Research Article

Graphene Oxide/Polyvinyl Alcohol/Fe₃O₄ Nanocomposite: An Efficient Adsorbent for Co(II) Ion Removal

Thu Dieu Le, Luyen Thi Tran, Hue Thi Minh Dang, Thi Thu Huyen Tran, and Hoang Vinh Tran

School of Chemical Engineering, Hanoi University of Science and Technology, 1 Dai Co Viet Road, Hanoi, Vietnam

Correspondence should be addressed to Hoang Vinh Tran; hoang.tranvinh@hust.edu.vn

Received 19 December 2020; Revised 3 February 2021; Accepted 26 February 2021; Published 9 March 2021

In this work, an effective nanocomposite-based adsorbent directed to adsorb cobalt (Co²⁺) ion was successfully synthesized from graphene oxide (GO), polyvinyl alcohol (PVA), and magnetite (Fe₃O₄) nanoparticles via a coprecipitation technique. The synthesized GO/PVA/Fe₃O₄ nanocomposite was applied for Co²⁺ ion removal with the optimized working conditions including 100 min of contact time, 0.01 g of adsorbent dosage, pH of 5.2, and 50°C of temperature. The investigation of adsorption kinetics showed that the adsorption of Co²⁺ ion onto the GO/PVA/Fe₃O₄ nanocomposite followed the pseudo-second-order kinetic model with the rate constant $k_2$ being 0.0026 (g mg⁻¹ min⁻¹). The Langmuir model is suitable to describe the adsorption of Co²⁺ ion onto the GO/PVA/Fe₃O₄ nanocomposite with the maximum sorption capacity ($q_{max}$) reaching 373.37 mg g⁻¹. The obtained results also indicated that the GO/PVA/Fe₃O₄ nanocomposite can adsorb/regenerate for at least 5 cycles with a little reduction in removal efficiency. Therefore, we believe that the GO/PVA/Fe₃O₄ nanocomposite could be used as a potential adsorbent for heavy metal treatment in terms of high adsorption capacity, fast adsorption rate, and recyclability.

1. Introduction

Nowadays, electronic devices are becoming more and more common in our life, in which rechargeable batteries are an indispensable item in every family and for every individual. However, the reality indicates that the manufacturing of rechargeable batteries, electrodes, gas turbine engines, hard permanent magnets etc. use a huge amount of cobalt (Co) and discharge a lot of cobalt ions (Co²⁺) into the environment. Inhalation of Co dust may cause adverse respiratory effects, also causing neurological symptoms and cancer in human beings with unknown mechanism [1–3]. Therefore, there are many kinds of technologies to reduce the concentration of Co²⁺ in water pollutants, such as nanofiltration, adsorption, and ion exchange, in which the adsorption process is the best choice because it is cheap and suitable to adapt with a vast range of working conditions to remove Co²⁺ ion from aqueous solutions [4–10]. In order to improve the adsorption efficiency, some advanced nanomaterials have been applied for enhancing the specific surface area of the adsorbent which favors adsorption using carbon nanotubes (CNTs) [11–13], activated carbon [14, 15], graphite [16], graphene oxide (GO) [17], or reduced graphene oxide [18]. These nanomaterials have many functional groups on the surface such as −COOH, −OH, and C=O which can be used as an electron-trapping site to attract metal ions or organic materials [11–14, 17]. Recently, GO is widely applied as an adsorbent directed to adsorb heavy metal ions from water because GO has a large surface area (which can be up to 2630 m² g⁻¹) and high water solubility [19–22]. In addition, GO has abundant oxygen-based groups on its surface such as hydroxyl, carboxylic, carbonyl, and epoxide groups, making GO a material of great interest in adsorption-based technologies of water treatment. GO adsorbents with excellent maximum adsorption capacity ($q_{max}$) were reported, such as $q_{max} = 198$ mg g⁻¹ for adsorption of Cr(VI) ion [23] and the $q_{max} = 46.6$ mg g⁻¹ for adsorption of Cu(II) ion [24]. However, GO is a nano/micromaterial and it has very low density; therefore, it is difficult to remove GO out of the water after adsorption.
processes. The hybrids of graphene with magnetic nanomaterials such as Fe₃O₄ nanoparticles have been used to solve the above problem. Fe₃O₄ is usually used for water purification due to its safety; in addition, the Fe₃O₄ is also used to generate magnetic properties for the adsorbent, which makes it easy to be collected after treatment by using an external magnet bar. Yao et al. [25] reported the use of GO/chitosan/Fe₃O₄ nanocomposite as a adsorbent for the removal of Co²⁺ ion. The black precipitate of Fe₃O₄ will be obtained. If the Fe₃O₄ is dispersed well, they are mixed with a mixture of Fe₃O₄ colloid, stirred for 10 minutes and filtered, washed many times with distilled water, and finally dried in an oven at 40°C for 1 day.

2.4. Batch Adsorption Experiments for Co²⁺ Ion Removal. 0.0406 g of CoCl₂·6H₂O was dissolved in 100 mL distilled water to obtain the stock solution of Co²⁺ ion (100 mg·L⁻¹). The stock solution was diluted to the desired solution. 0.01 g of GO/PVA/Fe₃O₄ nanocomposite as an adsorbent was added into 20 mL of the solution containing Co²⁺ ion; then, the mixtures were agitated at 30°C and pH 7 for 100 min. The residue Co²⁺ ion concentration in the solution was analysed by the spectrophotometric method (described in Section 3.5). The adsorption capacity, q (mg·g⁻¹), and the percentage removal (H, %) were calculated by the following equations:

\[
q = \frac{(C_0 - C_E) \cdot V}{m} \quad (\text{mg} \cdot \text{g}^{-1}),
\]

\[
H = \left(1 - \frac{C_E}{C_0}\right) \cdot 100\% \quad (\%),
\]

where \(C_0\) and \(C_E\) are the initial and equilibrium concentrations of Co²⁺ solution (mg·L⁻¹), respectively; \(C_0\) is the Co²⁺ ion concentration at time \(t\); \(V\) is the volume of the sample solution used for the experiment (ml); and \(m\) is the weight of the adsorbent (g). The adsorption of Co²⁺ ion onto GO/PVA/Fe₃O₄ was studied as a function of contact time, mass of adsorbent influent, pH of the solution, and temperature.

The used GO/PVA@Fe₃O₄ adsorbent was recovered by immersing it into 0.1 N NaOH solution for 1 day, and then, it was rinsed with distilled water and dried at 40°C in an oven for 12 h to obtain the regenerated GO/PVA@Fe₃O₄ adsorbent, which was reused to adsorb Co²⁺ ion.

2.5. Determination of Co²⁺ Ion Concentration. The Co²⁺ ion concentration after adsorption process is determined by the spectrophotometric method with the aid of many complexing reagents, which had been developed recently to monitor Co²⁺ concentration, with fast response, high sensitivity, and easy preparation compared to other methods. The common complexing reagents used include ninhydrin (optimum pH is 8.2; the complex is stable in 30 min) [30], 2-benzoylpyridine-4-phenyl-3-thiosemicarbazone [31], 2-pyridine carboxaldehyde isonicotinyl hydrazine (pH 9; the apparent molar adsorptivity is 7.1.10⁴ L·mol⁻¹·cm⁻¹) [32], dehydroacetic acid oxime (pH 5.8) [33], and 5-[3-(1,2,4-triazolyl-azo]-2,4-dihydroxybenzaldehyde [34]. In our work, we used NH₄SCN as a ligand in acetone solution and we have discovered that it can be stable up to more than 7 days. A typical procedure is followed: 1 ml of 18% HCl solution is added into 10 ml of residue solution at RT. Then, 0.5 ml of NH₄SCN saturated solution is added into the above mixture and the solution is mixed well. After that, 20 ml of concentrated acetone is added into this mixture and the solution will change from pink color to blue color in the following reaction:
CoCl₂ + 4NH₄SCN → (NH₄)₂[Co(SCN)₄] + 2NH₄Cl
(pink color) (blue color)

(2)

The absorbance of the mixture is then measured with an Agilent 8453 UV-Vis spectrophotometer, and the calibration curve is obtained (Figure S1). Each sample was measured in duplicate.

2.6. Characterizations.

XRD patterns of GO and GO/PVA/Fe₃O₄ were obtained on D8 Advance, Brucker AXS, operated at CuKα wavelength of 1.542 A in the range of 2θ = 5 to 70° at the room temperature. UV-Vis spectra were measured with an Agilent 8453 UV-Vis spectrophotometer system. The fractal surfaces of GO and GO/PVA/Fe₃O₄ were observed using a Hitachi S4500 Scanning Electron Microscope (SEM). The infrared (IR) spectra were recorded on a Nicolet FT-IR Spectrometer model 205 with KBr pellets in the region from 500 cm⁻¹ to 4000 cm⁻¹. Specific surface area and pore size distribution of the prepared GO/PVA/Fe₃O₄ sample were evaluated using low-temperature nitrogen adsorption isotherm by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods on the Tristar II plus System (Micromeritics, USA).

3. Results and Discussion

3.1. Characterization of the GO/PVA/Fe₃O₄ Nanocomposite.

The XRD patterns of GO and GO/PVA/Fe₃O₄ (Figure 1(a)) show a diffraction peak at 2θ = 10°, which is assigned to the crystalline of GO (curve A) with (001) reflection indicating that the oxygen functionality existence increases the distance between graphene layers. Using Bragg’s Law and Scherrer equation for this sharp peak, it is revealed that the interlayer space is about 0.885 nm and the number of layers in GO is 5. In case of GO/PVA/Fe₃O₄ (curve b), this peak disappears due to a very low content of GO in the sample; however, the characteristic peaks of Fe₃O₄ clearly appeared at 2θ = 30°, 35°, 57°, and 63° corresponding to the reflection of (220), (311), (511), and (440), respectively.

The FT-IR spectrum of GO/PVA/Fe₃O₄ (Figure 1(b), curve C) shows the band at 3221 cm⁻¹, which denotes to the O-H stretching of physisorbed water. The band at 2902 cm⁻¹ attributed to the C-H stretching vibration, and the characteristic peaks ascribed to C-OH groups (1413 cm⁻¹ and 1078 cm⁻¹) in PVA were found in both the FT-IR spectrum of PVA and GO/PVA/Fe₃O₄ (Figure 1(b), curve B and curve C, respectively) confirming the presence of PVA in the GO/PVA/Fe₃O₄ samples. A peak at 542 cm⁻¹ is attributed to the Fe-O group of Fe₃O₄ in GO/PVA/Fe₃O₄ samples (curve C), indicating that Fe₃O₄ is linked successfully to the GO and PVA. SEM images of GO (Figures 1(c) and 1(e)) show that the GO materials are arranged in sheets. SEM images of the GO/PVA/Fe₃O₄ adsorbent (Figures 1(d) and 1(f)) show an appearance of spherical particles with a size of about 15–20 nm, deposited on the GO sheets, nearly covering all the surface of GO sheets, making it difficult to see the GO sheets. It can be seen the Fe₃O₄ nanoparticles were well distributed on the GO sheets (Figure 1(f)); these Fe₃O₄ nanoparticles contribute to making the magnetic property recover the GO/PVA/Fe₃O₄ adsorbent from the solution after the adsorption process by using an external magnet. The hysteresis loop of the nitrogen adsorption-desorption isotherm of the GO/PVA/Fe₃O₄ nanocomposite (Figure 1(g)) exhibits type IVa hysteresis loops by IUPAC, which is specific to mesoporous materials with a pore width range from 4 to 50 nm [35]. The BJH pore size distribution of GO/PVA/Fe₃O₄ sample (Figure 1(h)) shows the main pore diameters to be less than 7 nm, which is in agreement with the shape of the hysteresis loop above (Figure 1(g)). The BET specific surface area and BJH average pore width of the synthesized GO/PVA/Fe₃O₄ sample is summarized in Table 1.

3.2. Optimization Conditions for Co²⁺ Ion Adsorption onto GO/PVA/Fe₃O₄ Nanocomposite.

Figure 2(a) shows that Co²⁺ ion adsorption capacity increased rapidly when contact time was from 3 to 100 minutes, with about 60% of the Co²⁺ removed, and thereafter, the adsorption capacity has a constant trend. The rapid uptake within 100 min was due to the large surface area, the presence of various oxygen functional groups of GO, and PVA that creates an electrostatic interaction with Co²⁺ ion. After that, the adsorption sites of the adsorbent were filled with Co²⁺ ions so the rate of adsorption becomes constant. The contact time here longer than that in other reported materials [36] can be attributed to higher of Co²⁺ initial concentration and lower used adsorbent dose (100 mg·L⁻¹, m = 0.01 g) as well. The influence of adsorbent dosage was evaluated by changing the mass of GO/PVA/Fe₃O₄ adsorbent from 0.0123 g to 0.034 g for treatment of 20 mL of Co²⁺ solution, and the obtained results show that with the increasing mass of the adsorbent, the adsorption capacity decreases and the optimal amount of absorbent is 0.0123 g with an adsorption capacity qₑ of 17.63 mg·g⁻¹ (Figure 2(b)). Figure 2(c) reveals that the qₑ increased with the increase in temperature, which suggested that the adsorption of Co²⁺ ion onto the GO/PVA/Fe₃O₄ adsorbent may be favored by high temperature and therefore the optimal temperature for this process was selected at 50 °C.

The influence of pH on the adsorption process was evaluated with pH change from pH 2 to pH 7 because at higher pH (pH > 7), Co²⁺ ion can be agglomerated as a Co(OH)₂ precipitate [37,38]. As shown in Figure 2(d), Co²⁺ ion removal was 61.7% with a qₑ of 121 mg·g⁻¹ at pH 2 (curve A) and the removal was about 64.0% with a qₑ of 127.3 mg·g⁻¹ at pH 5.2 (curve B), and the UV-Vis spectra at equilibrium time are shown in Figure S2. The obtained results can explain that the high concentration of H⁺ ion (at low pH value) led to the competition between positive charge ions to attach with negative charge oxygen functional groups on GO and PVA. Meanwhile, at higher pH, the concentration of H⁺ ions decreases so there is less competition, and the result is the adsorption increase. Therefore, the optimal pH for adsorption Co²⁺ ion onto GO/PVA/Fe₃O₄ was pH 5.2. Effect of K⁺ ion as an interference to the adsorption of Co²⁺ onto GO/PVA/Fe₃O₄ was also tested (Table 2). Results show that the presence of K⁺ ion did not...
Figure 1: (a) XRD patterns of GO (A) and GO/PVA/Fe₃O₄ (B) sample; (b) FT-IR of GO (A), PVA (B), and GO/PVA/Fe₃O₄ (C); (c–f) SEM images with different magnifications of (c, e) GO and (d, f) GO/PVA/Fe₃O₄, respectively; nitrogen (N₂) adsorption-desorption isotherm (g) and BJH pore size distribution (h) of the as-synthesized GO/PVA/Fe₃O₄ sample.
interfere with the adsorption efficiency of Co$^{2+}$ ion, even when the concentration of interfering K$^+$ ion was 10–80 times higher than the Co$^{2+}$ ion concentration, which is completely consistent with the previous report [39].

### Table 1: BET surface area analysis of as-synthesized GO/PVA/Fe$_3$O$_4$ sample.

| Surface area (m$^2$·g$^{-1}$) | Langmuir surface area | BET surface area | BJH pore area | BJH pore volume (cm$^3$·g$^{-1}$) | BJH average pore width (nm) |
|-----------------------------|-----------------------|-----------------|---------------|----------------------------------|-----------------------------|
| 122.328 ± 3.367            | 82.071 ± 0.163        | 97.218          | 0.137 ± 0.144 | 5.931 ± 6.725                   |

![Graphs and tables](image)

**Figure 2:** Optimization conditions for adsorption Co$^{2+}$ ion onto GO/PVA/Fe$_3$O$_4$ nanocomposite: (a) effect of contact time, (b) effect of the adsorbent dosage: (A) 0.03 g; (B) 0.02 g; (C) 0.01 g, respectively, (c) effect of temperature, and (d) effect of pH: (A) pH 2 and (B) pH 5.2 (inserted image: % removal of samples vs. pH).

### Table 2: The effect of K$^+$ as an interfering ion to the adsorption of Co$^{2+}$ ion onto GO/PVA/Fe$_3$O$_4$ nanocomposite$^\star$.

| Interfering ion | Fold ratio | Adsorption efficiency (%) |
|-----------------|------------|---------------------------|
| K$^+$           | 10         | 63.7                      |
| K$^+$           | 20         | 61.9                      |
| K$^+$           | 50         | 62.3                      |
| K$^+$           | 80         | 63.0                      |

$^\star$Experimental conditions: C$_{0}$ = 100 mg·g$^{-1}$, pH = 5.2, $T$ = 25°C, and $m_{adsorbent}$ = 0.01 g.

3.3. The Kinetics of Co$^{2+}$ Ion Adsorption onto GO/PVA/Fe$_3$O$_4$ Nanoadsorbent. In this work, two kinetic models including the pseudo-first-order and the pseudo-second-order
kinetic models were analysed, which can be represented as follows:

\[
\ln (q_e - q_t) = \ln q_e - k_1 t, \\
\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}
\]

where \(q_e\) is the adsorption capacity at equilibrium, \(q_t\) is the adsorption capacity at time \(t\) (min), and \(k_1\) is the pseudo-first-order rate constant of adsorption (min\(^{-1}\)), and \(k_2\) is the pseudo-second-order rate constant of adsorption (g·mg\(^{-1}\)·min\(^{-1}\)). As proved in the previous study [40], equation (2) can be written as follows:

\[
\ln \frac{C_t}{C_0} = \ln \left( \frac{A_t - A_e}{A_i - A_0} \right) = -k_1 \cdot t,
\]

where \(C_0\) and \(C_t\) are the initial concentration and concentration of Co\(^{2+}\) ion in solution, respectively, \(A_0\) and \(A_e\) are the initial and equilibrium absorbance; \(k_1\) was calculated from the slope of the plot of \(\ln (A_t - A_e)\) vs. \(t\) (Figure 3(a)); and \(k_2\) was calculated from the slope of the plot of \(t/q_t\) vs. \(t\) (Figure 3(b)). Based on comparison of the correlation coefficient \((R^2)\) of two plots, it can be seen that the adsorption of Co\(^{2+}\) ion onto the GO/PVA/Fe\(_3\)O\(_4\) adsorbent was fitted to the pseudo-second-order kinetic model than the pseudo-first-order kinetic model. The rate constant \(k_2\) was fitted at 0.0026 g·mg\(^{-1}\)·min\(^{-1}\).

3.4. Investigation of the Thermodynamic Parameters of the Adsorption Process. The thermodynamic parameters of the adsorption process such as enthalpy change \((\Delta H^0)\), entropy change \((\Delta S^0)\), and Gibbs free enthalpy change \((\Delta G^0)\) of reaction are calculated following the second law of thermodynamics, which have been described by the following equations:

\[
\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 = -R \cdot T \cdot \ln K_c,
\]

\[
K_c = \frac{q_e}{C_e},
\]

\[
\ln K_c = \frac{-\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R},
\]

where \(R\) is the gas constant \((R = 8.314 \text{ J·mol}^{-1}·\text{K}^{-1})\), \(K_c\) is the equilibrium constant of chemical reaction, and \(T\) is the absolute temperature \((K)\). \(\Delta H^0\) and \(\Delta S^0\) can be calculated from the slope and the intercept on the plot of \(\ln K_c\) vs. \(1/T\) following equation (4) and the obtained results are given in Table 3. The negative value of \(\Delta G^0\) indicates that the process is spontaneous for all evaluated temperatures. The positive value of \(\Delta H^0\) confirms that the adsorption is endothermic and favors at high temperature. The positive value of \(\Delta S^0\) shows the increase in the randomness of the adsorption on GO/PVA/Fe\(_3\)O\(_4\) for Co\(^{2+}\) ion.

3.5. Adsorption Isotherm. The Langmuir model (equation (5)) assumes a monolayer adsorption onto the homogeneous surface, and there is no transmigration of adsorbate on the surface plane. Meanwhile, the Freundlich model assumes a multilayer adsorption onto the heterogeneous surface (equation (5)).

\[
\frac{C_e}{q_e} = \frac{1}{(K_L \cdot q_{max})} + \frac{1}{q_{max}} \cdot C_e,
\]

\[
\lg q_e = \lg K_F + \frac{1}{n} \cdot \lg C_e,
\]
where \( q_{\text{max}} \) (mg·g\(^{-1}\)) is the maximum adsorption capacity of Co\(^{2+}\) ion onto the GO/PVA/Fe\(_3\)O\(_4\) adsorbent; \( K_L \) and \( K_F \) are the Langmuir constant and Freundlich constant, respectively; and \( n \) is a constant. Experimental results following the Langmuir and Freundlich adsorption isotherms are shown in Figure 4, and the fitting of the Langmuir and Freundlich constants is given in Table 4. It can be seen that, with the higher correlation coefficient, the Langmuir model fitted well for the adsorption of Co\(^{2+}\) ion onto GO/PVA/Fe\(_3\)O\(_4\) (Table 4). The maximum monolayer adsorption capacity \( q_{\text{max}} \) is 370.37 mg·g\(^{-1}\) and \( K_L \) is 0.0122. Compared to the other adsorbents in the literature for Co\(^{2+}\) ion removal (Table 5), the obtained result in our work is so high and impressive, which can be attributed to a very large surface area of GO, facilitating the adsorption process.

### Table 3: Thermodynamic parameters of the adsorption Co\(^{2+}\) ion on GO/PVA/Fe\(_3\)O\(_4\).

| \( \Delta G^0 \) (kJ·mol\(^{-1}\)) | \( \Delta H^0 \) (kJ·mol\(^{-1}\)) | \( \Delta S^0 \) (J·mol\(^{-1}\)·K\(^{-1}\)) |
|---|---|---|
| 298 K | 303 K | 313 K | 323 K |
| -9.8 | -10.07 | -10.06 | -12.38 |
| 22.04 | | | 106.47 |

### Table 4: The Langmuir and Freundlich isotherm parameters.

| Langmuir isotherm | Freundlich isotherm |
|---|---|
| \( q_{\text{max}} \) (mg·g\(^{-1}\)) | \( K_L \) | \( R^2 \) | \( K_F \) | \( N \) | \( R^2 \) |
| 370.37 | 0.0122 | 0.9993 | 15.8767 | 0.5485 | 0.9935 |

### Table 5: Comparison of various adsorbents for Co\(^{2+}\) ion removal.

| Adsorbent materials | \( q_{\text{max}} \) (mg·g\(^{-1}\)) | Ref. |
|---|---|---|
| Palygorskite | 8.88 | [41] |
| Lignocellulose/montmorillonite | 93.43 | [42] |
| Fe\(_3\)O\(_4\)/bentonite | 18.76 | [43] |
| Hydroxypatite | 22.50 | [44] |
| GO/PVA/Fe\(_3\)O\(_4\) | 370.37 | This work |

3.6. Recordation and Regeneration Studies. SEM images of GO/PVA/Fe\(_3\)O\(_4\) adsorbent before (Figure 5(a)) and after Co\(^{2+}\) adsorption process (Figure 5(b)) are not significantly different excepting several clusters of particles appearing on the surface of adsorbent after the adsorption process, and the surface of the GO/PVA/Fe\(_3\)O\(_4\) adsorbent after adsorption process is less porous than that before. These observations can be attributed to the presence of adsorbed Co\(^{2+}\) ion onto the GO/PVA/Fe\(_3\)O\(_4\) surface, which was confirmed by the EDS analyses. It can be seen that there was no cobalt element (0 wt.%) on the EDS spectrum of GO/PVA/Fe\(_3\)O\(_4\) before adsorption (Figure 5(c)); meanwhile, with the sample after Co\(^{2+}\) ion adsorption, the cobalt element reached 4 wt.% (Figure 5(d)), in which Co\(^{2+}\) ions were adsorbed onto the GO/PVA/Fe\(_3\)O\(_4\) adsorbent.

As shown in Figure S3, the regenerated GO/PVA/Fe\(_3\)O\(_4\) adsorbent can adsorb Co\(^{2+}\) ion with only a small decrease in adsorption capacity between the 1st cycle and the 5th cycle. The remaining adsorption efficiency of the 5th cycle was about 86% of the 1st cycle (Figure S3), which implies that the GO/PVA/Fe\(_3\)O\(_4\) material has a good stability and a high
degree of regeneration to use as an excellent adsorbent for removal of Co\textsuperscript{2+} ion in aqueous solution.

4. Conclusion

As described in this study, GO/PVA/Fe\textsubscript{3}O\textsubscript{4} nanocomposite as an effective adsorbent has been simply synthesized via a coprecipitation technique and it was directed to capture Co\textsuperscript{2+} ions from an aqueous solution via an adsorption process. The adsorption process of Co\textsuperscript{2+} ion onto the GO/PVA/Fe\textsubscript{3}O\textsubscript{4} adsorbent was evaluated by studying the effects of adsorbent dose, the solution pH, and temperature. At optimized adsorption conditions, this process followed the pseudo-second-order kinetic model and the adsorption isotherm was fitted to the Langmuir model with the maximum adsorption capacity to Co\textsuperscript{2+} ion estimated at 370.37 mg·g\textsuperscript{-1}. The GO/PVA/Fe\textsubscript{3}O\textsubscript{4} adsorbent can be regenerated for at least 5 cycles with the remaining adsorption efficiency after the 5th cycle being 86% compared to the first cycle. These findings indicate that the GO/PVA/Fe\textsubscript{3}O\textsubscript{4} nanocomposite can be considered as a good candidate for the removal of Co\textsuperscript{2+} ion from aqueous solutions.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was supported by the Ministry of Education Project, under code number B2020-BKA-15.

Supplementary Materials

Figure S1(a) UV-Vis spectra of various concentrations of Co\textsuperscript{2+} solution and (b) the calibration curve for Co\textsuperscript{2+} concentration measurement. Figure S2The UV-Vis spectra of samples at different pH values vs. equilibrium time: (i) pH 2 and (ii) pH 5.2. Experimental conditions: adsorbent dose 0.01 g, initial concentration of Co\textsuperscript{2+} ion 100 mg·L\textsuperscript{-1}, and temperature 25°C. Figure S3GO/PVA/Fe\textsubscript{3}O\textsubscript{4} regeneration results. Conditions: adsorbent dose 0.01 g, initial
concentration of Co²⁺ ions 100 mg L⁻¹, temperature 25°C, and pH = 5.2. (Supplementary Materials)

References

[1] F. Zheng, Z. Luo, C. Zheng et al., “Comparison of the neurotoxicity associated with cobalt nanoparticles and cobalt chloride in Wistar rats,” Toxicology and Applied Pharmacology, vol. 369, pp. 90–99, 2019.

[2] M. Abbass, M. Adil, S. Ehtisham-ul-Haque et al., “Vibrio fischeri bioluminescence inhibition assay for ecotoxicity assessment: a review,” Science of The Total Environment, vol. 626, pp. 1295–1309, 2018.

[3] M. Iqbal, “Vicia faba bioassay for environmental toxicity monitoring: a review,” Chemosphere, vol. 144, pp. 785–802, 2016.

[4] A. E. Burakov, E. V. Galunin, I. V. Burakova et al., “Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: a review,” Ecotoxicology and Environmental Safety, vol. 148, pp. 702–712, 2018.

[5] A. Awwand, M. Amer, and M. Al-aqarbeh, “TiO₂-Kaolinite nano composite prepared from the Jordanian kaolin clay: adsorption and thermodynamics of Pb(II) and Cd(II) ions in aqueous solution,” Chemistry International, vol. 6, pp. 168–178, 2020.

[6] A. Kanwal, H. N. Bhatti, M. Iqbal, and S. Noreen, “Basic dye adsorption onto clay/MnFe₂O₄ composite: a mechanistic study,” Water Environment Research, vol. 89, no. 4, pp. 301–311, 2017.

[7] G. Sharma and M. Naushad, “Adsorptive removal of noxious cadmium ions from aqueous medium using activated carbon/zirconium oxide composite: isotherm and kinetic modelling,” Journal of Molecular Liquids, vol. 310, 2020.

[8] M. Naushad, “Surfactant assisted nano-composite cation exchanger: development, characterization and applications for the removal of toxic Pb²⁺ from aqueous medium,” Chemical Engineering Journal, vol. 235, pp. 100–108, 2014.

[9] M. Naushad, A. Mittal, M. Rathore, and V. Gupta, “Ion-exchange kinetic studies for Cd(II), Co(II), Cu(II), and Pb(II) metal ions over a composite cation exchanger,” Desalination and Water Treatment, vol. 54, no. 10, pp. 2883–2890, 2015.

[10] S. M. Shaheen, J. Rinklebe, T. Frohne, J. R. White, and R. D. DeLaune, “Redox effects on release kinetics of arsenic, cadmium, cobalt, and vanadium in Wax Lake Deltaic freshwater marsh soils,” Chemosphere, vol. 150, pp. 740–748, 2016.

[11] Y.-H. Li, S. Wang, J. Wei et al., “Lead adsorption on carbon nanotubes,” Chemical Physics Letters, vol. 357, no. 3–4, pp. 263–266, 2002.

[12] J. Zhao, A. Buklum, J. Han, and J. P. Lu, “Gas molecule adsorption in carbon nanotubes and nanotube bundles,” Nanotechnology, vol. 13, no. 2, pp. 195–200, 2002.

[13] C. Chen and X. Wang, “Adsorption of Ni(II) from aqueous solution using oxidized multiwall carbon nanotubes,” Industrial & Engineering Chemistry Research, vol. 45, no. 26, pp. 9144–9149, 2006.

[14] A. Namane, A. Mekarzia, K. Benrachedi, N. Belhanechbensmra, and A. Hellal, “Determination of the adsorption capacity of activated carbon made from coffee grounds by chemical activation with ZnCl₂ and HPO,” Journal of Hazardous Materials, vol. 119, no. 1-3, pp. 189–194, 2005.

[15] Ihsanullah, F. A. Al-Khaldi, B. Abusharkh et al., “Adsorptive removal of cadmium(II) ions from liquid phase using acid modified carbon-based adsorbents,” Journal of Molecular Liquids, vol. 204, pp. 255–263, 2015.

[16] D. laoui, L. Österlund, and B. Kasemo, “Water adsorption on graphite (0001),” Vacuum, vol. 46, no. 8-10, pp. 1109–1112, 1995.

[17] S. Thangavel and G. Venugopal, “Understanding the adsorption property of graphene-oxide with different degrees of oxidation levels,” Powder Technology, vol. 257, pp. 141–148, 2014.

[18] K. Gupta and O. P. Khatri, “Reduced graphene oxide as an effective adsorbent for removal of malachite green dye: plausible adsorption pathways,” Journal of Colloid and Interface Science, vol. 501, pp. 11–21, 2017.

[19] S. Thangavel, S. Thangavel, N. Raghavan, K. Krishnamoorthy, and G. Venugopal, “Visible-light driven photocatalytic degradation of methylene-violet by rGO/Fe₃O₄/ZnO ternary nanohybrid structures,” Journal of Alloys and Compounds, vol. 665, pp. 107–112, 2016.

[20] V. Pandiyarasani, J. Archanà, A. Pavithra et al., “Hydrothermal growth of reduced graphene oxide on cotton fabric for enhanced ultraviolet protection applications,” Materials Letters, vol. 188, pp. 123–126, 2017.

[21] A. Fakhri, “Adsorption characteristics of graphene oxide as a solid absorbent for aniline removal from aqueous solutions: kinetics, thermodynamics and mechanism studies,” Journal of Saudi Chemical Society, vol. 21, no. Supplement 1, pp. S52–S57, 2017.

[22] H.-L. Ma, Y. Zhang, Q.-H. Hu, D. Yan, Z.-Z. Yu, and M. Zhai, “Chemical reduction and removal of Cr(VI) from acidic aqueous solution by ethylenediamine-reduced graphene oxide,” Journal of Materials Chemistry, vol. 22, no. 13, pp. 5914–5916, 2012.

[23] K. Zhang, H. Li, X. Xu, and H. Yu, “Synthesis of reduced graphene oxide/NiO nanocomposites for the removal of Cr(VI) from aqueous water by adsorption,” Microporous and Mesoporous Materials, vol. 255, pp. 7–14, 2018.

[24] S.-T. Yang, Y. Chang, H. Wang et al., “Folding/aggregation of graphene oxide and its application in Cu²⁺ removal,” Journal of Colloid and Interface Science, vol. 351, no. 1, pp. 122–127, 2010.

[25] Y. Y. Xiao, S. Miao, S. Liu, L. P. Ma, H. Sun, and S. Wang, “Synthesis, characterization, and adsorption properties of magnetic Fe₃O₄@graphene nanocomposite,” Chemical Engineering Journal, vol. 184, pp. 326–332, 2012.

[26] A. Uheida, G. Salazar-Alvarez, E. Björkman, Z. Yu, and M. Muhammed, “Fe₃O₄ and γ-Fe₂O₃ nanoparticles for the adsorption of Co²⁺ from aqueous solution,” Journal of Colloid and Interface Science, vol. 298, no. 2, pp. 501–507, 2006.

[27] Y. Li, P. Wang, C. Liu et al., “High strength polyvinyl alcohol/graphene oxide composite hydrogel,” Gaofenzi Cailiao Kexue Yu Gongcheng/Polymeric Materials Science and Engineering, vol. 31, pp. 161–166, 2015.

[28] N. Wang, P. R. Chang, P. Zheng, and X. Ma, “Graphene-poly(vinyl alcohol) composites: fabrication, adsorption and electrochemical properties,” Applied Surface Science, vol. 314, pp. 815–821, 2014.

[29] H. V. Tran, T. L. Tran, T. D. Le, T. D. Le, H. M. T. Nguyen, and L. T. Dang, “Graphene oxide enhanced adsorption capacity of chitosan/magnetite nanocomposite for Cr(VI) removal from aqueous solution,” Materials Research Express, vol. 6, no. 2, 2018.

[30] K. Mahmood, F. H. Wattoo, M. H. S. Wattoo et al., “Spec trophotometric estimation of cobalt with ninhydrin,” Saudi Journal of Biological Sciences, vol. 19, no. 2, pp. 247–250, 2012.
[31] H. Bingol and T. Atalay, “Study of kinetics of complexation re-
action of Co²⁺ with 2-benzoylpyridine-4-phenyl-3-thiosemicarba-
zezone and kinetic-spectrophotometric determination of cobalt,”
Acta Physico-Chimica Sinica, vol. 22, no. 12, pp. 1484–1488, 2006.
[32] S. Guzar and Q. Jin, “Simple, selective, and sensitive spect-
rophotometric method for determination of trace amounts of
nickel(II), copper(II), cobalt(II), and iron(III) with a novel reagent
2-pyridine carboxaldehyde isonicotinyl hydrazone,”
Chemical Research in Chinese Universities, vol. 24, no. 2,
pp. 143–147, 2008.
[33] J. Iqbal, F. Wattoo, S. Tirmizi, D. M. H. S. Wattoo, N. Ishrat,
and A. Memon, “Dehydroacetic acid oxime as a new ligand for
spectrophotometric determination of cobalt,”
Journal of Chemical Society of Pakistan, vol. 29, no. 2,
pp. 136–139, 2007.
[34] A. Khedr, M. Gaber, R. Issa, and H. Erten, “Synthesis and spectral
studies of 5-[3-(1,2,4-triazolyl-azo]-2,4-dihydroxybenzaldehyde
(TA) and its Schiff bases with 1,3-diaminopropane (TAAP)
and 1,6-diaminohexane (TAAH). Their analytical application for
spectrophotometric microdetermination of cobalt(II). Application
in some radiochemical studies,”
Dyes and Pigments, vol. 67,
no. 2, pp. 117–126, 2005.
[35] F. Sotomayor, K. A. Cychosz, and M. Thommes, “Charac-
terization of micro/mesoporous materials by physisorption:
concepts and case studies,”
Accounts of Materials & Surface Research, vol. 3,
pp. 34–50, 2018.
[36] I. Bernabé, J. M. Gómez, E. Díez, P. Sáez, and A. Rodríguez,
“Optimization and adsorption-based recovery of cobalt using
activated disordered mesoporous carbons,”
Advances in Materials Science and Engineering, vol. 2019,
no. 2, Article ID 3430176, 2019.
[37] K. A. Krishnan and T. S. Anirudhan, “Kinetic and equilibrium
modelling of cobalt(II) adsorption onto bagasse pith based
sulphurised activated carbon,”
Chemical Engineering Journal, vol. 137,
no. 2, pp. 257–264, 2008.
[38] E. Demirbaş, “Adsorption of cobalt(II) ions from aqueous
solution onto activated carbon prepared from hazelnut
shells,”
Adsorption Science & Technology, vol. 21,
no. 10, pp. 951–963, 2003.
[39] J. Fries and H. Getrost, Organic Reagents for Trace Analysis, E.
Merck Darmstadt, Darmstadt, Hessen, Germany, 1977.
[40] L. T. Tran, H. V. Tran, T. D. Le, G. L. Bach, and L. D. Tran,
“Studying Ni(II) adsorption of magnetite/graphene oxide/ chitosan nanocomposite,”
Advances in Polymer Technology, vol. 2019,
no. 3, Article ID 8124351, 2019.
[41] M. He, Y. Zhu, Y. Yang, B. Han, and Y. Zhang, “Adsorption of
cobalt(II) ions from aqueous solutions by palygorskite,”
Applied Clay Science, vol. 54, no. 3-4,
p. 292–296, 2011.
[42] X. Zhang, X. Wang, and Z. Chen, “Radioactive cobalt(II)
removal from aqueous solutions using a reusable nano-
composite: kinetic, isotherms, and mechanistic study,”
International Journal of Environmental Research and Public Health, vol. 14,
no. 12, p. 1453, 2017.
[43] S. Hashemian, H. Saffari, and S. Ragabion, “Adsorption of
cobalt(II) from aqueous solutions by Fe₃O₄/bentonite
nanocomposite,”
Water, air, & Soil Pollution, vol. 226, p. 2212,
2015.
[44] M. Ferri, S. Campisi, and A. Gervasini, “Nickel and cobalt
adsorption on hydroxypatite: a study for the de-metalation of
electronic industrial wastewaters,”
Adsorption, vol. 25, no. 3,
pp. 649–660, 2019.