Tracking the adsorptive effect of nano silicate–ginkgo residue composite for Sr(II) and Cd(II) removal from aqueous solutions

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Abstract
Ginkgo biloba (Ginkgo)/calcium silicate nanocomposite (NG-CSA) was prepared as a novel sorbent. Nanomaterial was characterized using different techniques such as Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray diffraction, differential thermal analysis and thermal gravimetric analysis (DTA and TG). Adsorption of Sr(II) and Cd(II) ions was performed taking into account significant parameters such as initial pH of the solution, shaking time and initial concentration of metal ions as well as temperature. The acquired results were disclosed that the adsorption of both ions is notably improved using NG-CSA composite. The monolayer capacity of NG-CSA for Sr(II) and Cd(II) from binary system is 122.45 and 64.68 mg/g for Sr(II) and Cd(II), respectively. The kinetic studies exposed that the adsorption process followed nonlinear pseudo-first-order model. The isotherm studies show that the extended Langmuir model is more applicable than Freundlich model for binary system adsorption process. The value of diffusion coefficient for the Sr(II) and Cd(II) is in range $10^{-10}$ m²/s which indicates the chemisorption nature of the process. The maximum value of desorption for the Sr(II) and Cd(II) is 98.41% and 97.66 utilized 0.3 M of nitric acid. This indicated that NG-CSA composite can be regenerated and reused for further adsorption of Sr(II) and Cd(II) from wastewater.

Keywords Ginkgo biomass composite · Sr(II) · Cd(II) · Adsorption

Introduction
The release of large amounts of radioactive waste during nuclear industries into the environment has received significant attention; thus, this waste must be removed in ways that protect humans and reduce the risks of radioactive waste to the environment. The removal of discharged waste into the environment is a significant issue, and it is a challenge for scientists to always search for the best ways to get rid of this waste (Sutirman et al. 2021; Abdel Maksoud et al. 2022; Li et al. 2020; Abdel Maksoud et al. 2021). There are different sources of waste in environment: one from man-made and the other from natural sources. The radioactive wastes can be generating during research reactor activities and the production of radioisotope also from the different applications that use the radioisotopes (Wang et al. 2020; Zhang et al. 2021; Hassan and Elmaghraby 2019). The handling of radioactive waste often includes the usage of several techniques such as chemical deposition, filtration, chemical precipitation, adsorption, ion exchange and evaporation. Many materials have been used for elimination hazardous elements such as zinc ferrite nanocrystals (Hassan et al. 2020a, b, c), nanosized calcium silicate (Hassan et al. 2020a, b, c), silica–chitosan nanocomposite (Dakrouy et al. 2020), activated carbon (Makarova et al. 2021) and waste biomass (Rostamian et al. 2015). Calcium silicates (CSA) have many characteristics that make it enter into wide fields (Estrada-Floresetal et al. 2018). Calcium silicate is an industrial mineral trioxide aggregate (MTA) or calcium metasilicate comprised of calcium, silicon and oxygen. Its molecular formula is CaSiO$_3$ and theoretically contains 48.28% CaO and 51.72% SiO$_2$. As far as the wollastonite properties, such as low dielectric constant, low...
dielectric loss, thermal stability, low thermal expansion and low thermal conductivity are concerned, it was widely used in ceramic fabrication, as a high frequency insulator, metallurgy and frictional product (Nabila et al. 2017). Elimination of harmful elements from wastewater was one of the CSA applications that made a significant impact. Guangxia et al. (2015), prepared CSA from fly ash and utilized in sorption of Co (II) (Guangxia et al. 2015). Also, calcium silicate materials are common use worldwide in immobilization strategies for radioactive waste. The widespread usage of calcium silicate materials in management of nuclear waste is in particular due to their general radionuclide fixation and immobilization properties including the low solubility of many metals at high pH, their low permeability and diffusivity, and the versatility in application (Steve et al. 2018). Tits et al. 2014 used CSA for immobilization some hazardous materials such as Th (IV) and U(VI). In last decades, many authors investigated the sorption behavior of different waste elements, $^{90}$Sr, $^{226}$Ra, $^{152}$Eu, $^{237}$Np and $^{248}$Cm (Tits et al. 2014). The use of bio-nanocomposite for wastewater treatment has recently attracted significant attention. This is due to their unique advantages such as non-toxicity, easy fabrication and cost viability (Ahmed et al. 2016; Ahmad et al. 2018). Waste plant resources present unique spherical surface structure characteristics and have been utilized for fabrication of nanocomposite (Verma et al. 2017). Ginkgo biloba leaves are the main by-product of Ginkgo biloba industry (Liang 2012). It is commonly used in medicinal extract process and additives in food and cosmetics, which produced a large available and inexpensive supply of ginkgo leaves residue (Zhang et al. 2015). These residues have no present commercial usage and are not eaten by livestock. There are no previous published reports on the use of ginkgo leaves residue after extraction process for Sr(II) and Cd(II) recovery from aqueous solution. In addition, the main components in Ginkgo biloba including lignin, cellulose and hemicellulose which could be contribute in the adsorption process (van Beek and Montoro 2009). Jiang et al. (2013) produced activated carbons from Ginkgo biloba leaves with good electronic conductivity and high surface areas (Jiang et al. 2013). However, there are still limited applications of the abundant Ginkgo biloba leaves. Therefore, more strategies for the application of Ginkgo biloba leaves need to be developed. So, the objective of this work is to develop a new composite material composed of calcium silicate CSA and biomass ginkgo biloba residue leaves extract G used as adsorbent material for the removal of Sr(II) and Cd(II) from wastewater. Many parameters that influence the sorption behaviour of both ions, such as contact time, pH change, and concentration effect, have been investigated. Various kinetic and isotherm models were applied. As expected, this study can open a new approach applied more generally to different biomaterials from nature.

Materials and methods

Preparation of adsorbent

Synthesis of ginkgo (G)

The crushed residue of Ginkgo biloba (Ginkgo) leaves was obtained as a by-product after extraction process. It was rinsed with diluted nitric acid 0.1 M in order to eliminate color. Sample was washed with distilled water, dried, grinded and sieved to the desired size 20 mesh. Phosphoric acid $H_3PO_4$ was used as activating agent in 1:1(w:w) at 110 °C for 2 h and at 500 °C for 4 h. The mixture was then dried over night at 105 °C to remove the excess acid until the solution become neutral pH 7. The final product was kept in oven for 12 h at temperature of 60–80 °C to remove moisture.

Synthesis of nano-ginkgo–calcium silicate composite (NG-CSA)

The synthesis procedure of nano-calcium silicate (NCSA) and different characterization techniques were illustrated elsewhere (Hassan et al. 2020a, b, c). In a typical synthesis, 1 g of activated ginkgo (G) was mixed with calcium silicate in ratio (1:1) with 20 ml distilled water and 30 ml ethanol solution. The mixture was stirring frequency (200 rpm). After 2 h of reaction, the product was separated from the solution and finally dried at 70 °C and the prepared adsorbent was labeled as NG-CSA.

Characterization of adsorbent

Physicochemical characterization of the NG-CSA was achieved using X-ray diffraction (XRD) (Philips, PW/1710). The surface morphology of NG-CSA and size of the prepared composite was assigned through sem (Philips XL 30 attached to EDX Unit) and transmission electron microscope.
(TEM) [JEM-HR-2100, Japan] to determine the nanosize of the prepared powder. The molecular structure and chemical composition were achieved using the KBr disk method and transmission % of the FTIR spectra (FTIR, model FT/IR-6100 type A, USA) with the range 4000–400 cm⁻¹. The weight loss and phase change of the NG-CSA powder were carried out using Shimadzu DTA-TGA system of type DTA-TGA-60 H, Japan. The pore size distribution and porosity of the NG-CSA powders were studied by applying mercury intrusion porosimetry technique with the aid of pore sizer chromatech 9320 (USA).

**Solubility studies**

Solubility studies of the NG-CSA composite, CSA composite and G material were achieved by contact of 0.5 g (w₁) of the solid materials with 10 mL of different molarities of eluents (HNO₃, HCl and NaOH) for overnight at 25 °C; then, the two phases were separated, and then, the weight of dried NG-CSA (w₂) was determined. The percentage of the solubility can be determined using the following equation:

\[ S = \frac{w_1 - w_2}{w_1} \times 100 \]  

(1)

**Saturation capacity of the under studied samples**

The saturation capacity of the prepared samples toward the adsorption of metal ions was studied. 0.01 g of sample with 10 mL of ions solution (200 mg/L) was conducted overnight to be sure that the equilibrium was reached. The solid sample was separated from the liquid phase, and the concentration of ions was determined. This process was repeated for several times using new volumes of metal ions (10 mL) until the adsorbent was completely saturated with the ions. The saturation capacity is expressed in Eq. (2):

\[ \text{Saturation Capacity} = \frac{\sum \text{Removal\%}}{100} \times C_o \times \frac{V}{m} \]  

(2)

**Adsorption analysis**

Different sorption experiments were conducted under equilibrium and kinetic conditions. A series of 100-mL glass flask containing 10 mL ion solution with 0.01 g of NG-CSA at temperature of 25 ± 1 °C onto shaker. Certain parameters, such as pH (1–9), initial concentration (50–500 ppm) and shaken time onto the ion adsorption, were studied. The pH values were adjusted with dilute solution of HCl or NaOH. The concentration of Cd(II) and Sr(II) in the aqueous phase was defined using the atomic absorption spectrophotometer (Buck Scientific, VGP 210). The amount of adsorbed ions, \( q_t \), and removal percentage were determined using the following equations:

\[ \text{Removal\%} = \frac{C_o - C_t}{C_o} \times 100 \]  

(3)

\[ q_t = \frac{C_o - C_t}{C_o} \times \frac{V}{m} \]  

(4)

where \( C_o \) and \( C_t \) represent the initial concentration of ions and concentration at time \( t \). \( V(L) \) is the volume of the solution and \( m (g) \) represents the mass of both ions.

**Adsorption isotherm**

Adsorption assays with starting ion concentrations ranging from 50 to 250 mg/L L were carried out to see how the amount of Cd(II) or/and Sr(II) uptake was affected by the initial ion concentration. For isotherm studies, a set of glass tubes containing 0.01 g of NG-CSA composite with 10 mL of the binary solution has been shaken at different temperatures (298, 303 and 313 K). After equilibrium, a volume of supernatant liquid (1 ml) was pulled and the concentration of both ions in the aqueous phase for all samples was determined. The amount concentration of both ions sorbed onto the NG-CSA at equilibrium, \( q_e \), was calculated using the following equation:

\[ q_e = \frac{(C_o - C_e)}{m} \times V \]  

(5)

where \( C_e \) is the equilibrium concentrations. The extended Freundlich and Langmuir isotherm models were used to studied the equilibrium isotherm for the adsorption of Sr(II) and Cd(II).

**Results and discussion**

**Characterization of NG-CSA**

**FTIR analysis**

FTIR is a significant technique to define functional groups of the prepared materials, which make the adsorption process possible. FTIR spectrum of calcium silicate was discussed before in detail (Hassan et al. 2020a, b, c). The
FTIR spectrum of ginkgo material is presented in Fig. 1a. The FTIR spectrum of G material presented a large number of peaks. Weak peak of ginkgo appears at 3384.43 cm\(^{-1}\) which represented the O–H modes of phenol group. The alkane CH group of each lipid and carbohydrate appears at 2919.51 and 2849.67 cm\(^{-1}\), respectively. The peak of G powder at 1576.90 cm\(^{-1}\) corresponds to amid group (Sangiliyandi et al. 2014). Also, the peak at 1176.00 cm\(^{-1}\) may be ascribed to bending stretching vibration of C–O–H. Peak at 1069.32 cm\(^{-1}\) is due to six-member cyclic ether. The peak corresponding to P-OH appears at 671.47 cm\(^{-1}\) (Han et al. 2011; Ahmad et al. 2009; El-Sayed et al. 2011; Deng et al. 2011; AL-Aoh et al. 2012). The spectra peaks in Fig. 1b represent NG-CSA functional groups. The peaks at 3415.46 and 2515.51 cm\(^{-1}\) are associated with OH and CH groups, respectively. Particularly, the absorption bands at 3415.46 are related to the stretching vibration of O–H in phenolic and/or carboxylic groups (Wanga and Chena 2014). The peaks at 1797.77 cm\(^{-1}\) assigned to the presence of C=O of NG-CSA. Moreover, the strong peak at 1429.46 cm\(^{-1}\) could be attributed to stretching N–H group. 1093.66 cm\(^{-1}\) is related to C=C stretching vibration. The peak at 879.75 cm\(^{-1}\) is due to a coupling of the vibrations of the Si–O–Si, Si–OH and Si(OSi)\(_3\)O–Ca groups. The peaks of NG-CSA powder appear at 713.45 and 671.51 cm\(^{-1}\) that were specified to Si–O and P-OH groups stretching.

Table 1 shows the data of specific surface area of prepared sample that displayed increase sing in specific surface area of NG-CSA composite than that in G and NCSA samples. G and NCSA have specific surface areas of 46.47 and 32.38 m\(^2\)/g, respectively, whereas NGCAS has a specific surface area of 104.23 m\(^2\)/g. The porosity and average pore diameter of NGCSA also rise. Also, the porosity of NG-CSA and the average pore diameter increase. The open and closed pores as well as volume of the powder materials are estimated by the bulk density. Also, the apparent density takes into consideration volume of the prepared materials and closed pores only. Regarding the data for the G and NCSA sample, the most of the existing pores were closed pores; however, in NG-CSA the most pores are open pores. Therefore, the improvement of NG-CSA composite was expected for the adsorption process.

XRD characterization of NG-CSA composite

The XRD analysis of the NCSA sample shows the crystallization of quartz (Ca\(_2\)SiO\(_4\)) and little of wollastonite (S. 1). But, at 1000 °C the wollastonite phase was the main phase (Hassan et al. 2020a, b, c). The crystalline structure of the G was further studied using XRD. The XRD pattern of G exhibits a characteristic peak at 2θ 25° and 2θ 40° which are close to that of pure G, as shown in Fig. 2. Sangiliyandi Gurunathan Jae Woong Han Jung Hyun Park Vasuki Eppakayala Jin-Hoi Kim, Ginkgo biloba: a natural reducing agent

| Sorbent | Specific surface area (m\(^2\)/g) | Average pore diameter (nm) | Bulk density (g/mL) | Apparent density (g/mL) | Porosity (%) |
|---------|----------------------------------|----------------------------|---------------------|-------------------------|--------------|
| G       | 46.47                            | 811                        | 0.51                | 0.72                    | 44.23        |
| NCSA    | 32.38                            | 805                        | 0.49                | 1.07                    | 31.75        |
| NG-CSA  | 104.23                           | 798                        | 0.45                | 1.63                    | 88.12        |
for the synthesis of cytocompatible graphene, International Journal of Nanomedicine 2014:9 363–377]. No patterns were seen in NG-CSA, which might be due to the creation of an infinite phase of NCSA with varied sizes capable of interacting with the G sample through aggregation onto the surface or adsorption (Gamal et al. 2021).

**Morphology of the prepared samples**

The SEM measurement was taken to emphasize the morphology of the NCSA (nano-calcium silicate) and NG-CSA composite materials. The SEM micrographs of NCSA sample are displayed in S.2. The composite material is composed of porous samples that were created by the assemblage of ultrafine nanoparticles. Figure 3A illustrates the SEM images of the Gingko (G) sample that display noticeable porosity, and the surface of materials is rough with appearing some cavities. The pores are produced from evaporating the chemical activating agent \((H_3PO_4)\) through carbonization process, leaving the sites previously occupied by acid molecules on the surface of G sample. Figure 3B shows the SEM images after coating NCSA with G; the surface of NG-CSA is imperishable rough and wrapped with G molecules.

TEM analysis of NCSA showed spherical grains in the nanoscale size, which was confirmed by the SEM micrographs (S.2). NCSA-based material showed irregular agglomerated particles. The particles size was ranged from 40 to 50 nm. Figure 3C presents TEM image of NG-CSA composite signalizes that the formed layer of ginko material covered the surface of aggregated NCSA particles. Therefore, the fixation of ginko on the NCSA surface is affirmed by this technique.

**Thermal properties of prepared samples**

The thermal analysis of prepared samples was studied to inquire into its thermal stability at elevated temperatures.

![SEM images of A G, B NG-CSA composite and C TEM of NG-CSA composite](image-url)
The DTA and TGA of materials were studied in the temperature range, 25–800 °C. (S.3) displays the curves of TGA and DTA for G and NG-CSA composite. The TGA curve exhibited three weight loss steps for the prepared samples. At low temperatures (up to 200 °C), the weight loss is reach to 13.09%, 9.03 for G and NG-CSA samples, respectively; this may be explained by losing the weakly water molecules bonded onto the surface of samples. The another weight loss stage is 8.07% and 10.06% for G and NG-CSA, respectively, that occurs at temperatures range from 200 to 500 °C; this loss coincides with the elimination of water molecules that chemisorbed onto the surface as well as lattice oxygen in the prepared samples (Handel et al. 2013). Finally, the samples were showed a higher degradation of 38.9 and 9.2% for G and NG-CSA, respectively, in this stage (600–800 °C). Differential thermal analysis was carried out from to 800 °C at constant heat rate of 10 °C/min. DTA curve shows one endothermic peaks and one exothermic peak; as shown in Fig. 4, the small endothermic peak at 90.9 °C is due to evaporation of adsorbed water, while the exothermic peak that located at 193 °C may correspond to the crystal structure of nano-NG-CSA.

**Solubility studies**

The solubility (S) of NG-CSA composite, NCSA composite and G material using various molarities of different eluents

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**Fig. 4** Thermal analysis for A G and B NC-CSA composite

**Fig. 5** Solubility of A G, B NG-CSA composite and C NCSA at room temperature
is displayed in Fig. 5. The result exhibits that increasing the solubility by increasing the eluents molarity and the rising in solubility follows the order: HNO$_3$ < HCl < NaOH. At low molarities of HNO$_3$ (< 3 M), the solubility of NG-CSA nanocomposite was less than 20%, while it was increased to be 97 at 5 and 6 M HNO$_3$ (Fig. 5B). While in the case of 3 M of HCl and NaOH solvents, the solubility of prepared samples became less than 15%, and the maximum value of solubility reached 96.8 and 95.1% at 6 M of HCl and NaOH, respectively. The results assessed that the solubility of G and NCSA samples is higher at low concentrations of the studied solvents than that of NG-CSA composite.

**Saturation capacity of the under studied samples**

Adsorption saturation capacity for the three samples under studied to the adsorption of Cd(II) and Sr(II) was achieved and computed by Eq. (2). The computed saturation capacities for Cd(II) have been 70.56, 56.76 and 95.32 mg/g to NCSA, G and NG-CSA composite, respectively, while they are 96.44, 78.43 and 210.54 mg/g for NCSA, G and NG-CSA composite, respectively, for Sr(II). These data assert the higher capacity of NG-CSA-composite to removing Cd(II) and Sr(II) from the aqueous solutions. This may be to the higher surface area of NG-CSA (104.23 m$^2$/g) and many active sites available for adsorption which created as the result from interactions between NCSA and G.

**Impact of sorbent mass**

Figure 6 displays the effect of sorbent quantity on adsorption behavior of Cd(II) and Sr(II) at initial concentration (200 mg/L) for single and binary system. The sorbent quantity effect was studied in the range 1 mg to 200 mg and the volume of ions solution 10 ml. After obtaining the equilibrium, the solutions were centrifuged and the concentration of ions in solution was measured. Figure 6 illustrates an increasing in removal efficiency with an increasing in the sorbent amount to a certain limit; then, the removal efficiency becomes constant. Optimum sorbent amount has been obtained at sorbent amount of 10 mg. The increasing in adsorption capacity with increasing sorbent amount is anticipated because as the amount of sorbent increases the number of active sites on the surface of composite increases (Hassan et al. 2019a, b). There is a disparity between removal efficiency of both ions as a function of sorbent amount; this indicates that the functional group on the composite surface is strong predilection toward Sr(II) than Cd(II) which is referred to the increasing in the hydration radius of cadmium ion compared to strontium ion (Hassan and Elmaghraby 2012).

**Impact of pH and speciation**

Figure 7 shows the relation between pH values and the percentage of removal efficiency for the Cd(II) and Sr(II) and the variation of distribution coefficient values of metal ions onto NG-CSA as a function of pH. It is observed that the values of $K_d$ increase with the increase in pH values as shown in Fig. 7b. At lower pH values (pH ≤ 4), $K_d$ of both ion was inhibited; this is attributed to the fact that when the pH is low, the presence of excess protons competes with ions in the solution and preferably occupies the binding sites available in the sorbent. At higher pH values, the $K_d$ values continuously increase with the increase in pH due to the decrease in proton competition. The $K_d$ values for Sr(II) and Cd(II) onto NG-CSA composite at pH 6.0 were found to be 1474 mL/g and 434, respectively. As can be seen, the value of $K_d$ for Sr(II) is greater than that of Cd(II); this means that Sr(II) are more able to diffuse through the sorbent and reach a higher number of active sites than Cd(II). This may be due to the ionic radii of Sr(II) is larger than that of Cd(II); hence, Sr(II) is less hydrated ionic radii and can be sorbed easily. The most favorable pH value has been choosing, pH 6. When the pH values are higher than pH > 6, both ions are precipitated and the discrimination between the quantity of ions adsorbed onto the NG-CSA composite and the precipitated quantity becomes more difficult (Hassan and Elsayed Elmaghraby 2019). So, the most favorable pH value has been acquired at pH = 6.

**Adsorption study**

The sorption study for binary system solution was achieved at various temperatures with a fixed weight of the prepared NG-CSA (0.01 g) at optimum pH (pH 5). The obtained
results of both ions are given in Fig. 8. It was observed that the sorption of each ion increases with contact time, which begins with high rate that decreases continuously. The sorption proceeds at slower rate to attain equilibrium after 60 min. After equilibrium, the sorption reached steady state. The amount of Sr(II) sorbed onto sample powder is greater than that of Cd(II); this indicates that both ions may be sorbed as hydrated ions, since the hydrated atomic radius of Sr(II) is smaller than that of Cd(II), because the atomic radius of Sr(II) is larger than that of Cd(II) (113 and 95 p.m., respectively). The largest atomic radius is the smallest hydrated atomic radius; hence, the amount sorbed of Sr(II) onto prepared composite is the highest. Also, as the
temperatures increase, the sorption rates of two ions increase and this proves the process endothermic.

**Kinetic studies**

The study of kinetics models for adsorption process is significant to describe of adsorption rate and estimated most favorable conditions for different applications (Motlochova et al. 2019). The prominent variation between the two kinetic models, pseudo-first order and pseudo-second order, is the mechanism difference of adsorption in both models. The pseudo-first-order model was inspired with the supposition applied in Langmuir isotherm model, in which each active site on the composite surface can adsorb one molecule only from the ions; in this case, the mechanism of the adsorption process is generally physisorption. But in pseudo-second-order model, one molecule of ions can be adsorb onto more than one active site onto adsorbent surface, and this model was identified as chemisorption mechanism that includes the covalent bonding as well as ion exchange (Hassan et al. 2020c). In this work, three kinetic models were applied to study the adsorption behavior of Sr(II) and Cd ions onto NC-CSA: pseudo-first-order, pseudo-second-order and Boyd models.

**Pseudo-first-order model**

This model presumes that the adsorption rate is limited by one mechanism on a single category of adsorbing sites and these sites are time-dependent. The adsorption rate relies on the adsorption capacity of ions. Lagergren was the first one proposed the pseudo-first-order model. The nonlinearized first-order kinetic model formula can be written as follows (Hassan et al. 2020c):

\[
q_t = q_e \left(1 - e^{-kt}\right)
\]  

(6)

where \(q_t\) and \(q_e\) represent the sorbed amount of studied ions at any time \(t\) and in equilibrium case, respectively (mg/g), the rate constant of this model, \(k_1\), min\(^{-1}\). Figure 9 illustrates the relation between \(q_t\) and \(t\). The pseudo-first-order parameters such as \(k_1\) and \(q_e\) can be estimated and are displayed in Table 2 along with \(R^2\) values. Although the calculated values of \(q_e\) close to the experimental values, the values of

![Fig. 9 Pseudo-first- and pseudo-second-order kinetic model for sorption of Sr(II) and Cd(II) onto NG-CSA at different temperatures](image)

| Metal ion | Temperature K | First-order kinetic parameters | Second-order kinetic parameters | \(q_e\), exp., mg/g |
|-----------|---------------|-------------------------------|---------------------------------|-------------------|
|           |               | \(k_1,\) min\(^{-1}\) | \(q_e\), calc. mg/g | \(R^2\) | \(k_2,\) g/mg min | \(q_e\), calc. mg/g | \(R^2\) |
| Sr(II)    | 298           | 0.07                          | 104.2                           | 0.99              | 0.09             | 119.13               | 0.92              | 100.81            |
|           | 303           | 0.08                          | 106.1                           | 0.99              | 0.11             | 119.22               | 0.93              | 103.03            |
|           | 313           | 0.09                          | 110.6                           | 0.98              | 0.13             | 123.4                | 0.92              | 107.87            |
| Cd(II)    | 298           | 0.08                          | 39.48                           | 0.99              | 0.12             | 46.17                | 0.91              | 40.8              |
|           | 303           | 0.11                          | 41.59                           | 0.98              | 0.18             | 47.22                | 0.92              | 43.0              |
|           | 313           | 0.11                          | 51.26                           | 0.97              | 0.18             | 55.64                | 0.91              | 50.8              |
The pseudo-first-order model constants are displayed in Table 2. The result shows the values of calculated \( q_e \) are closer to the values of experiment \( q_e \) and the \( R^2 \) values more than 0.99.

**Pseudo-second-order model**

This model has been applied to depict the kinetics of the adsorption process of binary system solution of studied ions onto NG-CSA at various temperatures. This model presumes a chemical rate controlling uptake process (chemisorption) (Garcia et al. 2019). This model can be written in the nonlinearized form as the following equation (Hassan et al. 2020c):

\[
q_t = \frac{(K_2 q_e^2 \cdot t)}{(1 + K_2 q_e \cdot t)}
\]

\( K_2 \) is symbolized to the constant of the pseudo-second-order model. Plotting of \( q_t \) with \( t \) for both Sr(II) and Cd(II) ions at 298, 303 as well as 313 K is displayed in Fig. 9. Table 2 shows the calculated values from ions sorbed onto NG-CSA; the values of calculated, \( q_e \), are not closer to the experimental ones, and the values of \( R^2 \) are less than those of pseudo-first-order model. So, the pseudo-first-order model is prevailing for the adsorption of Sr(II) and Cd(II) (Hassan et al. 2019).

**Boyd model (Helfferich 1962; Boyd et al. 1947)**

This model was studied to determine whether the sorption mechanism is film or particle diffusion. Many parameters in model have been determined by using the following expressions: is interest in studying whether the mechanism adsorption process is particle diffusion. Many parameters in this model can be specified using the following equations:

\[
F(t) = 1 - 6 \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -D_i \pi^2 \frac{m^2}{r_0^2} \right)
\]  

\( F(t) = 1 - 6 \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2Bt) \)  \( F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2Bt) \)

\[
B = \frac{\pi^2 D_i}{r_0^n}
\]

\[
F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left( -D_i \pi^2 \frac{m^2}{r_0^2} \right)
\]

\[
B = -0.4977 - \ln(1 - F)
\]

\( F \) represents the ratio between sorbed amount at equilibrium and at any time \( t \), \( F = \frac{q_t}{q_e} \) symbolizes time constant, \( D_i \) is exemplifying the effective coefficient of diffusion for ions, \( r_0 \) is the radius of the solid particle, and \( n \) is integers. The relation between \( Bt \) with \( t \) can define whether the adsorption process is controlled by particle diffusion or film. \( F \) values were acquired from Reichenberg’s table (Rechenberg 1953). The linear plots of \( Bt \) versus time were used to differentiate between film and particle diffusion controlling sorption process. The feature of linearity and the plot is a straight line passing through the origin; the rate of sorption has been fitted by particle diffusion.

![Fig. 10](image_url)  
**Fig. 10** Plot of \( Bt \) versus Time for the adsorption of Sr(II) and Cd(II) ions sorbed onto NG-CSA composite at different temperatures

Table 3 Diffusion coefficient and activation energy values for the adsorption of Sr(II) and Cd(II) onto NG-CSA composite

| Metal ion | \( D_i \times 10^{10} \), m²/s | \( R^2 \) | \( D_o \times 10^{7} \), m²/s | \( E_a \), kJ/mol | \( R^2 \) |
|-----------|-----------------------------|--------|-----------------------------|-----------------|--------|
| Sr(II)    | 8.06                        | 0.962  | 8.98                        | 16.561          | 0.987  |
| Cd(II)    | 10.37                       | 0.988  | 7.26                        | 5.76            | 0.877  |

Table 3 displays the diffusion coefficient and activation energy values for the adsorption of Sr(II) and Cd(II) onto NG-CSA composite.
mechanism. Nonlinearity and deviation of straight line about the origin indicate that the sorption rate has governed by film diffusion mechanism. Figure 10 reports the relation between Bt with time for Sr(II) and Cd(II) ions at 298, 303 and 313 K. The obtained plots are a straight lines pass through the origin point for each ions; these results propose that the adsorption behavior for both ions are particle diffusion at various temperatures. The values of effective coefficient of diffusion (Di) for Sr(II) and Cd(II) ions at 298, 303 and 313 K were defined from the slope. The data are displayed in Table 3. The adsorption nature is efficacious remarkably on the diffusion coefficient values (Di). If the values of Di range from $10^{-6}$ to $10^{-9}$ m²/s, the physical adsorption is prevalent, but for chemisorption, the values range from $10^{-15}$ to $10^{-17}$ m²/s. In this work, the chemisorption is predominant, and the values of Di are in the range $10^{-10}$ m²/s, for both Sr(II) and Cd(II) ions (Hassan et al. 2019; Walker and Weatherly 1999). Figure 4c displays the linear relationship between lnDi and $1/\text{T}$ that demonstrates the validation of the linear format of Arrhenius equation:

$$\ln D_i = \ln D_0 - \left(\frac{E_{ac}}{kT}\right)$$  \hspace{1cm} (12)

where $E_{ac}$ represents the activation energies for each ion and $D_0$ is a pre-exponential constant and can be computed these parameter from the slope and intercept of the linear plots. The obtained data are given in Table 3. The values of $E_{ac}$ for Sr(II) and Cd(II) were found to be 16.56 and 5.76 kJ/mol, respectively. From the data of $E_{ac}$ it is clear that the adsorption process is controlled by intra-particle diffusion (Walker and Weatherly 1999) (Figs. 11, 12, 13 and 14).

**Adsorption isotherms**

The presence of more than one component in the solution leads a competition among these various ions for the adsorption sites. Thus, the models used in adsorption of the single ions are not viable. Two isotherm models was applied to depict the adsorption isotherm of Sr(II) and Cd(II).
Extended Langmuir model

The extended Langmuir model was applied to describe the binary system. The equation of the extended Langmuir for the adsorption in a binary system is represented as follows:

\[
q_{e,i} = \frac{Q_0^i b_i C_{e,i}}{1 + \sum_j b_j C_{e,j}}
\]  

\[ \text{Eq. (13)} \]

Here, \( q_{e,i} \) refers to the equilibrium concentrations of the solute \( i \), and the amount of adsorbed ions at equilibrium was symbolized by \( q_{e} \) (mg/g). \( Q_0^i \) and \( b \) are the constants of Langmuir isotherm point out the capacity and adsorption energy, respectively. The extended Langmuir plot is illustrated in Fig. 5a; the values of different parameters of this model were estimated and are displayed in Table 4. Table 4 clearly shows that the \( Q_0^i \) values were increased with increasing the temperature because of the approachability of the active sites onto the surface of NG-CSA. The higher value of \( b \) indicated...
that the higher affinity of the NG-CSA to the sorbate. The difference between the $b_{\text{Sr(II)}}$ and $b_{\text{Cd(II)}}$ values displayed in Table 4 refers to a great affinity of the NG-CSA to Sr(II) regarding Cd(II) in binary system. These results are convenient with the hypothesis mention in other studies; the difference in affinity could be ascribed to the variation in ionic properties of ions such electronegativity and ionic radius (Ibrahima et al. 2018).

**Extended Freundlich model**

Freundlich isotherm is be contingent on the distribution of adsorbate between liquid as well as solid surface at equilibrium. The mathematical expression of Freundlich model can be written as follows (Ibrahima et al. 2018):

$$q_e = K_F i C_{e,i} (C_{e,i} + \sum_{j=1}^{N} a_{ij} C_{e,j})^{1/n}$$

where $K_F i$ is constant of Freundlich model for the solute $i$ that refers to adsorbent capacity (mg/g·(mg/L)$^{1/n}$), and $n$ is constant that displays the heterogeneity of the surface and also defined as adsorbent intensity. The Freundlich isotherm for binary system is plotted in Fig. 5b, and the parameters of this model are presented in Table 4. The higher values of correlation coefficients were acquired ($R^2 > 0.96$), but the $K_F i$ value is small compared with adsorption capacity in case of Langmuir model; this explains that the extended Langmuir model is more preferred than model better than Freundlich model (Tables 5 and 6).

**Desorption studies**

Regeneration of sorbent materials are requisite for the many applications in industrial field and clarifies the efficiency of materials and remarkably minimizes the operational cost and protection of the waste treatment plants. In this study, desorption experiments of Sr(II) and Cd(II) from loaded NG-CSA were achieved using acid (HNO$_3$) and base (NaOH).

| Table 4 | Extended Langmuir and Freundlich parameters for the adsorption of Sr(II) and Cd(II) onto NG-CSA composite |
|---------|-----------------------------------------------------------------------------------------------------|
| Metal ion | Temp (k) | **Langmuir isotherm model** | **Freundlich isotherm model** |
|          |          | $Q^o$ (mg/g) | $b$ (L/mg) | $R^2$ | $K_F$ (mg/g·(mg/L)$^{1/n}$) | $n$ | $R^2$ |
| Sr(II)  | 298      | 122.45      | 0.049      | 0.98   | 098.68 | 0.018 | 0.97  |
|         | 303      | 146.65      | 0.076      | 0.97   | 101.11 | 0.015 | 0.97  |
|         | 313      | 159.43      | 0.086      | 0.97   | 116.70 | 0.023 | 0.96  |
| Cd(II)  | 298      | 064.68      | 0.011      | 0.96   | 045.72 | 0.012 | 0.96  |
|         | 303      | 081.58      | 0.014      | 0.96   | 067.85 | 0.009 | 0.97  |
|         | 313      | 094.97      | 0.016      | 0.97   | 084.16 | 0.015 | 0.98  |

| Table 5 | Regeneration of Sr(II) and Cd(II) using 0.3 M of nitric acid |
|---------|-------------------------------------------------------------|
| Cycle no | Sorption, % | Desorption, % |
|          | Sr(II) | Cd(II) | HNO$_3$, 0.3 M | Sr(II) | Cd(II) |
| Cycle 1  | 98.87  | 88.45 | 98.41 | 97.66 |
| Cycle 2  | 85.74  | 82.55 | 93.78 | 91.51 |
| Cycle 3  | 69.39  | 71.68 | 90.98 | 88.32 |
| Cycle 4  | 49.81  | 43.61 | 86.88 | 84.99 |

| Table 6 | Sorption capacity of the prepared material in comparison with other sorbent materials |
|---------|-------------------------------------------------------------------------------------|
| Sorbents          | Capacity (mg/g) | References                          |
|                  | Sr(II) | Cd(II) |                                  |
| GO-EDTA           | 172.3  | –      | Amer et al. (2017)                |
| Dolomite          | 1.172  | –      | Ghaemi and Torab-Mostaedi (2011)   |
| Modified yeast cells | 140.8 | –      | Ji et al. (2010)                  |
| TiO2              | –      | 86.95  | Sharma (2014)                    |
| Sawdust           | –      | 221.45 | Hidalgo-vázquez (2011)            |
| Grape residues    | –      | 9.18   | Villaescusa et al. (2004)         |
| Dried cactus cladodes | –    | 30.42  | Barka et al. (2013)               |
| Alginate          | –      | 30.91  | Mata et al. (2009)                |
| Ginkgo biloba L. shells | –    | 42.59  | wang et al. (2007)                |
| NG-CAS            | 122.45 | 64.68  | This work                         |
reagent at 25 °C. The influence of reagent concentration on desorption process of the Sr(II) and Cd(II) was examined employing various molarities of HNO₃ and NaOH, ranged from 0.01 to 0.3 M. The desorption percentage ($D\%$) could be computed as follows:

$$DE\% = \frac{C_{aq} \times 100}{C_{si}}$$ (15)

The $C_{aq}$ and $C_{si}$ are symbolized to concentrations of the ions in the aqueous solution and solid medium, respectively. The data of desorption process are displayed in (S.5); the results clarifies that the desorption of the studied metal ions by means of nitric acid is greater than desorption of sodium hydroxide. The maximum desorption percentage obtained for Sr(II) and Cd(II) is 98.41% and 95.37, respectively, by applied 0.3 M of HNO₃. The regeneration of NG-CSA composite was achieved using the preferable concentration of nitric acid (0.3 M), and the regeneration process was achieved utilized for four cycles. In adsorption process, the first cycle attained 98.87 and 88.45% for Sr(II) and Cd(II), respectively, and become less to 49.81, 43.61% after four cycles. However, in desorption process after four cycles the desorption percentage of Sr(II) and Cd(II) was 86.88 and 84.99%, respectively. (S. 6) displays the results of the percent of adsorption–desorption process for each cycle. Data recommend that NG-CSA can be regenerated as well as reused for a new adsorption process.

**Comparative material**

The comparison among several types of sorbent materials is shown in (S.7). It clear that the prepared composite has a high adsorption capacity that can be used for Sr(II) and Cd(II) uptake from aqueous solutions.

**Conclusion**

In summary, novel bio-adsorbents from biomaterials including gingko leaves residue and calcium silicate were successfully fabricated. The results show that NG-CSA is an efficient sorbent material and advised for uptake of Sr(II) and Cd(II) from binary system solution. The study of the kinetic of the adsorption process disclosed that the adsorption follows the nonlinear pseudo-first-order model. The diffusion coefficient value ($D_i$) in the range of $10^{-10}$ m²/s indicates the adsorption process chemisorption process for the two metal ions. The isotherm studies explained that the extended Langmuir model is more preferable for the adsorption process of the two ions. The saturation capacity of NG-CSA was calculated and found to be 210.54 and 96.44 mg/g for Sr(II) and Cd(II), respectively. The maximum value of desorption for the Sr(II) and Cd(II) is 98.41% and 97.66 utilized 0.3 M of nitric acid. The regeneration of NG-CSA composite was achieved using the preferable concentration of nitric acid 0.3 M, and the regeneration process was achieved utilized for four cycles. The data uncovered that NG-CSA is a new sorbent material for the removal of Sr(II) and Cd(II) with repeated utilization.

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**Declarations**

**Conflict of interest** The author declares that he has no conflict of interests regarding the publication of this paper.

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