A comparative study of SDS- and DSS-functionalized graphene as adsorbents for removal of $^{137}$Cs ions from low level radioactive waste

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ABSTRACT

Graphene (GR) functionalized with Aerosol 501 “dicyt sulfo succinate sodium” (DSS/GR) and sodium dodecyl sulfate (SDS/GR) were synthesized and characterized by analytical techniques including BET surface area, X-ray diffractometry (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscope (HRTEM), Fourier transform infra-red (FTIR) and thermogravimetric analysis (TGA). The SEM images provide a direct evidence for the existence of sulfonic and sulfate anchors, respectively, by adding DSS and SDS surfactants to graphene structure where GR cavities effectively reduced. The XRD patterns of SDS/GR and DSS/GR exhibit reflection peaks at 2θ of 22.69° and 21.72° with interlayer spacings of 0.39 and 0.41 nm, respectively. These interlayer spacings were larger than that of GR, due to intercalating functional groups of SDS and DSS. The characteristic features of these samples were investigated as adsorbents to remove $^{137}$Cs ions from low level radioactive waste (LLW). It was found that adsorption of $^{137}$Cs ions onto GR, SDS/GR and DSS/GR were relatively fast and the equilibrium state reached after 60, 40, and 30 min, respectively. The maximum adsorption capacity ($Q_m$) of $^{137}$Cs ions inferred from the Langmuir model increases in the following order: GR < SDS/GR < DSS/GR. Results suggest that the sorption of $^{137}$Cs ions onto each samples followed the pseudo second-order model. The thermodynamics were discussed.

KEYWORDS: graphene; SDS; Aerosol 501; Sorption of $^{137}$Cs.

1. INTRODUCTION

Graphene has been attracting massive attention in the scientific community because of its unique properties for nanotechnological applications in many areas. Unlike the conventional 2D systems, which are usually formed at buried semiconductor interfaces, graphene is a one-atom-thick planar layer of sp²-hybridized carbon atoms arranged in a honeycomb crystal lattice and directly accessible to external perturbations which can interact with its π-electron system [1-3]. Graphene has been synthesized in various ways and on different substrates depending on targeted applications.

Graphene flakes are usually synthesizable at a size of several microns and thus have irregular shapes. The extraordinary electronic transport properties of graphene require structurally coherent graphene on a large scale (e.g., wafer-scale). The latter structure can be obtained with different types of functionalization in the context of providing an opportunity to obtain exfoliated graphene flakes. This can also modify the chemical nature of graphene [4], since the modifier molecule imparts specific properties to graphene after its attachment, along with minimizing the irreversibly aggregation of graphene layers into platelets.

Various investigations of the effects of commonly used surfactants as modifier molecules to graphene were studied [5]. Surfactant is considered an economical, safe and friendly process since water is the main solvent [6]. There are a number of studies on surfactants dispersed on graphene in water base system [7]. Among these surfactants, sodium dodecylsulfate (SDS) is a promising one as its dispersion can create large solvation around graphene [8]. Yet, one can also suggest Aerosol 501 (DSS), a proprietary sulfo succinate surfactant, that can substantially reduce surface tension, between graphene particles and aqueous medium, and thus lowers the energy of the formation of a new phase as well as increasing the dispersion of graphene, i.e., DSS/GR [9].

Therefore, the general physical properties of SDS/GR and DSS/GR such as electronic, optical, specific surface area and thermal behavior were compared. Furthermore, several solid state properties were described in detail, relating the fundamental and structural performance covered throughout the studied graphene systems [10].

The abundant functional moieties related to SDS/GR and DSS/GR could theoretically clean hazardous waste water from some ions. Cesium radioisotope $^{137}$Cs (t½ = 30.7 y) emit gamma radiation at 0.662 MeV, which found in radioactive liquid wastes originating from nuclear reactors and research institutes, mostly at levels exceeding the limits [11]. Because body can accumulate cesium at muscles so ingestion of this radio-isotope creates severe internal hazards [12]. We report a simple practical approach to use the synthesized graphene composites for assessment of $^{137}$Cs adsorption from low level wastewater (LLW).
2. EXPERIMENTAL

2.1. Materials

Natural graphite powder and H₂SO₄ (98 wt.%) were purchased from Merck. Potassium permanganate, aqueous hydrogen peroxide (H₂O₂ 30%), and hydrochloric acid solution (HCl, 37%) were used as received from Fisher Scientific and hydrizine hydrate (N₂H₂·H₂O, 64-65%) from Sigma Aldrich. The surfactants sodium dodecyl sulfate (C₁₂H₂₅NaO₄S, 99.0%, abbreviated as SDS) was purchased from Sigma and dioctyl sodium sulfosuccinate (Aerosol 501; C₂₀H₃₇NaO₂S; abbreviated as DSS) was gifted from the Egyptian British Co. For Chemicals & Auxiliaries and used as received.

2.2. Synthesis of graphene Oxide (GO)

Graphene (GO) was prepared from graphite as the starting material via a modification of the Hummers and Offeman method [13]. In brief, 1 g of graphite and 0.5 g of sodium nitrate were mixed together followed by the addition of 23 ml of concentrated sulfuric acid under constant stirring for 1 h. Afterward, 3 g of KMnO₄ was added gradually to the above solution while keeping the temperature less than 20°C to prevent overheating and explosion. The mixture was allowed to stir for 12 h and the resulting solution was diluted by adding 500 ml of distilled water under vigorous stirring. The oxidation reaction of graphite is driven to completion by further treatment of the bulk supernatant with 50 ml of 30% H₂O₂ solution. The resulting mixture was washed with HCl and H₂O, respectively, followed by filtration and drying to finally obtain graphene oxide (GO).

2.2.1. Preparation of graphene (GR)

0.1 g of GO was dispersed in 150 ml water and sonicated for 30 min. The reaction mixture was then transferred to a preheated oil bath at 60 °C and stirred for 24 h. Hydrazine monohydrate was added to the reaction mixture and the sample was allowed to reflux for 12 h at 100 °C. Finally, the product (GR) was filtered through 0.20 mm cellulose acetate membrane paper, washed with deionized water and dried in a vacuum at 60 °C for 72 h.

2.2.2. Functionalization of graphene by SDS and DSS

0.1 g of GR was dispersed in 150 ml distilled water and sonicated for 30 min. The desired amount (0.05 g) of the surfactant SDS or DSS was then dissolved in 100 ml of water while stirring at room temperature, followed by the addition of the aqueous graphene suspension to either SDS or DSS solution. The reaction mixture was then transferred to a preheated oil bath at 60 °C and vigorously stirred for 24 h to produce SDS/GR or DSS/GR.

2.3. Adsorption Experiments

100 ml of 75 ppm inactive cesium solution was prepared and traced with the radioactive isotope ¹³⁷Cs solution. Adsorption capacity determinations of ¹³⁷Cs using NaI scintillation crystal connected to an ACE° multichannel analyzer (ORTEC) were carried out. The uptake percent (U %) of ¹³⁷Cs ions was calculated from the following equation:

\[ U \% = \frac{A_o - C_i}{A_o} \times 100 \]  

(1)

where \( A_o \) and \( C_i \) are the activities expressed in counts per minute of 1 ml solution for the radioisotope before and after contacting with the sorbents GR, SDS/GR and DSS/GR. The solution pH was adjusted by adding 0.1 M of either NaOH or HCl solution.

2.4. Characterization

High resolution transmission electron microscope (HRTEM) was carried out using a Tecnai G2, FEI, Netherland.

The morphology and grain size of the particles were identified using Jeol scanning electron microscope of JSEM-6510A Model, Japan, operating with beams of primary electrons ranging from 5 to 30 keV.

X-ray diffraction (XRD) was measured using Shimadzu X-ray diffractometer (Shimadzu "Japan"). The samples were first ground, then introduced for analysis in the special sample holder. The analysis was carried out using a nickel–filter and CuKα radiation source (\( \lambda = 0.154 \text{ nm} \)) at 40 kV and 30 mA. The crystallite size of produced composite phase was calculated from line broadening of the main diffraction line at about 2θ of 22° of GR using Scherrer equation [14]:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

(2)

where \( D \) is the mean crystalline diameter, \( \lambda \) the X-ray wavelength, \( K \) the Scherrer constant (0.9), \( \beta \) the full width at half maximum (FWHM) of the diffraction peak of GR and \( \theta \) is the diffraction angle.
Fourier transform infrared (FT-IR) spectra were recorded via a single beam Perkin Elmer Spectrometer with a resolution of 2 cm$^{-1}$. The samples were ground with KBr (1:100) so as to form tablets. The measurements were recorded at the temperature 25 °C in the region 4000-400 cm$^{-1}$.

Thermal gravimetric analysis (TGA) of the materials was carried out on a TA-50 Shimadzu, JAPAN, at a heating rate of 20 °C/min under nitrogen atmosphere flowing at 30 mL/min.

3. RESULTS AND DISCUSSION

3.1. Characterization

3.1.1 High-resolution transmission electron microscope (HRTEM)

HRTEM was used to investigate the microstructure of GR, SDS/GR and DSS/GR (Fig. 1). The HRTEM image of GR shows the appearance of transparent graphene nanosheets that involve wrinkles and cracks due to the partial collapse of graphene sheet. On the contrary, SDS/GR and DSS/GR show a decrease in the wrinkles and crack growth in the graphene nanosheet. Here, GO platelets were covalently bonded to the polymer matrix through the sulfate and sulfonate as the hydrophilic groups in SDS and DSS, respectively. The appearance of a number of dark lines indicates the number of layers in graphene. Assuming that SDS and DSS influence the number of layers in the functionalized graphene, this would indicate that the remaining layers are reduced by analyzing the TEM images. The formation of a few layers of functionalized graphene in presence of either SDS or DSS suggests the formation of functionalized graphene with a semi crystalline nature [15].

![TEM photos of a- GR, b- SDS/GR and c- DSS/GR](image)

3.1.2 SEM

The morphology of graphene before and after functionalization was analyzed using SEM as shown in Fig. 2. The SEM images showed that GR effectively decrease the cavities of GR during functionalization as shown in Fig. 2b-c, and could indeed anchor different chemical groups including sulfate/sulfonic groups from added surfactants.
3.1.3 XRD

XRD analysis was performed to examine the impact of the SDS and DSS on the crystal structures of the final GR products. The diffraction pattern of GR shows an intense diffraction peak at 2θ of 22.76° that reveals the dominant presence stacked graphene sheets (Fig. 3), along with an additional shoulder at 2θ of 26.06° [16]. This shoulder corresponds to 002 plane of graphite with interlayer spacing of 0.34 nm. The patterns of SDS/GR and DSS/GR exhibit the same reflection peak at 2θ of 22.69° and 21.72° with interlayer spacing of 0.39 and 0.41 nm, respectively. These interlayer spacings are larger than that of GR, due to intercalating functional groups of SDS and DSS. This shows effective incorporation of hydrophilic, with oxygen-containing groups, SDS and DSS into the graphene interlayer. The average particle sizes were calculated using the Scherrer equation and listed in Table 1.

Table 1: The average particle size (nm) calculated from XRD of the studied graphenes

<table>
<thead>
<tr>
<th>Material</th>
<th>2-Theta (deg.)</th>
<th>d (nm)</th>
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<tbody>
<tr>
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<td>22.76</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>42.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44.00</td>
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</tr>
<tr>
<td>SDS/GR</td>
<td>12.67</td>
<td>29.1</td>
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<tr>
<td></td>
<td>40.20</td>
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</tr>
<tr>
<td>DSS/GR</td>
<td>22.42</td>
<td>21.4</td>
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3.1.4 Thermogravimetric analysis (TGA)

Thermal stabilities of GR, SDS/GR and DSS/GR were examined by TGA up to 800 °C as shown in Fig. 4. The TG profile of GR exhibits one clear step of a weight loss, while surface species associated with SDS/GR and DSS/GR decomposes in three steps. The first weight loss at 80–120°C relates to the loss of water molecules in all TGA profiles. The second step observed from 200 to 300°C in SDS/GR and DSS/GR may result from the decomposition of oxygen-containing moieties, and the third step 450–550°C to unstable carbon remaining in the structure and pyrolysis of oxygen functional groups in the main structure of surfactants to yield CO and CO$_2$ [17]. The GR profile shows similar characteristic weight losses but to lesser extent, compared to those of SDS/GR and DSS/GR. This could be explained by successful inclusion of oxygen functional groups in the structure of the latter samples.

Table 2: The weight loss values from TGA thermograms of the studied graphenes

<table>
<thead>
<tr>
<th>Sample</th>
<th>1st range 80-120 °C</th>
<th>2nd range 200-300 °C</th>
<th>3rd range 450-550 °C</th>
<th>Total weight loss</th>
</tr>
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<tr>
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<td>3</td>
<td>4</td>
<td>6</td>
<td>17</td>
</tr>
<tr>
<td>SDS/GR</td>
<td>5</td>
<td>8</td>
<td>8</td>
<td>25</td>
</tr>
<tr>
<td>DSS/GR</td>
<td>8</td>
<td>12</td>
<td>15</td>
<td>38</td>
</tr>
</tbody>
</table>
3.1.5 Surface area

Specific surface area $S_{BET}$ (m$^2$ g$^{-1}$) is an important feature of graphene that determines the interface interaction between the prepared graphene and functional groups in the functionalized graphene. Surface areas of different few layer graphene samples have been measured by the Brunauer–Emmett–Teller (BET) method and are in the range of 270–1550 m$^2$ g$^{-1}$[18]. Therefore, few-layer graphenes show large surface areas, some of them approaching the value of single layer graphene. In our case, BET analysis shows that GR possessed a relatively high surface area (300 m$^2$ g$^{-1}$). Nevertheless, SDS/GR and DSS/GR demonstrate about two-fold increase in surface area, i.e. 750 and 620 m$^2$ g$^{-1}$, respectively. This might be due to the large open surface area created by fewer layers in these two samples, in compatible with the TEM images. Alternatively, SDS/GR and DSS/GR would form mesoporous flakes with high surface areas.

3.1.6 FT-IR spectra

The FT-IR spectra of GR, SDS/GR and DSS/GR are presented in Figure 5. The graphs show the stretching of hydroxyl group at 3450 cm$^{-1}$, the C=O carbonyl stretching at 1728 cm$^{-1}$, and the C–O epoxide group stretching at 1229 and 1061 cm$^{-1}$[19]. The high intensity of the main peaks in SDS/GR confirms the presence of a large amount of oxygen functional groups after the functionalization process. The peak at 1627 cm$^{-1}$ is related to the vibrations of adsorbed water molecules. After the GR was functionalized, hydroxyl and alkoxy groups were significantly decreased Fig. (5), and the phenol C=C ring stretching at 1585 cm$^{-1}$ was present [20]. In order to effectively show the oxygen bond from sulphonic functional group on carbon planes the symmetric stretching and asymmetric stretching bands were observed at 1119 and 1044 cm$^{-1}$ respectively[21]. These observations suggest that SDS and DSS surfactant molecules were successfully adsorbed and modified the graphene surfaces.

3.2 Adsorption of Cesium (I)

Exploring the adsorption of $^{137}$Cs ion on the studied sorbent graphenes based on the consideration of various factors affecting the uptake process as contact time, pH and $^{137}$Cs ion concentration.
3.2.1 Effect of contact time

The influence of contact time on $^{137}$Cs ions adsorption on the sorbents under study was at the range of 0 - 120 min at pH 6.0 and 298 K for 100 mg L$^{-1}$ of $^{137}$Cs. It can be noted from Fig. (6) that the sorption increases with increasing contact time and equilibrium attains after 60 min after which the sorption remains constant. The adsorption process onto graphenes composite functionalized with sulphonic and carboxylic groups is more intense than non functionalized graphene [22].

![Graph showing effect of contact time on sorption of $^{137}$Cs ions]

**Fig. 6**: Effect of contact time on the sorption of $^{137}$Cs ions using GR, SDS/GR and DSS/GR sorbents

3.2.2 Effect of pH

Several sorption experiments were carried out to study the effect of initial solution pH at the range of 3-8. As shown in Fig. (7), the obtained curves have the same shape characterized by a strong increase of the amount of $^{137}$Cs ions sorbed during the first minutes of contact solution–sorbent, followed by a slow increase until it reaches the equilibrium state. The maximum removal rate of functionalized graphene is realized at the pH of 6. Hence, SDS/GR, DSS/GR exhibit higher adsorption capacity than GR in the weak acid medium. The amount of $^{137}$Cs ions sorbed at the equilibrium increases with the solution equilibrium state depending on the initial pH of solution [23].

![Graph showing effect of pH on sorption of $^{137}$Cs ions]

**Fig. 7**: Effect of pH on the sorption of $^{137}$Cs ions using GR, SDS/GR and DSS/GR sorbents
3.2.3 Effect of $^{137}$Cs ion concentration

The effect of $^{137}$Cs ion carrier concentration on the amount of graphene sorbents is illustrated in Fig.(8) which indicates the amount of $^{137}$Cs uptake increases in the order: GR < SDS/GR < DSS/GR which may be due to the smaller number of active sites the higher concentration of $^{137}$Cs and the stability increases by the amount of adsorbed cesium as the $^{137}$Cs ion concentration increases[24].

![Graph showing the effect of $^{137}$Cs ion concentration on the amount of graphene sorbents](image)

Fig. 8: Effect of initial ion concentration on the sorption of $^{137}$Cs ion using GR, SDS/GR and DSS/GR, sorbents

3.2.4. Adsorption isotherm study

Adsorption isotherm plays an important role in the predictability of modeling procedures for the analysis and design of an adsorption system. Hence, the adsorption data of Cs (I) was examined by Langmuir and Freundlich isotherm models which are the most widely referred equations. The various constants of the two models were calculated and listed in Table 4. The Langmuir isotherm equation is as follows [25].

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{1}{q_m} C_o$$

$$R_L = \frac{1}{1 + b C_o}$$

Where $q_e$ is the equilibrium adsorption capacity (mg g$^{-1}$), $C_o$ is the initial ion concentration (mg L$^{-1}$), $C_e$ is the equilibrium concentration of the solution (mg L$^{-1}$), $q_m$ is the maximum adsorption capacity (mg g$^{-1}$), $b$ is a Langmuir constant related to the affinity of the binding sites and energy of adsorption (L g$^{-1}$). A straight line is obtained on plotting $C_e/q_e$ against $C_e$ Fig. 9 (a, b and c), where $q_m$ and $b$ were evaluated from the slope and intercept, respectively (Table4). The maximum monolayer adsorption capacity ($q_m$) of the GR, SDS/GR and DSS/GR composite was found to be 42, 62 and 73 mg g$^{-1}$, respectively for Cs (I) at 50ºC. Thus, a greater uptake capacity of Cs (I) onto graphene and its composites decreases on the order DSS/GR>SDS/GR>GR which may be due to high surface area of the composite. The $R_L$ values at 50ºC lie between 0 and 1, indicating a favorable adsorption process of Cs (I) onto the GR, SDS/GR and DSS/GR surface [26].

![Graph showing the Langmuir sorption isotherm for Cs (I) ion onto GR at 50 ºC.](image)

Fig. (9-a): The Langmuir sorption isotherm for Cs (I) ion onto GR at 50 ºC.

![Graph showing the Langmuir sorption isotherm for Cs(I) ion onto SDS/GR at 50 ºC.](image)

Fig. 9-b: The Langmuir sorption isotherm for Cs(I) ion onto SDS/GR at 50 ºC.
Table 4: Langmuir and Freundlich parameters for sorption of Cs (I) ions onto GR, SDS/GR and DSS/GR.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q(mg/g)</td>
<td>R_L</td>
</tr>
<tr>
<td>GR</td>
<td>42.83</td>
<td>0.023</td>
</tr>
<tr>
<td>SDS/GR</td>
<td>62.00</td>
<td>0.929</td>
</tr>
<tr>
<td>DSS/GR</td>
<td>73.00</td>
<td>0.705</td>
</tr>
</tbody>
</table>

Freundlich isotherm model assumes heterogeneity of adsorption surfaces that commonly can be expressed as follows:

\[
\log q_e = \log K + \frac{1}{n} \log C_e
\]

Where \(q_e\) (mg g\(^{-1}\)) is the amount adsorbed at equilibrium, \(K\) (L g\(^{-1}\)) is Freundlich constant, which indicates the relative adsorption capacity of the adsorbent, and \(n\) is the heterogeneity factor related to the adsorption intensity. A straight line is obtained by plotting \(\log q_e\) versus \(\log C_e\) as \(n\) and \(K\) could be evaluated from the slope and intercept, respectively.

Fig. (9-c): The Langmuir sorption isotherm for Cs(I) ion onto GR at 50°C.

Fig. (10-a): The Freundlich sorption isotherm for Cs ion onto GR at different temperatures.

Fig. 10-b: The Freundlich sorption isotherm for Cs ion onto SDS/GR at 50°C.

Fig. 10-c: The Freundlich sorption isotherm for Cs ion onto DSS/GR at 50°C.
SDS/GR, DSS/GR composites as assumed by the Langmuir model and as shown by the high \( R^2 \) values \( (R \approx 0.999) \) at the different adsorption temperatures.

### 3.2.5. Adsorption kinetics

In order to investigate the kinetics of adsorption of Cs(I) onto the modified graphenes, the pseudo-first-order and pseudo-second-order kinetic models are employed in this study. The linearized-integral form for pseudo-first-order model is expressed as [27]:

\[
\log \left( q_e - q_t \right) = \log q_e - \frac{k_1}{2.303} t
\]  

(7)

Where \( q_e \) and \( q_t \) are the amounts of adsorption capacity (mg/g) on the adsorbents at equilibrium time and at time \( t \), respectively, while \( k_1 \) represents the rate constant of pseudo-first-order (min.\(^{-1}\)), which is determined by plotting \( \log (q_e - q_t) \) versus \( t \) (Fig. 11 a & b & c). The parameter values of the kinetic models at initial concentrations are presented in Table (5, 6, and 7). The calculated \( q_e \) values show nearly agreement with the experimental values, and the values of \( R^2 \) are more than 0.999 which indicates that this model could fit well the adsorption of Cs(I) onto the various surfaces of modified graphenes.

The linearized-integral form of the pseudo-second-order model is expressed as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]  

(8)

Where \( k_2 \) is the pseudo-second-order rate constant \( (g/ (mg \text{ min})) \) which is determined by plotting \( t/q_t \) versus \( t \). The parameter values of the kinetic models are listed in Fig. 12 (E, F, and G) and Table (5, 6, and 7). The calculated \( q_e \) values show nearly agreement with the experimental values, and the values of \( R^2 \) are more than 0.999 which indicates that this model could fit well the adsorption of Cs(I) onto the various surfaces of modified graphenes.
Table 5: The pseudo-first order and pseudo-second order parameters for sorption of Cs (I) ions onto GR.

<table>
<thead>
<tr>
<th>C₀ (ppm)</th>
<th>qₑ(cal.) (mg/g)</th>
<th>qₑ(exp.) (mg/g)</th>
<th>K₁ (g/mg.min)</th>
<th>R²</th>
<th>C₀ (ppm)</th>
<th>qₑ(cal.) (mg/g)</th>
<th>qₑ(exp.) (mg/g)</th>
<th>K₂ (g/mg.min)</th>
<th>R²</th>
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<td>75</td>
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<td>0.9758</td>
<td>25</td>
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<tr>
<td>150</td>
<td>14.41</td>
<td>38.74</td>
<td>0.041</td>
<td>0.9862</td>
<td>75</td>
<td>36.7</td>
<td>38.74</td>
<td>0.0039</td>
<td>0.9998</td>
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Table 6: The pseudo-first order and pseudo-second order parameters for sorption of Cs (I) ions onto SDS/GR.

<table>
<thead>
<tr>
<th>C₀ (ppm)</th>
<th>qₑ(cal.) (mg/g)</th>
<th>qₑ(exp.) (mg/g)</th>
<th>K₁ (g/mg.min)</th>
<th>R²</th>
<th>C₀ (ppm)</th>
<th>qₑ(cal.) (mg/g)</th>
<th>qₑ(exp.) (mg/g)</th>
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Table 7: The pseudo-first order and pseudo-second order parameters for sorption of Cs (I) ions onto DSS/GR.

<table>
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<tr>
<th>C₀ (ppm)</th>
<th>qₑ(cal.) (mg/g)</th>
<th>qₑ(exp.) (mg/g)</th>
<th>K₁ (g/mg.min)</th>
<th>R²</th>
<th>C₀ (ppm)</th>
<th>qₑ(cal.) (mg/g)</th>
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<th>K₂ (g/mg.min)</th>
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<td>46.13</td>
<td>44.34</td>
<td>0.005</td>
<td>0.9996</td>
</tr>
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</table>

3.2.6. Thermodynamic study

To evaluate the influence of temperature on adsorption process of Cs (I) onto sorbent surfaces, the thermodynamic parameters such as standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) are computed using the following equations [28]:

\[ ΔG° = -RT \ln k_d \]  \hspace{1cm} (9)

\[ ΔG° = ΔH° - TΔS° \]  \hspace{1cm} (10)
Where R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K), and $K_d$ is adsorption equilibrium constant, the values of the of $K_d$ are calculated using the values of Langmuir constants ($b \cdot q_m$) at different temperatures. The values of enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) were calculated from slope and intercept respectively of the plot of ln$K_d$ versus 1/T (Van’t Hoff plot). The thermodynamic parameters are listed in Table (8). The positive values of ($\Delta S^0$) reflects the increased randomness at the solid/solution interface during the adsorption process and may be due to the fixation of ion on the exchange sites of the randomly distributed surfactant species[29] as well as indicated the increase in number of species and degrees of freedom.

Inspection of the Table (8) indicated that the standard free energy $\Delta G^0$ decreased with increasing the temperature thereby indicating an increase in adsorption at higher temperature as well as it perhaps the surfactant molecules have more affinity toward the metal ions revealing the feasible spontaneous adsorption process. On the other hand, the positive $\Delta H^0$ values reveal the endothermic nature of Cs (I) adsorption. Hence, it would be expected that the higher solution temperature the larger adsorption capacity, as shown in Table (8),i.e. the sorption of Cs(I) increased with increasing temperature, confirming that sorption is an endothermic process and energetically stable. The $\Delta H^0$ values are found to be less than 40 kg mol$^{-1}$ indicating a physisorption process and which confirmed with the $\Delta G^0$ values which are in between 0 and -20kJmol$^{-1}$ [30].

**Fig. 13-a:** Van’t Hoff plot for adsorption of Cs(I)ion on to GR.

**Fig. 13-b:** Van’t Hoff plot for adsorption of Cs(I)ion on to SDS/GR.

**Fig. 13-c:** Van’t Hoff plot for adsorption of Cs(I)ion on to DSS/GR.
CONCLUSIONS

In this study, GR, SDS/GR and DSS/GR nanocomposites were prepared and characterized by TEM, SEM, XRD, TGA, SA and FTIR. Batch experiments were conducted and showed that the adsorption of $^{137}$Cs ions depends upon time, pH and ion concentration. The introduction of SDS and DSS groups to the GR surface can significantly increase its adsorption capacity of $^{137}$Cs removal. The kinetics of $^{137}$Cs ions was experimentally studied and the obtained data were analyzed using pseudo first-order and pseudo second-order kinetic models. Results suggest that the sorption of $^{137}$Cs ion onto each samples followed the pseudo second-order rate model. Equilibrium study have been determined and tested for different isotherms and the sorption data were successfully modeled using Langmuir isotherm than that of Freundlich model.

The results showed that these adsorbents decreased in the following order DSS/GR>SDS/GR>GR, respectively. The SDS or DSS on the GR surfaces can enhance the sorbent DSS/GR to be a promising sorbent for the environmental friendly removal of radioactive $^{137}$Cs ions from actual LLW solutions.

REFERENCES


Table 8: Thermodynamic parameters for adsorption of Cs(I) onto GR, SDS/GR and DSS/GR.

<table>
<thead>
<tr>
<th>Tem. K</th>
<th>$K$ mL/g</th>
<th>$\Delta H$ KJ/mol</th>
<th>$\Delta S$ J/mol.K</th>
<th>$-\Delta G$ KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GR</td>
<td>SDS/GR</td>
<td>DSS/GR</td>
<td>GR</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>6.4</td>
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<td></td>
<td>333</td>
<td>3.86</td>
<td>19</td>
<td>3.343</td>
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</table>

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R e f e r e n c e s


