Research Article

Green Synthesis Ca-MgO Nanosorbent for the Uptake of Cobalt Ions from Aqueous Media

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Ca-doped magnesium oxide nanosorbent has been prepared by sol-gel in the presence of gum arabic extract and assessed for the removal of cobalt ions (Co (II)) from aqueous media. X-ray diffraction analysis indicates the formation of MgO and CaO composites with a mean crystallite size of 6 nm having a large surface area of 50 m²/g. Scanning and transmission electron microscopy observations reveal spherical-shaped particles at the nanoscale around 20 nm. Besides, X-ray photoelectron spectroscopy and Fourier transform infrared analyses manifest the existence of functional groups, which will facilitate the adsorption of metal ions. The adsorption capability of the CaO-MgO nanosorbent achieved 469.5 mg/g for Co (II) ions under optimum operating conditions. Furthermore, the experimental data elucidate that the adsorption process is primarily diffusion-based and that both intraparticle and boundary layer diffusion appear to play a key role in the rate-controlling step. The findings of this study highlight the remediation of contaminated water by cobalt ions by CaO-MgO nanostructure and can be extended to other metal ions and organic pollutants.

1. Introduction

Cobalt is a naturally occurring chemical element with an atomic number of 27, belongs to the d sublevel elements, and is located at the top of the ninth group of elements in the periodic table, chemically classified as a transition metal [1, 2]. Cobalt is found in nature, mainly in the Earth’s crust in various minerals such as cobaltite, and it is not found in its natural, free form [3]. In contrast, the free element is produced from the reductive smelting of its ores. On the other hand, the pure state is found in the form of shiny silver-gray metal [4, 5]. Additionally, cobalt has been found to be a component of vitamin B12, which plays a significant role in blood pressure regulation and thyroid function [6].

Nowadays, water contamination by heavy metals is one of the most critical and challenging environmental problems facing the world [7]. In particular, cobalt (II) is a nonbiodegradable, cancerous, and pathogenic contaminant found in natural, industrial, and artificial processes [8]. Cobalt is a metal used in various industries, including nuclear medicine, surface coatings, optoelectronics, milling machines, glassware, and ceramic decorating, and metal processing [9]. Furthermore, it is also used as a drier for lacquers, varnishes, paints, and foaming stabilization in beer [10]. The continual release of various cobalt effluents from multiple industries endangers the environment and harms human health [11]. Cobalt (II) contamination of wastewater is a serious issue due to its toxicity at higher levels [12]. Cobalt has many
adverse health consequences, including cardiovascular disease, asthma, heart failure, goiter, and liver disorders [13]. Humans require water to survive; however, the quality of water available is insufficient to meet their basic needs [14]. Therefore, the quality control of water that has been contaminated with metal ions including Co (II) has become an increasingly important concern in recent years [15]. Numerous physicochemical approaches have been developed to effectively remove Co (II) ions from wastewater [16, 17], such as adsorption, membrane filtration, sedimentation, coprecipitation, and biotechnology [18, 19]. However, most of these technologies have substantial drawbacks such as low removal efficiency, high costs, operating requirements sensitivity, and secondary effluent generation [20]. Nonetheless, the adsorption method is considered the most suitable for removing Co (II) ions because of its low cost and high efficiency even in small quantities [21]. On the other hand, traditional sorbents have a limited binding capability and insufficient active surface sites, resulting in poor regeneration of particular metal ions from massive volumes of solution [22]. Consequently, the search for novel adsorbents with enhanced characteristics including high surface area, high efficiency, and fast segregation for vast volumes is of great importance [23].

Metallic oxide nanoparticles have been extensively investigated as potential sorbents, thanks to their exceptional characteristics and high efficacy [24, 25]. In this regard, magnesium oxide (MgO) has been examined due to its high capacity for the removal of metal ions in aqueous solutions [26, 27]. Recently, nanosized MgO nanoparticles have been widely used as nanosorbent to remediate contaminated water, owing to the large surface area and negligible impact on the environment [28, 29]. Furthermore, the adsorption capacity of MgO nanoparticles can be improved by surface modifications through physical coatings, alloying, doping, and covalent bonding to enable specific metal complexes [30, 31].

Green synthesis has been adopted by using the extract of the Acacia Senegal plant as a reducing and capping agent. The aim of this research is to synthesize Ca-doped MgO (CaO:MgO) nanopowder by the sol-gel method in the presence of Acacia Senegal solution and to examine its performance for the removal of Co (II) ions from aqueous solution. XRD, BET, FTIR, and SEM characterizations are performed for the removal of Co (II) ions from an aqueous solution. XRD, BET, FTIR, and SEM characterizations are performed for the removal of Co (II) ions from an aqueous solution. XRD, BET, FTIR, and SEM characterizations are performed in order to determine the phase composition, chemical bondings, surface properties, and particle morphology and size. The influence of the operating parameters such as Co (II) concentration, contact time, and pH on the adsorption capacity of Ca-doped MgO nanosorbent is also investigated. Furthermore, kinetic and isotherm adsorption tests are performed, the obtained data are modelled, and subsequently, a plausible adsorption mechanism is proposed.

2. Experimental Process

Ca-doped MgO oxide nanopowder was synthesized using by green sol-gel method aided by the Acacia Senegal solution. A 0.5 L of distilled water (DW) was dissolved in 0.249 mol. of magnesium carbonate dehydrate (MgCO₃) and 0.0249 mol. of calcium carbonate (CaCO₃). Then, 125 mL of NaOH ethanolic solution (0.02 M) was added dropwise for 30 min during sonication. Subsequently, 25 mL gum arabic (Acacia Senegal) solution (5 g in 100 ml DW) was added followed by sonication for 15 min, and afterward, the mixture was allowed to stand for 24 h. The as-formed white gel was washed with DW and dried at 90°C for 5 h. The final product was then calcined at 700°C for 2 h.

A Rigaku Mini Flex 600 (Tokyo, Japan) diffractometer equipped with a CuKα radiation source (λ = 1.5418 Å) was used to identify the crystal structure and phase purity. The surface area and pore size of the nanopowder were determined using a Micrometric ASAP 2020 analyzer, and Brunauer, Emmett, and Teller (BET) formula as well as Lippens and de Boer’s t-plot method. A Shimadzu FT-IR spectrometer was used to investigate the vibrational modes of the prepared nanopowder before and after Co (II) ions adsorption. Morphological observations were performed using scanning electron microscopy (SEM) by means of a JEOL JEM-6700F instrument equipped with electron dispersive X-ray spectroscopy (EDS) for the elemental chemical composition. Transmission electron microscopy (TEM) images were acquired at a 200 kV accelerating voltage using an FEI Tecnai G20 instrument. The surface chemical species were analyzed using the X-ray photoelectron spectroscopy (XPS) technique on a Thermo Scientific XPS (VG ESCALAB 220i-XL, UK) equipped with a monochromatic Al K (1486.6 eV) reference.

Adsorption experiments were conducted in a 25 mL glass vial containing 10 mg of nanosorbent powder and 25 mL of Co (II) ions at various concentrations (5, 15, 30, 45, 60, 100, and 200 ppm) under electromagnetic stirring for a contact time of 1440 min. Following the elimination equilibrium study, the mixture was centrifuged and separated to estimate the residual Co (II) ions concentration [29]:

\[ Q_e = \frac{V}{w} (C_i - C_e), \]

where \( Q_e \) (mg/g) denotes the ability of Co (II) ions to be removed by the mass of sorbent nanopowder, and \( C_e \) denotes the equilibrium Co (II) concentration in mg/L.

The adsorption procedure was used to determine the rate of Co (II) removal by the as-prepared nanosorbent (Ca-doped MgO). A 150 mL of Co(II) volume was stirred with 60 mg of nanosorbent at an initial concentration of 60 ppm to investigate the kinetics and contact time. A small suspension volume was withdrawn at preset time intervals and then centrifuged to determine the residual Co (II) concentration. Then, the amount of Co (II) separated per gram of nanosorbent at every period (min) was calculated by applying the following equation [32]:

\[ Q_t = \frac{V}{w} (C_i - C_t), \]

where \( Q_t \) (mg/g) is the capability of Co (II) to be removed per mass of nanosorbent (g) at each time \( t \) (min), \( C_i \) and \( C_t \) are the Co (II) concentrations (ppm) before and after introducing Co (II) at each time, and \( V \) is the volume of the solution mixture (mL).
3. Results and Discussion

3.1. Ca-Doped MgO Nanosorbent Characteristics. Figure 1(a) depicts the XRD pattern of the as-prepared Ca-doped MgO-powdered sample. The major peaks located at $2\theta = 36.9, 42.9, 62.2, 74.6,$ and $78.6^\circ$ are indexed as (111), (200), (220), (311), and (222) reflections of MgO phase with a face-centered cubic-FCC-rock salt-type structure (space group Fm$ar{3}$m—No. 225 and lattice constant $a = 4.213$ Å) [33] and consistent with JCPDS card No. 78-0430. The two small peaks observed at $2\theta = 36.9$ and 42.9$^\circ$ are attributed to the gum arabic extract [34] whereas the remaining peaks at $2 = 32.3$ and 53.9 are indexed as (110) and (202) reflections of the cubic CaO phase (space group Fm$ar{3}$m—No. 225 and lattice parameter $a = 4.801$ Å) [35], in agreement with JCPDS card no. 77-2376. Hence, the as-prepared Ca-doped MgO is in fact a nanocomposite composed mainly of MgO and CaO phases. The crystallite size calculated using the Sherrer formula is found to be around 5.98nm [36]; hence, a high surface area of the as-prepared nanopowder consequently enhanced adsorption efficiency.

For the fabrication of an effective adsorbent, such as CaO:MgO nanopowder, it is high desirable the presence of a large number of active sites at particles’ surface, besides a high surface area with large pore-volume. The nitrogen adsorption-desorption isotherms (Figure 1(b) (inset pore size)) demonstrate that the as-prepared CaO:MgO nanocomposite is a mesoporous material with an IUPAC class IV adsorption isotherm. The isotherm is connected to a type H1 hysteresis, implying a limited dispersion of homogenous mesoporous particles and limited networking effects [37, 38]. The nanosorbent CaO:MgO possesses a relatively high surface area to 50 m$^2$/g with a total pore volume of 0.277 cc/g and an average pore size of 11.79 nm. The adsorbent’s important surface area and porosity are expected to expose many adsorption sites, leading to a high adsorption capacity.

Furthermore, FTIR analysis was used to identify the chemical bonds and composition (purity) of the synthesized nanosorbent, see Figure 1(c). The broad band at 3465 cm$^{-1}$ is assigned to the O–H group’s asymmetric stretching [39], while the band at 1639 cm$^{-1}$ corresponds to the adsorbed water molecule’s –OH stretching mode [40]. The three bands observed at 1524, 1406, and 1056 cm$^{-1}$ are associated with an unknown carbonate adsorbed on the nanoparticles' surface [41]. The unique band at 420 cm$^{-1}$ is attributed to the Mg–O vibration mode [42], hence confirming the formation of the MgO phase. Meanwhile, the band at 871 cm$^{-1}$ is related to CaO stretching [43]. The FTIR analysis corroborates with the XRD analysis by confirming the formation of CaO:MgO nanocomposite material.

The SEM image displayed in Figure 2(a) reveals irregular-shaped spherical crystalline particles at the nanoscale with dimensions approximately around 20 nm. The corresponding EDX spectrum (Figure 2(b)) manifests intense signals at 3.7, 1.2, and 0.5 keV corresponding to Ca, Mg, and O, respectively. No additional peaks can be detected signifying the purity of the as-prepared nanosorbent. Furthermore, according to the chemical composition shown as an inset in Figure 2(b), the weight proportions of the components are compatible with the initial chemical composition. The TEM images as illustrated in Figures 2(c) and 2(d) indicate the presence of irregular and spherical particles with dimensions around 20 nm, in good agreement with SEM analysis.

XPS analysis has been used to determine the chemical state of the elements on the surface of CaO:MgO nanostructure, see Figures 3(a)–3(d). Ca-2p, Mg-2p, O-1s, and O-2s peaks are detected in the recorded survey scan (Figure 3(a)). The existence of an Mg-2p peak at around 52.50 eV is attributed to surface magnesium in an oxidized state, indicating the formation of Mg-O [44]. The Ca-2p peaks at 348.13 and 351.2 eV correspond to the divalent oxidation states of calcium oxygen molecules (Ca-2p3/2 and Ca-2p1/2), confirming the existence of calcium oxide (CaO) [45, 46]. The three O-1s peaks observed at 531.4, 532.5, and 533.8 eV correspond to Ca-O, Mg-O, and hydroxyl group in water molecules, respectively (see Figure 3(b)) [47]. The peaks at 42.0 and 51.1 eV may be ascribed to the typical Mg-2p and Mg-2s peaks of the MgO phase as shown in Figure 3(c) [48]. Moreover, the O-1s peak at 533.8 eV confirms the Mg-O bonding (Figure 3(d)) [49, 50]. It can be concluded that XPS analysis indicates the presence of Ca, Mg, and O species only without any additional peaks belonging to impurities, which corroborates with the results obtained by XRD, FTIR, and EDS analyses. Furthermore, the XPS results indicate that CaO:MgO nanostructure' surface is hydroxylated, which is consistent with FTIR analysis (the strong band for the O-H group in FTIR indicates the hydroxylation of the nanostructure).

3.2. Co (II) Removal onto CaO:MgO Nanosorbent

3.2.1. Influence of the Initial Co (II) Concentration. The influence of the initial Co (II) concentration in the range of 5–200 mg/L on the adsorption efficiency of CaO:MgO nanosorbent has been examined under the following operating conditions: contact time 1440 min, room temperature, pH 5, 350 rpm stirring speed, and a sorbent dose 10 mg. As shown in Figure 4, increasing the starting Co (II) concentration from 5 to 200 mg/L improved the adsorption capacity significantly from 12.5 to 462.23 mg/g but reduced slightly the adsorption rate and elimination efficiency of Co (II) from 100 to 92.45%. These results indicate that at lower concentrations, Co (II) ions in the reaction medium interact more efficiently with the top layer of the sorbent particles due to the large amount of vacant active sites. On the contrary, the ratio of accessible sites for Co (II) ions declines with a further rise in the concentration attributed to potential binding saturation.

3.2.2. Influence of pH on Co (II) Removal by the Nanosorbent. The pH of the solution governs the sorption affinity of the adsorbent by tuning the type of charge on the surface of the adsorbent, speciation of the metal in the solution, and ionizing strength of the adsorbent [51]. The influence of pH can also be described through the point of zero charges (pHpzc). It is known that pHpzc refers to the pH at which the surface of the adsorbent has a zero net charge. The evolution of
(pH_{\text{final}} - pH_{\text{initial}}) vs. pH_{\text{initial}}, as illustrated in Figure 5(a), indicates that the value of pH_{pzc} is 4.02. This result suggests that the surface of the adsorbent is positively charged and favors the sorption of anions for the solution with pHs < pH_{pzc} (9.97). In contrast, it becomes negatively charged to favor the sorption of cations for the solution with pHs > pH_{pzc}. To examine the optimal pH for the Co (II) removal, the pH has been varied from 1 to 8. The effect of pH on Co (II) uptake is depicted in Figure 5(b). As can be seen, the amount of the adsorbed Co (II) increases significantly reaching a maximum capacity of 130.36 mg/g at pH 5. Increasing pH reduces the amount of H\(^+\), thus reducing competition for adsorption sites onto particle surfaces between metal ions and protons [52]. The other aspect that may aid in metal ions’ sorption is the rise in the pH, which promotes their precipitation from solution as hydroxides. Consequently, the adsorption is reduced due to the formation of soluble hydroxyl complexes [53]. Hydroxonium ions (H\(_3\)O\(^+\)) may be tightly coupled with the surface of the adsorbent at low pH through a repulsive effect, leading to a decrease in metal ions elimination [54]. The Lewis base (lone pair electron) that is present in some of the functional groups of defatted CaO-MgO nanosorbent may play a significant role in eliminating metal ions by (Lewis acid) defatted CaO-MgO nanosorbent. The elimination of Co (II) from sewage by sorbents includes a more complex mechanism that is partly governed by sorption and chemical precipitation at the sewage-solid interface and the mechanism of its pore filling. Therefore, it is suggested that inner sphere complexes between CaO-MgO nanosorbent and metal ions may have formed. When hydroxyl groups occupy the place of metal ligands inside the inner coordination sphere, ions will undergo hydrolysis [55]. This replacement occurs following the removal of the metal cation-hydration outer sphere. Moreover, the findings of several studies in the literature corroborate the reported association between metal ions’ adsorption and a more comprehensive pH range [56].

3.2.3. Effect of Co (II) Contact Time and Adsorption Kinetic Studies. Figure 6(a) depicts the correlation between Co (II) adsorption by CaO-MgO nanosorbent and the contact time.
The adsorption capacity and removal efficiency are found to increase with the contact time, reaching equilibrium at 18 min. Beyond this equilibrium threshold, the adsorption capacity is in dynamic equilibrium with the amount of adsorbed Co (II), as demonstrated by a negligible rise in Co (II) percentage. The first % elimination of Co (II) is rapid (Figure 6(a)), owing to a large number of adsorbent’s active sites and the short diameter of Co (II) ions. After 18 min, Co (II) ions cannot penetrate the adsorbent’s inner pores, which are attributed to Co (II) monomolecular saturation at the pores’ surface. Additionally, the data from Figure 6(a) manifest that the equilibrium period is unrelated to the original Co (II) concentration.

The adsorption kinetics quantifies the rate of solute adsorption at the solid-liquid interface and provides critical information on the equilibrium time, which is necessary for the design and operation of an adsorption process [57]. Co (II) adsorption kinetics by the CaO.MgO nanosorbent has been examined by adopting pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models as displayed in Figures 6(b) and 6(c). On the basis of the adsorbent capacity, a pseudo-first-order model is established. It states that the rate at which adsorbate consumption changes with time is directly proportional to the difference in saturation concentration levels. The corresponding equation’s linear form is denoted in Table 1.

Table 1 summarizes the calculated model parameters under the studied experimental conditions. Although the fitted model has a high $R^2$ value of 0.9038, the computed $Q_{\text{max}}$ value for initial Co (II) concentrations differs significantly from the experimental $Q_{\text{max}}$ values. This discrepancy implies that the pseudo-first-order equation may not sufficiently describe the Co (II) adsorption pathway onto the surface of CaO.MgO nanoparticles, implying the necessity to examine the effectiveness by testing another kinetic model. The pseudo-second-order model may appropriately explain

Figure 2: SEM image (a), EDX (b), and TEM images (c) and (d) of the prepared CaO.MgO nanosorbent.
Figure 3: XPS spectra of (a) survey, (b) Ca-2p, (c) Mg-2p, and (d) O-1s for CaO.MgO nanosorbent.

Figure 4: Evolution of the adsorption rate as a function of Co (II) initial concentration by CaO.MgO nanosorbent.
the experimental adsorption kinetics data. It states that the rate of adsorption sites’ occupation is related to the square of the number of available sites. The formula denoting the PSO linear model’s form is given in Table 1. Figure 6(c) depicts the nonlinear curves of $Q_t$ vs. $t$. The extremely high $R^2$ value of 0.9999 is obtained using the model parameters calculated in Table 1. The results reveal that the pseudo-second-order equation provides a perfect match compared to the pseudo-first-order model. It can be seen that the differences between the model estimated $Q_{\text{max}}$ values and the experimental $Q_{\text{max}}$ values for the studied Co (II) concentrations are negligible. Hence, the best fit of the pseudo-second-order model implies the concentration of Co (II) in the solution, and the accessible active sites onto CaO: MgO nanosorbent can be used to explain the intrinsic kinetic adsorption constant mathematically [58–60]. Figure 6(d) depicts the intraparticle diffusion plot. It can be observed that the adsorption process occurs upon two distinct stages. The first stage reflects the transport of Co(II) ions from the bulk solution through the boundary layer to the surface of CaO:MgO nanosorbent, whereas the second stage manifests the equilibrium state in which intraparticle diffusion starts to diminish due to low Co(II) concentration.

3.2.4. Adsorption Modeling of Co (II) onto CaO:MgO Nanosorbent. The maximum amount of Co (II) ($Q_{\text{max}}$) adsorbed by the sorbent presents another critical feature for evaluating the high adsorption ability displayed by CaO:MgO nanocomposite. To assess its absorption capability, the adsorption data have been evaluated using several adsorption isotherms models, namely Freundlich and Langmuir as illustrated in Figures 7(a) and 7(b). The formulas corresponding to each isotherm model and the computed parameters are given in Table 2.

As can be noted from the isotherm graphs and the experimental data for Co (II) adsorption over CaO:MgO nanosorbent, the Langmuir adsorption isotherm has the highest $R^2 = 0.9979$. The equilibrium value of $R_L$ is around 0.0021, suggesting a desirable adsorption equilibrium [63]. These findings indicate that the Langmuir adsorption isotherm curve is more accurate to fit the experimental data. The greatest sorption capacity of CaO:MgO nanosorbent for Co (II) is found to be 469.5 mg·g$^{-1}$, as given in Table 2.

The capability of CaO:MgO to adsorb cobalt ions from aqueous media was compared to other adsorbents previously described in the literature. As shown in Table 3, the obtained Ca-MgO nanosorbent has a greater capacity for Co (II) ions removal than previously reported sorbents, indicating its potential as a promising nanosorbent for the removal of cobalt ions from aqueous media.

3.3. Adsorption Mechanism. FTIR analysis has been assessed to propose a plausible mechanism for Co (II) ions adsorption onto CaO:MgO nanosorbent. The FTIR spectra before and after Co (II) ions adsorption are shown in Figure 8(a). The position of the OH stretching vibration band has been shifted significantly, as illustrated in Figure 7(a), indicating that Co (II) interacts with the OH in MgO to establish an O–Co bond. The displacement of the CaO vibration band at 871 cm$^{-1}$ confirms the interaction between Co (II) ions and the oxygen of CaO [39]. In addition, the FTIR bands of unidentate carbonate onto the particles’ surface are shifted after Co (II) ions adsorption. This finding indicates that the unidentate surface carbonate
Figure 6: Effects of duration time (a), PFO (b), PSO adsorption kinetics models (c), and intraparticle diffusion of Co (II) onto CaO.MgO nanosorbent.

Table 1: Kinetics models for Co (II) adsorption onto CaO.MgO nanosorbent.

<table>
<thead>
<tr>
<th>Kinetics model</th>
<th>Kinetic equation</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFO [59]</td>
<td>$\ln (Q_e - Q_t) = \ln q_e - k_1 t$</td>
<td>$Q_e$ (mg/g)</td>
<td>14.38 ± 1.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_1$ (min$^{-1}$)</td>
<td>0.0174 ± 0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.9038</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Q_m$ (exp) (mg/g)</td>
<td>113.5 ± 1.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Q_m$ (cal) (mg/g)</td>
<td>112.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_2$ (g/mg.min)</td>
<td>0.0029 ± 0.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$h_0$ (mg/g.min)</td>
<td>36.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$t_{1/2}$ (min)</td>
<td>3.044</td>
</tr>
<tr>
<td>PSO [59]</td>
<td>$t/Q_t = [1/k_2 Q_e^2] + (1/Q_e)t$</td>
<td>$K_{dif1}$ (mg. min$^{1/2}$/g)</td>
<td>19.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_1$</td>
<td>5.997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.9671</td>
</tr>
<tr>
<td>Intraparticle diffusion [60]</td>
<td>$q_t = k_{dif} t^{1/2} + C$</td>
<td>$K_{dif2}$ (mg. min$^{1/2}$/g)</td>
<td>0.816</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_2$</td>
<td>109.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.6783</td>
</tr>
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</table>
Figure 7: Experimental adsorption data fitted with the Langmuir (a) and Freundlich (b) models.

Table 2: Equilibrium isotherm models for Co (II) adsorption onto CaO.MgO nanosorbent.

<table>
<thead>
<tr>
<th>Equilibrium model</th>
<th>Linear form</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir [61]</td>
<td>$C_e/q_e = 1/q_mK_L + C_e/q_m$</td>
<td>$q_m$ (mg/g)</td>
<td>469.5 ± 4.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_L$ (mg/g)</td>
<td>0.2341 ± 1.22 × 10^{-3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.9979</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N$</td>
<td>2.847 ± 0.128</td>
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<tr>
<td>Freundlich [62]</td>
<td>$\ln q_e = \ln K_F + (1/n)\ln C_e$</td>
<td>$K_F$ (L/mg)</td>
<td>155.9 ± 5.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.9568</td>
</tr>
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Table 3: Adsorption capability of various cited sorbents for the Co (II) ions removal.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg/g)</th>
<th>Time (min.)</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>Ion-imprinted polymer</td>
<td>23.1</td>
<td>10</td>
<td>[64]</td>
</tr>
<tr>
<td>Nanosponge biopolymer</td>
<td>7.8</td>
<td>80</td>
<td>[18]</td>
</tr>
<tr>
<td>Carbon@UiO-66 bio-nanocomposite</td>
<td>44.5</td>
<td>20</td>
<td>[65]</td>
</tr>
<tr>
<td>Modified chitosan nanocomposites</td>
<td>43.9</td>
<td>60</td>
<td>[66]</td>
</tr>
<tr>
<td>GO-BSA membrane</td>
<td>180</td>
<td>80</td>
<td>[20]</td>
</tr>
<tr>
<td>Doped glycerol</td>
<td>117.9</td>
<td>70</td>
<td>[67]</td>
</tr>
<tr>
<td>Carbon-modified zirconia/spinel ferrite</td>
<td>82.5</td>
<td>60</td>
<td>[68]</td>
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<tr>
<td>Amination graphene oxide</td>
<td>116.3</td>
<td>5</td>
<td>[69]</td>
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<tr>
<td>Ca-MgO</td>
<td>469.5</td>
<td>18</td>
<td>Present study</td>
</tr>
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</table>
may have been involved in the removal of Co (II) ions. Wu et al. established by FTIR and XPS analyses that the surface monodentate carbonate species contributed to the As (V) adsorption mechanism [41]. Figure 8(b) illustrates the plausible adsorption mechanism of Co (II) ions onto the CaO.MgO nanosorbent.

4. Conclusion

CaO.MgO nanosorbent fabricated through a sol-gel method exhibits remarkable adsorption ability to remove Co (II) from an aqueous solution effectively. Structural, microstructural, and physicochemical characterizations indicate the formation of CaO.MgO composite with a relatively high surface area (50 m²/g) and pore size (11.79 nm), and porous nanostructure formed the irregular spherical particles (20 nm), besides the presence of functional groups at the particles’ surface. The adsorption kinetics process fits well with the pseudo-second-order kinetic model (PSO). The adsorption of Co (II) obeys the Langmuir adsorption isotherm, with an excellent removal capacity of 469.5 mg/g and a very high correlation coefficient ($R^2 = 0.9979$). This study demonstrates that the bio-fabricated cost-effective CaO.MgO nanosorbent possesses superior characteristics for the removal of Co (II) in an aqueous solution and can be assessed for the removal of other heavy metal ions and organic pollutants.

**Data Availability**

The data used in this study are available from the main author upon request.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

**Authors’ Contributions**

The study plan, preparation of materials, data collection, and analyses were carried out by the authors with their contributions throughout the reviewing process. All authors read and approved the final work before it was published.

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