STUDIES OF EQUILIBRIUM AND KINETICS OF ADSORPTION OF CESIUM IONS BY GRAPHENE OXIDE

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ABSTRACT

Cesium is one of the fission products of major radiological concern, it is often found in nuclear radioactive waste generated at nuclear power plants. Graphene Oxide (GO) has attracted great attention due to its functionalized surface, which includes hydroxyl, epoxy, carbonyl and carboxyl groups, with great capacity of complexation with metal ions and can be used as adsorbent to remove cations from aqueous solutions. In this work, a treatment of radioactive waste containing ^{137}Cs was studied. For the batch experiments of Cs^+ removal, ^{133}Cs concentrations remained after the adsorption were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and the results obtained were analyzed according to the Langmuir and Freundlich isotherms models. The kinetics of adsorption and Gibbs free energy were also determined. The Langmuir model was the best fit and defined a favorable adsorption. The cesium adsorption process is the pseudo-second model and the Gibbs free energy calculation indicated that the adsorption process is spontaneous.

1. INTRODUCTION

In the operation of nuclear reactors for energy production, as well as in the production and use of radioisotopes in industry, medicine and research, radioactive waste is generated that can pose a risk to man and the environment, and a its safe management is required.

^{137}Cs is one of the products of nuclear fission of major radiological concern in the radioactive waste of the nuclear fuel cycle. This isotope has a half-life of about 30 years and can be easily spread in aqueous medium. The chemical properties of ^{137}Cs are similar to K^+, and this one compete with it in the activation of several enzymes [1, 2, 3].

Further studies with various carbon-based nanomaterials have been made for the removal of radionuclides, mainly uranium from aqueous solutions. Recently, a new nanomaterial has been outstanding in the removal of heavy metals from aqueous solutions: graphene oxide (GO).

The presence of epoxy, hydroxyl, carbonyl and carboxyl groups in the GO structure enhances the adsortion capacity of metal cations and GO is also a promising adsorbent in the removal of organic contaminants [4] and inorganic from aqueous solutions [5]. In the treatment of liquid radioactive waste the GO has a high adsorption capacity [6, 7].

In the present work, the study of equilibrium and kinetics aims to understand the characteristics and parameters of the adsorption process of cesium from aqueous solutions by GO.

2. EXPERIMENTAL

2.1. Materials

Standard solution of cesium chloride, 1.0 g.L^{-1} (Fluka Chemika) and graphene oxide, synthesized using the modified Hummers method (1958) [8].

2.2. Analyses by Absorption Spectrometry in the Infrared Region (FTIR)

The spectrometer used was the Perkin-Elmer Frontier-100 model and the samples were dispersed in potassium bromide (KBr) and pressed, obtaining a tablet with which the absorbance measurements were made. FTIR was used to characterize synthesized GO, and to confirm the presence of Cs$^+$ in GO, after the adsorption tests.

2.3. Analysis of Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope (SEM), model TM3000, Hitashi, was used for the characterization of the synthesized GO. In order to confirm the presence of Cs$^+$ in GO, after the adsorption tests the Scanning Electron Microscope (SEM), Philips XL-30, was coupled to the dispersive energy detector (EDS).

2.4. Adsorption Process

A standard 1.0 g.L^{-1} solution of cesium chloride was diluted in plastic bottles at concentrations ranging from 12 to 123 mg.L^{-1} in three replicates, the pH was adjusted to 6.5, and 20 mg of the adsorbent were added to the flasks and left under stirring for 60 minutes. The solutions were filtered through syringe filters (0.2μm / 15mm / Sartorius) for removal of the adsorbent and the remaining cesium in the solution was analyzed by ICP-OES (Optically Coupled Plasma Inductively Coupled Spectrometry) - Perkin Elmer Optima model 7000DV.

2.5. Determination of Langmuir / Freundlich Isotherms for GO

The adsorption isotherm is a mathematical expression that relates the equilibrium between the amount of the adsorbed material and the concentration of this material in the solution [9]. For the Langmuir model (equation 1)

$$Q_{eq} = \frac{Q\,K_L C_{eq}}{1 + K_L C_{eq}} \tag{1}$$

where:
Q_{eq} - amount of solute adsorbed on the adsorbent (mg.g^{-1})
C_{eq} - concentration of adsorbate (mg.L^{-1}) in solution
Q - maximum adsorption capacity (mg.g^{-1})
K_L - Langmuir adsorption constant (L.mg^{-1})

The Freundlich model can be applied in non-ideal systems with heterogeneous surfaces and adsorption in multilayers, characterized by the exponential distribution [7]. The value of n is calculated by equation 2

$$Q_{eq} = K_F C_{eq}^{1/n} \qquad (2)$$

where:
K_F - Freundlich adsorption constant (L.g^{-1})
$1/n$ - heterogeneity factor
C_{eq} - concentration of adsorbent (mg.L^{-1}) in solution
Q_{eq} - maximum adsorption capacity (mg.g^{-1})

2.6. Models of Lagergren of Pseudo-first and Pseudo-second Order

To determine the sorption rate of a sorvate in a solution, they are represented by equations 3 and 4 of pseudo-first and pseudo-second order respectively.

$$\ln(Q_{eq} - Q_t) = \ln Q_{eq} - K_1 t \qquad (3)$$

where:
K_1 - reaction rate constant (g.mg^{-1}.min^{-1})
Q_{eq} - quantity adsorbed at equilibrium (mg.g^{-1})
Q_t - amount of adsorbate at any time t (mg.g^{-1})
t - contact time (min)

$$\frac{t}{Q_t} = \frac{1}{K_2 Q^2} + \frac{1}{Q} t \qquad (4)$$

where:
K_2 - reaction rate constant (g.mg^{-1}.min^{-1})
Q - theoretical amount of removal (mg.g^{-1})
Q_t - amount of adsorbate at any time t (mg.g^{-1})
t - contact time (min)

2.7. Gibbs Free Energy and Adsorption Kinetics for GO

The free energy of Gibbs (ΔG), equation 5, shows that if temperature and pressure remain constant, it is possible to predict whether a process is spontaneous only in terms of the thermodynamic properties of the system. The reactions are spontaneous when the value of ΔG is negative [10].

$$\Delta G = -RT \ln(K_L) \qquad (5)$$

Where:
R = universal constant of the perfect gases, 8.314 J.K^{-1}.mol^{-1}
T = absolute temperature in kelvin (K)
K_L = Langmuir constant (L.mol^{-1})

3. RESULTS AND DISCUSSION

3.1. Characterization of Graphene Oxide (GO)

In the characterization of graphene oxide synthesized by infrared absorption spectrometry (FTIR), we observed the presence of bands characteristic of the functional groups of the carboxyl (1700-1730 cm^{-1}) and epoxy (1000-1300 cm^{-1}) [11]. The results obtained in the present study were similar to those reported in the literature.

3.2. Characterization of GO After Adsorption Test of Cesium Ions (GO/Cs)

The presence of cesium ions on the surface of the adsorbent was confirmed by Scanning Electron Microscopy (SEM) with dispersive energy spectroscopy (EDS) and by comparison of the FT-IR spectra of GO and GO/Cs.

The presence of the cesium ions was indicated by deformations in the bands between 1200 and 1300 cm^{-1}, characteristics of the axial deformation of the carboxyl group. This result suggests that the carboxyl groups present in the GO are responsible for the cesium sorption.

3.3. Isotherms Studies

The graphs of the linear form of the Langmuir isotherm and the Freundlich isotherm are shown in Fig.1.
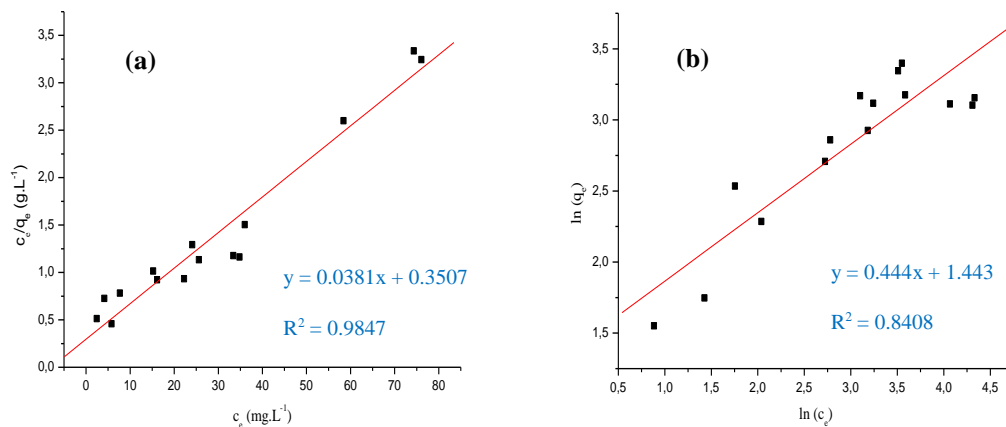

Figure 1: The linear form of Langmuir isotherm (a) and linear Freundlich isotherm (b).

In Table 1 are shown the calculated parameters of the linearized forms of the isotherms.

Table 1: Adsorption Parameters

Langmuir			Freundlich		
K_L (L.mg^{-1})	Q (mg.g^{-1})	R_2	K_F (L/mg^{-1})	1/n	R_2
0.1062	26.25	0.9847	1.443	0.444	0.8408

The Table 1 shows that the linear form of Langmuir isotherm (a) fits better than the linear Freundlich isotherm (b), considering the values of R^2, indicating that there is an equilibrium between the sorption and desorption process and it is a monolayer phenomenon, that is, each site accommodates only one adsorbed species.

The value of n represents the distribution of ions adsorbed in the active sites in the adsorbent. The value higher than 1 indicates that the Cesium ions are favorably removed. Q indicates the ability of the GO to adsorb the ions of Cs^+.

3.4. Chemical Kinetics Study

The linear graphs of pseudo-first order and pseudo-second order kinetics are shown in Fig.2.
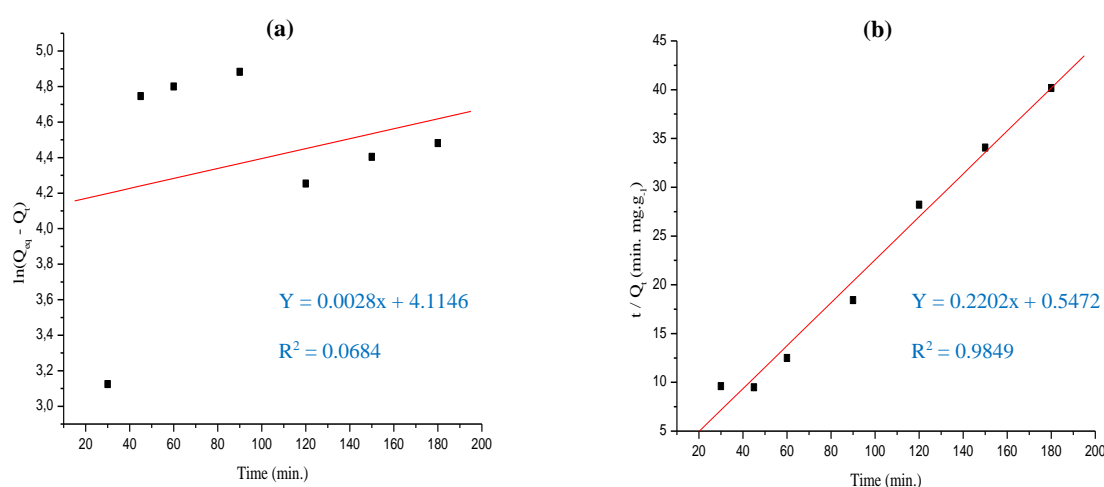

Figure 2: (a) Pseudo-first order and (b) Pseudo-second order

From the linearized forms of the pseudo-first order and pseudo-second order the parameters were calculated as shown in Table 2.

Table 2: Parameters of adsorption kinetics in GO.

Pseudo-first order			Pseudo-second order			
K_1 (g(mg^{-1}.min^{-1}))	Q_{eq} (mg.g^{-1})	R^2	K_2 (g(mg^{-1}.min^{-1}))	Q_t	Q (mg.g^{-1})	R^2
0.090	26.25	0.0684	1.443	4.54	4.80	0.9849

The kinetics fit better on the pseudo-second order as shown on Table 2, the R^2 value of pseudo-first order is smaller (0,0684) than the R^2 value of pseudo second order (0,9849) indicating that this order is indicated. The approximate values of theoretical Q_t and experimental Q, 4.54 and

4.80, respectively, confirm that the pseudo-second order model explains the adsorption kinetics of cesium ions remotion by GO.

The calculated value for Gibbs free energy (ΔG) was -14,691.82 kJ.mol^{-1}, and the negative value indicates that the process of adsorption of cesium ions by GO spontaneous.

4. CONCLUSIONS

The characterization of GO before and after the cesium adsorption experiments confirmed the presence of cesium on the surface of the adsorbent. The study of the adsorption isotherms indicated that the adsorption process was favorable and the model that better fitted was Langmuir one, indicating that there was equilibrium between the sorption and desorption process and that it was monolayer phenomenon.

For the kinetics of the adsorption process was adequate to the pseudo-second order model. The calculated value for Gibbs free energy indicated that the adsorption process was spontaneous. These results showed that graphene oxide is a very promising adsorbent to the treatment of radioactive liquid wastes that contain ^{137}Cs.

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