 100 mg of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid was mixed with 10 mL of Cr(VI) solution at pH 3. The loaded surface was then washed with HCl then DW several times and dried in an oven to be ready for further application after recycling operation. As illustrated in Fig. 13, five cycles were performed and the removal percentages of Cr(VI) by the recycled Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid decreased from 95.21 to 70.04% after the fifth regeneration step. This decline may be attributed to the possible weight loss of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid. The outlined data in Fig. 13 prove the successful reusability of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid.

| Cr(VI) | ΔG$^\circ$ | ΔH$^\circ$ | ΔS$^\circ$ |
|--------|----------|----------|----------|
| 5 mg L$^{-1}$ | $-5.89$ | $-5.00$ | $-4.65$ | $-3.26$ | $-3.07$ | $-34.47$ | $-93.65$ |
| 10 mg L$^{-1}$ | $-6.27$ | $-5.13$ | $-4.59$ | $-3.45$ | $-1.64$ | $-47.43$ | $-134.47$ |
| 15 mg L$^{-1}$ | $-3.86$ | $-3.60$ | $-2.63$ | $-1.73$ | $-0.96$ | $-33.22$ | $-95.41$ |

Table 3. Thermodynamic parameters.

![Figure 12. Effect of NaCl electrolyte on removal of Cr(VI) onto Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO.](image-url)
Application of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO in Cr(VI) removal from real specimens. The validity of utilization of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid as efficient adsorbent material for the of hexavalent chromium ion from three different actual water specimens (tap, seawater, and wastewater) was studied by the batch technique. The water specimens were spiked with hexavalent chromium solution to obtain the three required concentrations of hexavalent chromium ion (5, 10 and 15 mg L$^{-1}$). Then, the optimum conditions were used by adjustment of pH at 3 and using 70.0 mg of nanohybrid mass. The removal percentage values of hexavalent chromium from tap, seawater and wastewater were found to be more than of 98% as illustrated in Table 4. The outlined results emphasize that the prepared and investigated Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid has been validated as an excellent regenerable adsorbent for removal of Cr(VI) from various water samples.

Conclusion

A novel nanohybrid (Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO) has been prepared and investigated for remediation of water from hexavalent chromium. Inclusion of Fe$_{0.75}$Cu$_{0.25}$-BDC MOFs into Alg-MoO$_3$/GO was accomplished by a simple and facile solvothermal process. Characterization of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO confirmed the successful preparation of with distributed particles homogeneously and uniformly at average particle size from 4.19 to 8.33 nm based on the TEM analysis and the point of zero charge of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO was found pHPzc = 3.8. Various parameters were studied to figure out the optimum conditions for extraction of Cr(VI) from aqueous solution (pH = 3 dosage, initial concentration of hexavalent chromium ion = 5, 10 and 15 mg L$^{-1}$, shaking time = 5–10 min). The collected results from the kinetic study clarified that pseudo-second order model is the most convenient one to depict the adsorption behavior of Cr(VI) onto Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanohybrid and the adsorption behavior was suggested to rely on a chemisorption mechanism. The impact of ionic strength by the presence of NaCl was found to slightly enhance the removal percentage of Cr(VI) due to the ability of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO to carry a more positive charge. The isotherm modeling study evaluated Langmuir model as the most valid model with a correlation coefficient $R^2 = 0.9934$. The impact of temperature and characterized thermodynamic parameters revealed that the adsorption mechanism of Cr(VI) by Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO was a spontaneous and exothermic process. The pseudo-second order model was proved as the most convenient model with $R^2$ close to one (1.000, 0.9998 and 0.9993). Finally, the emerged Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO nanocomposite was compared with previously reported adsorbents as compiled in in Table 5, indicating the superiority of the assembled and investigated Fe0.75Cu0.25-BDC@Alg-MoO3/GO nanocomposite in removal of Cr(VI) from aqueous solutions versus other previously reported adsorbent.

Table 4. Adsorptive removal of Cr(VI) by Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO from real water samples at optimum conditions (Cr (VI) concentrations (5, 10 and 15 mg L$^{-1}$) and 70 mg of adsorbent and pH 3).

| Water sample | Percentage removal of Cr (VI) |
|--------------|-------------------------------|
|              | 5 mgL$^{-1}$                  | 10 mgL$^{-1}$ | 15 mgL$^{-1}$ |
| Tap water    | 98.72                         | 98.77         | 98.4          |
| Sea water    | 98.62                         | 98.50         | 98.20         |
| Wastewater   | 98.83                         | 98.01         | 98.85         |

Figure 13. Recycling/reusability of Fe$_{0.75}$Cu$_{0.25}$-BDC@Alg-MoO$_3$/GO.
1. Wu, Q., Siddique, M. S. & Yu, W. Iron-nickel bimetallic metal-organic frameworks as bifunctional Fenton-like catalysts for enhanced... reasonable request.

The datasets used and/or analyzed during the current study are available from the corresponding author on request.

The maximum removal percentage of Cr(VI) by different adsorbents.

Table 5. Comparison of the maximum removal percentage of Cr(VI) by different adsorbents.

| Contaminant | sorbent | Results (Maximum removal percentages) | Optimum pH | References |
|-------------|---------|---------------------------------------|------------|------------|
| Cr(VI)      | Fe0.75Cu0.25-V2O5@Ch/Cu-TMA nanobiosorbent | > 98% from tap, sea and wastewater | 3 | This study |
|             | Cd-TIPA (Photocatalyst) | high catalytic efficiency 93% | - | - |
|             | GO-CS@MOF [Zn(BDC)(DMF)] | > 92% | 3 | - |
|             | ZrPO4·PPY nanocomposite | > 98.8% occurred in 80 min | - | - |
|             | ZIF-8 | > 85% | - | - |
|             | UiO-66 | > 80 | - | - |
|             | ZIF-8@ABs | Uio-66@Abs | > 60% | 6 |
|             | Fe2O3/ SiO2/CS-TETA | 96.4% | 2.5 | - |
|             | V2O5@Ch/Ga-TMA nanobiosorbent | 96.61%, 96.95% and 95.72% from tap, sea and wastewater | 3 | - |
|             | Fe202Cu49.72-BDC@Alg-MoO3-GO | > 98% from tap, sea and wastewater | 3 | - |

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Received: 25 April 2022; Accepted: 1 November 2022
Published online: 09 November 2022

References

1. Wu, Q., Siddique, M. S. & Yu, W. Iron-nickel bimetallic metal-organic frameworks as bifunctional Fenton-like catalysts for enhanced adsorption and degradation of organic contaminants under visible light: Kinetics and mechanistic studies. J. Hazard. Mater. 401, 123261 (2021).
2. Zhao, Q. et al. Potential health risks of heavy metals in cultivated topsoil and grain, including correlations with human primary liver, lung and gastric cancer, in Anhui province, Eastern China. Sci. Total Environ. 470, 340–347 (2014).
3. Zou, H. et al. Recent advances in removal techniques of Cr(VI) toxic ion from aqueous solution: a comprehensive review. J. Mol. Liq. 329, 115062 (2020).
4. Chen, Y. et al. Efficient removal of Cr(VI) from aqueous solution by natural pyrite/rhodochrosite derived materials: Performance, kinetic and mechanism. Adv. Powder Technol. 32(10), 3814–3825 (2021).
5. Yang, W. et al. Photocatalytic reduction of Cr(VI) over cinder-based nanoneedle in presence of tartaric acid: Synergistic performance and mechanism. Res. J. Environ. Sci. 107, 194–204 (2021).
6. Ding, J. et al. Synergetic adsorption and electrochemical classifications of Cr(VI) and dyes in synthetic dyeing wastewater. Chem. Eng. Res. Des. 384, 123232 (2020).
7. Brohi, R. O. Z., Khuwawar, M. Y., Mahar, R. B. & Ibrahim, M. A. Novel bimetallic nanoparticle for sorption of mercury (II) from drinking water: adsorption experiment and computational studies. J. Water Process Eng. 39, 101727 (2021).
8. Lu, J. et al. Nano iron oxides impregnated chitosan beads towards aqueous Cr(VI) elimination: Components optimization and performance evaluation. Colloids Surf. A Physicochem. Eng. 625, 126902 (2021).
9. Zou, H. et al. Ball milling biochar iron oxide composites for the removal of chromium (Cr (VI)) from water: Performance and mechanisms. J. Hazard. Mater. 413, 125252 (2021).
10. Guo, C., Wu, S., Gao, X., Li, M. & Long, H. Mechanistic study of Cr(VI) removal by modified alginate/GO composite via synergistic adsorption and photocatalytic reduction. Int. J. Biol. Macromol. (2021).
11. Guo, J. et al. Polyprrole modified benzonate nanocomposite and its application in high-efficiency removal of Cr(VI). J. Environ. Chem. Eng. 9(6), 10663 (2021).
12. Lim, J. Y., Mubarak, N. M., Abdallah, E. C., Nizamuddin, S. & Khalid, M. Recent trends in the synthesis of graphene and graphene oxide based nanomaterials for removal of heavy metals—A review. J. Ind. Eng. Chem. 66, 29–44 (2018).
13. Dhaka, S. et al. Metal–organic frameworks (MOFs) for the removal of emerging contaminants from aquatic environments. Coord. Chem. Rev. 380, 330–352 (2019).
14. Phan, D. P. et al. Effect of amino-defective-MOF materials on the selective hydrodeoxygenation of fatty acid over Pt-based catalysts. J. Catal. 400, 283–293 (2021).
15. Mahmoud, M. E., Amira, M. F., Azab, M. M. & Abdel fattah, A. M. Effective removal of levofloxacin drug and Cr (VI) from water by a composed nanobiosorbent of vanadium pentoxide/chitosan@MOFs. Int. J. Biol. Macromol. 188, 879–891 (2021).
16. Gaikwad, S., Cheedarala, R. K., Gaikwad, R., Kim, S. & Han, S. Controllable Synthesis of 1, 3, 5-tris (1H-benzo [d] imidazole-2-yl) Benzene-Based MOFs Appl. Surf. Sci. 413(21), 8956 (2021).
17. Huang, Z. H., Liu, G. & Kang, F. Glucose-promoted Zn-based metal-organic framework/graphene oxide composites for hydrogen sulfide removal. ACS Appl. Mater. Inter. 4, 4942–4947 (2012).
18. Wang, L., Xu, H., Gao, J., Yao, J. & Zhang, Q. Recent progress in metal-organic frameworks-based hydrogels and aerogels and their applications. Coord. Chem. Rev. 398, 213016 (2019).
19. Petit, C. & Bandosz, T. J. Exploring the coordination chemistry of MOF-graphite oxide composites and their applications as adsorbents. Dalton Trans. 41, 4027–4035 (2012).
20. Haeri, Z., Ramezanzadeh, B. & Ramezanzadeh, M. Recent progress on the metal-organic frameworks decorated graphene oxide (MOFs-GO) nano-building application for epoxy coating mechanical-thermal/flame-retardant and anti-corrosion features improvement. Prog. Org. Coat. 163, 106645 (2022).
21. Ventura, K. et al. Superparamagnetic MOF@GO Ni and Co based hybrid nanocomposites as efficient water pollutant adsorbents. *Sci. Total Environ.* **738**, 139213 (2020).

22. Chen, J., Yao, B., Li, C. & Shi, G. An improved Hummers method for eco-friendly synthesis of graphene oxide. *Carbon* **64**, 225–229 (2013).

23. El-Sharkawy, R. M., Allam, E. A. & Mahmoud, M. E. Functionalization of CeO2-SiO2-(CH3)3-Cl nanoparticles with sodium alginate for enhanced and effective CdII, PbII, and ZnII ions removal by microwave irradiation and adsorption technique. *Environ. Nanotechnol. Monit. Manag.* **14**, 100367 (2020).

24. You, Y. et al. Sodium alginate templated hydroxyapatite/calcium silicate composite adsorbents for efficient dye removal from polluted water. *Int. J. Biol. Macromol.* **141**, 1035–1043 (2019).

25. Naseem, T. & Durrrani, T. The role of some important metal oxide nanoparticles for wastewater and antibacterial applications: A review. *J. Environ. Chem. Eng.* **3**, 59–75 (2021).

26. Huang, S. et al. Multifunctional molybdenum oxide for solar-driven water evaporation and charged dyes adsorption. *Appl. Surf. Sci.* **491**, 328–334 (2019).

27. Chen, Y. et al. Pomegranateline N, P-doped Mo2C-C nanospheres as highly active electrocatalysts for alkaline hydrogen evolution. *ACS Nano* **10**, 8851–8860 (2016).

28. Huang, D. et al. Optimal preparation of catalytic Metal-organic framework derivatives and their efficient application in advanced oxidation processes. *Chem. Eng. J.* **421**, 127817 (2021).

29. Chang, W.-T. et al. Graphene oxide synthesis using microwave-assisted vs. modified Hummer’s methods: Efficient fillers for improved ionic conductivity and suppressed methanol permeability in alkaline methanol fuel cell electrolytes. *J. Power Sour.* **414**, 86–95 (2019).

30. Allam, E. A., El-Sharkawy, R. M., Gizawy, M. A. & Mahmoud, M. E. Assembly of CeO2–MoO3–SiO2(CH2)3-(Alginate)2 As A micro-composites with graphite, graphene and graphene oxide for lithium ion batteries. *Electrochim. Acta* **365**, 137355 (2021).

31. Almodôvar, P. et al. Synthesis, characterization and electrochemical assessment of hexagonal molybdenum trioxide (h-MoS3) micro-composites with graphite, graphene and graphene oxide for lithium ion batteries. *Electrochim. Acta* **241**, 129002 (2020).

32. Ai, L., Zhang, C., Li, L. & Jiang, J. Iron terephthalate metal–organic framework: revealing the effective activation of hydrogen peroxide for the degradation of organic dye under visible light irradiation. *Appl. Catal. B.*** **148**, 191–200 (2014).

33. Li, X. et al. Three hidden talents in one framework: a terephthalic acid-coordinated cupric metal–organic framework with cascade cysteine oxidase-and peroxidase-mimicking activities and stimulus–responsive fluorescence for cytotoxic sensing. *J. Mater. Chem. B.*** **6**(39), 6207–6211 (2018).

34. Sun, Q. et al. Synthesis of Fe/M (M= Mn Co, Ni) bimetallic metal organic frameworks and their catalytic activity for phenol degradation under mild conditions. *Inorg. Chem. Front.* **4**(1), 144–153 (2017).

35. Ismail, Z. Green reduction of graphene oxide by plant extracts: A short review. *Ceram. Int.* **45**(18), 23857–23868 (2019).

36. Suman, A. et al. Graphene oxide synthesized from zinc-carbon battery waste using a new oxidation process assisted sonoication: Electrochemical properties. *Mater. Chem. Phys.* **275**, 125308 (2022).

37. Vadav, N., Poorabdollah, M. & Rajabi, L. Graphene oxide and silane-modified graphene oxide/unsaturated polyester resin nano-composite: A comparative cure kinetic and diffusion study. *Thermochim. Acta* **707**, 179081 (2021).

38. Kolanthai, E. et al. Graphene oxide—a tool for the preparation of chemically crosslinking free alginate–chitosan–collagen scaffolds for bone tissue engineering. *AACS Appl. Mater. Interfaces* **10**, 12441–12452 (2018).

39. Gv, Y. D., Prabhu, A., Anil, S. & Venkatesan, J. Preparation and characterization of dexamethasone loaded sodium alginate-graphene oxide microspheres for bone tissue engineering. *J. Drug Deliv. Sci. Technol.* **64**, 102624 (2021).

40. Gv, Y. D., Prabhu, A., Anil, S. & Venkatesan, J. Preparation and characterization of dexamethasone loaded sodium alginate-graphene oxide microspheres for bone tissue engineering. *J. Drug Deliv. Sci. Technol.* **64**, 102624 (2021).

41. Ramar, V. & Ralalbaraman, K. Optical and highly enhanced solar light-driven photocatalytic activity of reduced graphene oxide wrapped a-MoO3 nanoflakes. *Sol. Energy* **194**, 1–10 (2019).

42. Do, T. L., Ho, T. M. T., Doan, V. D., Le, V. T. & Hoai Thuong, N. Iron-doped copper 1, 4-benzenedicarboxylate as photo-Fenton catalyst for degradation of methylene blue. *Toxicol. Environ. Chem.* **101**, 13–25 (2019).

43. Yonita, M., Pandele, M. A. & Iovu, H. Sodium alginate/graphene oxide composite films with enhanced thermal and mechanical properties. *Carbohydr. Polym.* **94**, 339–344 (2013).

44. Soman, S. A., Gul, I. H., Naseer, H., Marwat, S. & Mujahid, M. Improved performance of CuFe2O4/GO nanohybrid as an anode material for lithium-ion batteries prepared via facile one-step method. *Curr. NanoSci.* **15**(4), 420–429 (2019).

45. Rahmani, B. et al. Gas sensing properties of thermally evaporated lamellar MoO3. *Sens. Actuators B Chem.* **145**(1), 13–19 (2010).

46. Pujari, R., Lokhande, V., Kumbhar, V. & Divakar, C. D. Hexagonal microrods architectured MoO3 thin film for enhanced and effective CdII, PbII, and ZnII ions removal by microwave irradiation and adsorption technique. *Environ. Nanotechnol. Monit. Manag.* **14**, 100367 (2020).

47. You, Y. et al. Sodium alginate templated hydroxyapatite/calcium silicate composite adsorbents for efficient dye removal from polluted water. *Int. J. Biol. Macromol.* **141**, 1035–1043 (2019).

48. Dastbaz, A., Karimi-Sabet, J. & Moosavian, M. A. Intensification of hydrogen adsorption by novel Cu-BDC@rGO composite. *Chem. Eng. Process* **135**, 245–257 (2019).

49. Mahmoud, M. E. & Abdelfattah, A. M. Mechanism of Cr(VI) uptake onto sagwan sawdust derived biochar and statistical optimization via response surface methodology. *Biomass Convers. Biorefin.* **1–17** (2020).

50. Mahmoud, M. E., Nabil, G. M. & Elweshahy, S. M. T. Novel NTiO2-chitosan@NZrO2-chitosan nanocomposite for effective adsorp-tive uptake of trivalent gadolinium and samarium ions from water. *Powder Technol.* **378**, 246–254 (2020).

51. Qi, X. et al. Removal of copper ions from water using polyacrylic acid-constructed hydrogels. *Carbohydr. Polym.* **209**, 101–110 (2019).

52. Gupta, G. K. & Mondal, M. K. Mechanism of Cr(VI) uptake onto sagwan sawdust derived biochar and statistical optimization via response surface methodology. *Biomass Convers. Biorefin.* **1–17** (2020).

53. Mahmoud, M. E., Abdelfattah, A. M., Tharwat, R. M. & Nabil, G. M. Adsorption of negatively charged food tartrazine and sunset yellow dyes onto positively charged triethylentetramine biochar: optimization, kinetics and thermodynamic study. *J. Mol. Liq.* **318**, 114297 (2020).
60. Akram, M., Nawaz Bhatti, H., Iqbal, M., Noreen, S. & Sadaf, S. Biocomposite efficiency for Cr(VI) adsorption: Kinetic, equilibrium and thermodynamics studies. *J. Environ. Chem. Eng.* 5, 400–411 (2017).
61. Dao, T. H. *et al.* Adsorption behavior of polyelectrolyte onto alumina and application in ciprofloxacin removal. *Polymers* 12, 1554 (2020).
62. Dubey, S. P. & Gopal, K. Adsorption of chromium (VI) on low-cost adsorbents derived from agricultural waste material: A comparative study. *J. Hazard. Mater.* 145(3), 465–470 (2007).
63. Mahmoud, M. E., Osman, M. M., Abdel-Aal, H. & Nabil, G. M. Microwave-assisted adsorption of Cr (VI), Cd (II) and Pb (II) in presence of magnetic graphene oxide-covalently functionalized-tryptophan nanocomposite. *J ALLOY COMPD* 823, 153855 (2020).
64. Niu, G. *et al.* An electron-rich metal-organic framework for highly efficient photocatalytic reduction of Cr (VI). *J. Alloys Compd.* 830, 154696 (2020).
65. Samuel, M. S. *et al.* A GO-CS@ MOF [Zn (BDC)(DMF)] material for the adsorption of chromium (VI) ions from aqueous solution. *Compos. B. Eng.* 152, 116–125 (2018).
66. Noraei, Z., Jafari, A., Ghaderpoori, M., Kamarehie, B. & Ghaderpoury, A. Use of metal-organic framework to remove chromium (VI) from aqueous solutions. *J. Environ. Health Sci.* 17(2), 701–709 (2019).
67. Behera, A. *et al.* Polypyrrole modified zirconium (IV) phosphate nanocomposite: An effective adsorbent for Cr (VI) removal by adsorption-reduction mechanism. *Mater. Chem. Phys.* 290, 126540 (2022).
68. Daradmare, S., Xia, M., Kim, J. & Park, B. J. Metal–organic frameworks/alginate composite beads as effective adsorbents for the removal of hexavalent chromium from aqueous solution. *Chemosphere* 270, 129487 (2021).
69. Wang, X. *et al.* Triethylenetetramine-modified hollow Fe3O4/SiO2/chitosan magnetic nanocomposites for removal of Cr (VI) ions with high adsorption capacity and rapid rate. *Micropor. Mesopor. Mater.* 297, 110041 (2020).

**Author contributions**
All authors reviewed the manuscript, Conceptualization, Data curation, and Methodology.

**Funding**
Open access funding provided by The Science, Technology & Innovation Funding Authority (STDF) in cooperation with The Egyptian Knowledge Bank (EKB).

**Competing interests**
The authors declare no competing interests.

**Additional information**
**Correspondence** and requests for materials should be addressed to A.M.A.

**Reprints and permissions information** is available at [www.nature.com/reprints](http://www.nature.com/reprints).

**Publisher’s note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit [http://creativecommons.org/licenses/by/4.0/](http://creativecommons.org/licenses/by/4.0/).

© The Author(s) 2022