Insights into the Synergistic Removal of Copper(II), Cadmium(II), and Chromium(III) Ions Using Modified Chitosan Based on Schiff Bases-\textit{g}-poly(acrylonitrile)

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1. INTRODUCTION

The extended growth of water contamination occurred basically because of the huge growth of business technology. To decrease those unsafe contaminants, various attempts were carried out. Those attempts specifically aimed to prevent the harmful outcomes generated through the pollution of animals, plants, and mankind. Pollutions throw using heavy metal ions has recently turned out to be major vital trouble due to the persistence and accumulation of those metal ions within the environment. The toxic heavy metals in the environment have originated from electronics, food, cosmetics, paints, plastics, herbicides, pesticides, vehicle traffic emissions, etc. The effluents of industrial wastewater in almost all cases contain large quantities of polluting and toxic heavy metals like mercury, lead, copper, chromium, etc. The toxic heavy metals have become a severe environmental issue due to their significant toxic effects on living organisms. Since these toxic heavy metals cannot be degraded by the biological systems, they mostly bioaccumulate in living creatures through the main food chain.

Many methods such as adsorption, chemical deposition, coagulation, photocatalytic degradation, solid–liquid phase extraction, electrochemical, membrane systems, and ionic exchange have been developed. However, a lot of these methods have restrictions in use due to their slow sorption process, very low removal capacity, and poor stability and the fact that they cannot be reused. Material science technology faces considerable challenges to reach a method that faces high requirements for high removal capacity, sensitivity, selectivity, reusability, and stability. The uptake of heavy metal ions from aqueous solution media by adsorption is considered one of the highly efficacious methods used, related to its ease of uptake, low cost, ease, and high selectivity.

Many biosorptions like fungi, algae, seaweed, microorganisms, and several biopolymers were applied in the metal ion uptake from wastewater. The polysaccharides are renewable, biodegradable, plentiful, and...
inexpensive and are the perfect choice in water purification and excellent ones for saving the environment.\textsuperscript{27–30} Also, chitosan and its derivatives are natural low-cost polymers and have shown biodegradability with amine groups on its backbone structure. Therefore, this work is expected to provide new avenues with regard to the facile synthesis of high-performance green adsorbent materials. It is shown to be the most efficient and durable for the uptake of heavy metal pollution by the adsorption process.\textsuperscript{31}

The repeating units of N-acetyl-d-glucosamine linked by β-(1 → 4) bonds are called chitin. Because of its intractable characteristic, it is frequently deacetylated to chitosan (2-amino-2-deoxy-(1 → 4)-β-D-glucan) using hot alkali media.\textsuperscript{32} Chitosan’s chemical modification has an essential role in the manufacturing of bifunctional materials. The chemical modification of chitin and chitosan by the grafting copolymerization process and their applications have been mentioned.\textsuperscript{33} Chitosan’s properties include its biocompatibility, biodegradability, nontoxicity, and antimicrobial activity against bacteria and fungi; also, chitosan is used in different applications such as medical and pharmaceutical applications, environmental safety like wastewater treatment, textiles, biotechnology, cosmetics, food processing, and agriculture.\textsuperscript{34–36}

Both the reactive amino and hydroxyl groups of chitosan can be used to modify chitosan under certain reaction conditions.\textsuperscript{37} The presence of such groups results in the opportunity for numerous chemical modifications, such as graft copolymerization. Graft copolymerization onto chitosan using acrylonitrile as monomer where poly(acrylonitrile) (PAN) used in the removal of heavy metals such as mercury;\textsuperscript{38} also, it is the most important fiber-forming polymer and has been used in textiles due to its excellent physical and chemical properties. PAN is an ideal polymeric matrix with a series of merits such as solvent resistance, thermal and mechanical stability, abrasion resistance, and high tensile strength.\textsuperscript{39} Active nitrile groups (CN) in PAN can easily be converted into a number of new functional groups via special reactions.

On the other hand, the amino groups present in the repeated units of chitosan result in the opportunity for chemical modifications including the preparation of Schiff bases (−N═CH–R) via reaction with aldehydes, ketones, and acylation using acid chloride. Schiff base ligands bearing nitrogen/oxygen donor atoms have been shown to exhibit ionophoric properties, especially toward heavy metal ions.\textsuperscript{40} These properties have been investigated by their application as a modifier of octadecyl disks for separation—concentration of trace amounts of metal ions.\textsuperscript{41} Moftakhar et al. (2016) used a Schiff base for the removal of copper, lead, zinc, cadmium, cobalt, and nickel ions from aqueous solutions.\textsuperscript{42} Also, Moradinasab and Behzad (2014) used a Schiff base to remove Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, and Ni\textsuperscript{2+} ions from water.\textsuperscript{43}

In our study, (i) we prepared chitosan−graft-poly(acrylonitrile) using potassium persulfate as initiator and modification of chitosan by the synthesis of Schiff base derivatives using salicylaldehyde and P-anisaldehyde as efficient adsorption materials for high-efficiency removal of metal ion pollutants. (ii) The prepared material was characterized by using various techniques of analysis to investigate their chemical and physical properties. (iii) The prepared materials were used for scavenging of Cu\textsuperscript{2+}, Cd\textsuperscript{2+}, and Cr\textsuperscript{3+} metal ions at different conditions of pH, adsorbent dose, initial metal ion concentrations, and time until equilibrium. The isotherms and kinetics of metal ion adsorption onto synthesized materials were determined using batch method experiments.

\section{2. MATERIALS AND METHODS}

\subsection{2.1. Materials}

Chitosan (Ch; Bio Basic, ON, Canada) with degree of deacetylation 96\%, acrylonitrile and salicylaldehyde (Loba Chemie, India), P-anisaldehyde (Sigma-Aldrich, USA), potassium persulfate, propan-2-ol, CrCl\textsubscript{2}, 6H\textsubscript{2}O, CdCl\textsubscript{2}, H\textsubscript{2}O, and CuCl\textsubscript{2}, 2H\textsubscript{2}O (Oxford Laboratory, India), and ethyl alcohol (Piochem, Egypt) were used in the study. All analytical reagents were high grade and used as received without any more purification. Ultrapure water was used throughout this study.

\subsection{2.2. Preparation of the Adsorbents}

\subsubsection{2.2.1. Preparation of Grafted Chitosan with Acrylonitrile (Ch-g-PAN)}

A predetermined amount of chitosan (1 g) was dissolved in 100 mL of 1\% aqueous acetic acid solution, placed in a flat-bottom three-neck flask, and stirred till the formation of the chitosan solution. During that time, nitrogen was purged by putting it at a constant temperature (60 °C) through the stirred solution. Then, a solution of potassium persulfate (0.01 mol L\textsuperscript{−1}) that was freshly prepared was added followed by dropwise addition of acrylonitrile (3 mol L\textsuperscript{−1}). The reaction was left to conduct for 2 h with stirring and then at room temperature for another 15 min; the final product was taken and precipitated out using isopropyl alcohol (2 vol/mL), filtered, and dried. The N,N-dimethylformamide (DMF) was used for Soxhlet extraction for 8–12 h to solubilize and remove any homopolymer and finally lyophilized.\textsuperscript{44}

\subsubsection{2.2.2. Modification of the Ch-g-PAN Using Salicylaldehyde and P-Anisaldehyde}

One millimole of Ch-g-PAN, 2 mmol of

\section*{Figure 1. Modification of chitosan−graft-polyacrylonitrile.}
aldehyde, and 1 mL of glacial acetic acid were added to 20 mL of absolute ethanol. The solution was stirred for 48 h at room temperature and then left to reflux for 24 h at 85 °C. The product was filtered and washed using methanol to remove any excess aldehyde and acetic acid and finally collected and dried in a vacuum oven at 40 °C for 24 h, which is presented in Figure 1.

2.3. Characterizations of the Prepared Material. The formed materials had been characterized by XRD (PANalytical Empyrean, Sweden). The accelerating voltage used was 40 kV with a current of 30 mA, a scan angle ranging from 5 to 60°, and a scan step of 0.05. To determine the vibration of chemical bonds, a Bruker Germany (Vertex 70 FTIR Raman) spectrophotometry (serial number 1341) covering the frequency range of 400–4000 cm⁻¹ had been applied using a potassium bromide disc. The morphology of materials had been estimated by a scanning electron microscope (SEM) (JEOL (JSM-5200), Japan). EDX was taken by a Quanta FEG250. The stability of the suspensions of material was examined using zeta potential on a Malvern (Malvern Instruments Ltd.)

2.4. Metal Ion Adsorption. The batch adsorption runs were performed by shaking vigorously the prepared materials with Cu²⁺, Cd²⁺, or Cr³⁺ metal ion solution using an orbital shaker (200 rpm) at room temperature. The adsorbents’ adsorption ability was investigated via the factors of batch adsorption by adjusting the solution pH (3–7), initial metal concentrations (300–900 mg L⁻¹), and contact time till equilibrium (2–24 h). After each (batch) adsorption process was completed, the solution was then centrifuged for 5 min at 5000 rpm to separate the adsorbent. The remaining concentration of metal ions was estimated by applying an atomic absorption spectrometer (Agilent Technologies, 200 Series AA Systems, USA).

Adsorption experiments were performed by mixing 50 mL of Cu²⁺, Cd²⁺, or Cr³⁺ solutions (starting concentrations 300–900 mg L⁻¹) with 0.05 g of the synthesized polymers. The adsorbent–adsorbate mixtures were mixed at 200 rpm for 24 h. The adsorbed copper metal ion quantities at equilibrium (qₑ) were calculated using eq 1:

### Table 1. The Adsorption Isotherm and Kinetics Models

| Isotherm models | Equations | Kinetics models | Equations |
|-----------------|-----------|----------------|-----------|
| Langmuir        | \( \frac{C_{eq}}{C_{ads}} = \frac{bC_{eq}}{K_L} + \frac{1}{K_L} \) | pseudo-first-order | \( \log(q_e - q_i) = \log q_e - \frac{K_L}{2.303} \) |
| Freundlich      | \( \log q_e = \log K_f + \frac{1}{n} \log C_e \) | pseudo-second-order | \( \frac{t}{q_e} = \frac{1}{K_f q_e^2} + \frac{1}{q_0} \) |

Figure 2. XRD of (a) chitosan, (b) grafted chitosan, (c) grafted chitosan Schiff base using salicylaldehyde (Ch-g-Sch I), and (d) grafted chitosan Schiff base using P-anisaldehyde (Ch-g-Sch II).
The efficiency for absorbing metal ions on Ch-g-Sch I and Ch-g-Sch II was determined according to eq 2:

\[ q_e = \frac{(C_0 - C_e)V}{W} \]  

\[ Q\% = \frac{C_o - C_i}{C_o} \times 100 \]  

Figure 3. SEM of (a) chitosan, (b) Ch-g-PAN, (c1) Ch-g-Sch I, and (d1) Ch-g-Sch II at ×20,000 magnification and of (c2) Ch-g-Sch I and (d2) Ch-g-Sch II at ×2000 magnification.

Figure 4. Effect of pH on the adsorption of Cr\(^{3+}\), Cd\(^{2+}\), and Cu\(^{2+}\) ions by (1) Ch-g-Sch I and (2) Ch-g-Sch II.

The efficiency for absorbing metal ions on Ch-g-Sch I and Ch-g-Sch II was determined according to eq 2:
where $Q$ is the absorptivity (%), $C_o$ is the initial concentration of ions, and $C_t$ is the ion concentration (mg L$^{-1}$) after adsorption at the time $t$ (h).

Two isotherm models were used to fit the experimental adsorption data: Langmuir and Freundlich. Experiments of the kinetics study were applied to calculate the uptake in which 0.05 g of adsorbents was added in 50 mL of 300 mg L$^{-1}$ initial concentration of metal ions at optimized pH. The sample solutions were shaken slowly, and then the solutions of samples were collected at examined intervals of time for measurements. The contact time was from 2 to 24 h. The experimental kinetics data were fitted by two kinetics models: pseudo-first-order and pseudo-second-order. The equations of the adsorption isotherm and kinetic models are shown in Table 1.

### 3. RESULTS AND DISCUSSION

#### 3.1. Material Characterizations

FT-IR spectra of chitosan, Ch-g-PAN, Ch-g-Sch I, and Ch-g-Sch II are shown in Figure S1a,b,c, and f. The characteristic peaks of the saccharide structure (chitosan) appeared at 1149, 1063, 1024, and 893 cm$^{-1}$, and a very strong broad peak at 3352 cm$^{-1}$ corresponded to the stretching vibration of the $-\text{OH}$ groups, the extension vibration of $-\text{NH}_2$, and the intermolecular hydrogen bonds between the polysaccharide. For Ch-g-PAN, a peak appeared at around 2244 cm$^{-1}$ corresponding to the $-\text{CN}$ (nitrile) group. For Ch-g-Sch I and Ch-g-Sch II, peaks appeared at 1627 and 1454 cm$^{-1}$ corresponding to the imine group (N$\equiv\text{CH}$) and the (C$\equiv\text{C}$) of the aromatic ring, respectively, which confirm the Schiff base reaction. The special peak of salicylaldehyde also appeared at 3745 cm$^{-1}$ that corresponded to the stretching vibration of the $-\text{OH}$ group, which confirms the chemical modification of the Ch-g-PAN through Schiff base formation using salicylaldehyde, and the special peak of P-anisaldehyde appeared at 2848 cm$^{-1}$ that corresponded to the methoxy group ($-\text{OCH}_3$), which confirms the chemical modification of Ch-g-PAN through Schiff base formation using P-anisaldehyde.

![Langmuir plot for the adsorption of (a) Cr$^{3+}$ ions, (b) Cd$^{2+}$ ions, and (c) Cu$^{2+}$ ions onto the Ch-g-Sch I copolymer.](https://doi.org/10.1021/acsomega.2c03809)
X-ray diffraction of chitosan, Ch-g-PAN, Ch-g-Sch I, and Ch-g-Sch II is shown in Figure 2. The characteristic peaks of native chitosan at around $\theta = 11$ and $20^\circ$ showed the overlapped diffraction from chitosan’s crystal planes. For grafted chitosan, two peaks appeared at $\theta = 16.06$ and $29.04^\circ$; this difference in the crystalline structure of chitosan confirms the grafting of acrylonitrile onto chitosan. For the Ch-g-PAN Schiff base, it is clear that its crystalline structure was different than the parent Ch-g-PAN, where Ch-g-Sch I had peaks at $\theta = 16.6$ and $20.2^\circ$, while Ch-g-Sch II had a single peak at $\theta = 16.97^\circ$. Also, the crystallite size for chitosan and its graft (Ch-g-PAN) was 10.98 and 1.27 nm, respectively, while the crystallite size for Ch-g-Sch I and Ch-g-Sch II was 9.6 and 5.999 nm, respectively, which confirmed chitosan modification.

The scanning electron microscopic (SEM) images of chitosan, Ch-g-PAN, Ch-g-Sch I, and Ch-g-Sch II are shown in Figure 3. The images illustrated that the surface morphology of the Ch-g-Sch II copolymer is different from the grafted chitosan and native chitosan. The morphology of the native chitosan surface indicates that its surface is relatively homogeneous fibers without any pores, but after grafting, the surface becomes softer and more porous. Also, after Schiff base modification, the surface of Ch-g-Sch I becomes like accumulated layers with small distribution pores, and the surface of Ch-g-Sch II becomes like arranged layers with larger pores than Ch-g-Sch I. The nanoporous nature (higher surface area) and the self-assembly of fine nanoparticles (high hot spot density) are very crucial parameters that enhance Ch-g-Sch II capabilities toward the heavy metals.

The scanning electron microscopic (SEM) images of chitosan, Ch-g-PAN, Ch-g-Sch I, and Ch-g-Sch II are shown in Figure 3. The images illustrated that the surface morphology of the Ch-g-PAN Schiff base is different from the grafted chitosan and native chitosan. The morphology of the native chitosan surface indicates that its surface is relatively homogeneous fibers without any pores, but after grafting, the surface becomes softer and more porous. Also, after Schiff base modification, the surface of Ch-g-Sch I becomes like accumulated layers with small distribution pores, and the surface of Ch-g-Sch II becomes like arranged layers with larger pores than Ch-g-Sch I. The nanoporous nature (higher surface area) and the self-assembly of fine nanoparticles (high hot spot density) are very crucial parameters that enhance Ch-g-Sch II capabilities toward the heavy metals.

Table 2. Langmuir Isotherm Parameters and $C_{\text{max}}$ for Copper, Cadmium, and Chromium onto the Ch-g-Sch I and Ch-g-Sch II Copolymers

| Metal Ions | $K_L$ (dm$^3$ g$^{-1}$) | $b$ (dm$^3$ g$^{-1}$) | $C_{\text{max}}$ (mg g$^{-1}$) | $R^2$ |
|------------|----------------------|----------------------|----------------------|-----|
| Ch-g-Sch I | | | | |
| Cu$^{2+}$  | 1.311                | 0.0254               | 51.614               | 0.775 |
| Cd$^{2+}$  | 4.613                | 0.0251               | 183.784              | 0.935 |
| Cr$^{3+}$  | 1.385                | 0.0252               | 52.960               | 0.566 |
| Ch-g-Sch II | | | | |
| Cu$^{2+}$  | 8.563                | 0.0254               | 337.125              | 0.760 |
| Cd$^{2+}$  | 8.170                | 0.0253               | 322.924              | 0.752 |
| Cr$^{3+}$  | 2.472                | 0.0250               | 98.880               | 0.693 |

X-ray diffraction of chitosan, Ch-g-PAN, Ch-g-Sch I, and Ch-g-Sch II is shown in Figure 2. The characteristic peaks of native chitosan at around $2\theta = 11$ and $20^\circ$ showed the overlapped diffraction from chitosan’s crystal planes. For grafted chitosan, two peaks appeared at $2\theta = 16.06$ and $29.04^\circ$; this difference in the crystalline structure of chitosan confirms the grafting of acrylonitrile onto chitosan. For the Ch-g-PAN Schiff base, it is clear that its crystalline structure was different than the parent Ch-g-PAN, where Ch-g-Sch I had peaks at $2\theta = 16.6$ and $20.2^\circ$, while Ch-g-Sch II had a single peak at $2\theta = 16.97^\circ$. Also, the crystallite size for chitosan and its graft (Ch-g-PAN) was 10.98 and 1.27 nm, respectively, while the crystallite size for Ch-g-Sch I and Ch-g-Sch II was 9.6 and 5.999 nm, respectively, which confirmed chitosan modification. The scanning electron microscopic (SEM) images of chitosan, Ch-g-PAN, Ch-g-Sch I, and Ch-g-Sch II are shown in Figure 3. The images illustrated that the surface morphology of the Ch-g-PAN Schiff base is different from the grafted chitosan and native chitosan. The morphology of the native chitosan surface indicates that its surface is relatively homogeneous fibers without any pores, but after grafting, the surface becomes softer and more porous. Also, after Schiff base modification, the surface of Ch-g-Sch I becomes like accumulated layers with small distribution pores, and the surface of Ch-g-Sch II becomes like arranged layers with larger pores than Ch-g-Sch I. The nanoporous nature (higher surface area) and the self-assembly of fine nanoparticles (high hot spot density) are very crucial parameters that enhance Ch-g-Sch II capabilities toward the heavy metals.
Sch II higher than Ch-g-Sch I, obtained that the grafted chitosan Schiff base with P-anisaldehyde removed heavy metal ions more than with salicylaldehyde, also attributed to the methoxy group is more electron donating group than hydroxyl group, where the electron-donating group, as a substituent, showed a greater activity toward metal ions.

3.2. Adsorption Investigation. 3.2.1. Effect of pH. The adsorption efficacy of Ch-g-PAN Schiff base copolymers was affected by the pH of the solution. pH is the master parameter that had a vital impact on metal adsorption in the aquatic medium related to the metal speciation (charge of metal ions and the hydrolyzed species) and to the charged surface of the sorbent functional groups, of the physicochemical properties (as in protonation/deprotonation).

The pH of the solution was varied from 3 to 7. To examine the effect of pH on metal ion removal efficacy, the adsorption of Cu^{2+}, Cd^{2+}, and Cr^{3+} ions by Ch-g-Sch I and Ch-g-Sch II is presented in Figure 4. The pH of the solution has an influence on the charged surface of the adsorbents.\textsuperscript{37} It is acknowledged that metal species [M^{3+} = Cu^{3+}] existed in deionized water as M^{2+}, M(OH)\textsubscript{2}.\textsuperscript{38} By increasing the acidic pH of the solution, the level of metal ion uptake to the adsorbent increased.\textsuperscript{39} From Figure 3, it can be noticed that pH clearly affects the adsorption process of all metal ions. Better results were reached at pH \( \approx 5 \) for Cu^{2+}, Cd^{2+}, and Cr^{3+} metal ions. The increasing ion removal percent with increasing acidic pH media can be illustrated by considering a decrease in competition between the proton and metal cations for the same functional groups and a decrease in positive surface charge, which lead to less electrostatic repulsion between the surface and the metal ions.\textsuperscript{40} The maximum % removal by Ch-g-Sch I for Cu^{2+}, Cd^{2+}, and Cr^{3+} ions was about 83, 35, and 82%, respectively, at pH 5, while the removal percent by Ch-g-Sch I for Cu^{2+}, Cd^{2+}, and Cr^{3+} ions was about 44, 20, and 30%, respectively, at pH 7. The maximum % removal by Ch-g-Sch II for Cu^{2+}, Cd^{2+}, and Cr^{3+} ions was about 91, 83, and 86%, respectively, at pH 5, while the removal percent by Ch-g-Sch II for Cu^{2+}, Cd^{2+}, and Cr^{3+} ions was about 77, 66, and 79%, respectively, at pH 7.

3.2.2. Effect of the Initial Concentration. At a high level of metal ion concentration, the accessible sites of adsorption become fewer. This conduct is associated with the competitive diffusion process of the Cu^{2+}, Cd^{2+}, or Cr^{3+} ions through the microchannel and pores in Ch-g-Sch I and Ch-g-Sch II. This competitive diffusion will lock the inlet of a channel on the surface and keep the metal particles from passing profoundly inside the adsorbent; i.e., the adsorption happens at the surface.

Figure 7. Freundlich plot for the adsorption of (a) Cr^{3+} ions, (b) Cd^{2+} ions, and (c) Cu^{2+} ions onto the (Ch-g-Sch I) copolymer.
These findings show that energetically less suitable sites are formed by increasing metal ion concentration in the medium. These results are found to match with other studies.

The removal efficiency of Cu\(^{2+}\), Cd\(^{2+}\), or Cr\(^{3+}\) ions on Ch-g-Sch I and Ch-g-Sch II at different initial concentrations (300–900 mg L\(^{-1}\)) is shown in Figure S2. The results indicated that the removal percentage of Cu\(^{2+}\), Cd\(^{2+}\), and Cr\(^{3+}\) ions using the Ch-g-PAN Schiff base decreases as the initial concentration of Cu\(^{2+}\), Cd\(^{2+}\), or Cr\(^{3+}\) ions increases. For example, the maximum removal percent by Ch-g-Sch I on Cu\(^{2+}\), Cd\(^{2+}\), and Cr\(^{3+}\) ions is found to be 80, 60.8, and 72.2\%, respectively, at 300 mg L\(^{-1}\), while it is found to be 20.3, 17.8, and 19\%, respectively, at 900 mg L\(^{-1}\). Also, the maximum removal percent by Ch-g-Sch II on Cu\(^{2+}\), Cd\(^{2+}\), and Cr\(^{3+}\) is 89, 84, and 82\%, respectively, at 0.003 g L\(^{-1}\), while it is found to be 77, 50, and 66\%, respectively, at 900 mg L\(^{-1}\). On the other hand, comparing the removal percent between Ch-g-Sch I and Ch-g-Sch II, it is found that Ch-g-Sch II removed the heavy metal ions from the aqueous solution more than Ch-g-Sch I, and both removed Cu\(^{2+}\) metal ions more than Cr\(^{3+}\) and Cd\(^{2+}\) metal ions.

### 3.3. Adsorption Isotherm.

The adsorption efficiency process could be illustrated by the adsorption isotherm. Langmuir and Freundlich models are the most popular parameter models (Table 1) to explain the adsorption isotherms.

The Langmuir equation has been commonly used to provide the sorption equilibrium.\(^{55}\) The Langmuir adsorption is based on every adsorption site being identical and energetically equivalent (thermodynamically, each site can hold one adsorbate molecule). The Langmuir isotherm is the most widely used to describe monolayer sorption onto a surface with a

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Table 3. Freundlich Isotherm Parameters for Copper, Cadmium, and Chromium onto Ch-g-Sch I and Ch-g-Sch II Copolymers

| Metal ions | Freundlich parameters: Ch-g-Sch I | N | R\(^2\) |
|------------|-----------------------------------|---|--------|
| Cu\(^{2+}\) | K\(_f\) (mg g\(^{-1}\)) | 1.538 | 1.620 | 1.598 |
| Cd\(^{2+}\) | 0.751 | 1.076 | 0.999 |
| Cr\(^{3+}\) | 0.905 | 0.972 | 0.994 |

| Metal ions | Freundlich parameters: Ch-g-Sch II | N | R\(^2\) |
|------------|-----------------------------------|---|--------|
| Cu\(^{2+}\) | K\(_f\) (mg g\(^{-1}\)) | 3.677 | 3.676 | 3.612 |
| Cd\(^{2+}\) | 1.002 | 0.994 | 0.412 |
| Cr\(^{3+}\) | 0.999 | 0.996 | 0.906 |

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![Figure 8](https://example.com/f8.png)

Figure 8. Freundlich plot for the adsorption of (a) Cr\(^{3+}\) ions, (b) Cd\(^{2+}\) ions, and (c) Cu\(^{2+}\) ions onto the (Ch-g-Sch II) copolymer.
finite number of identical sites, and it is presumed that the uptake of metal ions takes place on a homogeneous surface. The linearity of the Langmuir isotherm facilitates the calculation of adsorption capacities and Langmuir constant.

The Langmuir plot ($C_{eq}/C_{ads}$ vs $C_{eq}$) for the adsorption of Cr$^{3+}$, Cd$^{2+}$, and Cu$^{2+}$ ions onto Ch-g-Sch I and Ch-g-Sch II copolymers yielded a straight line (see Figures 5 and 6), ensuring the applicable effect of the Langmuir adsorption isotherm. Table 2 shows the calculated results of the Langmuir isotherm constants and $C_{max}$. From the results, it is evident that the adsorption of Cr$^{3+}$, Cd$^{2+}$, and Cu$^{2+}$ onto Ch-g-Sch I and Ch-g-Sch II copolymers correlates well with the Langmuir equation under the concentration studies. Also, the $C_{max}$ value is greater for cadmium ion compared with other metal ions in the case of the Ch-g-Sch I copolymer, but the $C_{max}$ value is greater for copper ions compared with others metal ions in the case of the Ch-g-Sch II copolymer.

The Freundlich isotherm is commonly used to describe the adsorption characteristics of heterogeneous surface energies. It represents the initial surface adsorption followed by a condensation effect resulting from strong adsorbate−adsorbate interaction. The most widely used Freundlich isotherm, which is a nonlinear sorption model, may be written in the general form:

$$q_e = K_f C_0^{1/n}$$

Figure 9. Pseudo-first-order kinetic plot for the adsorption of Cr$^{3+}$ ions, Cd$^{2+}$ ions, and Cu$^{2+}$ ions onto (a) Ch-g-Sch I and (b) Ch-g-Sch I copolymers.

Figure 10. Pseudo-second-order kinetic plot for the adsorption of Cr$^{3+}$ ions, Cd$^{2+}$ ions, and Cu$^{2+}$ ions onto (a) Ch-g-Sch I and (b) Ch-g-Sch I copolymers.

Table 4. Pseudo-first-order ($k_1$) and Pseudo-second-order ($k_2$) Kinetics Rate Constants for Copper, Cadmium, and Chromium Ions onto Ch-g-Sch I and Ch-g-Sch II Copolymers

| Metal Ions | pseudo-first-order | pseudo-second-order |
|------------|--------------------|---------------------|
|            | $q_e$ (mg g$^{-1}$) | $k_1$ (h$^{-1}$)   | $R^2$  | $q_e$ (mg g$^{-1}$) | $k_2$ (g mg$^{-1}$ h$^{-1}$) | $R^2$ |
| Cr$^{3+}$  | 952 0.015 0.635 477 | 0.00036 0.992      |
| Cd$^{2+}$  | 82 0.059 0.533 559 | 0.00024 0.907      |
| Cu$^{2+}$  | 485 0.032 0.536 535 | 0.00013 0.849      |
The Freundlich plot for the adsorption of Cr\(^{3+}\), Cd\(^{2+}\), and Cu\(^{2+}\) ions onto Ch-g-Sch I and Ch-g-Sch II copolymers yielded a straight line (see Figures 7 and 8), and Freundlich isotherm parameters are listed in Table 3. In a comparison between \(R^2\) values of Langmuir and Freundlich isotherm models in both copolymers (Ch-g-Sch I and Ch-g-Sch II), the Freundlich adsorption model was best fitted with an experimental value that indicated multilayer more than monolayer adsorption. These results are found to match with other studies reported by AlOthman et al. (2013) and Naushad (2014)\(^{51,57}\).

### 3.4. Kinetics Studies

The adsorption efficacy of Ch-g-PAN Schiff base copolymers was affected by contact time (Figure S3), keeping the other parameters constant. The rise in the removal percent with the increase in contact time can be attributed to the fact that more time will be available for metal ions to make an attractive complex with Ch-g-Sch I and Ch-g-Sch II copolymers.\(^{51,58}\) In the beginning, the adsorbing process was slow, and then it accelerated hurriedly, achieved equilibrium and saturation, and gave a constant adsorption value. For that reason, the results illustrated that the maximum removal percent using Ch-g-Sch I on Cu\(^{2+}\), Cd\(^{2+}\), and Cr\(^{3+}\) was 56, 40, and 60%, respectively, after 24 h. Also, the maximum removal percent using Ch-g-Sch II on Cu\(^{2+}\), Cd\(^{2+}\), and Cr\(^{3+}\) was 77, 50, and 62%, respectively, after 24 h. The contact time effects to give more proved that Ch-g-Sch II most removal the heavy metal ions than Ch-g-Sch I.

Adsorption kinetics depends on the adsorbate–adsorbent interaction and system condition, which has been investigated for its suitability for an application in water pollution control. The kinetics of adsorption can be represented by two models: pseudo-first-order kinetic and pseudo-second-order kinetic models (Table 1).

The linear plots of \(\log(q_e - q_t)\) versus \(t\) and \((t/q_t)\) versus \(t\) are drawn for the pseudo-first-order and the pseudo-second-order models, respectively (Figures 9 and 10). The values of \(k_1\) can be determined from the slope of the linear plot of \(\log(q_e - q_t)\) versus \(t\), and \(k_2\) can be calculated from the slope of the linear plot \((t/q_t)\) versus \(t\). The values of \(k_1, k_2, q_e\), and the correlation coefficient \((R^2)\) obtained from the linear plots are shown in (Table 4).

A comparison between \(R^2\) values of the pseudo-first-order and the pseudo-second-order models in both copolymers (Ch-g-Sch I and Ch-g-Sch II) showed that the pseudo-second-order linear plots resulted in higher \(R^2\) values than the pseudo-first-order, except for the \(R^2\) value of Cu\(^{2+}\) ions onto the Ch-g-Sch I copolymer, where the \(R^2\) value of the pseudo-first-order was higher than the \(R^2\) value of the pseudo-second-order. But mostly, the pseudo-second-order was the best description model for the adsorption process.

#### 3.5. Ch-g-Sch II Adsorbent Recycling and Reusability

Ch-g-Sch II reusability was evaluated through 10 cycles, as presented in Figure 11. The adsorption performance of Cu\(^{2+}\) onto Ch-g-Sch II does not considerably differ (nearly 3%) up to the sixth cycle. This illustrates the high stability of Ch-g-Sch II and its ability to be reused for up to six cycles as shown in Figure 11.

#### 3.6. The Effect of Ionic Strength on Cr\(^{3+}\) Adsorption

As shown in Figure 12, we find that as the ionic strength of the solution increases, the adsorption decreases. This behavior was related to the charge of the adsorbent. The zeta potential obtained under different ionic strengths gave evidence to support the interpretation. The value of the zeta potential of prepared material indicated that the potential at the adsorption plane decreased with the increase in ionic strength, so the repulsion between partials decreased and the stability of the adsorbent decreased.

#### 3.7. Mechanism of Cu\(^{2+}\) Adsorption Using Ch-g-Sch II

The mechanism of the ability of Ch-g-Sch II for Cu\(^{2+}\) adsorption was illustrated via different ways, as follows:

First, for approving the adsorption of Cu\(^{2+}\) ions into the matrix of Ch-g-Sch II, there is a significant difference in the surface morphology of the prepared Ch-g-Sch II before (Figures 1d1 and 1d2) and after Cu\(^{2+}\) adsorption (Figure 13). When observing its surface morphology after Cu\(^{2+}\) adsorption, the material surface is clearly slightly rougher than that before Cu\(^{2+}\) adsorption. It appears as if there were stacked layers that were aggregated to roll on themselves as a result of metal adsorption. In addition, most of the pores that were present on the surface were filled up due to the adsorption of metal ions on these pores, which can confirm the effect of adsorption on the surface morphology. The Cu\(^{2+}\) adsorption onto Ch-g-Sch II is based on strong surface interactions (chelation, electrostatic forces, etc.) not only on diffusion phenomena into the matrix but also on the observed homogeneous distribution of Cu\(^{2+}\) on the surface of Ch-g-Sch II through EDX analysis. As can be seen from Figure 14, the distribution of Cu\(^{2+}\) on Ch-g-Sch II was uniform. There are traces of Cu\(^{2+}\), which confirm the interaction of metal ions with the active site of Ch-g-Sch II. Therefore, the particular phenomenon seems to be qualitatively, not quantitatively, interactive.\(^{59}\)

Second, the possible mechanism is also confirmed through the formation of coordination sites between imine groups of the grafted chitosan Schiff base and the heavy metal ions. Also, the
Figure 13. SEM of Ch-g-Sch II after Cu$^{2+}$ adsorption.

Figure 14. EDX analysis illustrates the distribution and existence of Cu$^{2+}$ on the surface of Ch-g-Sch II.
Figure 15. FTIR spectra of Ch-g-Sch I and Ch-g-Sch II after adsorption.

Table 5. Comparison of Maximum Adsorption Capacities for Other Chitosan-Based Adsorbents at Variable Process Parameters

| adsorbent                                                      | metal   | dose (g L\(^{-1}\)) | pH | time (h) | adsorption capacity (mg g\(^{-1}\)) | ref |
|----------------------------------------------------------------|---------|----------------------|----|----------|------------------------------------|-----|
| chitosan-g-poly(acrylic acid)-bentonite composite              | Cu\(^{2+}\)  | 0.01–2               | 6  | 24       | 88.5 mg g\(^{-1}\)                  | 64  |
| EGTA-chitosan                                                  | Cd\(^{2+}\) | 6                    |    |          | 51.5 mg g\(^{-1}\)                  |     |
| CTS-ECH-TPP                                                   | Cd\(^{2+}\) | 2.0                  | 4  | 24       | 83.1 mg g\(^{-1}\)                  | 65  |
| cross-linked chitosan graft acrylonitrile copolymer            | Cd\(^{2+}\) | 1.0                  | 6  | 30       | 130.7 mg g\(^{-1}\)                 | 66  |
| chitosan/sporopollenin microcapsules                          | Cu\(^{2+}\) | 6                    | 5.5| 2        | 1.3 mmol g\(^{-1}\)                 | 67  |
|                                                                  | Cd\(^{2+}\) | 5.5                  | 4  |          | 0.77 mmol g\(^{-1}\)                |     |
| cross-linked chitosan graft acrylonitrile copolymer            | Cr\(^{3+}\) | 4                    | 4  |          | 0.99 mmol g\(^{-1}\)                |     |
| CS/PAA-GLA                                                    | Cu\(^{2+}\) | 5                    |    |          | 119.9 mg g\(^{-1}\)                 | 68  |
| CS/PVAm                                                       | Cu\(^{2+}\) | 0.15                 | 4.5| 5        | 192.5 mg g\(^{-1}\)                 | 69  |
| CS/PVA/MWCNTNH2                                                | Cu\(^{2+}\) | 5.5                  | <4 |          | 20.1 mg g\(^{-1}\)                  | 70  |
| chitosan-modified MnFe\(_2\)O\(_4\) nanoparticles             | Cu\(^{2+}\) | 3.33                 | 6.5| 5        | 65.1 mg g\(^{-1}\)                  | 71  |
| Ch-g-Sch I                                                    | Cu\(^{2+}\) | 0.05                 | 5  | 24       | 51.6 mg g\(^{-1}\)                  |     |
|                                                                  | Cd\(^{2+}\) | 5                    |    |          | 183.7 mg g\(^{-1}\)                 |     |
| Ch-g-Sch II                                                   | Cr\(^{3+}\) | 5                    |    |          | 52.9 mg g\(^{-1}\)                  |     |
|                                                                  | Cu\(^{2+}\) | 0.05                 | 5  | 24       | 337.1 mg g\(^{-1}\)                 |     |
|                                                                  | Cd\(^{2+}\) | 5                    |    |          | 322.0 mg g\(^{-1}\)                 |     |
|                                                                  | Cr\(^{3+}\) | 5                    |    |          | 98.8 mg g\(^{-1}\)                  |     |

representative samples are shown in Figure15. We noted that there were a slight shift in the frequency of some peaks and also changes in the peak’s intensity due to the interaction between the adsorbent and the adsorbed metals, where the special peaks of Ch-g-Sch I/Cu\(^{2+}\) after adsorption become 1632, 1446, and 3407 cm\(^{-1}\), corresponding to the imine group (N=CH), the (C=C) of the aromatic ring, and the stretching vibration of the −OH group, respectively. Also, the special peaks of Ch-g-Sch II/Cr\(^{3+}\) after adsorption become 1635, 1447, and 2933 cm\(^{-1}\), corresponding to the imine group (N=CH), the (C=C) of the aromatic ring, and the methoxy group (−OCH\(_3\)), respectively. Also, the intermolecular hydrogen bonds between the saccharide units have a great effect on the physical and chemical properties of the material and also relate to the crystallinity degree, the crystal system regularity, and the amount of adsorbed water molecules bound.\(^{42,43}\) The hydrogen bond intensity was calculated as the ratio of the absorbance bands at 3735 and 3441 cm\(^{-1}\) (for the −OH stretching vibration) and 1627 and 1627 cm\(^{-1}\) (for the extension vibration of −NH) in Ch-g-Sch I and Ch-g-Sch II before metal adsorption, respectively. The ratio of the absorbance bands at 3407 and 2993 cm\(^{-1}\) (for the −OH stretching vibration) and 1632 and 1635 cm\(^{-1}\) (for the extension vibration of −NH) in Ch-g-Sch I/Cu\(^{2+}\) and Ch-g-Sch II/Cr\(^{3+}\) after metal adsorption. The obtained absorbance ratio illustrated decreases from 2.29 to 2.08 after metal adsorption in the case of Ch-g-Sch I/Cu\(^{2+}\) and from 2.11 to 1.83 in the case of Ch-g-Sch II/Cr\(^{3+}\). The decrease of hydrogen bond intensity is related to the replacement of hydrogen with metal ions and confirms the complex reaction mechanism.

Finally, we investigated the charge and the stability of the adsorbent before and after adsorption through measuring the zeta potential. The measured value of the zeta potential for Ch-g-Sch II was 13.50 mV before adsorption and 14.90 mV after adsorption of Cu\(^{2+}\) or Cr\(^{3+}\) metal ions as a specific effect on the formation of the complex and the coordination site that may increase or decrease the coordination capacity of the molecules.\(^{60}\) Thus, the methoxy groups in Ch-g-Sch II are the more electron-donating group than hydroxyl groups Ch-g-Sch I, where the electron-donating group, as a substituent, showed a greater activity toward metal ions.

The third tool for confirming is FTIR analysis, and FT-IR spectra after adsorption of Cu\(^{2+}\) or Cr\(^{3+}\) metal ions as a substituent, showed a greater activity toward metal ions.

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(dH) of the prepared material measured by DLS was 1780 and 1790 nm before and after adsorption, respectively. This observation is probably due to the interactions of the Cu²⁺ metal cations with the adsorbent.

A comparison of prepared materials with other adsorbents is shown in Table 5. To further investigate the significance of synthesized materials for wastewater remediation from heavy metal ions, the maximum adsorption capacity of metal ions on these synthesized materials is carefully compared with those on other adsorbents. By considering the high adsorption capacity, it seems that the as-prepared materials can be potentially used for the cost-effective adsorbents for Cu²⁺, Cd²⁺, and Cr³⁺ metal ion polluted aquatic systems.

Finally, the observed values of adsorption capacity of our study are more significant than those previously obtained for many polymer grafted chitosan adsorbents, as shown in Table 5. This result confirmed that the Ch-g-Sch I and Ch-g-Sch II adsorbents are effective materials for water remediation.

4. CONCLUSIONS
The FT-IR results confirmed that the chitosan-g-PAN copolymer and its Schiff base derivatives (Ch-g-Sch I and Ch-g-Sch II) were successfully synthesized. X-ray diffraction showed changes in the crystallinity of Ch-g-PAN and its Schiff base derivatives (Ch-g-Sch I and Ch-g-Sch II) compared to chitosan. Also, scanning electron microscopy showed changes in the surface morphology of Ch-g-PAN and its Schiff base derivatives compared to chitosan. Investigations have been done to evaluate the capacity of Ch-g-Sch I and Ch-g-Sch II copolymers to adsorb Cr³⁺, Cd²⁺, and Cu²⁺ ions. The observed outcomes indicated that the change of initial concentration, pH, and contact time had a pronounced effect on the removal of metal ions from aqueous solutions and that the adsorption capacity for the metals on Ch-g-Sch I and Ch-g-Sch II copolymers follows the sequence Cu²⁺ > Cd²⁺ > Cr³⁺. Both monolayer and multilayer adsorptions of heavy metal ions were proven by conducting adsorption studies of Ch-g-Sch I and Ch-g-Sch II copolymers by adsorption isotherms (Freundlich and Langmuir isotherms). In addition, the adsorption processes on Ch-g-Sch I and Ch-g-Sch II copolymers were fitted with pseudo-second-order. In addition, the mechanism of Cu²⁺ adsorption using Ch-g-Sch II was illustrated in different ways. Finally, the formed copolymers were acclimated for the remediation of abundant metal ions in the wastewater (Scheme 1).

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03809.

FTIR of different polymer samples (chitosan, Ch-g-PAN, Ch-g-Sch I, and Ch-g-Sch I-Cu) and grafted chitosan Schiff base in addition to the effect of the initial concentration of Cr³⁺, Cd²⁺, and Cu²⁺ ions and effect of contact time on the adsorption of Cr³⁺, Cd²⁺, and Cu²⁺ ions (PDF)

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ABBREVIATIONS
Ch, chitosan; Ch-g-PAN, chitosan-graft-polyacrylonitrile; Ch-g-Sch I, grafted chitosan Schiff base using salicylaldehyde; Ch-g-Sch II, grafted chitosan Schiff base using P-anisaldehyde; Q, the adsorptivity (%); Ceq, the initial concentration of ions; Ce, the ion concentration in (mg/L) after adsorption at the time t (h); Cads, the amount of metal ions adsorbed (mg g⁻¹); Ceq, the equilibrium concentration of metal ion in solution (mg dm⁻³); Kf, the Langmuir constant (dm³ g⁻¹); B, the Langmuir constant (dm³ g⁻¹); Cads, the maximum metal ion to adsorb onto 1 g of adsorbent (mg g⁻¹); Ceq, the equilibrium concentration of adsorbate in the solution after adsorption (mg dm⁻³); Kd, the empirical Freundlich constant or capacity factor (mg g⁻¹); 1/n, the Freundlich exponent; qe, the adsorption capacity (mg g⁻¹) of the adsorbent at equilibrium; qd, the adsorption capacity (mg g⁻¹) of the adsorbent at time t; k₁ (h⁻¹), the pseudo-first-order rate constant; k₂ (g mg⁻¹ h⁻¹), the pseudo-second-order rate constant.

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