Using nano-magnesium oxide/bentonite composite for cadmium removal from industrial wastewater

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ABSTRACT
Nowadays, the removal of toxic heavy metals from industrial wastewater is a long standing problem due to the industrial progress worldwide. This study mainly focused on the production of a novel nMgO-bentonite nanocomposite using sol–gel method to enhance Cd ions removal from industrial wastewater. The nMgO-bentonite nano-composite was characterized for structural morphology and presence of functional groups using SEM/EDS, XRD and FTIR analysis. Cadmium sorption equilibrium and kinetic data were well fitted to Langmuir and power function models respectively as confirmed by the highest R² (0.965), and the lowest SE (38*10⁻⁶) values among other studied models. The Langmuir removal capacity of the nanocomposite is 200 mg/g which is 60 times greater than that of bentonite. Increased Cd sorption on nano-composite with increased temperature from 287 to 307K and the thermodynamic results revealed that Cd adsorption process was endothermic and spontaneous. The data also showed highly repetitive application of nano-composite during six cycles of adsorption/ desorption experiment. The final results pointed out that nMgO-bentonite nano-composite has great adsorption affinity for Cd and could potentially employ as a cost-effective, ecofriendly and efficient sorbent for Cd removal from contaminated wastewater.

Keywords: Industrial wastewater, nMgO-Bentonite composite, Sorption isotherm, kinetic, Thermodynamic

1. Introduction
Water contamination is a widespread issue that threatens worldwide human health. The discharge of untreated industrial effluents into water bodies is seriously contaminating fresh water with heavy metals [1, 2]. Due to non-biodegradability nature of the toxic metals, they can easily transfer into bio-organisms and seriously affect human health [3, 4]. Among these metals, cadmium which is a toxic element for living organisms, can interfere with plants-metabolism reactions and consequently bio-pile into aquatic organisms and step inside the food chain [5]. The carcinogenic effect of cadmium on all living organisms is related to nephrology, teratogenicity, and reproductive system toxicity [6]. Thus, from the human health point of view, an efficient remediation strategy is demanding for wastewater remediation to achieve safe water supply [7].

Different conventional and modern methods -like adsorption, precipitation and ion exchange- have been employed to decontaminate heavy metals-polluted water [8]. For example, Cd can be removed from aqueous solution using solvent displacement [9], electrochemical processing [10], ion flotation and substitution [11-13]. Nevertheless, these methods are costly and require high pollutant concentrations and few heavy metal ions can be recovered effectively [14]. Among these approaches, adsorption process is preferred as a result of its suitability, easy to run, high removal rate, and wide applicability in water pollution control [15].

A number of adsorbents including bentonite [16], magnetite [17], chitosan [18], etc., have been employed for removal of heavy metal ions from aqueous solutions. However, these adsorbents usually suffer from low adsorption capacities or removal efficiencies of heavy metal ions. Recently, considerable studies concerning the use of nano adsorbents for the removal of heavy metals from
industrial effluent have been done [19]. Metals oxides like magnesium oxide nanoparticles (nMgO) have attracted researchers worldwide due to its large specific surface area, low-density, non-toxicity, cheap manufacturing, and better physical characteristics which can efficiently remove heavy metals [20], Feng et al. [21] reported mesoporous MgO nanosheets had the maximum adsorption capacity of 168.25 mg/L for Ni(II) removal from aqueous solutions. Because bentonite possesses excess negative charges on its lattice and swells into very large surface area [16], we hypothesized that modification of bentonite surface by coating with Mg oxides nanoparticles as a new technique may greatly enhance the reactivity and the adsorption affinity of bentonite for Cd ions.

To the best of our knowledge, this study reports for the first time the synthesis of a novel nano-composite sorbent (nMgO-Bentonite) by depositing MgO nanoparticles onto bentonite to increase sorption capability of both sorbents for Cd removal from wastewater. The specific objectives of this study were to (i) produce nMgO-Bentonite nano-composite and characterizes its surface morphology and chemical composition using microscopy/spectroscopy and x-ray tools, (ii) determine Cd adsorption capacity under optimal conditions of pH, sorbent dose, competitive cations, contact time and temperature, (iii) examine the reutilizing prospect of the sorbent, and (iv) evaluate the efficiency of the produced nano-composite for Cd removal from industrial wastewater.

2. Materials and Methods

2.1. Synthesis of (nMgO-Bentonite) Composite

The nMgO were synthesized using sol-gel method. Magnesium acetate tetra hydrate [Mg(C₂H₃O₂)₂·4H₂O] was used as the initial precursor and ammonia solution as the precipitating agent. Typically, 0.1 mol/L magnesium acetate tetra hydrate (mol wt.214.45) was dissolved in 200 mL of distilled water. It was then stirred on the magnetic stirrer for about 10 h. Then, 15 mL of ammonium solution (NH₄OH) was added drop wise into the solution maintaining the pH of 8 with the heating at 80°C temperature and simultaneous stirring of the solution for about 16 h using temperature controlled Orbital Shaker to get the white precipitate. The resulting precipitate of Mg(OH)₂ was then dried at 120°C for 3 h and then crushed into fine powder with the help of mortar pestle. Finally, powder was annealed at a temperature of 600°C for 6 h and then crushed again to get the white powder of magnesium oxide. Bentonite clay was obtained from Egyptian nano-technologies Company at Borg El Arab city and sieved using 53 μm sieve. The nano-composite (nMgO-Bentonite) was obtained by adding nMgO to aqueous suspension of bentonite and stirred for 24 h. The resulting solid phase was separated by decantation, washed several times with distilled water, and then dried at 105°C for 24 h.

2.2. Characterization

Scanning electron microscope equipped with energy dispersive spectroscopy (SEM-EDS) (INCAx-Sight, Oxford Instruments, UK) was used for morphological characterization and elemental content determination of nMO, Bentonite, and (nMgO-Bentonite) nano-composite. The crystalline kernel of the obtained sorbents was investigated using Bruker AXS D8 Advance X-ray Diffractometer [22]. The specific surface area of the sorbents was determined according to Brunauer–Emmett–Teller method [23] using surface area analyzer (Quantachrome, USA). The functional groups of the sorbent surfaces were clarified using Fourier transform infrared spectroscopy (FTIR).

2.3. Adsorption Kinetics

Kinetic adsorption experiments were carried out in 50 ml polyethylene centrifuge tubes by adding 0.2 g of nMgO, Bentonite, or (nMgO-Bentonite) nano-composite to 500 ppm Cd solution as CdCl₂. The centrifuge tubes were shaken in an end-over-end shaker for different time intervals (5 min–24 h). The Cd-sorbent mixtures were centrifuged at 4,000 rpm for 10 min and filtered through a 0.45 μm Millipore filter. Total Cd concentrations were measured in the filtered solutions using atomic absorption spectrometer (contrAA 300). The kinetics of sorbed Cd onto the three sorbents were modeled using first-order [24], Elovich [25], Intraparticle diffusion [26], and power function [27] kinetic models.

2.4. Adsorption Isotherms

The adsorption experiments were conducted in batch system. A 0.2 g of each sorbent was shaken with CdCl₂ solution ranging from 40 to 640 mg L⁻¹ in 50 mL polyethylene centrifuge tubes using an end-over-end shaker for 24 h (predetermined equilibrium adsorption time). Centrifugation, filtration, and Cd concentrations measurement were run as mentioned in adsorption kinetics section. The sorption data were applied to Langmuir, Freundlich, Elovich, Temkin, Fowler–Guggenheim (FG), Kiselev, and Hill-de Boer mathematical isotherm models.

2.5. Thermodynamic Parameters

The thermodynamic parameters including change in the Gibbs free energy (ΔG°, J mol⁻¹), enthalpy (ΔH°, J mol⁻¹) and entropy (ΔS°, J mol⁻¹ K⁻¹) were studied to understand the effects of temperature on Cd adsorption process. These parameters were determined using the following equations:

\[ \Delta G^\circ = -RT \ln K_c \]  \hspace{1cm} (1)

\[ K_c = C_{qe}/C_S \]  \hspace{1cm} (2)

Where:

\[ R = \text{The gas constant } [8.314 \text{ kJ/ (mol K)]} \]

\[ K_c = \text{the equilibrium constant} \]

\[ C_{qe} = \text{The amount of Cd(II) adsorbed on the adsorbent from the solution at equilibrium (mg/L)} \]

\[ C_S = \text{The equilibrium concentration of Cd (II) in the solution (mg/L)} \]

\[ \Delta H^\circ \text{ and } \Delta S^\circ \text{ were calculated from the plot of } \Delta G^\circ \text{ versus } T \text{ (Fig. 8), by the following equation:} \]

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]  \hspace{1cm} (3)
2.6. Adsorbent Reusability
The reusability of (nMgO-Bentonite) nano-composite was tested for 6 consecutive cycles using 0.01M HCl solution. The Cd loaded nano-composite was dried and soaked in 50 mL HCl (0.01M), then shaken for 120 min at room temperature. The suspensions were then filtered and dried and the regenerated nano-composites were then reused for Cd removal. The adsorption-desorption process was repeated and tested for 6 cycles.

2.7. The Cd Adsorptive Removal Efficiency of Nanocomposite
2.7.1. Batch study
The efficiency of (nMgO and Bentonite) nano-composite for Cd (II) removal was evaluated by setting up a batch experiment using real wastewater from Al-Bilali agricultural drainage and industrial effluents of paper manufacturing factory (Rakta). The chemical analysis of the wastewaters used in the study is presented in Table S4. Because the agricultural drainage sample was free of cadmium it was spiked with 5 mg L⁻¹ Cd.

2.7.2. Column (continuous) study
The efficiency of nano-composite for Cd removal under flow through conditions was studied. Packed-bed reactors 20 cm high with 2.5-cm internal diameter were used to test the filter media (homogeneously mixed (nMgO –Bentonite) nano-composite and sands at a 1:2 mass ratio). A peristaltic pump was continuously delivering Cd-containing waste water to a reservoir connected with the column. Solution flow gravitationally through the columns and leachate was collected and analyzed. The schematic diagram of the experimental columns is shown in Fig. S3.

3. Results and Discussion
3.1. Characterization of Bentonite, nMgO and Nano-composite
3.1.1. Bentonite
The SEM images of bentonite sample clearly showed different sizes and shapes and the representative individual particle size of nMgO lies in the nanostructure zone (< 100 nm) (Fig. 2 & Fig. S4). The EDX analysis of bentonite reveals that the major elements of bentonite are O, Na, Mg, Al, Si and Fe in 53.08, 2.25, 1.14, 10.08 and 23.38%, respectively (data not shown). The XRD patterns of bentonite demonstrate that bentonite sample is mainly containing high percentage of silicon oxide (2θ = 26.495 and 28.25%), sodium iron oxide (2θ = 19.739, 14.2%), titanium Oxide (2θ = 20.41 and 11.83%), Quartz (2θ = 50.43 and 9.42%), Potassium Iodate (2θ = 54.09 and 11.25%) and calcium iron oxide (2θ = 62.26 and 8.71%) (Fig. 1(a)).

3.1.2. nMgO
The SEM images indicate that nMgO sample possess spherical structure in the 29–80 nm size range (Fig. 2 & Fig. S4). The EDX analysis of nMgO revealed that MgO represents 97.96% whereas CaO represent 2.04% (data not shown). The XRD analysis showed high percentage of MgO₂ at (2θ = 42.61) and presence of MgO at (2θ = 62.26) (Fig. 1(b)).

3.1.3. n(MgO-Bentonite) nano-composite
The XRD patterns of composite sample (Fig. 1(c)) is mainly containing high percentage of aluminum silicate (2θ = 26.189 and 38.34%), calcium iron oxide (2θ = 34.412 and 15.30%), potassium aluminum (2θ = 24.141 and 14.78%), calcium aluminum oxide (2θ = 50.375 and 12.38%) and tridymite (2θ = 20.282 and 5.08%).

The SEM and EDX analyses of (nMgO-Bentonite) nano-composite are shown in Fig. 2. Bentonite flakes are clearly visible in SEM image and spherical shaped nMgO are dispersed on bentonite
It is clear that the bentonite is not in nanoscale range, whereas the diameters of the spherical dispersed nMgO particles on bentonite surface are of the nano-range size (< 100 nm) (Fig. 2(a), (c)). The two SEM images (Fig. 2(a), (c)) clearly show that the measured diameters of the representative dispersed nMgO particles on bentonite surfaces before and after Cd saturation are in the size range of 29-80 nm which is definitely < 100 nm. The EDS analysis (Fig. 2(b)) reveals that the major elements of nMgO-Bentonite nano-composite are O, Mg, Al, Si and Fe in 59.42, 13.33, 4.05, 8.93 and 2.49%, respectively. The presence of Mg, confirms the existence of nMgO and the presence of base cations (i.e. Ca, Mg, Fe) could be an aid to Cd adsorption by nano-composite. The SEM and EDX analysis of Cd saturated nano-composite are shown in Fig. 2(b). The EDX analysis (Fig. 2(d)) revealed the presence of Cd ions in high concentration (21%). The level of cations (particularly Mg) decreased significantly from 13.33 to 9.16 indicating higher neutralization potential on the synthesized nano-composite material. Such potential is expected to play significant role in creating favorable conditions for Cd adsorption.

3.2. Fourier Transmission Infrared (FTIR) Spectroscopy and Functional Groups

The FTIR spectra of nMgO and bentonite prior/after Cd adsorption are presented in Fig. 3. Prior Cd addition to MgO nanoparticles Fig. 3(a) showed three bands at 3,696, 3,417 and 1,430 cm^{-1} correspond to the OH group, pure nMgO, and Mg-O stretching vibration respectively [28, 29]. After Cd addition, changes in the FTIR spectra of nMgO have been noticed. The intensity of the band at 3,696 cm^{-1} increased, while the two bands at 3,417 and 1,430 cm^{-1} increased in intensity and shifted to new sites at 3,443 and 1,446 cm^{-1}, respectively. Such changes indicate obvious interaction between Cd (II) ions and OH functional group and Mg-O stretching vibration. In respect of bentonite after Cd adsorption (Fig. 3(b)), the disappearance of the band at 3,426 cm^{-1} that belongs to OH stretching of hydroxyl groups demonstrates the role of OH group on Cd adsorption onto bentonite.

Similarly, the FTIR spectra of (nMgO and Bentonite) nano-composite before Cd adsorption is shown in Fig. 3(c). The two bands at 3,697 and 3,623 cm^{-1} correspond to stretching vibrations OH groups coordinated to two Al atoms whereas the band at 3,444 cm^{-1} is referred to Cd captured by nMgO. Retention of Cd onto nano-composite surface caused some spectral changes such as emerging of a new band belongs to CO3 at 860 cm^{-1}, shifting the band at 1,484 cm^{-1} to a new site at 1,423 cm^{-1} with intensity increase as well as increasing the intensity of the two bands at 1,033 and 914cm^{-1} which indicate the active role of Al-O-Si, Al-OH-Al, Si-O stretching groups in Cd removal by nano-composite (nMgO-bentonite).
3.3. Adsorption Kinetics

Adsorption kinetics experiments were performed to determine the equilibrium time for Cd (II) sorption onto nMgO, Bentonite and nano-composite (nMgO-Bentonite). For bentonite and (nMgO-Bentonite) nanocomposite, the system reached equilibrium after 2 h, while the nMgO system reached equilibrium after 16 h. These data are substantial because equilibrium time is considered the core parameter in wastewater treatment field [30]. Fig. 4(a) clearly shows that incorporation of nMgO into bentonite creates more adsorption sites and greatly enhances the adsorption capacity of the nano-composite. Moreover, in all the sorbents studied, ~92% of Cd was sorbed at initial five minutes and slowed down until reach equilibrium (Fig. 4(a)). This could be explained on the bases that adsorption of Cd is a surface phenomenon and the unoccupied sites in the sorbent surface may be filled up rapidly and subsequently slowed down.

The kinetic data for Cd adsorption onto nMgO, bentonite and nano-composite were fitted to first order, Elovich, parabolic diffusion, and power function kinetic models. The kinetics model constants, determination coefficient ($R^2$) and standard error of estimate (SE) values for cadmium sorption by the studied sorbents are given in Table S1. The determination coefficient ($R^2$) and the standard error of estimate (SE) values are indicators of how well the model fits the data. The highest $R^2$ value and the lowest SE value signalize the good fitness of the model to kinetics of Cd sorption process. The Lowest SE values in Table S1 affirmed that Cd adsorption onto the studied sorbents fitted well to power function model. The SE values of Elovich, intraparticle diffusion and first order models were much higher than those of power function model (Table 1). Thus, Cd sorption by the three studied sorbents was best described by power function model (Fig. 4(b)) which suggests the dominance of chemisorption reaction [31, 32].
3.4. Adsorption Isotherms

Sorption isotherm is a very useful tool for the evaluation of the most efficient sorbent and the optimum experimental conditions [33]. Therefore, sorption isotherms of nMgO, bentonite and nano-composite (nMgO- Bentonite) were performed to demonstrate the metal intake of these sorbents at different concentrations (40–640 mg/L (Fig. 5(a)). A continuous increase of sorbed Cd by nMgO, bentonite and (nMgO- Bentonite) nano-composite with increasing Cd concentration is noticed. The Cd sorption capacity of nano-composite (nMgO- Bentonite) was much higher than either nMgO or bentonite clay. Interestingly, the shape of nano-composite sorption isotherm is an 'H' type isotherm (Fig. 5(a)) which clearly indicates the vigorous association between Cd and the nano-composite sorbent [34]. In contrast, the shape of Cd sorption isotherm of bentonite and nMgO were L-type isotherms indicating intermediate affinity for Cd.

Seven sorption isotherm models (Freundlich, Langmuir, Elovich, Temkin, Fowler–Guggenheim, Kiselev, and Hill–deBoer) were used for fitting the experimental equilibrium isotherm data and to evaluate the interaction between Cd and adsorption equilibrium state of the three sorbents studied. The adsorption isotherm models and their fitting parameters are presented in Table 1. As shown in Table 1, Langmuir model well fitted Cd sorption data onto the three studied sorbents as evidenced by its highest R² and Lowest SE values (Fig. 5(b)). It is, therefore, suggested that the monolayer mode of adsorption is responsible for Cd adsorptive removal from the surface of the studied sorbents [35]. The Langmuir maximum adsorption capacity (qmax) of the nano-composite (200 mg/g) was 4 and 60 times higher than those of nMgO and bentonite sorbents respectively (Table 1).

3.5. Effect of Initial Solution pH on Cd Adsorption by Nanocomposite

The solution pH greatly affects the adsorption process; since it determines the charges of the surface sites of nano-composite and control Cd (II) action and Cd(II) species in the solution [36]. The effect of initial solution pH ranged from 4 to 9 at the sorbent dose of 0.2 g and different temperature range (287–307K) on the sorption process was monitored (Fig. 6). The results indicated that percent of Cd ions removal was low at pH 4 and gradually increased until peaking to ~95% at pH 9. Alteration in the removal of Cd ions as a result of changing pH can be referred to sorbent surface characterization and Cd speciation [37]. It is plausible that at low pH (4), nano-composite surfaces is covered with hydronium ions (H+) that compete with Cd ions and causing a low removal percentage. Increasing the pH may reduce the repulsive forces between the positively charged metal ions and the nanoparticles’ surface was reduced, causing a higher Cd removal [38].

3.6. Effect of Competitive Cations on Cd Removal by the Sorbents Studied

The industrial wastewater effluents contain many metal ions that could compete for binding sites of the sorbents. It is, therefore, important to study the competition between the heavy metals for Cd adsorption onto the studied sorbents. To evaluate the Cd% sorbed by nMgO, bentonite and nano-composite (nMgO and
Table 1. Equilibrium Model Constants and Determination Coefficients and Standard Error of Estimate for Cadmium Adsorption by Three Different Sorbents

| Models          | Parameter                           | nMgO  | Bentonite | Composite |
|-----------------|-------------------------------------|-------|-----------|-----------|
|                 | $K_F$ (mL g$^{-1}$)                 | 23,908.76 | 15,832.18 | 65,643.9  |
| Freundlich      | $1/n$                               | 0.9999 | 0.9508    | 1.013     |
|                 | $R^2$                               | 0.893  | 0.688     | 0.937     |
|                 | SE                                  | 0.415  | 0.709     | 0.317     |
| Langmuir        | $q_{\text{max}}$ (µg g$^{-1}$)     | 50,000 | 3333      | 200,000   |
|                 | $K_L$ (L mg$^{-1}$)                 | 1.6666 | 0.75      | 0.5       |
|                 | $R^2$                               | 0.923  | 0.939     | 0.965     |
|                 | SE                                  | 30*10$^{-6}$ | 43*10$^{-6}$ | 38*10$^{-6}$ |
| Elovich         | $q_{\text{max}}$ (µg g$^{-1}$)     | 111111 | 58823     | 2,000,000 |
|                 | $K_D$ (L mg$^{-1}$)                 | 214,000.000 | 60,000,000 | 1,520,000,000 |
|                 | $R^2$                               | 0.350  | 0.467     | 0.166     |
|                 | SE                                  | 0.336  | 0.519     | 0.290     |
| Temkin          | $\Delta Q$ (kJ mol$^{-1}$)          | 1.487  | 4.380     | 24.446    |
|                 | $K_D$ (L g$^{-1}$)                  | 2.092  | 4.133     | 18.107    |
|                 | $\theta = RT/\Delta Q \ln K_D C_e$ | 0.612  | 0.534     | 0.757     |
|                 | SE                                  | 0.350  | 0.575     | 0.069     |
| Fowler-Guggenheim(FG) | $K_{FG}$ (L mg$^{-1}$) | 0.7407 | 0.0542    | 0.3449    |
|                 | $R^2$                               | 0.427  | 0.795     | 0.510     |
|                 | SE                                  | 0.42399 | 0.940     | 0.295     |
| Kiselev         | $k_1$ (L mg$^{-1}$)                 | -1.4695 | 76.136    | 5.171644  |
|                 | $k_n$                               | 76.136 | 5.171644  | 5.171644  |
|                 | $K_{\text{I}}$ (Lmg$^{-1}$)         | 0.8050 | 0.0004    | 0.026     |
| Hill-deBoer     | $K_2$ (kJ mol$^{-1}$)               | -1.866 | -74.7892  | 9.026     |
|                 | $K_1 C_e = (1-k_1 \theta) \exp(2 \theta w/RT)$ | 0.857 | 0.0009    | 0.885     |
|                 | $R^2$                               | 0.112  | 0.859     | 0.736     |
|                 | $K_2$ (kJ mol$^{-1}$)               | -1.866 | -74.7892  | 9.026     |
|                 | $K_1$                               | 0.585  | 5.529     | 0.307     |
|                 | $K_2$ (kJ mol$^{-1}$)               | -1.866 | -74.7892  | 9.026     |
|                 | $K_1$                               | 0.585  | 5.529     | 0.307     |

Model parameters are defined in appendix A: Supporting information

Fig. 7. Effect of competitive cations (Zn, Cu, Ni) (a), and sorbent dose (0.1, 0.2, 0.3 g) (b) on Cd sorption by the three sorbents.
charged species. These results agree with other observations regarding efficiency of sorbents to bind heavy metals in presence of competing cations [39-41].

3.7. Effect of Sorbent Dose on Cd Removal
The effect of the mass of the three sorbents studied on Cd (II) uptake was performed by adding 20 mL of 500 mg L⁻¹ initial Cd (II) concentration to different dosages of the three sorbents studied for 60 min contact time. The effect of each sorbent mass on the corresponding Cd uptake percentage and the equilibrium sorption capacity is shown in Fig. 7(b). The results show substantial variations in Cd sorption ability among different doses. Increasing the dosage of each sorbent from 0.1 to 0.3 g significantly increased Cd removal. The increase of mass sorbent has led to a greater surface area and that augments the number of active sites available for Cd binding.

3.8. Effect of Temperature on Cd Sorption by Nano-composite
Effect of temperature on Cd(II) sorption by nano composite (nMgO and Bentonite) was studied at three different temperatures (287, 297 and 307 K) and four different Cd concentrations (100, 250, 500 and 1,000 mg L⁻¹). The adsorbed Cd onto studied sorbents increased with increasing the temperature from 287K to 307K (Fig. 6). The Langmuir sorption capacity of nano-composite for Cd increased from 200 to 279 mg g⁻¹ with increasing temperature from 287K to 307K. Fig. 6 shows that the highest efficiency of Cd removal by (nMgO and Bentonite) nano-composite was at temperature of 307 K and pH 9. These findings are coincided with Ismail et al. (2009) [42] who found an increase of Cd adsorption by powdered corn cobs with increasing temperature from 25 to 55°C. The enhanced adsorption at higher temperature is attributed to the increase of surface reaction and kinetic energy of sorbate [43].

3.9. Thermodynamic Parameters of Cd Sorption on Nano-composite
Thermodynamic parameters of Cd sorption by nano-composite (nMgO and Bentonite) were determined using the equilibrium constants [44], to fully understand the nature of the sorption process (Table S2). The change in standard free energy (ΔG°) for Cd (II) sorption at initial concentration of (100 mg L⁻¹) and pH 7 was observed to be -21,142.097, -24,076.274 and -26,220.009 J mol⁻¹, onto (nMgO and Bentonite) composite at 14, 24, and 34°C, respectively (Table S2). The negative values of ΔG° point out the ease of Cd sorption reaction and the spontaneous nature of Cd sorption onto nano-composite sorbent [45]. The decrease in ΔG° (i.e. increase negative) values indicated the increase in the extent of the adsorption. Data in Table S2 and Fig. S1 showed decrease of ΔG° values with increasing temperature suggesting more effective sorption at higher temperatures. In addition, it is noticed a negativity increase in ΔG° values with increasing solution pH values which indicates more sorption with increasing pH values from 49 [46, 47].

The values of ΔS° were in the ranges of -241.81 to -439.45 and -197.30 to -231.77 J mol⁻¹K⁻¹ for Cd adsorption on nanocomposite at of 100 and 1,000 mg L⁻¹ initial Cd concentration, respectively. The negative values of ΔS° suggest decreasing randomness at the solid/solution interface and no significant changes occur in the internal structure of the adsorbent through the adsorption [48]. The negative values of ΔS° obtained in this study suggest that the Cd (II) sorption process involves a dissociative mechanism. The positive values of ΔH° for Cd sorption on nano-composite at different initial solution concentration suggested that sorption was endothermic in nature (Table 3) [48]. If the ΔH° or the heat of sorption ranges from 2.1–20.9 kJ mol⁻¹, the sorption is physical in nature, and if it ranges from 20.9–418 kJ mol⁻¹, the process is chemisorption [49]. In the current study, ΔH° values suggest that chemisorption was the dominant process for Cd(II) removal by nano composite.

3.10. Suggested Cd Adsorption Mechanisms
To elucidate Cd adsorption mechanisms onto (nMgO and Bentonite) nano-composite, SEM, EDX and FTIR analyses were performed to characterize the nano-composite before and after Cd adsorption. The EDX analysis revealed the presence of Cd ions on the nano-composite in high concentration (21%) after adsorption (Fig. 2(d)). The FTIR spectra of nMgO and (nMgO and Bentonite) nano-composite after Cd adsorption confirm the obvious interaction between Cd (II) ions and OH functional group and Mg-O stretching vibration. Indeed, the considerable decrease in Mg content of Cd-saturated nano-composite from 13.33 to 9.16% could be evidence for cation exchange reaction (Fig. 2(c), (d)). In addition, the FTIR analyses confirmed the role of CO₃ in Cd precipitation reaction as evidenced from the appearance of CO₃ band at 630 cm⁻¹ after adsorption of Cd onto nano-composite (Fig. 3(b)). Thus, it is proposed that the mechanism of Cd sorption onto nano-composite can be mainly referred to cation exchange and precipitation reactions as described in the following equations:

\[
\text{MgO + H}_2\text{OH} = \text{Mg(OH)}_2 \quad \text{(hydroxylation ability of MgO)} \quad (1)
\]
\[
\text{MgO + Cd = CdO + Mg} \quad \text{(cation exchange reaction)} \quad (2)
\]
\[
\text{Mg(OH)}_2 + \text{Cd = Cd(OH)}_2 + \text{Mg} \quad \text{(precipitation reaction)} \quad (3)
\]
\[
\text{Cd(OH)}_2 + \text{CO}_3^- + (\text{H}_2\text{O})^n = \text{CdCO}_3 + (\text{H}_2\text{O})^n \quad \text{(more stable complexes formation)} \quad (4)
\]

The suggested mechanisms of Cd adsorption by the nano-composite are in accord with Xu et al. (2019) [50] who concluded that both cation exchange and precipitation reactions control sorption process of Cd on mesoporous MgO ceramic fibers. They demonstrated that Cd can be adsorbed on MgO to form CdO as a result of cation exchange reaction between Mg and Cd. Because of the strong attraction of H towards oxygen of MgO, MgOH may release considerable OH into solution and precipitate Cd as Cd(OH)₂. In addition, they noticed that Cd(OH)₂ can be progressively transformed into more stable compound of CdCO₃ in the case of presence of CO₃ in aqueous solution..
The efficiencies of the nano-composite at a flow rate of 2 mL min\(^{-1}\) of 91\%, and 93\% were observed for Cd removal from industrial wastewater and drainage water respectively. Overall, the findings of the present study revealed that the novel (nMgO–Bentonite) nano-composite would be a superior ecofriendly and recycled adsorbent for efficient removal of Cd from wastewater.

Comparative overview for adsorptive capacity of nanocomposite (200 mg/g) for Cd removal with the various adsorbents studied in literature is presented in Table S3. Application of hydrous iron oxide, Spirulina maxima, hydroxyapatite biomaterial and manganese oxide/active carbon fiber resulted in quite low adsorption of Cd (14.86–72 mg g\(^{-1}\)). Using of modified apple pomace, Birnessite (powder), Zeolite composite and Cryptomelane (powder) in Cd removal showed good adsorption capacity (112–196) but lower than the nMgO-bentonite nano-composite. Therefore, the currently suggested nanocomposite was exhibited by more efficient Cd adsorption capacity compared to the various adsorbents reported in literature. Moreover, the nanocomposite demonstrated a superior reusability and applicability in Cd removal that making the nanocomposite more efficient and desirable for removal of heavy metals.

4. Conclusions

The novel nano-composite (nMgO-bentonite) was successfully produced and characterized by XRD, SEM-EDX and FTIR. The power function model and Langmuir adsorption isotherm model preferably described the adsorption process. The Langmuir maximum adsorptive capacity of bentonite for Cd increased substantially from 3.33 to 200 mg/g in case of applying the nanocomposite. The kinetics and the thermodynamics data suggest the spontaneous and endothermic nature of Cd adsorption process onto nanocomposite. The possible mechanisms of Cd adsorption on the nanocomposite involved cation exchange and precipitation reactions. The Cd removal efficiencies of nanocomposite in industrial wastewater and drainage water were 91 and 93\%, respectively for packed columns. The Cd removal efficiency of the nano-composite was not significantly altered after six successive cycles suggesting its excellent reusability. The current findings revealed that nano-composite (nMgO-bentonite) has excellent adsorption affinity towards Cd and can be potentially employed as a superior adsorptive removal of Cd from industrial wastewater.

Conflict-of-Interest

The authors declare that they have no conflict of interest.

Author Contributions

E.E. (professor) conceptualization, supervising investigation, writing, editing and revising. M.M. (Professor) supervising, investigation, writing and editing. A.S. (Professor) supervising investigation, writing. F.A. (Master student) investigation, determination and writing.
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