Batch and fixed bed column investigations of the sorptive removal of cesium ions from aqueous solutions using modified graphene-alginate nanocomposite beads

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ABSTRACT
Cesium radioisotopes are among the majors that are presented in liquid radioactive waste causing long-term environmental threats. The mandatory treatment of these streams is regenerative in which adsorption techniques are focal. Calcium alginate/graphene-sodium dodecyl sulfate (CA/GR-SDS) nanocomposite beads were synthesized/characterized and their sorption properties toward Cs⁺ were evaluated. Beads were of amorphous nature and the essential components were detected by FT-IR. Batch and fixed-bed column studies were explored. The highest sorbed Cs⁺ amounts were acquired within the 1st-30 min of contact time. The pseudo 2nd-order model gave the best fitting of the experimental kinetic data. Simple thermodynamic models have been applied to the isotherm sorption data and the relevant thermodynamic parameters were determined from the graphical presentation of these models. Increasing temperature gave lower quantities of sorption capacities. The estimated thermodynamic parameters disclosed the exothermic spontaneous ease of all sorption processes where negative ΔH° and ΔG° quantities were gained. Curves of Cs⁺ breakthrough from CA/GR-SDS were constructed at varied bed depths (2.0, 4.0, and 8.0 cm) and flow rates (1.0 and 2.0 mL/min). Increasing the bed depth to 8.0 cm, slower exhaustion time was observed (15.5 h). Capacities and performances of beds were increased from 24.85 to 214.46 mg/g and from 13.67 to 29.89%, respectively, by increasing bed depths from 2.0 to 8.0 cm. A fast exhaustion time were observed with increasing the flow rate to 2.0 mL/min (1.17 h).

1. Introduction

Nanocomposites became significant in a great diversity of industrial and research sectors to promote processes or develop new ones. The nanoparticle have unique characteristics (Alvarez & Cervantes, 2011). A new carbon nanomaterial, graphene, has distinctive physical, chemical, electrical, and mechanical features (Balandin et al., 2008; Navarro et al., 2008; Park et al., 2008) and is proper for providing devices and composites in nano-scales (Ang et al., 2008; Yang et al., 2010). Recently, graphene(oxide) (GO) was applied for removing methyl orange (Li et al., 2011b; Li et al., 2011a), naphthalene (Zhao et al., 2011), 1-naphthol (Zhao, Li, Wang et al., 2011), arsenic (Chandra et al., 2010), and fluoride (Li et al., 2011c) from solutions and showed high rates of sorption for heavy metals (HMs) removal (Chandra & Kim, 2011; Deng et al., 2010). The high hydrophilicity/surface area of GO maximized its interaction with contaminants via the implanted active sites. These attributes make GO highly desirable for water remediation applications. It has demonstrated, few-layered GO had superior adsorptive capability to eliminate various HMs like Cd²⁺, Co²⁺ and Pb²⁺ (Zhao, Li et al., 2011). Modified graphene(s) implemented with varied functional groups were evaluated to provide an opportunity to tune the physicochemical properties of graphene (Mali et al., 2015; Sayed et al., 2016a).

However, an increasing fear is spreading throughout the communities toward GO/graphene’s hazards on health during the production, utilization, and disposal, once uptaken by living beings (Schinwald et al., 2012; Wang et al., 2011). Common awareness has not been established; ahead of that, some safety measures are welcome to avoid the thinkable environmental hazards. Current research on nanocomposites of graphene-based polymer has been fast motivated as a result of improvement in the attributes of the nanocomposites (Zhenghai, Yanda, Baochun, Liqun, & Demin, 2012; Rama, Sanjoy, & Arun, 2012). Immobilization/encapsulation of GO deserves as an option.

Alginate, a hetero-polysaccharide composed of β-D-manuronic acid and α-L-guluronic acid, widely distributes in diverse seaweeds and bacteria. It constitutes stable gels cross-linked by various di/trivalent cations like Ba²⁺, Ca²⁺, and Fe³⁺. Many authors were focused on removal/separation of metal ions and dyes applying in this regard the alginate beads (Ai et al., 2011; Kemp et al., 2013; Papageorgiou et al., 2006; Park & Chae, 2004; Rocher et al., 2008) indicating high selectivity for...
water treatment. Incorporation of GO in the usual adsorbent polymers, such as, chitosan, improves its mechanical property, and produced an efficient and biodegradable monolith (Zhang et al., 2011).

The main goal of the present work deals with synthesis/characterization of calcium alginate/graphene-sodium dodecyl sulfate (CA/GR—SDS) nanocomposite beads for the removal of Cs⁺ from aqueous solutions to as low as reasonable achievable limits under batch and continuous flow conditions in a fixed bed mode. Characterizations were established using X-ray diffraction (XRD), Fourier transform infrared (FT–IR), and scanning electron microscope (SEM) techniques. The batch kinetic data were analyzed by pseudo 1st- and 2nd-order models while the equilibrium data were analyzed by Langmuir, Freundlich, and Dubinin-Radushkevich models. Rates of breakthrough of Cs⁺ from CA/GR—SDS beds having varied depths were obtained.

2. Materials and Methods

2.1. Materials

Natural powder of graphite (C, repeated units) and H₂SO₄ (98.0 wt. %) were purchased from Merck (Germany). Potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂), sodium alginate (C₆H₇O₇Na), anhydrous CaCl₂ (96.0%); and HCl (38.0 wt. %) were received from Fisher Scientific. Hydrate monohydrate (Na₂H₂O₂-64–65%) was product of Aldrich while sodium dodecyl sulfate (SDS) (C₁₃H₂₇O₃NaSO₄; 99.0%) was received from Sigma. Cesium chloride (99.98%) was product of British Drug Houses (BDH).

2.2. Synthesis of Modified Graphene-alginate (CA/GR-SDS) Nanocomposite Beads

The obtained natural powder of graphite was modified to GO according to Hummers and Offeman (Marcano et al., 2010) where oxidizing agents and hydrazine monohydrate were utilized and then the product was functionalized with SDS to obtain GR-SDS nanocomposite (Sayed et al., 2016b). Sodium alginate gel (4% w/v) was prepared. About 5.0 mL of the prepared sodium alginate solution was mixed with a definite weight of GR-SDS, and then pumped into CaCl₂ solution (100 mL; 2%). The formed CA/GR-SDS nanocomposite beads (each of 2.5–3.0 mm in diameter) were left for 1 h in the caustic solution with gentle stirring and then washed by distilled water. The elaborated beads were kept at 4°C for use (Omar et al., 2010).

2.3. Characterizations

XRD, FT-IR, and SEM techniques were used to characterize the synthesized CA/GR-SDS nanocomposite beads. XRD Patterns were collected by Philips X-ray diffractometer (nickel filter of Cu Kα radiation type; λ = 1.540600 Å; 2θ range of 1–90°). FT-IR spectra were recorded on Nicolet iS10 (Thermo Scientific) where tablets of the nanocomposite mixed with KBr were used. SEM photographs of both GO and the CA/GR-SDS nanocomposite beads were used to examine their surface morphologies (JEM-1200EX II).

2.4. Sorption Studies

Sorption of Cs⁺ onto CA/GR-SDS beads was accomplished by batch and fixed-bed column techniques. Experiments were designed using the one-factor-at-a-time method to achieve the primary goal. The parametric effect of pH was preliminary studied in a wide range from 3.5 to 10.5 (± 0.02). By designing preliminary studies about the effect of nanocomposite dosage, a definite weight (0.15 g) of CA/GR-SDS nanocomposite beads was contacted with aqueous Cs⁺ solution (50 mL; 500 mg/L) in 150 mL capacity conical flasks. At constant temperature (298 K), bottles were sealed and then were shaken till equilibrium. A digital pH meter (Hanna Instruments) was used to adjust the pH values using 0.1 M of NaOH and/or HCl. The applied liquid volume (V, mL)/solid weight (m, g) was selected to supply sufficient driving force between aqueous and solid phases. Eq. 1 was applied to evaluate the higher uptake percentage (% R) of Cs⁺. Such value of pH was applied along with all sorption experiments, in triplets. The spectrophotometric analysis of liquid phases toward Cs⁺ was achieved at wavelengths of 455 nm (Buck Scientific, VGP 210 using air acetylene flame, Kyoto-Japan).

\[ \% \ R = \frac{C_o - C_e}{C_o} \times 100 \]  

(1)

Where C₀ and Cₑ are the initial and equilibrium concentrations of Cs⁺, respectively, in the liquid phases (mg/L).

2.4.1. Sorption Kinetic Investigations

This investigation was done to identify the effect of contact time on the sorption of Cs⁺ onto the synthesized CA/GR-SDS nanocomposite beads. Batches were designed at a temperature range of 298–318 K and an optimum pH of ~ 5.0 ± 0.02. Solid/liquid phases were separated at time 5 to 120 min. Data were collected and expressed as sorbed amounts at time t (qt, mg/g):

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

(2)

Both of the pseudo first- (Eq. 3; Lagergren, 1898) and pseudo second- (Eq. 4; Ho & McKay, 1999) order kinetic models were utilized to predict the rates of sorption.

\[ q_t = q_{max} \left(1 - \exp^{-kt}\right) \]  

(3)
2.4.3. Fixed-bed sorption.

These investigations and their parameters can explicit the surface characteristics of a sorbent and its affinity (El-Kamash, 2008). Batches were designed using a wide concentration range of Cs\(^+\) (125–1000 mg/L) and were shaken for 24 h. with 0.15 g of CA/GR-SDS nanocomposite beads, at different temperatures. Data were collected in this wide range and were graphed in terms of concentration of Cs\(^+\) at equilibrium, in liquid phase (\(C_e\) mg/L), versus its corresponding one in the solid phase (\(Q_e\) mg/g). Langmuir (Eq. 5) (Langmuir, 1918), Freundlich (Eq. 6) (Freundlich, 1906) and Dubinin–Radushkevich (D-R) (Eq. 7) (Dubinin & Radushkevich, 1947) isotherm models are effective in describing sorption mechanisms.

\[
Q_e = \frac{Q^\circ b C_e}{1 + b C_e}
\]  
(5)

Where \(Q^\circ\) is the monolayer sorption capacity (mg/g) and \(b\) is the constant related to the free energy of sorption.

\[
Q_e = K_f C_e^{1/n}
\]  
(6)

Where \(K_f\) is a constant indicative to the relative sorption capacity of the sorbent (mg/g) and \(1/n\) is a constant indicative to the intensity of sorption process.

\[
Q_e = q_m \exp(-\beta \varepsilon)
\]  
(7)

Where \(\beta\) is a constant related to the sorption energy, \(q_m\) is the theoretical maximum saturation capacity and \(\varepsilon\) is the Polanyi potential.

2.5. Sorption/desorption cycles

The CA/GR-SDS nanocomposite beads were eluted using different concentrations of HCl, and then were rinsed with distilled water until pH of 6.0–6.5. Three repeating cycles were done using the highest eluting HCl concentration. The equilibrium desorbed concentration of Cs\(^+\) was analyzed to calculate the corresponding desorption ratio using Eq. 12

\[
\text{Desorption ratio} = \frac{C_d}{C_e} \times 100
\]  
(12)

Where; \(C_d\) is the equilibrium desorbed cesium concentrations in 1 N HCl, mg/L.

3. Results and Discussion

3.1. Characterizations

3.1.1. XRD examination

Figure 1 shows the XRD pattern of the synthesized CA/GR-SDS nanocomposite beads. The presented diffraction pattern recorded a wide and broad peak around 25.81° with d-spacing of 3.45 Å reflecting the amorphous nature of the synthesized beads. The obtained data were in harmony with those obtained by Lin and coworkers (Lin et al., 2013). The obtained pattern recorded the absence of any intense or relatively broad peaks around 26.59° or 10.85°, respectively. These observations revealed two facts one of them is the complete transformation of graphite while the other is the complete destroying of the interlayer spacing of GO under the influence of hydrazine monohydrate (Lin et al., 2013).

3.1.2. FT-IR examination

FT–IR spectra of CA/GR–SDS nanocomposite beads before and after loading with Cs\(^+\) are illustrated in Figure 2. It can be seen that the observed bands at 3442 cm\(^{-1}\) may be due to stretching
vibrations (st. v.) of −OH groups (Xiao et al., 2014). The breadth of such band reflected the extensive intermolecular hydrogen bonding which associated with the bending vibrations (ben. v.) of water molecules observed at 1641 cm⁻¹. Bands arising at 2925 and 2856 cm⁻¹ may be due to the st. v. of CH₃ and CH₂, respectively, in the long chain of SDS (Javadian et al., 2020). The symmetric and asymmetric st. v. of −COO⁻ groups in the gulopyranuronate structure of CA were detected at 1566 and 1469 cm⁻¹, respectively, which associated with their st. v. of C = O observed at 1740 cm⁻¹. Bands arising at 1130 and 1036 may refer to the asymmetric and symmetric stretches of S = O in SDS structure, respectively (El-Naggar et al., 2019). An additional band was detected at 763 cm⁻¹ in Cs⁺ − CA/GR − SDS referring to −O − Cs bonding vibration which made an evident of sorption of Cs⁺ onto CA/GR − SDS nanocomposite beads.

3.1.3. SEM examination
Morphologies of GO nanopowder – before and after loading of both SDS and CA – are illustrated in Figure 3a&b. Verifying the nanoscale particle size of the synthesized GO was done in our previous study using high-resolution transmission electron microscope (HR-TEM) (Sayed et al., 2016b). Inspection of graphene oxide (Figure 3a) revealed the uniform distribution of the granular particles. Figure 3b shows the morphology of GO in presence of SDS, as a soft template, and CA. Data show a plate-like structure due to the addition of SDS, tied to the side of a flat structure of CA.

3.2. Preliminary Investigations
The effects of CA/GR-SDS nanocomposite dosage and solution pH (at initial metal ion concentration of 500 mg/L) on sorption of Cs⁺ were preliminary studied to achieve optimum choices. Figure 4 shows the increase in sorption of Cs⁺ by increasing the solution pH reaching maximum value at pH of 5.0. At higher pH values, uptakes were decreased. This may be attributed to deformed active sites as a result of the chain expansion from the ionic carboxylate group of alginate at higher pH values (Pawar & Edgar, 2012). Results
revealed that the removal percentage was high at high sorbent dose of beads (figure omitted).

3.3. Batch Sorption Kinetics

3.3.1. Effect of Contact Time

The sorbed amounts of Cs\(^+\) (mg/g) as effect by contact time and temperature was studied (Figure 5). The highest sorbed amounts were obtained within the first 30 min of contact time with an exothermic nature which may be due to better availability of Cs\(^+\) around the environment of the CA/GR-SDS nanocomposite beads during this period. After 1 h of contacting, the sorbed amounts were increased to 81.4 mg/g at 298 K with almost constant values till 120 min., which then was held as typical sorption duration.

3.3.2. Kinetic Modeling

3.3.2.1. Pseudo first-order kinetic model. For solid/liquid systems, Lagergren equation was the first in describing the sorption processes (Lagergren, 1898) with an assumption that each molecule can be sorbed onto one surface-active site. The integrated form (Eq. 3) can be linearized into:

$$\log(q_{e,cal} - q_t) = \log q_{e,cal} - \frac{k_1}{2.303}t$$  \hspace{1cm} (13)

Where \(q_{e,cal}\) is the calculated amount of ion sorbed at equilibrium (mg/g). Slopes and intercepts of the linear fitting of \(\log(q_{e,cal} - q_t) vs. t\) plots (Figure 6a) were used to investigate how fast the equilibrium can be achieved \((k_1, \text{min}^{-1})\) and to determine the parameter \(q_{e,cal}\) (mg/g), respectively. Parameters of
Figure 5. Effect of contact time on the sorbed amounts (mg/g) of $\text{Cs}^+$ onto CA/GR – SDS nanocomposite beads, at different temperature values. ($pH = 5.0 \pm 0.02$; Liquid/solid = 0.33 L/g; initial concentration = 500 mg/L).

Figure 6. Batch kinetic modeling of the sorption of $\text{Cs}^+$ onto CA/GR – SDS nanocomposite beads using a) pseudo first-order and b) pseudo second-order kinetic models, as affected by temperature.

Table 1. Fitting parameters of pseudo first- and second-order kinetic models for the sorption of $\text{Cs}^+$ onto CA/GR – SDS nanocomposite beads, as affected by temperature.

| Metal ion | Temperature, K | $K_1$, min$^{-1}$ | $q_{ex}$, mg/g | $R^2$ | $K_2$, g/mg min | $q_{ex}$, mg/g | $h$, mg/g min | $R^2$ | $q_{ex}$, mg/g |
|-----------|----------------|-------------------|----------------|-------|----------------|----------------|---------------|-------|----------------|
| $\text{Cs}^+$ | 298 | 2.85 E-2 | 14.92 | 0.947 | 5.33 E-3 | 83.33 | 37.04 | 0.999 | 81.40 |
| | 308 | 2.48 E-2 | 32.73 | 0.943 | 1.66 E-3 | 76.92 | 9.82 | 0.999 | 71.58 |
| | 318 | 2.45 E-2 | 30.15 | 0.956 | 1.64 E-3 | 62.50 | 6.40 | 0.999 | 58.28 |

This model for the studied sorption processes, as affected by temperature, are given in Table 1. The given parameters indicated that values of $q_{ex}$ (mg/g) were away from those obtained experimentally, where their obtained correlation coefficients ($R^2$) were ranged from 0.943 to 0.956.

3.3.2.2. Pseudo second-order kinetic model. Parameters of this model can be estimated when Eq. 4 is transformed into the linear form (Eq. 14):

$$
\frac{t}{q_t} = \frac{1}{K_2q_{ex}} + \frac{1}{q_{ex}}t
$$

(14)
If the initial sorption rate \( h \), mg/g min is:
\[
h = k_2q^2_{\text{calc}}
\]  
Eq. (15) became:
\[
\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_{\text{calc}}}\frac{t}{q_t}
\]  
(16)

This model can express a sorption process when the plot of \( t/q_t \) against \( t \) should give a linear fit, from which the model parameters can be estimated. Figure 6b represents the plotting of \( t/q_t \) vs. \( t \) for the studied sorption systems of Cs\(^+\) onto CA/GR-SDS nanocomposite beads. The calculated sorbed amounts (\( q_{\text{calc}} \), mg/g) and rate constants \( k_2 \), g/mg min were estimated from slopes and intercepts, respectively (Table 1). Data indicated the applicability of this model to the studied sorption systems \( (R^2 = 0.999) \). Also, values of \( q_{\text{calc}} \) were close to \( q_{\text{exp}} \), at the studied temperature range assuming that the chemisorption mechanism (exchanging or sharing electrons between sorbate and sorbent) controls all processes (Costodes et al., 2003; El-Naggar et al., 2013).

3.4. Batch Equilibrium Investigations

Along with the kinetics of sorption, equilibrium investigations are commonly carried out to stand on the mechanisms of sorption, designing the adsorption systems, and are critical in optimizing the sorbents use. These investigations are commonly expressed by isotherms which are relations between \( q_e \) (mg/g) and \( C_e \) (mg/L) at constants of pH, temperature, and concentration (Zhou et al., 2014). Figure 7 represents the isotherms of Cs\(^+\) onto CA/GR-SDS nanocomposite beads, at different temperatures. The regularity and positiveness of all isotherms with \( C_e \) were obvious. Fitting of data using Langmuir, Freundlich, and D-R isotherm equations were carried out.

3.4.1. Langmuir Isotherm Model

This model is among the most excessively used equations in describing what happened in sorption between solid/liquid phases. This model characterizes the distribution of sorbate molecule in homogeneous monolayer onto identical active sites of sorbent. The monolayer sorption capacity \( (Q^0, \text{mg/g}) \) and the constant which is related to the free energy of adsorption \( (b \propto e^{-\Delta G/RT}) \) can be determined graphically by linearizing and rearrangement of Eq. 5:
\[
\frac{C_e}{Q_e} = \frac{1}{Q^0b} + \frac{1}{Q^0}C_e
\]  
(17)

Figure 8 represents the graphical plotting of Langmuir isotherm model in its linear form \( (C_e/Q_e \text{vs. } C_e) \). Slopes and intercepts of the fitted data were used to calculate the model parameters (Table 2). Increasing temperature led to decrease the monolayer capacities from 144.30 to 102.88 mg/g. This effect of temperature may be attributed to possible availability of active sites at lower temperatures. Values of an important parameter of Langmuir at equilibrium, \( R_l \), were calculated using Eq. 18 and are given in Table 2.
\[
R_l = \frac{1}{1 + bC_o}
\]  
(18)

Where \( C_o \) equals \( 10^3 \text{ mg/L} \) of Cs\(^+\). The importance of this parameter can be attributed to its capability to distinguish the nature of an isotherm which may

![Figure 7](image-url)  
**Figure 7.** Sorption isotherm of Cs\(^+\) sorbed onto CA/GR—SDS nanocomposite beads, as affected by temperature. \((pH = 5.0 \pm 0.02; \text{Liquid/solid} = 0.33 \text{ L/g; initial concentration} = 125–1000 \text{ mg/L}).**
be, favorable \((0 < R_L < 1)\), unfavorable \((R_L > 1)\), irreversible \((R_L = 0)\) or linear \((R_L = 1)\). Data in Table 2 illustrated that the constructed isotherms are favorable, along with the studied temperature range.

**Figure 8.** Plots of Langmuir isotherm model for the sorption of Cs\(^+\) onto CA/GR – SDS nanocomposite beads, as affected by temperature.

**Table 2.** Langmuir, Freundlich and D-R isotherm model parameters of Cs\(^+\) sorbed onto CA/GR – SDS nanocomposite beads, as affected by temperature.

| Temp., K | \(Q_o\), mg/g | \(b\), L/mg | \(R^2\) | \(R_L\) | \(K_L\), mg/g | \(R^2\) | \(\beta\), mol\(^2/\text{kJ}\) | \(q_{max}\), mmol/g | \(\beta^2\) | \(E_s\), kJ/mol |
|---------|----------------|-------------|---------|---------|----------------|---------|----------------|------------------|---------|---------------|
| 298     | 144.30         | 9.30E-3     | 0.958   | 0.097   | 2.83           | 12.89   | 0.948          | −5.88E-3         | 23.69E-2 | 0.964         | 13.04       |
| 308     | 118.34         | 10.1E-3     | 0.974   | 0.090   | 2.99           | 12.08   | 0.963          | −5.67E-3         | 19.59E-2 | 0.989         | 13.28       |
| 318     | 102.88         | 10.5E-3     | 0.979   | 0.087   | 3.21           | 12.05   | 0.960          | −5.61E-3         | 17.88E-2 | 0.983         | 13.35       |

**Figure 9.** Plots of Freundich isotherm model for the sorption of Cs\(^+\) onto CA/GR – SDS nanocomposite beads, as affected by temperature.
3.4.2. Freundlich Isotherm Model

This model describes sorption processes involving energetically different active sites at heterogeneous sorption surfaces. The logarithmic form of Eq. 6 gives a linear relation of Freundlich isotherms model as shown by Eq. 19.

\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \]  

Equation (19)

The equilibrium data for sorption of Cs\(^+\) onto CA/GR-SDS nanocomposite beads were analyzed by Freundlich’s logarithmic formula by plotting \( \log Q_e \) vs. \( \log C_e \) values (Figure 9). Slopes and intercepts were used to estimate the parameters of this model (\( K_f \) and \( 1/n \)), after applying the linear fitting (Table 2). According to the \( n \) values, isotherms may be favorable, unfavorable or irreversible when \( 0 < 1/n < 1 \) or \( 1/n = 0 \), respectively. Data revealed a decrease in values of relative sorption capacities (\( K_F \), mg/g) by increasing temperature reflecting the tendency of the synthesized nanocomposite beads toward Cs\(^+\) at lower temperature. Values of \( K_F \) were compared with those obtained by Sayed and coworkers who recorded much lower values at different temperatures which ranged from 0.75 to 0.85 mg/g (Sayed et al., 2016b). It was observed that all \( 1/n \) values were \( 0 < 1/n < 1 \) indicating the favorability of all sorption processes (Gouda et al., 2019).

3.4.3. Dubinin–Radushkvice (D–R) Isotherm Model

Nature of the studied sorption processes can be determined by the aid of this model when equilibrium data were analyzed according to Eq. (20):

\[ \ln Q_e = \ln q_m - \beta \varepsilon^2 \]  

Equation (20)

Where \( q_m \) is the maximum sorbed amount of Cs\(^+\) (sorption capacity, mmol/g) per unit weight of sorbent, \( \beta \) (mol\(^2\)/kJ\(^2\)) is a constant relevant to the free energy of sorption (\( E \), kJ/mol) (Eq. 21) and \( \varepsilon \) is the Polanyi potential \( (\varepsilon = RT \ln (1 + 1/C_e)) \), where \( R \) (kJ/mol\( \cdot \)K) is the gas constant, and \( T \) (K) is the absolute temperature. If one mole of Cs\(^+\) is devolved to the surface of the CA/GR-SDS nanocomposite beads a change in the free energy occurs (kJ).

\[ E = (-\beta)^{-1/2} \]  

Equation (21)

Helfferich (1962) relates the quantity of to the happened reaction mechanism. When the quantity range of \( E \) lies between 8 and 16 kJ/mol, then the sorption mechanism is ion exchange. When the quantity of \( E \) recorded less than 8.0 kJ/mol, then the sorption mechanism may be affected by physical forces (Helfferich, 1962). Figure 10 correlates the experimental data to the linear form of D–R isotherm. Parameters of the D-R model with their corresponding \( R^2 \) are given in Table 2. Data reflected better fitting of the D–R isotherm model where it recorded better \( R^2 \) values than those of Langmuir and Freundlich ones. The synthesized CA/GR-SDS nanocomposite beads recorded sorption capacity toward Cs\(^+\) ranged from 23.69E-2 to 17.88E-2 mmol/g, as affected by temperature. The ion exchange mechanism controlled the sorbed amounts where values of mean free energy were in the range of 8 and 16 kJ/mol (Helfferich, 1962) which means that the counter ions in the solid phase were replaced by those presented in the liquid phase.

![Figure 10](image-url)  

Figure 10. Plots of D-R isotherm model for the sorption of Cs\(^+\)onto CA/GR – SDS nanocomposite beads, as affected by temperature.
3.5. Thermodynamic Parameters

The characteristic thermodynamic constant of equilibrium ($K_t$) was estimated from parameters of Langmuir model ($Q^* b$) which in turn applied to calculate the excess in Gibbs free energy (Gouda et al., 2019):

$$
\Delta G^o = -RT \ln K_t
$$

(22)

The spontaneous nature of a given sorption system can be specified depending on its free energy. The system takes place in spontaneous nature if its $\Delta G^0$ value records – ve quantity and non-spontaneous if the value is + ve. The enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) were also determined according to:

$$
\Delta G^0 = \Delta H^0 - T \Delta S^0
$$

(23)

$\Delta H^0$ and $\Delta S^0$ values were calculated from slopes and intercepts of $\Delta G^0$ versus $T$ plots according to Eq. 23, as shown in Figure 11. The calculated thermodynamic parameters are recorded in Table 3. $\Delta H^0$ was of – ve sign reflecting the exothermic nature of the sorption processes which may be attributed to the thermal destabilization that causes the increase in mobility of Cs$^+$ upon surface of the studied nanocomposite and subsequent inhibition of sorption with increasing temperature. $\Delta G^0$ was of -ve sign reflecting the spontaneous nature of Cs$^+$ onto the studied sorbent material. Values of $\Delta S^0$ were very small indicating the stability of Cs$^+$ on the active sites (Chen et al., 2007).

3.6. Column Investigations

The time at which breakthrough appeared and its shape are very important characteristics for determining the dynamics of sorption column operation. The breakthrough curves were constructed by plotting $C_{\text{eff}}/C_{\text{in}}$ vs. $V_{\text{eff}}$.

3.6.1. Effect of Bed Depth

The breakthrough curves of Cs$^+$ sorption by CA/GR-SDS nanocomposite beads were studied using bed depths 2.0, 4.0, and 8.0 cm, at constant influent concentration (100 mg/L) and flow rate (1.0 mL/min) (Figure 12a). At bed depths of 2.0 and 4.0 cm, the breakthrough (exhaustion) time was 0.97 and 2.92 h, respectively. By increasing the bed depth to 8.0 cm, slower exhaustion time was observed (15.5 h) shifting the breakthrough curve right. The integrated form of Eq. 9 gave the total adsorbed amount of Cs$^+$ ($Q_{\text{tot}}$, mg) at different bed depths which in turn was applied to calculate the column parameters (Table 4). The bed capacities (mg/g) and column performance (%) were increased from 24.85 to 214.46 mg/g and from 13.67 to 29.89%, respectively, by increasing bed depths from 2.0 to 8.0 cm.

![Figure 11. InKc versus 1/T plots for the sorption of Cs+ onto CA/GR - SDS nanocomposite beads.](image)

Table 3. Thermodynamic parameters of Cs$^+$ sorbed onto CA/GR - SDS nanocomposite beads.

| Temperature, K | Kc | $\Delta G^0$, kJ mol$^{-1}$ | $\Delta H^0$, kJ mol$^{-1}$ | $\Delta S^0$, J mol$^{-1}$ K$^{-1}$ |
|---------------|----|--------------------------|--------------------------|--------------------------|
| 298           | 1.34 | $-0.729$ | $-8.59$ | $-26.40$ |
| 308           | 1.20 | $-0.449$ |       |         |
| 318           | 1.08 | $-0.201$ |       |         |

3.6.2. Effect of flow rate

Figure 12b represents the breakthrough curves of Cs$^+$ sorption by CA/GR-SDS nanocomposite beads at different flow rates (1.0 and 2.0 ml/min) of constant influent concentration (100 mg/L) through a fixed bed
height of 4.0 cm. A fast breakthrough and exhaustion time were observed with increasing the flow rate from 1.0 to 2.0 mL/min (from 2.92 to 1.17 h). The flow rate also influenced the Cs\(^+\) removal capacity as 70.0 and 51.39 mg/g dry beads weight were obtained at flow rates of 1.0 and 2.0 mL/min, respectively, (Table 4). This reduction in bed capacity at higher flow rates may be related to the shorter contact time of Cs\(^+\) with CA/GR-SDS nanocomposite beads at the given flow rate which made the residence time of the solute in the column not long enough to reach equilibrium (Ghorai & Pant, 2005).

### 3.7. Desorption investigations

Elution of Cs\(^{±}\) from three different cycles of CA/GR-SDS nanocomposite beads was done using an optimum concentration of HCl (1.0 N) (Figure 13). Data indicated that the removal percentages were decreased through the reused cycles.

### 4. Conclusions

Here, calcium alginate/graphene-sodium dodecyl sulfate (CA/GR-SDS) nanocomposite beads were synthesized. The product was characterized by XRD, FT-IR, and SEM techniques and its sorption properties toward removal of Cs\(^+\) from aqueous solutions were evaluated. XRD pattern reflected the amorphous nature of the synthesized beads. The essential bond vibrations and the plate-like structure were detected by FT-IR and SEM methodologies, respectively. The batch kinetic studies revealed that the highest sorbed amounts of Cs\(^+\) were obtained within the first 30 min with an exothermic nature. The subsequent mathematical modeling of the kinetic data indicated that the chemisorptions mechanism controlled all sorption processes. The equilibrium sorption isotherms were constructed and data were analyzed by linear forms of Langmuir, Freundlich, and D-R equations. Data analysis by Langmuir and Freundlich equations gave the monolayer and relative sorption capacities of beads with an impression that the constructed isotherms were favorable. The maximum sorbed amounts of Cs\(^+\) were theoretically calculated using the D-R equation and were found to be 23.69 E-2, 19.59 E-2, and 17.88 E-2 mmol/g at 298, 303, and 313 K, respectively. These amounts were sorbed by the ion exchange mechanism where their mean free energy values were in the range of 8–16 kJ/mol. The thermodynamic parameters (changes in free energy, entropy, and enthalpy) were calculated and the sorption systems were found to take place in exothermic spontaneous natures. Sorption of Cs\(^+\) onto
the synthesized nanocomposite beads under continuous flow conditions in a fixed-bed mode was evaluated. The breakthrough curves were constructed at different bed depths and flow rates. Increasing the bed depth led to slower exhaustion times with an increase in both bed capacity and column performance. A fast breakthrough and exhaustion time were observed with increasing the flow rate. Based on the obtained data, the application of the synthesized nanocomposite beads in the treatment of radioactive waste streams containing cesium radionuclides is recommended.

Acknowledgments

Authors are acknowledged staff members of the Radioactive Waste Management Division, Hot Lab. Center, Egyptian Atomic Energy Authority.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

Ai, L., Zhang, C., & Chen, Z. (2011). Removal of methylene blue from aqueous solution by a solvothermal-synthesized graphene/magnetite composite. Journal of Hazardous Materials, 192(3), 1515–1524. https://doi.org/10.1016/j.jhazmat.2011.06.068

Alvarez, L. H., & Cervantes, F. J. (2011). (Bio)nanotechnologies to enhance environmental quality and energy production. Journal of Chemical Technology and Biotechnology, 86(11), 1354–1363. https://doi.org/10.1002/jctb.2697

Ang, P. K., Chen, W., Wee, A. T. S., & Loh, K. P. (2008). Solution-entrapped epigallocatechin as pH sensor. Journal of the American Chemical Society, 130(44), 14392–14393. https://doi.org/10.1021/ja805090z

Balandin, A. A., Ghosh, S., Bao, W., Calizo, I., Teweldebrhan, D., Miao, F., & Lau, C. N. (2008). Superior thermal conductivity of single layer graphene. Nano Letters, 8(3), 902–907. https://doi.org/10.1021/nl0731872

Chandra, V., & Kim, K. S. (2011). Highly selective adsorption of Hg^{2+} by a polypyrrole-reduced graphene oxide composite. Chemical Communications, 47(13), 3942–3944. https://doi.org/10.1039/c1cc00005e

Chandra, V., Park, J., Chun, Y., Lee, J. W., Hwang, I.-C., & Kim, K. S. (2010). Water-dispersible magnetite-reduced graphene oxide composites for arsenic removal. ACS Nano, 4(7), 3979–3986. https://doi.org/10.1021/nn1008897

Chen, C., Li, X., Zhao, D., Tan, X., & Wang, X. (2007). Adsorption kinetic, thermodynamic and desorption studies of Th(IV) on oxidized multi-wall carbon nanotubes. Colloids and Surfaces A, Physicochemical and Engineering Aspects, 302(1–3), 449–454. https://doi.org/10.1016/j.colsurfa.2007.03.007

Costodes, V. C., Fauduet, H., Porte, C., & Delacroix, A. (2003). Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of Pinus sylvestris. Journal of Hazardous Materials, 105(1–3), 121–142. https://doi.org/10.1016/j.jhazmat.2003.07.009

Deng, X., Lu, L., Li, H., & Luo, F. (2010). The adsorption properties of Pb(II) and Cd(II) on functionalized graphene prepared by electrolysis method. Journal of Hazardous Materials, 183(1–3), 923–930. https://doi.org/10.1016/j.jhazmat.2010.07.117

Dubinin, M. M., & Radushkevich, L. V. (1947). Equation of the characteristic curve of activated charcoal. Proceedings of the Academy of Sciences, Physical Chemistry Section, 55, 331.

El-Kamash, A. M. (2008). Evaluation of zeolite A for the sorptive removal of Cs+ and Sr^{2+} ions from aqueous solutions using batch and fixed bed column operations. Journal of Hazardous Materials, 151(2–3), 432–445. https://doi.org/10.1016/j.jhazmat.2007.06.009

El-Naggar, M. R., Aglan, R. F., & Sayed, M. S. (2013). Direct incorporation method for the synthesis of molybdophosphate/MCM-41 silica composite: Adsorption study of heavy metals from aqueous solutions. Journal of Environmental Chemical Engineering, 1(3), 516–525. https://doi.org/10.1016/j.jece.2013.06.026

El-Naggar, M. R., El-Masy, E. H., & El-Sadek, A. A. (2019). Assessment of individual and mixed alkali activated binders for solidification of a nuclear grade organic resin loaded with 134Cs, 60Co and 152+154Eu radionuclides. Journal of Hazardous Materials, 375, 149–160. https://doi.org/10.1016/j.jhazmat.2019.04.063

Freundlich, H. (1906). Über die absorption in lösungen. Universität.

Ghorai, S., & Pant, K. K. (2005). Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. Separation and Purification Technology, 42 (3), 265–271. https://doi.org/10.1016/j.seppur.2004.09.001

Gouda, M. M., Dawood, Y. H., Zaki, A. A., Ibrahim, H. A., El-Naggar, M. R., & Gad, A. (2019). Adsorption characteristic of Cs+ and Co^{2+} ions from aqueous solutions onto geological sediments of radioactive waste disposal site. Journal of Geochemical Exploration, 206, 106366. https://doi.org/10.1016/j.gexplo.2019.106366

Helfferich, F. (1962). Ion Exchange. Mc Graw Hill.

Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. Process Biochemistry, 34(5), 451–465. https://doi.org/10.1016/S0032-9592(98)00112-5

Javadian, H., Ruiz, M., Taghvai, M., & Sastre, A. M. (2020). Novel magnetic nanocomposite of calcium alginate carrying poly(pyrimidine-thiophene-amide) as a novel green synthesized polyamide for adsorption study of neodymium, terbium, and dysprosium rare-earth ions. Colloids and Surfaces A, 603, 125252. https://doi.org/10.1016/j.colsurfa.2020.125252

Kemp, K. C., Seema, H., Saleh, M., Le, N. H., Mahesh, K., Chandra, V., & Kim, K. S. (2013). Environmental applications using graphene composites: Water remediation and gas adsorption. Nanoscale, 5(8), 3149–3171. https://doi.org/10.1039/c3nr33708a

Lagergren, S. (1898). Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska, etenskapsakademien [To the theory of the so-called adsorption of dissolved substances]. Handlingar, 24(4), 1–39.

Langmuir, I. (1918). THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM. Journal of American Chemical Society, 40(9), 1361–1403. https://doi.org/10.1021/ja02242a004

Li, N., Zheng, M., Chang, X., Ji, G., Lu, H., Xue, L., Pan, L., & Cao, J. (2011a). Preparation of magnetic CoFe_{2}O_{4}-functionalized graphene sheets via a facile hydrothermal method and their adsorption properties. Journal of Solid State Chemistry, 184(4), 953–958. https://doi.org/10.1016/j.jssc.2011.01.014
Sayed, M. S., Bakr, M. F., Salama, T. M., El Dakrory, A. M., Ibrahim, I. A., & Maree, R. M. (2016a). A comparative study of SDS- and DSS-functionalized graphene as adsorbents for removal of $^{137}$Cs ions from low level radioactive waste. Global Journal of Chemistry, 3(1), 111–124.

Sayed, M. S., Salama, T. M., Bakr, M. F., El Dakrory, A. M., Maree, R. M., & Ibrahim, I. A. (2016b). Synthesis of graphene functionalized with SDS for removal of $^{137}$Cs and $^{134}$Cs ions from radioactive waste. Journal of International Environmental Application & Science, 11(1), 110–123. https://dergipark.org.tr/en/download/article-file/571718

Schinwald, A., Murphy, F. A., Jones, A., MacNee, W., & Donaldson, K. (2012). Graphene-based nanoplatelets: A new risk to the respiratory system as a consequence of their unusual aerodynamic properties. ACS Nano, 6(1), 736–746. https://doi.org/10.1021/nn204229f

Wang, K., Ruan, J., Song, H., Zhang, J. L., Wo, Y., Guo, S. W., & Cui, D. (2011). Biocompatibility of Graphene Oxide.. Nanoscale Research Letters, 6(1), 8–15. https://doi.org/10.1007/s11671-010-9751-6

Xiao, Q., Gu, X., & Tan, S. (2014). Drying process of sodium alginate films studied by two-dimensional correlation ATR-FTIR spectroscopy. Food Chemistry, 164, 179–184. https://doi.org/10.1016/j.foodchem.2014.05.044

Yang, S.-T., Chang, Y., Wang, H., Liu, G., Chen, S., Wang, Y., Liu, Y., & Cao, A. (2010). Folding/aggregation of graphene oxide and its application in Cu$^{2+}$ removal. Journal of Colloid and Interface Science, 351(1), 122–127. https://doi.org/10.1016/j.jcis.2010.07.042

Zhang, N., Qiu, H., Si, Y., Wang, W., & Gao, J. (2011). Fabrication of highly porous biodegradable monoliths strengthened by graphene oxide and their adsorption of metal ions. Carbon, 49(3), 827–837. https://doi.org/10.1016/j.carbon.2010.10.024

Zhao, G., Jiang, L., He, Y., Li, J., Dong, H., Wang, X., & Hu, W. (2011). Sulfonated graphene for persistent aromatic pollutant management. Advanced Materials, 23(34), 3959–3963. https://doi.org/10.1002/adma.201101007

Zhao, G., Li, J., Ren, X., Chen, C., & Wang, X. (2011). Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. Environmental Science & Technology, 45(24), 10454–10462. https://doi.org/10.1021/es203439v

Zhao, G., Li, J., & Wang, X. (2011). Kinetic and thermodynamic study of 1-naphthol adsorption from aqueous solution to sulfonated graphene nanosheets. Chemical Engineering Journal, 173(1), 185–190. https://doi.org/10.1016/j.cej.2011.07.072

Zhenhai, T., Yanda, L., Baouchun, G., Liqun, Z., & Demin, J. (2012). The use of rhodamine B-decora ted graphene as a reinforcement in polyvinyl alcohol composites. Polymer, 53, 673–680.

Zhou, C., Wu, Q., Lei, T., & Negulescu, I. I. (2014). Adsorption kinetic and equilibrium studies for methylene blue dye by partially hydrolyzed polyacrylamide/cellulose nanocrystal nanocomposite hydrogels. Cellulose Engineering Journal, 251, 17–24. https://doi.org/10.1016/j.cej.2014.04.034