Preliminary Study of the Potential Graphene Oxide as Radioactive Clinical Wastewater Adsorbability in Nuclear Medicine

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Abstract. This paper reports the ability of graphene oxide (GO) as a radionuclide adsorbent material for an alternative approach in nuclear medicine radioactive waste management. Notable physicochemical properties of GO mainly consist of oxygen-containing functional groups on its basal plane and edges site in the form of epoxy, hydroxyl, and carboxyl groups, making it a promising candidate for radionuclide extraction material from aqueous solution. Herein, GO was synthesised via a simplified Hummers method. The radioactive clinical waste, which is urine, was collected right after the scanning procedure and mixed with GO in various concentrations: 1 mg/ml, 1.5 mg/ml, 2 mg/ml, 2.5 mg/ml, and 3 mg/ml. The mixture was then filtered using micropore filter paper, leaving sediments on the filter paper and wastewater residues. The radioactivity of sediment and water residue was determined by using a well counter after 3, 6, 9, and 12 hours of filtration process. The activities of the sediment and water residues were found to be decreased with increasing GO concentrations. The FESEM image revealed high agglomeration structure when the sample was treated with GO of 3 mg/ml concentration. Further analysis via EDX showed the presence of other elements in the urine, which led to its attraction to the GO-layered sheets. This analysis also confirmed the presence of oxygen-functioning group in GO that facilitated the agglomeration process and solidified the radionuclide waste.

1. Introduction

Technetium-99m (^{99m}Tc) serves as the radionuclide of choice for diagnostic imaging in nuclear medicine. Among the isotopes currently available, ^{99m}Tc is the most radioactive chemical compound used in hospital practice for nuclear imaging, owing to its ideal nuclear properties and convenient supply method through a commercial generator system [1–3]. The common use of ^{99m}Tc in nuclear medicine had drawn attention towards the sustainable disposal of clinical radioactive waste generated from human [4]. In hospitals, the toilet outlets for patient undergoing diagnostic procedures are connected to the delay tank meant for collecting clinical radioactive waste, especially those from isolation ward. Delay tank works as an underground tank to delay the discharge of clinical radionuclide waste at a certain level of radioactivity before it is released into the ordinary sewage system [5]. Toilet waste (e.g., feces and

urine) from diagnostic patients goes into the delay tank, subsequently increasing the volume of waste collected [4]. As a consequence, the limited volume and size of delay tank, along with periodical clearance, places a severe limitation on the number of patient admission for nuclear imaging. Hence, exploring a new, efficient, and economical disposal of radioactive waste is vital to sustain the radioactive waste management from nuclear medicine department, which remains a challenge among researchers and practitioner to date.

A convenient way of overcoming this problem is to extract and solidify the radionuclide by a special adsorbent material for fast disposal [6]. This paper, therefore, is set out to propose graphene oxide (GO) as an efficient adsorbent material for ^{99m}Tc extraction from radioactive clinical wastewater. Its potential is believed to be attributed to its large surface area that is abundant with reactive oxygen functional groups for example epoxy, hydroxyl, and carboxyl [7], which are essential for preconcentration and solidification of radionuclide [8–11]. Furthermore, with exceptional properties such as extremely high contact surface, large pore volumes, and high chemical stability, GO seems to outperform other materials as a radionuclide adsorbent [8-9].

To date, a number of studies have proclaimed the ability of GO as radionuclide adsorbent, including the adsorption of Cs, Eu, Sr, U, and I-131 [6, 8, 11-12]. A recent study demonstrated the ability of GO as ^{99m}Tc adsorbent via GO membrane permeability through size-exclusion mechanism [13]. However, the adsorbent of GO with ^{99m}Tc in urine (as the most prominent clinical waste in nuclear medicine imaging) is still not comprehensively studied. This issue would be critical if spillage or contamination from this clinical radioactive waste were to occur. In such cases, rapid decontamination process should be done efficiently. Here, the potential of higher affinities of Tc in the form of TcO^-_4 towards GO is demonstrated and compared with other competing ions in the urine (Cl^- and SO_4^{2-}), which is attributed by its low hydration free energy nature. Overall, GO serves as the most promising candidate in removing radionuclide from contaminated solutions through sorption technique [14-15].

2. Methodology

This study involved patients who had been administered with ^{99m}Tc for nuclear diagnostic imaging. The urine samples were collected at the ablation ward, Nuclear Medicine Department of Advanced Medical and Dental Institute, Universiti Sains Malaysia; where patients were quarantined prior to and post of the nuclear imaging process. Six urine samples from patients containing ^{99m}Tc tagged with sestamibi were collected after the scanning procedure, with each measured at 0.25 ml, as shown in Figure 1 (a). Geiger-Muller (GM) survey meter was used to obtain the background exposure (mSv/h) during sample collection for radiation protection purposes. The experiment was conducted after the approval from Human Research Ethics Committee (HREC) of Universiti Sains Malaysia (USM) was obtained.

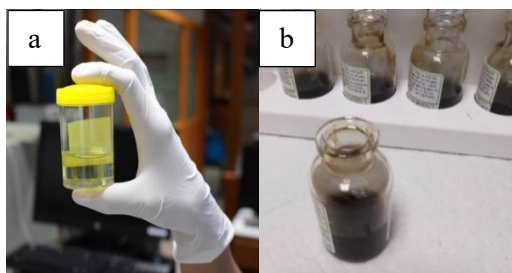*2.1. Synthesis of Graphene Oxide*

The GO solution was synthesised via a simplified Hummers method, as shown in Figure 1 (b) [6, 16]. Generally, 3 g of graphite was mixed into a solution of H_2SO_4 and H_3PO_4 (ratio of 4:1), followed by the addition of $KMnO_4$. The mixture was continuously stirred for three days. Then, the mixture was poured onto 400 ml of ice cubes, along with 27 ml of H_2O_2 (30%). The mixture was then centrifuged at 10,000 g (gravity) until pH 5 is reached. Final concentration of the GO solution was determined by dropping 1 ml of the solution on an identified weight filter paper before reweighing it to obtain the concentration in mg/ml. Characterisation of layered GO nanosheets from the final solution was performed using field emission scanning electron microscope (FESEM) model FEI Quanta 450 FEG at the School of Health Science, Universiti Sains Malaysia as shown in Figure 2 (a) and (b). In addition, the concentrations of GO solution used in this study were varied by diluting the solution with deionised water, as shown in Table 1, where it was calculated using Equation 1:

$$M_1 V_1 = M_2 V_2 \qquad (1)$$

where, M_1 = initial concentration of GO (mg/ml); V_1 = initial volume of GO (ml); M_2 = GO concentration after dilution (mg/ml); and V_2 = final volume of GO after dilution (ml).

Table 1. Ratio of GO concentrations and radioactive clinical waste mixtures.

| Concentration of GO (mg/ml)	Volume of GO (ml)	Volume of water added to GO (ml)	Volume of sample from urine	Volume of sample before filtration (ml)
1.0	0.075	0.175	0.25	0.5
1.5	0.113	0.138	0.25	0.5
2.0	0.150	0.100	0.25	0.5
2.5	0.188	0.062	0.25	0.5
3.0	0.225	0.024	0.25	0.5

Figure 1. (a) Radioactive urine sample collected from patient undergoing nuclear imaging procedure; (b) GO synthesised using simplified Hummers method.
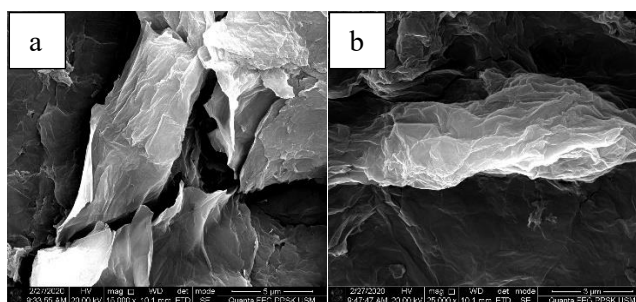
Figure 2. Characterisation of GO nanolayers; (a) GO nanolayers with non-uniform structures; (b) agglomerated GO tissues-wax nanolayers.

2.2. Radionuclide extraction

The initial activity (Ao) of each radioactive waste sample was measured using a well counter model Biodex, Atomlab 500 at the Radionuclide Laboratory, Advanced Medical and Dental Institute, Universiti Sains Malaysia. Subsequently, GO with varied concentrations of 1 mg/ml, 1.5 mg/ml, 2 mg/ml, 2.5 mg/ml, and 3 g/ml were added to each radioactive waste sample. One of the radioactive waste samples was left alone as a control sample. The ^{99m}Tc:GO sediments were then collected by filtering the mixture using a micropore filter paper, as shown in Figures 3 (a) and 3 (b). The physical adsorption properties of the sediment were characterised using FESEM and Energy-Dispersive X-ray (EDX) to investigate the morphological and elemental compositions.
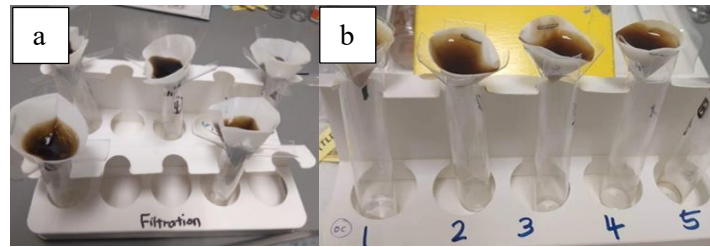
Figure 3. (a) ^{99m}Tc:GO filtering process using micropore filter paper, (b) sediment of ^{99m}Tc:GO formed on filter paper used for characterisation

3. Results and discussions

3.1. Kinetic study

The kinetic data, which is the radioactivity of ^{99m}Tc:GO sediment with residue (Bq), were fitted into an exponential graph against the concentration of GO (mg/ml) over the function of time (initial 15 minutes, after 3 hours, 6 hours, and 12 hours). Herein, the kinetic data were approximated by using the radioactive decay equation, as shown in Equation 2:

$$ln\left(\frac{A}{A_o}\right) = -\lambda t \qquad (2)$$

where, A = radionuclide activity; Ao = Initial radionuclide activity; λ = decay constant; and t = decay time.

Figure 4 shows the exponential decay rate of ^{99m}Tc:GO when the activity was measured at 3, 6, 9, and 12 hours after filtration process by using well counter and extrapolated with Equation 2. The graph provides the intercorrelation between the activity of sediment with residue and the concentration of GO. Overall, the radioactivity of the samples exponentially decreased with increasing GO concentration. In maintaining the initial concentration of adsorbate whilst increasing the adsorbent dosage, the increasing adsorption efficacy are ascribed to the enlarging surface area and the rising number of active sites for adsorption [7, 17]. Howbeit, a constant line was generated, suggesting that the radionuclides might be totally adsorbed due to decay norms after 12 hours of filtration, where the activity of the samples is very low. The findings provide evidence of active interaction between GO and clinical wastewater samples at high radioactivity [6]. This is due to more radionuclide being trapped and filtered by the high concentration of GO.

The GO surface functionalised with epoxy, hydroxyl, and carboxyl moieties is well suited for the interaction of adsorbent with ^{99m}Tc present in the form of pertechnetate (TcO$^-_4$) anion [18]. The phenomenon shows that higher GO concentration has higher affinity in radionuclide adsorbability and thereby reducing the amount of sediment, which directly resulted in less count of activity. This is due to the large surface area that leads to more functional groups and active sites availability [7], for radionuclide binding interaction to occur in high concentration solution [18]. The anion of TcO$^-_4$ radionuclide also has a unique attraction towards the surface of GO layers as a result of its low hydration free energy, in which it is consistent with the experimental evidence of TcO$^-_4$ having a high affinity for porous carbons [3, 5]. Another postulated interaction would be the anion TcO$^-_4$ adsorbed from wastewater by means of selective permeability through GO membranes, which is known to swell when immersed in water and selectively permeates ion according to size-exclusion mechanism [3-4].
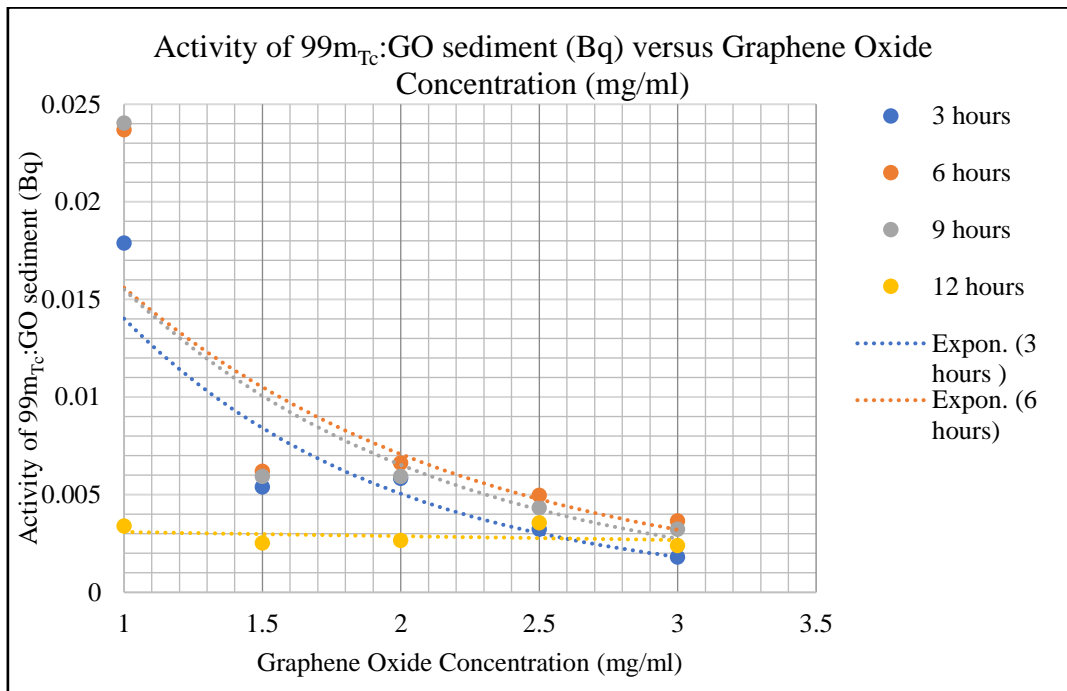
**Figure 4.** Extrapolation of ^{99m}Tc:GO sediment activity (Bq) versus GO concentration (mg/ml)

3.2. Radionuclide characterization

The ^{99m}Tc:GO sediment were morphological and elementarily characterised using FESEM and EDX, respectively. The analysis was conducted on samples treated with minimum and maximum concentration of GO of 1.0 mg/ml and 3.0 mg/ml, respectively. The morphologies of the extracted radionuclide with 1.0 mg/ml GO concentration and 3.0 mg/ml GO concentration are shown in Figure 5 (a) and Figure 6 (a), respectively. Meanwhile, the elemental compositions from EDX analysis for samples treated with minimum and maximum concentration of GO are shown in Figure 5 (b) and Figure 6 (b), respectively.
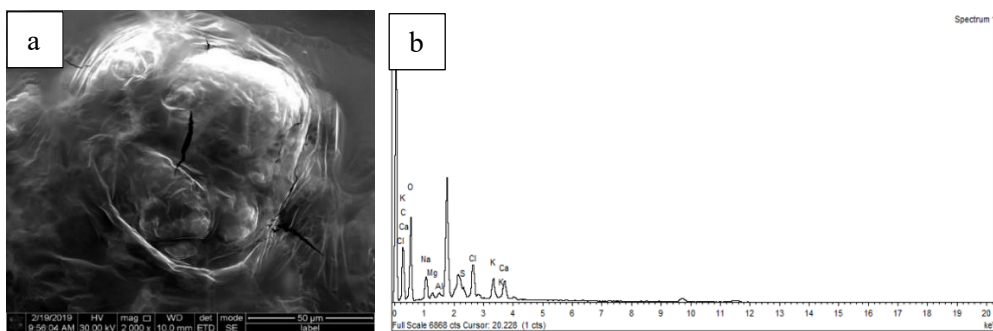
Figure 5. (a) Morphology of ^{99m}Tc radionuclide clinical wastewater mixture with 1 mg/ml of GO concentration appears transparent with thin coating layers; and (b) Elemental composition of ^{99m}Tc radionuclide clinical wastewater with 1 mg/ml GO concentration.
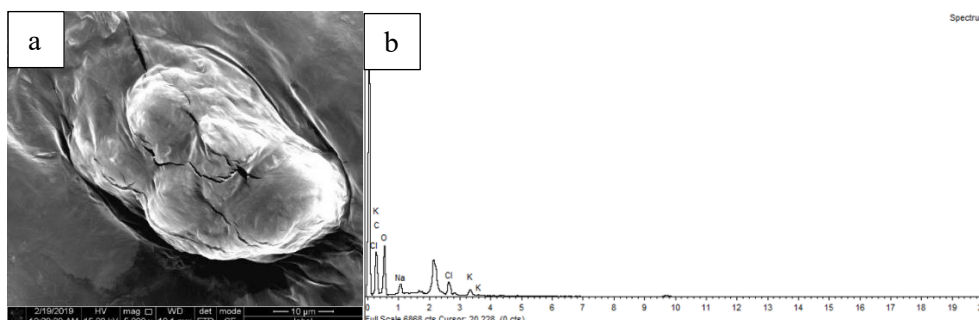
Figure 6. (a) Morphology of ^{99m}Tc radionuclide clinical wastewater mixtures with 3 mg/ml GO concentration appears tight with thick coating layers; and (b) Elemental composition of ^{99m}Tc radionuclide wastewater with 3 mg/ml of GO concentration.

Figure 5 (a) and Figure 6 (a) demonstrate the surface morphology of GO structure portrayed as the background layer in the image, coating the radionuclide and forming an agglomerated structure. The agglomerated structure suggests the trapping of ^{99m}Tc with other elements existed in the urine sample. This agglomerated structure is attracted by the background, which directly suggests that there might be an interaction between radionuclide and the GO surface via surface complexation as a result of abundant functional group (e.g., hydroxyl, carboxyl, and epoxy) on the GO surfaces [1, 7-8]. The FESEM images show the adsorption of radionuclide with maximum GO concentration strongly trapped to hold the substances within the tight and thick coating layers, compared with the minimum concentration that is loosely coated with nearly transparent layers surrounding the substances.

The findings proposed that the adsorbability of GO on the radionuclide is dependent on the concentration of GO. Figure 5 (b) and 6 (b) exhibit the elemental analysis via EDX of ^{99m}Tc:GO sediment at two selected GO concentrations, which are 1.0 mg/ml and 3.0 mg/ml. The oxygen-containing functional group molecules showed higher percentage of carbon, potassium, and chlorine, as shown from the EDX spectrum. High amount of C and O is due to the origin of the GO itself, which is made from hydrocarbon layers [6]. The carbon/oxygen (C/O) atomic ratio plays an important role as an indicator for the degree of graphene oxidation, and for assessing the nature of oxygen functionalities [19]. The oxygen-containing functional groups (e.g., C-O, C=C, and C=O) presented on the surface of GO are crucial for the preconcentration and solidification of radionuclides from aqueous solution [7-8]. Moreover, elements such as sodium (Na), chlorine (Cl), potassium (K), and magnesium (Mg) were also found from the sample analysis. The presence of these elements is suggestive of the patient consumption. Technetium (Tc) element with an atomic number 43 did not appear on the spectrum, which might be due to the limitation of EDX system to eject its K-shell electron due to the requirement needed to overcome 21.05 keV of binding energy [20].

Conclusion

Graphene oxide demonstrated adsorption affinity towards radioactivity from clinical wastewater contaminated by ^{99m}Tc. Kinetic study reveals the dependency of GO adsorption efficiency on the concentration of GO. Postulated interaction of GO with radionuclide via surface complexation and membrane permeability was found to be viable with increasing GO concentration. In addition, morphological analysis via FESEM depicts a highly agglomerated structure with tighter GO wax coating to the radioactive wastewater when treated with 3 mg/ml concentration, compared with the lower concentration. Furthermore, the EDX analysis confirmed the presence of C and O in the sample, which is believed to be attributed by the abundant functional groups within the GO layers. The oxygen functional group is crucial for the solidification and preconcentration of radionuclide wastewater. In brief, this paper highlights the potential of GO as a novel approach in extracting radionuclide from radioactive clinical waste via the adsorption technique for nuclear medicine waste management.

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