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# Preparation of a core-double shell chitosan-graphene oxide composite and investigation of Pb (II) absorption

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## Abstract

The need for new and impactful materials to address the global problem of water pollution continues to be driving force in chemical research. This report presents the preparation of a core-double shell composite consisting of sand base substrate onto which sequential layers of chitosan and graphene oxide (GO) are deposited. The adsorption characteristics of this material for Pb (II) from aqueous solutions is investigated. Specifically, different initial lead concentrations are allowed to reach equilibrium with the chitosan-graphene oxide composites, after which the remaining abundance of lead in the aqueous phase is analyzed by atomic emission spectrometry. In many cases, the resulting equilibrium lead concentration of the treated water reached below the detection limit of the method used (<15 ppb) in less than three hours. Furthermore, the data from the adsorption experiments are plotted for comparison against two different isotherm models. This study suggests that the interaction between lead and the GO-chitosan composite more closely resembles characteristics anticipated by the Freundlich adsorption isotherm than that expected by Langmuir-like properties.

Keywords: Environmental science, Materials chemistry, Materials science

## 1. Introduction

Over 71% of Earth's surface is covered with water and additional water lies beneath its surface [1]. However, of the all the water existing on earth, only freshwater is potentially safe for drinking, which makes up only 2.5% of all Earth's water [2]. Just a minute fraction of this fresh water ( $\sim 1.2\%$ ) is accessible as surface freshwater [2]. Furthermore, much of the accessible freshwater is contaminated with toxic agents, such as heavy metals or organic pollutants, mostly originating from chemical enterprises. In total, this leaves very little water that is both potable and easy to access, demonstrated by the fact that 2.1 billion people currently lack sufficient access to clean water from their homes [3].

Finding new methods to produce potable water from contaminated sources is a continuing challenge. Reverse osmosis [4], chemical precipitation [5], electrochemical precipitation [6], ion exchange [7], and adsorption [8] have been among the traditional workhorses for removal of heavy metals from water. Each of these methods, however, suffer from their own current limitations, including prohibitive costs in terms of either time, money, and/or energy to sufficiently address the scope and magnitude of the global drinking water crisis. Of these methods, adsorptive materials are perhaps among the most appealing routes to pursue due to their comparatively inexpensive cost and the ability of some adsorbents to sequester multiple toxic metal types [9, 10, 11, 12]. Although many diverse organic [13, 14], inorganic [15, 16], biological [10, 17, 18], and hybrid materials [12, 19, 20] have been investigated as adsorbents for toxic metals, insufficient adsorption capacity remains a recurring obstacle to large-scale water remediation via adsorption.

One common approach to increase adsorption capacity of a material is to increase its surface area. Nanomaterials represent an extreme case increasing surface area and presumably a corresponding influence on adsorption. In addition, modification of the size and surface of nanomaterials may provide avenues for further optimization of their adsorption properties. Carbon-based nanomaterials, due to their particularly unique properties, have been initially evaluated for water treatment applications including removal of toxic metals [21]. A particularly relevant property of graphene is that it is permeable to water but is otherwise impermeable to many salts, gases, and metals [22]. Previous research has demonstrated that a container filled with a variety of gases and covered with a graphene film will allow only water vapor to escape. This finding suggests that graphene-based systems might be suitable for water purification and has already been investigated prior to discovery of this remarkable property [23, 24].

Graphene oxide (GO), a form a graphene that is water-soluble, may possess qualities for heavy metal adsorption that are superior to graphene [25]. It is known that the GO surface can be readily modified to further alter its properties [26, 27]. With all the

promise and potential, relatively little is known about the safety of carbon-based nanomaterials, including nanotubes, graphene, and their derivatives. Thus, it is desirable to minimize the persistence of the graphene oxide-based adsorbents in treated water. However, removal of GO from water has proven to present its own challenges [9].

Here, we propose to bind GO to sand particles to create an adsorbent for Pb (II) ions. In binding GO to macroscopic grains of sand, the GO should be removed from the treated water with the sand upon simple filtering. This approach is similar to previous studies demonstrating GO-modified sand as a flexible adsorbent for treatment of a broad range of pollutants [26]. In order to promote adhesion between the sand and graphene oxide, we have employed the use of chitosan as a primer. In this way, sand forms the core particle that becomes deposited with two distinct layers, which we call a core-double shell composite. Interestingly, it is also known that in addition to its adhesive characteristics, chitosan itself (and other related saccharides) have been investigated as a component in systems for lead removal [28, 29]. In addition to the preparation of this material, we also attempt to initially characterize this material's interaction with aqueous Pb (II).

## 2. Experimental

### 2.1. Preparation of core-double shell composites

The sand used as the core to be layered was obtained from Fisher Chemical and was of "Sea Washed" grade. Prior to use, the sand was washed by placing it in a büchner funnel and rinsing it once with deionized water, then 10% aqueous HCl, and then again with deionized water until the conductivity of water after being passed through the sand in the funnel was lower than 20  $\mu$ S/cm. The sand was then dried in an oven at 200 °C for 2 hours or until completely dry. Five grams of chitosan (MP Biomedicals LLC, Solon, OH) were mixed with 100 grams of sand and 300 mL of 5% HCl, using the rotary evaporator's spin function to apply gentle agitation for 5 hours. This mixture was then placed in a vacuum oven to dry at 150 °C for 2 hours. Graphene oxide (Graphenea, Cambridge, MA), obtained at a stock concentration of about 4 mg/mL, is then added to the chitosan-coated sand and mixed well at a ratio of 0.34 g GO to 100 g chitosan-coated sand. This resulting mixture is dried again in a vacuum oven at 150 °C for 2 hours. The same batch of coated sand is treated again with a second aliquot of aqueous GO at the same concentration and dried under identical conditions prior to use in lead adsorption trials.

### 2.2. Lead adsorption trials

Adsorption studies for lead removal were conducted under batch conditions. Half a gram of dried GO-chitosan coated sand and 20 mL of a lead solution were combined

in vial and allowed to equilibrate for up to three hours with intermittent agitation. Eighteen different aliquots of Pb (II) solutions were combined with GO-chitosan composites such that triplicates could be sampled 5, 10, 30, 60, 120, and 180 minutes after the point of mixing, with intermittent agitation. Initial concentrations between nominal values of 250 and 2,500 ppb were tested, which were prepared from a 1000 ppm  $\pm$  1% lead reference standard (Fischer Scientific, NJ). The resulting mixture was allowed to settle before sampling the supernatant for analysis of the equilibrium concentration of lead in solution via atomic emission spectrometry.

### 2.3. Regeneration of the core-double shell composite sorbent

Individual aliquots of the core-double shell composite sorbent were reused for multiple experiments. To render a clean substrate surface, copious volumes of deionized water were initially filtered through the medium, followed by an hour soak in acetone as prescribed by Gupta et al. [30] The sorbent was then washed further with deionized water until the eluent measured a conductivity of 20  $\mu$ S/cm or less.

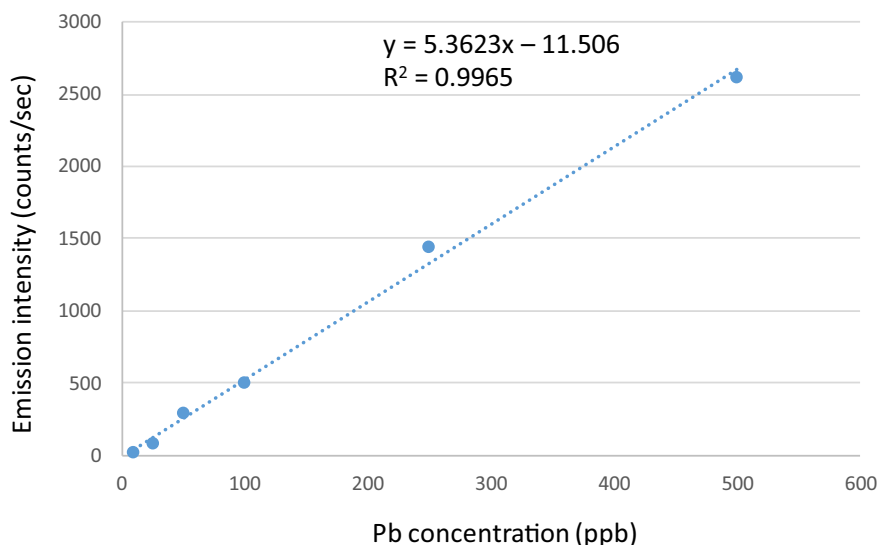
### 2.4. Instrumentation for lead analysis

Atomic emission measurements were performed on an Agilent Technologies 4200 Microwave Plasma Atomic Emission Spectrometer. A lead reference standard was diluted from the stock concentration of 1000 ppm  $\pm$  1% to solutions for use as calibrants in the range of 500 to 10 ppb. Emission intensities were monitored at 405.781 nm and recorded as the average of a triplicate set of 10-second scans for each standard and sample unless otherwise stated. Samples were infused into the spectrometer via the instrument's peristaltic pump and nebulizer after filtering through a Millex-HV 0.45  $\mu$ m PVDF syringe filter (MilliporeSigma, St. Louis, MO).

## 3. Results and discussion

### 3.1. Establishing instrument calibration and detection limit

The calibration curve obtained on the atomic emission spectrometer for these studies is shown in Fig. 1, along with the correlation coefficient from linear regression. The 10 ppb standard included in the calibration proved to be very near the limits of the capabilities of the instrument as operated. A separate 15 ppb standard was infused as a test sample; the spectrum obtained for this sample is shown in Fig. 2a with a blank shown for comparison in Fig. 2b. The baseline noise in each spectrum is similar and be approximated as 25 counts peak-to-peak noise ( $\sim$  15 counts positive spike and  $\sim$  -10 counts negative spike). Assuming Gaussian statistics for random noise, we can express the root-mean-squared (rms) noise as one standard deviation of the peak-to-peak noise, which in this case gives rms noise as 5 counts. The 15 ppb standard gives a signal average of about 35 counts against a roughly zero mean baseline.



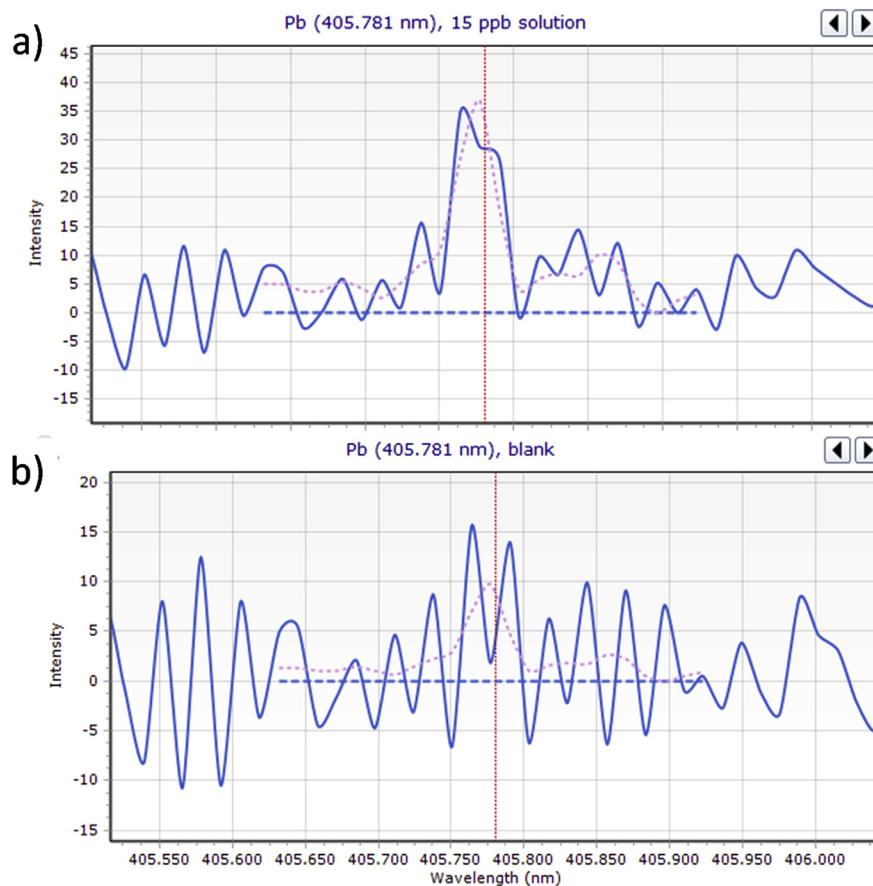
**Fig. 1.** Calibration of instrument response (emitted photons counted per second) to lead concentration in ppb. Calibrant solutions were prepared at 500, 250, 100, 50, 25, and 10 ppb.

Thus, the signal-to-noise ratio for the scan of the 15 ppb standard is approximately 7. This demonstrates a conservative limit of detection of the technique at 15 ppb, which is also the safety limit set by the EPA for lead in drinking water [31]. Therefore, we are confident that in our data that follows, those samples that fall below this detection limit also satisfy the criterion for water quality.

### 3.2. Time trials for estimating equilibrium conditions

Data from the 1,000 ppb Pb (II) initial concentration absorption experiment are shown in Fig. 3. The first measurement, taken after just five minutes of mixing, showed a dramatic decrease in the lead concentration with nearly a 90% reduction in the solution concentration. The lead concentration continued to drop in the expected decay functional form until it ceases to change significantly past approximately 120 minutes. At this point, the lead concentration has approached or fallen beneath the limit of detection of the analysis (<15 ppb).

Table 1 illustrates the effect of GO-chitosan composite material upon exposure to aqueous Pb (II) solutions over a range of concentrations representative of contaminated drinking water. Final concentrations of lead for those experiments beginning with lead concentration starting at 250, 500, and 750 ppb had final equilibrium concentrations that fell below the detection limit (<15 ppb), suggesting the treated water would be safe for consumption directly after treatment with the GO-chitosan composites. The most extreme concentration (~2,500 ppb) was shown to equilibrate at approximately 175 ppb. In each case, the same time period of between 2 to 3 hours showed to be sufficient to reach equilibrium conditions.

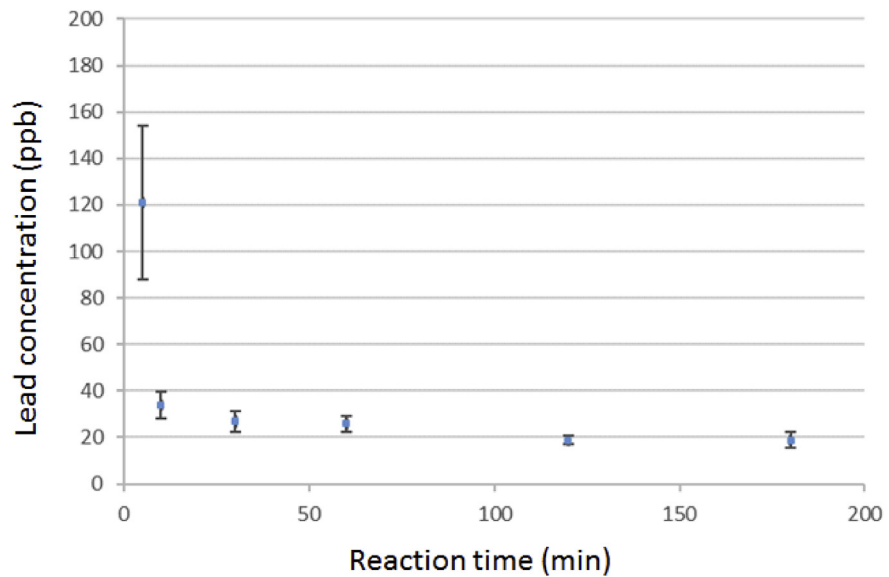


**Fig. 2.** Screen captures of the spectra viewed on the instrument as a demonstration of detection limit for the method. Panel a) shows the response for a 15 ppb standard showing a discernable peak in the baseline noise observed for panel b) of a deionized water solution. Average noise level for each spectrum is about 5 counts/second whereas the 15 ppb lead standard gives a response of more than 35 counts/second, thereby exhibiting a S/N ratio of roughly 7.

### 3.3. Adsorption isotherm analysis

Adsorption isotherm models describe the relationship between adsorbents and adsorbates at equilibrium. The two most popular are the Langmuir and the Freundlich models. To create adsorption isotherms, fixed amounts of adsorbents (GO in this case) are combined with fixed volumes of different concentrations of the adsorbates (Lead ions in this case). The relationship between the amount of adsorbed metal and the remaining concentration of metal ion in solution is described by the isotherm studies. Two of the most commonly modeled isotherm types are those set forth by Langmuir and Freundlich.

Langmuir isotherm theory assumes a mono-layer adsorption onto a surface containing a finite number of identical adsorption sites, each with uniform capability for



**Fig. 3.** Aqueous Pb (II) at roughly 1000 ppb initial concentration is mixed with the graphene-chitosan composite and the supernatant is sampled as a function of time. Average values are plotted with standard deviations as brackets. The lead concentration appears to reach a steady equilibrium condition within two hours.

adsorption and with no transmigration of adsorbate in the plane of the surface. This is a theoretical model and can be expressed by Eq. (1) [32].

$$\frac{Q_e}{Q_{max}} = \frac{k_L C_e}{1 + k_L C_e} \quad (1)$$

The quantity  $Q_e$  is the amount of lead adsorbed at equilibrium in mg/g, and is calculated by Eq. (2):

$$Q_e = \frac{(C_o - C_e) V}{W} \quad (2)$$

Where  $C_o$  and  $C_e$  are the initial and equilibrium concentrations of lead (mg/L) respectively,  $V$  is the volume of lead solution in liters and  $W$  is the weight of GO used for the equilibrium batch experiments in grams.  $Q_{max}$  (mg/g) is the maximum amount of metal ion (adsorbate) adsorbed per unit mass of adsorbent;  $C_e$  is the equilibrium concentration of the adsorbate (mg/L);  $K_L$  is the Langmuir binding constant and is related to the energy of adsorption. Eq. (1) can be linearized and cast into the form given in Eq. (3) for purposes of linear regression analysis:

$$\frac{1}{Q_e} = \frac{1}{Q_{max} k_L} \frac{1}{C_e} + \frac{1}{Q_{max}} \quad (3)$$

**Table 1.** Initial and equilibrium concentrations of lead upon treatment with graphene oxide-chitosan composite material.

Pb Concentration (ppb) Pre- and Post-Treatment	
Initial Pb concentration	Equilibrium Pb concentration
2120.6	174.8
1673.4	85.6
1279.9	30.2
788.8	22.6
635.1	n.d.
416.6	n.d.
199.9	n.d.

n.d. – not detected.

The other model we consider here is the Freundlich isotherm. Unlike the Langmuir model, the Freundlich isotherm is based on an empirical equation for adsorption on a heterogeneous surface [33]. The equation is represented by Eq. (4):

$$Q_e = k_f C_e^n \quad (4)$$

Where  $k_f$  is a rough indicator of adsorption capacity and  $1/n$  is an indication of the adsorption intensity. In its linear form the equation is represented in Eq. (5):

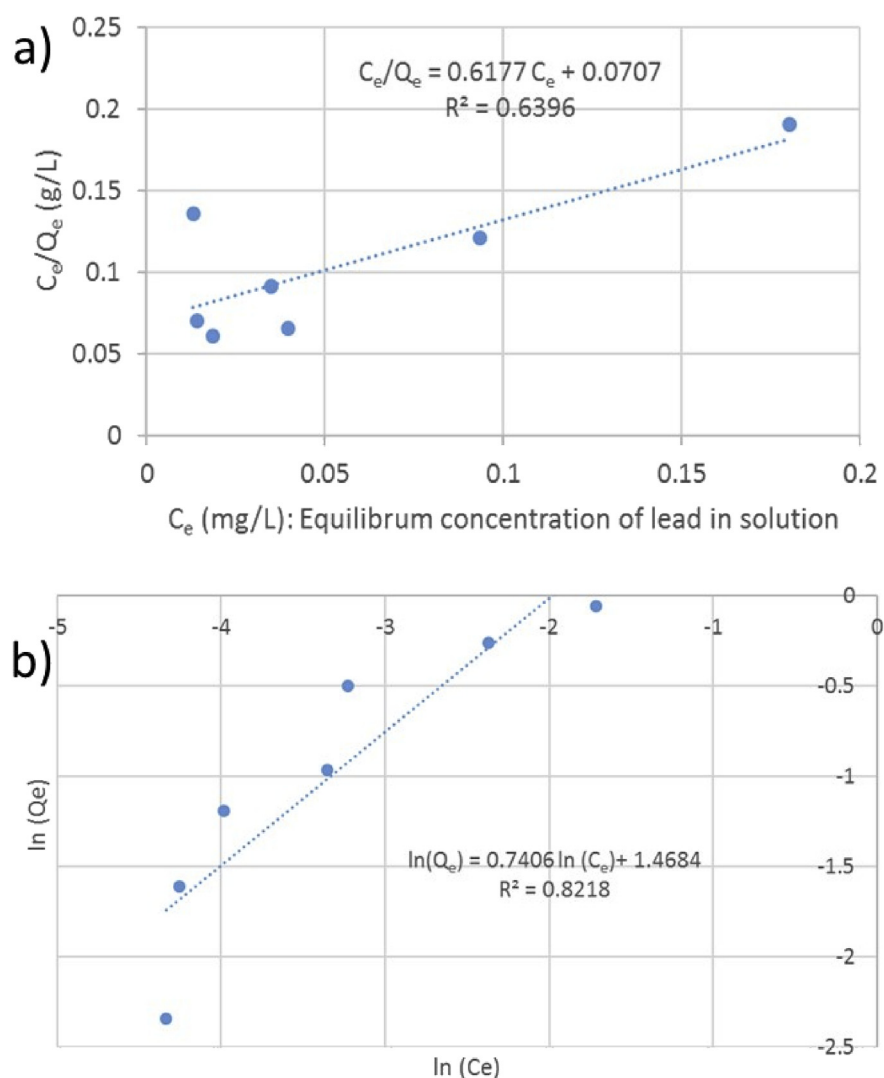
$$\ln Q_e = \ln(k_f) + \frac{1}{n} \ln(C_e) \quad (5)$$

$Q_e$  and  $C_e$  have the same definitions as described earlier. It is noted that when  $1/n$  is between 0.1 to 1 the adsorption process is favorable [34]. Further if  $n$  is below 1 the adsorption process is chemical while if it exceeds 1 it is a physical process [35].

The experimental results from this study were fitted according to both models; panel a) of Fig. 4 shows the fit expected to give a linear relationship for a Langmuir-like adsorption isotherm, whereas panel b depicts the data plotted according to the Freundlich casting of variables. Each plot features a data point that deviates significantly from the linear trend at one of the boundaries. Overall, these representations of our data suggest the GO-chitosan composites and their adsorption of Pb (II) appear to fit better the Freundlich model as indicated by its significantly higher coefficient of correlation ( $R^2 = 0.63$  vs  $R^2 = 0.82$ ). Furthermore, the linear regression analysis of Eq. (5) provides an estimate of  $n$  as 1.35, suggesting a physical adsorption between Pb(II) and the GO-chitosan composite.

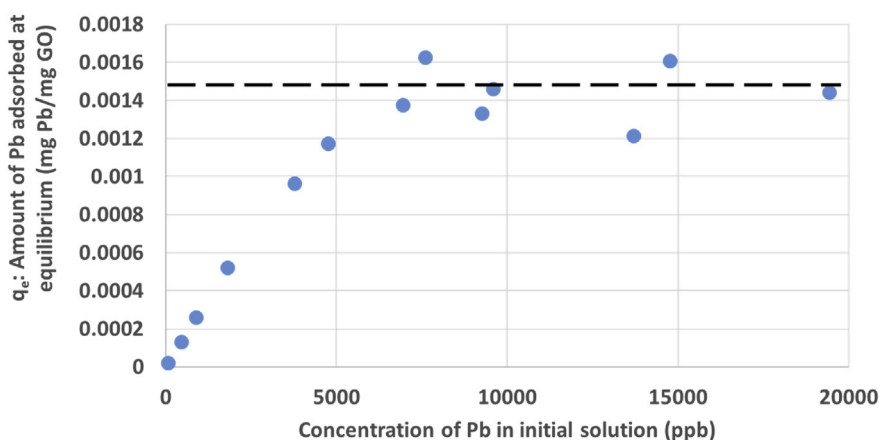
Although it is not the favored model for comparison, the Langmuir isotherm fitting of the experimental data may still be used to arrive at an approximation of the adsorption parameters  $K_L$  and  $Q_{max}$ . Of particular interest is the quantity  $Q_{max}$ ,





**Fig. 4.** Experimental fits to the adsorption data for the chitosan-GO composites for Pb (II) using Langmuir (a) and Freundlich (b) isotherm models. Each y-axis represents a form of the amount of depleted lead as a function of adsorbent mass, while the x-axis represents functional forms of the concentration of lead remaining in solution once equilibrium between the adsorbent and solution is established.

which along with extraction rate, are the parameters that most directly affect the feasibility of an adsorbent to be deployed at large scales [36].  $Q_{max}$  can be found experimentally by taking aliquots of a fixed mass of adsorbent and exposing it to incrementally larger abundances of Pb (II). The amount of Pb (II) absorbed, calculated by the volume of solution and the difference in the initial and equilibrium concentrations of Pb (II), will reach a maximum values at high concentration. A plot of this experiment is shown for the GO-chitosan composites in Fig. 5. From the approximately flat plateau region on the plot,  $Q_{max}$  for Pb (II) adsorbed onto the GO-chitosan composite is found to be approximately 1.5 mg Pb per gram of GO.



**Fig. 5.** Evaluation of the maximum adsorption capacity of the graphene oxide-chitosan composites as a function of mass of graphene oxide.

Although this adsorption capacity is markedly lower than reported in other studies on GO and GO-derived materials, it should be noted that two key differences exist between these substances. First, the composite presented here is a GO-functionalized macroparticle (sand) and is not entirely nanomaterial in nature. Secondly, the anchoring of GO to the macroparticle presumably takes away from the number of sites on the GO surface available to interact with and sequester Pb(II). Both of these influences could be anticipated to detract from the overall adsorption capacity for the composite. Adhering GO to sand, however, should solve the problematic issue of removing GO from treated water, as the GO-chitosan composite can be simply removed via gravity filtration or settling.

#### 4. Conclusions

This report shows that GO-chitosan core-double shell composites show a remarkable affinity for Pb (II). The composites have been demonstrated to reduce the concentration of Pb (II) in solution by  $\sim 50$ -fold, potentially within the safe drinking limit on a timescale that is sufficiently fast to allow for effective batchwise treatment of water [36]. The adsorption isotherm analysis for their affinity seems to best follow Freundlich-like characteristics with a maximum adsorption capacity estimated from Langmuir theory of 1.5 mg Pb (II) per gram of GO. Although lower than other reported adsorption capacities, the composite material exhibits favorable properties regarding reuse and removal of GO from treated water. It may be possible to take advantage of the heteroatom sites present on the GO surface of the composites to further optimize the adsorption capacity of the material. The macroparticle sand substrate also makes these composites amenable to development of filtration-based systems for water purification on large scale.

## Declarations

### Author contribution statement

Ankush K. Dhawan, Jeffery W. Seyler: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Brian C. Bohrer: Analyzed and interpreted the data; Wrote the paper.

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### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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