Synthesis of Graphene Functionalized with (SDS) for Removal of $^{137}$Cs(I) and Ce(III) Ions from Radioactive Waste

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Abstract: Sodium dodecyl sulfate (SDS) was chosen to obtain a sandwich type assembly of SDS and graphene (GR) sheets. The modified (SDS/GR) and unmodified GR were characterized by powder X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), Fourier transform infra-red (FTIR) spectroscopy, as well as thermal (TG) and TMA analyses. The SDS obviously prompts the dispersion of GR into a typical wrinkled layered structure. The addition of SDS into GR has lowering the coefficient of thermal expansion (CTE). $^{137}$Cs is the most currently radioactive isotope generated in the area around the Chernobyl disaster. Cerium is quantitatively concentrated and separated from Egyptian monazite by leaching the monazite lanthanide oxides cake. So, SDS/GR was applied to remove Cs(I) and Ce(III) from aqueous solutions using a batch technique. The factors pH, contact time, temperature, and dosage were investigated. The highest adsorption capacity of SDS/GR is found to be $44$ and $60$ mg g$^{-1}$ for $^{137}$Cs(I) and Ce(III), respectively. The adsorption of Cs(I) and Ce(III) onto SDS/GR fitted the pseudo-second-order model. It was found that the adsorption processes have reached their equilibrium state in about 2h, which is faster than most of carbon-based adsorbents can do. From the thermodynamic parameters the sorption process was endothermic and spontaneous in nature.

Keywords: Graphene; Sodium Dodecyl Sulphate; Characterization; Cs(I), Cerium(III); Sorption kinetics.

Introduction

Graphene is a one-atom-thick planar sheet of densely packed sp$^2$-hybridized carbon atoms arranged in a honeycomb crystal lattice with delocalized π electrons. It shows the combination of superior mechanical strength, carrier mobility, thermal and electrical properties (Lonkar et al., 2014). Modified graphene with different types of functionalization has been studied in the context of providing an opportunity to tune physical and chemical properties of graphene (Mali et al., 2015). This can afford ideal candidates for many applications, such as polymer composites, energy-related materials, sensors, paper-like materials, field-effect transistors (FET), and biomedical applications (Pham et al., 2010, Xu et al., 2011; Uddin et al., 2013). In particular, chemically modified graphenes (CMGs) derived from the interaction between dispersed graphene oxide (GO) and organic surfactant matrices, can successfully be used to develop graphene-based nanocomposites after being reduced by hydrazine and subsequent thermal annealing (Sungjin et al., 2011). Current research on graphene-based polymer nanocomposites has been fast motivated owing to the remarkable improvement in the mechanical properties and thermal properties of the nanocomposites (Yuxi et al., 2009, Zhengha et al., 2012, Li et al, 2011, Rama et al. 2012).

It has been shown (Tapas et al., 2012) the necessity to exfoliate graphene sheets in which loosely aggregated GR can be separated from one another, and thus maximizing the interfacial interaction between GR and the polymer matrix. This approach requires sufficient energy input, as depicted via ultrasonication in an aqueous solvent and by using charged surfactants, such as sodium dodecyl sulphate (SDS) (Andrew et al., 2013). SDS is dispersed into mostly individual sheets, leading to SDS-modified GR (SDS/GR) due to the attractive Vander Waals forces once the energy input from ultrasonication taking place and through coagulation as the proposed mechanism (Maa et al., 2010).
Treatment of liquid radioactive waste is an important phase in the management of all waste types, it aims to reduce the volume of generated wastes to enhance the safety and/or reduce the costs of further management phases. These wastes split into two portions after the treatment phase. The first portion is a small volume containing the bulk of radionuclides that is kept in the management system, and the second is a large volume one having such low levels of radioactivity as to be discharged to the environment after meeting the regulatory requirements (IAEA-TECDOC-1504-2006).

Cesium and cerium radioisotopes as $^{137}$Cs ($t_{1/2} = 30.7$ y) and $^{144}$Ce ($t_{1/2} = 284.91$ d) emit gamma radiation of energies 0.662 and 0.145 MeV, respectively, which are frequently found in radioactive liquid wastes originating from nuclear reactors and research institutes, mostly at levels exceeding the standards (Abdel Rahman et al 2011). Because body can accumulate cesium and cerium specially in spleen, liver, bone and lung, so ingestion of their radio-isotopes creates severe internal hazards (Ashraf et al 2014). Thus, SDS/GR which is non-conductive, hydrophilic and easily suspended in water was applied to clean up radionuclide-contaminated solution by agglomerating contaminants into solid phase (Attallah et al 2015). Herein, we report a simple and practical approach to use the synthesized SDS/GR composite for assessment of Cs(I) and Ce(III) adsorption from low level wastewater. Exploring the mechanism of ions adsorption on SDS/GR was undertaken based on the consideration of various factors affecting the uptake process.

Materials and Methods

Materials
Natural graphite powder and H$_2$SO$_4$ (98 wt.%) were purchased from Merck (Germany). Potassium permanganate (KMnO$_4$), H$_2$O$_2$ and HCl were used as received from Fisher Scientific. Hydrazine monohydrate from Sigma Aldrich (64-65%). SDS (sodium dodecyl sulfate) from Sigma (99.0%) $C_{12}H_{25}NaO_4S$ was used as received.

Synthesis of graphene oxide
Graphene oxide (GO) was prepared from graphite as a starting material via a modification of the Hummers and Offeman method (Marcano et al 2010).

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 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 to produce.

Modification of graphene oxide with SDS (SDS/GR)
0.1 g of GO was dispersed in 150 ml water and sonicated for 30 min. The desired amount (0.05 g) of the surfactant SDS was then dissolved in 100 ml of water by stirring at room temperature, followed by the addition of the dispersed GO in solution to the SDS solution. 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 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 to produce.

Adsorption Experiments

Ion solution preparation
100 ml of 200 ppm inactive cesium solution were prepared and traced with the radioactive isotope $^{137}$Cs solution. Activity determination using NaI scintillation crystal connected to a ACE™ multichannel analyzer (ORTEC) were done. The uptake percent (U%) of $^{137}$Cs was calculated from the following equation:

$$U\% = \left(\frac{(A_o - C_t)}{A_o}\right) \times 100$$

(1)
Where \( A_o \) and \( C_t \) are the activities expressed in counts per minute of 1 ml solution for the radioisotope before and after contacting with the biosorbent SDS/GR or GR. The pH was adjusted using appropriate amount of 0.1 M NaOH or HCl. 100 ml of 200 ppm of Ce III was prepared as stock solutions by dissolving an exactly weighted quantity from (CeCl\(_3\).7H\(_2\)O) salts in distilled water to obtain a concentrated solutions and other concentrations were obtained by dilution and measured through calibration curve for range of known concentrations (25-100ppm). The (\( \lambda \) max) of the Ce III ion is 252 nm. Spectrophotometric measurements were carried out using Shimadzu-160 UV/visible recording double beam spectrophotometer (Japan).

**Sorption isotherm**

Uptake experiments of the studied ion were carried out at pH of 6 by placing 0.05 g portions of GR or SDS/GR in a series of flasks containing 100 ml metal ions at initial concentration ranged 25-200 ppm. The contents of the flasks were equilibrated on a shaker for 1 h then the residual concentration of either \(^{137}\)Cs or Ce(III) in each flask was determined. After adsorption equilibration, radioactivity for the former or concentration for the latter in aqueous solutions was estimated and the amount \( q \) (mg/g) of metal ion adsorbed on adsorbent was calculated from the relation:

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

where \( C_o \) and \( C_e \) are the initial and equilibrium concentration of ions in aqueous solution, respectively. \( V \) and \( m \) are volume of solution and weight of adsorbent, respectively.

**Characterization**

High resolution transmission electron microscope (HR-TEM) was carried out using a Tecnai G2, FEI, Netherland. Two different modes of imaging were employed; X-ray diffraction (XRD) was measured using a Philips diffractometer (type PW-3710). Fourier transform infrared (FT-IR) spectra were recorded via a single beam Perkin Elmer Spectrometer (RXI FT-IR), 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 room temperature in the region 4000-400 cm\(^{-1}\).

In order to measure the dimensional stability of the samples, thermo- mechanical analysis (TMA) was carried out with a TMA Q 400 (TA instruments, USA) at a heating rate of 3 °C/min. TMA is used to determine the linear thermal coefficient of GR and SDS/GR, and was defined as follows (Jeffrey et al 2011):

\[
\alpha = \frac{dL}{dT} L^o
\]

where \( L^o \) is the original length of the sample and \( dL/dT \) is the slope of the TMA curve. The calculated value of \( \alpha \) is temperature dependent.

Thermal analysis of the prepared samples through (DSC and TGA) was carried out on a TA-50 Shimadzu, JAPAN, at a heating rate of 20 °C/ min in nitrogen atmosphere.

**Results and Discussion**

**Characterization**

**High-resolution TEM (HRTEM)**

The morphological structures of GR and SDS/GR were characterized by HRTEM (Fig. 1). Figure 1a shows that the GR layers display interplanar stacking disorder. Conversely, the TEM image of Fig. 1b shows that SDS/GR exhibits a curved thin flaky appearance in few layered structure with some wrinkled and folded regions. Due this fact GR sheets in SDS/GR can be stabilized by the SDS surfactant (Michael et al 2007).
Figure 1. TEM images of (a) GR and (b) SDS/GR

X-ray diffraction (XRD) analysis

Fig. 2 shows the XRD patterns of the graphite Gt, GO, GR, and SDS/GR. Graphite showed a sharp diffraction peak at 2θ of 26.2°, corresponding to the normal interlayer distance of 3.35 Å between graphite planes. After oxidation, this characteristic graphite peak disappeared and is replaced by a sharp, strong peak at 2θ of 11.23° corresponding to an interlayer distance of 7.87 Å in a typical layer-like structure of GO (Hawelek et al. 2013). The presence of oxygen based functional groups interacting into the interlayer of GO could lead to hydration and exfoliation of GO sheets in aqueous media. The diffraction pattern of GR is shown to exhibit a broad diffraction at 2θ of 22.76° which indicates a random of pucking of graphene sheets. After reduction of GO was undertaken by continuous stirring with hydrazine hydrate, the hydrophilicity of water-dispersed GO sheet gradually decreased, leading to an irreversible agglomeration of GR sheets. However, this reflection peak corresponds to a co-facial π-π stacking interlayer distance of 3.9 Å, as a result of oxygen removal from GO. The XRD pattern of SDS/GR shows a strong and sharp characteristic peak at 2θ of 22.69° corresponding to an interlayer distance of 3.91 Å, and thus GR is fully exfoliated into single graphene sheets in the SDS matrix. So, SDS can stabilize and disperse graphene, to prevent the formation of new stacked layers (Worsley et al. 2011).

Figure 2. XRD of Graphite (Gt), graphite oxide (GO), graphene (GR), and (SDS/GR)

FTIR Spectra

Figure 3 represents the FTIR spectra of GO, GR and SDS/GR. The spectrum of GO showed a broad band with a maximum at about 3383 cm⁻¹ characteristic of the stretching O–H vibration of compounds in which the hydroxyl functional group is bound to a carbon atom. The broadening of this band indicates an extensive intermolecular hydrogen bonding and thus could be associated with the presence of adsorbed water at 1620 cm⁻¹. The IR spectrum of GO also indicates the presence of the oxygen-containing functional groups; bands at 1059, 1226 and 1385 cm⁻¹ correspond to C–O
vibration of alkoxide, epoxy and hydroxyl group; and a band at 1720 cm$^{-1}$ to the C=O stretching vibration in $\text{COOH}$ group. For the spectrum of GR, these peaks have almost disappeared due to the removal of the carbonyl-based functional groups during the reduction process of GO (Si and Samulski 2008). The peak at about 3382 cm$^{-1}$ was significantly reduced in intensity for GR and centered at 3435 cm$^{-1}$, indicating that C–OH still exists. The SDS/GR does have additional drawbacks except the 3435 cm$^{-1}$ band was markedly decreased in intensity. This suggests that the SDS molecules diminish intermolecular hydrogen bonding localized in graphene interlayer spacing, and therefore enhanced graphene exfoliation which was significantly reduced due to hydrazine addition (Thayumanavan et al 2015).

![FTIR spectra of GO, GR and SDS/GR](image)

**Figure 3:** FTIR spectra of GO, GR and SDS/GR

**Thermo-mechanical analysis (TMA)**

From the TMA curves shown in Fig. 4, the coefficients of thermal expansion (CTE) for the two studied samples were calculated over two different temperature ranges, the first between 25 and 40 $^\circ$C and the second between 100 and 150 $^\circ$C. These coefficients were determined individually from the linear portions of each thermogram below 40 $^\circ$C and above 100 $^\circ$C. A low-expansion was observed for the two samples. The corresponding curves obtained for plain GR and SDS/GR have the same shape. Figure 4 illustrates the plots of dimension change (μm) vs temperature for the studied samples. Figure 4 shows that the GR undergoes a thermal expansion with a rate of 0.009 $\times$ 10$^{-6}$/K from 25 -40 $^\circ$C where as SDS/GR undergoes a thermal expansion at a rate of 0.01 $\times$ 10$^{-6}$/K; at the same temperature range. The thermal expansion coefficient $\alpha$ was calculated and listed at Table 1. This indicate that functionalization with SDS decrease the thermal expansion coefficient to approximately the half graphene value at the studied temperature ranges. This may be due to decreasing the mobility of the carbon atoms at the graphene sheets in presence of sulphonate group of SDS (Tapas et al 2012).

![TMA Thermogram for GR and SDS/GR](image)

**Figure 4.** TMA Thermogram for GR and SDS/GR
Table 1. Calculated thermal expansion coefficient of GR and SDS/GR at two different temperature range

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. range</th>
<th>Slope μm/K X</th>
<th>Thermal expansion coefficient X 10^6 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR</td>
<td>25-40</td>
<td>0.009</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>100-150</td>
<td>0.0024</td>
<td>0.25</td>
</tr>
<tr>
<td>SDS/GR</td>
<td>25-40</td>
<td>0.01</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>100-150</td>
<td>0.003</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Differential scanning calorimetry (DSC)

A typical DSC curve with a heating rate of 20 °C/min is shown in Fig. 5. A wide exothermic crystallization peak was observed around 40 °C for GO. This exothermic peak was not apparent for SDS/GR and GR, indicating no phase transition occurred at the preparation and functionalization steps for latter two graphens (Kuibo et al, 2011).

Figure 5. DSC Thermograms of GO, GR and SDS/GR

Thermogravimetric analysis (TGA)

As shown in Fig. 6, the TGA profiles of the studied samples showed successive weight loss processes as temperature increases at a heating ramping rate of 20 °C min⁻¹ under flowing nitrogen gas. A weight loss at room temperature up to 100 °C in the thermogram of GO could be primarily noticed due to thermodesorption of physically adsorbed water molecules held to GO (Richard et al 2009) [27]. This weight loss is approximately 11 wt. %. GR and SDS/GR had comparatively smaller weight loss, i.e. ~5 wt.%, indicating that these samples do not contain much water as previously reported (Stankovich et al 2007). However, GO exhibited a significant weight loss of approximately 15 wt.% from 100 to 250 °C that mainly contributed by the removal of oxygen-containing functional groups (Hao et al 2015). On the contrary, less weight losses of 2 and 5 wt.% occurred for GR and SDS/GR, respectively, over the same temperature range, suggesting that a significant amount of oxygen-containing functional groups was removed essentially by the hydrazine reduction of GO. Thus, such weight loss occurred to a lesser extent for SDS/GR than for GR. Finally, the former showed a significant endothermic peak near 500-600 °C accompanied by a weight loss representing the thermal decomposition of the dopant SDS surfactant.
Adsorption Study

Effect of pH

The adsorption capacity of $^{137}$Cs and Ce(III) on SDS/GR as a function of pH is shown in Fig. 7. At pH 3–5, the adsorption with 75 ppm by the various adsorbents was found to be very low, meaning the competition of an excess of hydrogen ions with these cations for bonding sites. At pH 5–7, the adsorption capacity increases sharply with increasing pH. Thus, the adsorption of either $^{137}$Cs(I) or Ce(III) is strongly dependent on pH. The hydrogen atoms will compete with the positively charged metal ions on the active sites of SDS/GR in the solution (Sepehrian et al 2013). So, the pH affect the sort and behavior of the SDS/GR in the solution, as well as with the adsorbed ions. Adsorbent functional groups such as carboxyl or hydroxyl are negatively charged so, the electrostatic attraction of positively charged $^{137}$Cs(I) onto the adsorbents enhances the capacity greatly. At pH > 8, the maximum Ce(III) removal is attributed to the formation of hydrolysis species [i.e. Ce(OH)$^+$, Ce(OH)$_2^+$] (Awual et al 2013).

Effect of contact time

For the evaluation of contact time effect, 0.05g of SDS/GR was treated with 20 mL Cs (I) and Ce(III) at an initial concentration ranged from 25–150 ppm at pH 6.0 at various time intervals. The dependence of ion adsorption upon contact time is shown in Fig. 8 (a and b). As the contact time increases, the capacity (mg g$^{-1}$) of SDS/GR increases. It could be observed that the process is quite rapid and is significant by 20 min after the addition of SDS/GR. The maximum adsorption capacity of either Cs (I) or Ce(III) was achieved after 120 min. This is a quite rapid ion removal due to the nanosize scale of SDS/GR which enhances either adsorption or diffusion of cations to the functional sites (Yan et al 2013). Also, Ce (III) ion uptake shows about two times higher than Cs(I) ion uptake may be due increase of e/r (Charge/ionic radius) value from 16.483 to 8.747, respectively (Deiseroth 2004).
The adsorbent dose in solution will affect the metal adsorption capacity of either Cs (I) or Ce(III) ions. It can be shown in Fig. 9, the adsorption rate of ions increased with increasing SDS/GR due to more surface area will be available which exposed more active sites for binding of metal ions. For a given initial concentration of ions, further increase of the sorbent mass up to 0.1 g doesn’t possess any influence on the adsorption rate of the studied ions.

Adsorption isotherm study

Adsorption isotherm plays a crucial role in the predictive modeling procedures for the analysis and design of an adsorption system. Therefore, the adsorption data of Cs (I) and Ce (III) were tested with Langmuir and Freundlich isotherm models at varying metal ion concentrations ranging from 25 to 150 ppm at 20-60 °C. The various constants of the two models were calculated and listed in Table 2 & 3. The Langmuir isotherm equation is described as follows (Ansari et al 2010).

\[
\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{1}{q_m} C_e
\]

(4)

\[
R_L = \frac{1}{1 + b C_e}
\]

(5)

where \(q_e\) is the amount adsorbed at equilibrium (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. 10 (a and b), where \(q_m\) and \(b\) were evaluated from the slope and intercept, respectively (Table 2). The maximum monolayer adsorption capacity \((q_m)\) of the SDS/GR composite was respectively found to be 44 and 60 mg g\(^{-1}\) for Cs(I) and
Ce(III) at 60 °C. Thus, a greater uptake capacity of SDS/GR was achieved for Ce (III) than Cs (I). The \( R_L \) values at all temperatures lie between 0 and 1, indicating a favorable adsorption process of Cs(I) and Ce(III) onto the SDS/GR surface (Mishra et al 2011).

**Table 2:** Langmuir and Freundlich parameters for sorption of Cs(I) ions onto SDS/GR.

<table>
<thead>
<tr>
<th>Temp.(k)</th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q(mg/g) R_L b(L/mg)</td>
<td>R²</td>
</tr>
<tr>
<td>293</td>
<td>22.21 0.0452 0.865</td>
<td>0.99451</td>
</tr>
<tr>
<td>298</td>
<td>23.11 0.0412 0.861</td>
<td>0.99651</td>
</tr>
<tr>
<td>303</td>
<td>24.62 0.0325 0.850</td>
<td>0.99384</td>
</tr>
<tr>
<td>313</td>
<td>37.84 0.0440 0.405</td>
<td>0.99989</td>
</tr>
<tr>
<td>323</td>
<td>42.83 0.0229 0.457</td>
<td>0.99988</td>
</tr>
<tr>
<td>333</td>
<td>44.12 0.0239 0.0463</td>
<td>0.99978</td>
</tr>
</tbody>
</table>

**Table 3:** Langmuir and Freundlich parameters for sorption of Ce(III) ions onto SDS/GR.

<table>
<thead>
<tr>
<th>Temp.(k)</th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q(mg/g) R_L b(L/mg)</td>
<td>R²</td>
</tr>
<tr>
<td>293</td>
<td>40.5 0.9199 0.0087</td>
<td>0.9994</td>
</tr>
<tr>
<td>298</td>
<td>51.5 0.9326 0.0072</td>
<td>0.9991</td>
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<td>303</td>
<td>60.2 0.9403 0.0064</td>
<td>0.9992</td>
</tr>
<tr>
<td>313</td>
<td>61.8 0.9376 0.0067</td>
<td>0.9982</td>
</tr>
<tr>
<td>323</td>
<td>62.0 0.9293 0.0076</td>
<td>0.9993</td>
</tr>
<tr>
<td>333</td>
<td>63.1 0.9213 0.0085</td>
<td>17.3 4.45 0.9928</td>
</tr>
</tbody>
</table>

**Figure 10-a:** Langmuir isotherm plots for adsorption of Cs (I)

**Figure 10-b:** Langmuir isotherm plots for adsorption of Ce(III)

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.11 (a&b). As cited in Tables 2&3, the values of \( K \) and \( n \) for adsorption of Ce(III) onto SDS/GR increased with increasing temperature, indicating that the adsorption is favorable at higher temperatures (Rahmani et al 2010). On the contrary, the values of these parameters decrease for Cs(I) as the temperature increases denoting that the adsorption process is favorable at lower temperatures. The Langmuir isotherm model fits the experimental data very well which perhaps due to homogeneous distribution of active sites on the.
SDS/GR composite as assumed by the Langmuir model and as shown by the high $R^2$ values ($R \approx 0.999$) at the different adsorption temperatures.

**Fig.(11-a):** Freundlich isotherm plots for adsorption of Cs (I)  
**Fig.(11-b):** Freundlich isotherm plots for adsorption of Ce (III)

### Adsorption kinetics

In order to investigate the kinetics of adsorption of either Cs(I) or Ce(III) onto SDS/GR, 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 (Ruparelia et al 2008):

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$  \hspace{1cm} (7)

where $q_e$ and $q_t$ are the amounts of adsorption capacity (mg/g) on SDS/GR at equilibrium time and at time t, respectively, while $k_1$ (L/min) representing rate constant of pseudo-first-order (min$^{-1}$), $k_1$ is determined by plotting log ($q_e - q_t$) versus t (Fig. 12 a&b). The parameter values of the kinetic models at initial concentrations are presented in Table (4). The results tell us that the experimental $q_e^{\text{exp.}}$ values disagree with calculated $q_e^{\text{cal.}}$ and the coefficients of determination $R^2$ is low. Therefore, the adsorption of either Cs(I) or Ce(III) onto SDS/GR does not fit with the pseudo-first order kinetic model.

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} t$$  \hspace{1cm} (8)

where $k_2$ is the pseudo-second-order rate constant (g/(mg min)) which is determined by plotting t/q versus t. The parameter values of the kinetic models are listed in Fig. 13 (a & b) and Table (4 &5). The calculated $q_e$ values show nearly an agreement with the experimental values, and the values for coefficient of determination ($R^2$) are more than 0.999 indicating that the second-order kinetic model could fit well and the adsorption of either Cs (I) and Ce (III) on SDS/GR surface.

**Figure (12-a):** Pseudo-first order plot for the sorption of Cs(I) ion on SDS/GR  
**Figure (12-b):** Pseudo-first order plot for the sorption of Ce(III) ion on SDS/GR
Figure (13-a): Pseudo-second order plot for the sorption of Cs(I) ion on SDS/GR

Figure (13-b): Pseudo-second order plot for the sorption of Ce(III) ion on SDS/GR

Table 4: The pseudo-first order and pseudo-second order parameters for sorption of Cs(I) ions on SDS/GR.

<table>
<thead>
<tr>
<th>Co (ppm)</th>
<th>qe(cal) (mg/g)</th>
<th>qe(exp) (mg/g)</th>
<th>K1 (g/mg.min)</th>
<th>R2</th>
<th>Co (ppm)</th>
<th>qe(cal) (mg/g)</th>
<th>qe(exp) (mg/g)</th>
<th>K2 (g/mg.min)</th>
<th>R2</th>
</tr>
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<tr>
<td>25</td>
<td>1.83</td>
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<td>0.03715</td>
<td>0.9976</td>
<td>25</td>
<td>4.8</td>
<td>4.6</td>
<td>0.038342</td>
<td>0.999</td>
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<td>50</td>
<td>3.5</td>
<td>8.6</td>
<td>0.032703</td>
<td>0.9976</td>
<td>50</td>
<td>9.1</td>
<td>8.6</td>
<td>0.017551</td>
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<tr>
<td>75</td>
<td>4.9</td>
<td>12.3</td>
<td>0.034637</td>
<td>0.9986</td>
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<td>12.9</td>
<td>12.3</td>
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<td>0.999</td>
</tr>
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<td>100</td>
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<td>0.9986</td>
<td>100</td>
<td>16.8</td>
<td>16</td>
<td>0.01006</td>
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</tr>
<tr>
<td>150</td>
<td>14.9</td>
<td>22.8</td>
<td>0.0433654</td>
<td>0.9798</td>
<td>150</td>
<td>24.9</td>
<td>22.8</td>
<td>0.004126</td>
<td>0.999</td>
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<tr>
<td>200</td>
<td>12.98</td>
<td>24</td>
<td>0.04984</td>
<td>0.9456</td>
<td>200</td>
<td>22.5</td>
<td>24</td>
<td>0.009584</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 5: The pseudo-first order and pseudo-second order parameters for sorption of Ce(III) ions on SDS/GR.

<table>
<thead>
<tr>
<th>Co (ppm)</th>
<th>qe(cal) (mg/g)</th>
<th>qe(exp) (mg/g)</th>
<th>K1 (g/mg.min)</th>
<th>R2</th>
<th>Co (ppm)</th>
<th>qe(cal) (mg/g)</th>
<th>qe(exp) (mg/g)</th>
<th>K2 (g/mg.min)</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>12.6</td>
<td>13.4</td>
<td>0.042</td>
<td>0.9758</td>
<td>25</td>
<td>15.4</td>
<td>13.4</td>
<td>0.0039</td>
<td>0.9974</td>
</tr>
<tr>
<td>50</td>
<td>13.42</td>
<td>20.54</td>
<td>0.027</td>
<td>0.9697</td>
<td>50</td>
<td>22.4</td>
<td>20.54</td>
<td>0.0029</td>
<td>0.9924</td>
</tr>
<tr>
<td>75</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>
</tr>
<tr>
<td>100</td>
<td>15.4</td>
<td>39.18</td>
<td>0.033</td>
<td>0.9743</td>
<td>100</td>
<td>51.95</td>
<td>47.18</td>
<td>0.0017</td>
<td>0.9895</td>
</tr>
<tr>
<td>150</td>
<td>16.2</td>
<td>40.18</td>
<td>0.033</td>
<td>0.9743</td>
<td>150</td>
<td>55.95</td>
<td>49.18</td>
<td>0.0017</td>
<td>0.9895</td>
</tr>
</tbody>
</table>

Thermodynamic study
To evaluate the influence of temperature on adsorption process of both Cs(I) or Ce(III) onto SDS/GR surface, 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: (Çavuş and Gürdağ 2009).

\[ ΔG° = -RT \ln K_d \]
\[ ΔG° = ΔH° - TΔS° \]
\[ ln K_d = \frac{ΔS°}{R} - \frac{ΔH°}{RT} \]
\[ K_d = b \cdot q_m \]

where R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K), and Kd is adsorption equilibrium constant, the values of the of Kd are calculated using the values of Langmuir constants (b .q_m) at different temperatures .The values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from slope and intercept respectively of the plot of lnKd versus 1/T (Van't Hoff plot). The thermodynamic parameters are listed in Table (6). The positive values of (ΔS°) reflects the increased randomness at the solid/solution interface during the adsorption process. Also, the positive
ΔS values may be due to the fixation of ion on the exchange sites of the randomly distributed surfactant species (Fan et al 2012). Inspection of the Table (6) indicated that the standard free energy ΔG decreased with increase in temperature thereby indicating an increase in adsorption at higher temperature and the negative values of ΔG which perhaps that the surfactant molecules have more affinity toward the metal ions which point to the feasible spontaneous adsorption process and the positive ΔH values reveal the endothermic nature of Ce(III) adsorption more than Cs(I). Hence, it would be expected that an increase in solution temperature would lead to an increase in adsorption capacity, as shown in Tables (6) the sorption of both Cs(I) and Ce(III) increased with increasing temperature, confirming that sorption is an endothermic state and their uptake process is energetically stable. The ΔH \(^0\) values are found to be less than 40 kg mol\(^{-1}\) indicating a physisorption process and which confirmed with the ΔG values which are in between 0 and -20kJmol\(^{-1}\) (Humelnicu et al 2014). The positive ΔS \(^0\) for this process indicated the increase in number of species and degrees of freedom.

![Figure 14-a](image1.png)  
**Figure (14-a):** Van’t Hoff plot for adsorption of Cs(I) ion on SDS/GR

![Figure 14-b](image2.png)  
**Figure (14-b):** Van’t Hoff plot for adsorption of Ce(III) ion on SDS/GR

### Table 6. Thermodynamic parameters for adsorption of Cs(I) and Ce (III) onto SDS/GR.

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>Kd, mL/g</th>
<th>ΔH(^o) KJ/mol</th>
<th>ΔS(^o) J/mol.K</th>
<th>ΔG(^o) KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2.65</td>
<td>6.4</td>
<td>-2.35</td>
<td>-3.87</td>
</tr>
<tr>
<td>298</td>
<td>2.80</td>
<td>7.4</td>
<td>-2.52</td>
<td>-4.23</td>
</tr>
<tr>
<td>303</td>
<td>2.88</td>
<td>8.4</td>
<td>-2.69</td>
<td>-5.15</td>
</tr>
<tr>
<td>313</td>
<td>3.096</td>
<td>12</td>
<td>+7.612</td>
<td>+33.77</td>
</tr>
<tr>
<td>323</td>
<td>3.55</td>
<td>17</td>
<td>-3.03</td>
<td>-6.43</td>
</tr>
<tr>
<td>333</td>
<td>3.86</td>
<td>19</td>
<td>-3.37</td>
<td>-7.73</td>
</tr>
</tbody>
</table>

### Conclusions

This work describes the synthesis of graphene (GR) as well as SDS/GR as the anionic functionalization using SDS surfactant on graphene (GR) and its use for treatment of liquid waste contain either Cs (I) or Ce (III). The surface structure of sorbent (SDS/GR) was characterized using SEM, TEM, XRD, FT-IR, TMA, DSC and TGA. Finally, the effect of experimental condition on sorption process and evaluation of the thermodynamic parameters as free energy of ion adsorption onto the SDS/GR were attained following that adsorption on the surface of SDS/GR was physisorption process for Cs (I) or Ce (III). The optimal pH for the removal of Cs (I) or Ce (III) is about 6.0. The adsorption of Cs (I) fits Freundlich equation while Ce (III) adsorption fits the Langmuir equation well. The highest adsorption capacity of SDS/GR was found to be 44 and 63 mg/g for Cs (I) or Ce (III), respectively. The results illustrate that the adsorption of the studied ions onto SDS/GR fitted the pseudo-second-order model. It is found in this study that the adsorption processes have reached their equilibrium state in about 2 h, which is faster than most of carbon-based adsorbents can do. The calculated thermodynamic parameters indicate that the adsorption of the studied ions is an endothermic and spontaneous process and more preferable in case of Ce (III) than...
This research demonstrates that SDS/GR can be an effective adsorbent for radioactive and hazardous ions removal.

References
Deiseroth HJ, (2004) Advanced Inorganic Chemistry (part 1) basic solid state chemistry WS 05/06.


