Fabrication of Graphene Sand Hybrid Using Green Method for Remediation of Lead and Tetracycline Contaminated Groundwater

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Abstract

The objective of this investigation involved the green synthesis of Graphene Sand Hybrid (GSH) with the sustainable carbon source provided from the pyrolysis of low-quality dates; it was evaluated for its use in permeable reactive barrier (PRB) technology for treating lead- (Pb) and tetracycline- (TC) contaminated groundwater, as a cost effective and highly reactive material. The GSH thus produced was evaluated by testing its properties through a variety of testing procedures. From these tests the GSHs prepared were proven to be composed of graphene structures on the inorganic sand, with the capacity to treat simulated contaminated groundwater. The experimental experiments of this study were done using batch and continuous mode. In the batch experiments, different factors that affect the sorption process were studied and the sorption data were explained using the Langmuir and Freundlich isotherm models, whereas the kinetic process of sorption was ascertained through the use of the three kinetic models (pseudo first- and second-orders and intra particle diffusion). From the results it was evident that the Langmuir model shows a good fit for the sorption data, better than the Freundlich isotherm model does, and the pseudo second-order model shows a better fit for the kinetic data than does the first-order model. The continuous mode was performed employing a series of column experiments. Besides, using the COMSOL Multiphysics software, a solved numerical model was advanced for simulation of the one-dimensional equilibrium conveyance. The results depicted that the GSH can be effective and economically reactive material in PRB.

1. Introduction

Recently, over the past few years, the rapid rate of international industrialization and urban development posed a considerable risk to the groundwater supply, caused particularly by the antibiotics and heavy metals being irresponsibly discharged into it (Minale et al. 2021). Several scientists considered lead as significant among the heavy metals, as it causes strong negative effects on public health and the environment. In human beings, Tetracycline has been identified as the second most commonly used antibiotic in treating diseases (Pulicharla et al. 2017). Extensively used in clinical and veterinary practice Tetracycline is also used in the feedstuff industry, as it has been shown to be a good growth promoter (Chen et al. 2016). After the animal consumes tetracycline, it is absorbed by the digestive tract. Due to the Tetracycline interacting with the heavy metal ions such as lead (Pb), the reaction products showed higher stability which were more hazardous and easier to transport than parent materials (Minale et al. 2021).

To counteract the adverse influence, tetracycline and lead must necessarily be removed, efficiently and effectively, from the polluted water bodies. In general, groundwater is utilized in greater quantities than surface water. However, this does not imply that it is not susceptible to contamination because chemical compounds are easily soluble and can penetrate through the soil, reach the groundwater and contaminate it. Due to the burgeoning demand for surface water and its myriad sources of pollution from a variety of pollutants, a sharp decrease was noted in terms of quantity and quality (Abd Ali 2021a). Therefore, the focus was turned towards groundwater and the development of methods of protection from pollutants, as well as treatment techniques, as it continues to be among the vital sources of usable
water for most of the population. Contaminated groundwater can be treated by a plethora of methods, the most effective one, from the perspective of efficiency and economics, is the Permeable Reactive Barrier (PRB) technology (Faisal and Ali 2015). This technology is dependent upon the reactive material present deep in the soil, and identified along the down gradient of the source of contamination to impede the propagation of the plume and ultimately remove it via many mechanisms like adsorption (Faisal and Ali 2014; Abd Ali and Ismail 2020). One fundamental facet of this methodology is the selection of an environmentally-friendly reactive filler, with neither negative chemical reactions, nor pollutant source nor high cost (Allègre et al. 2006).

Despite the availability of a wide range of natural and very affordable reactive materials suitable for PRB and that can be used currently, investigations are ongoing to produce a sorbent with good capacity for removal, besides being efficient and inexpensive (Bulut and Aydin 2006). With the advancements in nanotechnology, much research is being done on the use of carbon nanomaterials in water purification, to identify new and beneficial methods of controlling the current water shortages. Graphene, the newest addition to the carbon group, is an innovative, 2D nanomaterial sheet, where the hybrid carbon atoms are arranged in a honeycomb-like structure and which, because of its unique physicochemical and mechanical properties, has garnered substantial scientific attention for research in recent times (Zhu et al. 2010). However, due to some of its limitations, like steep costs, and prerequisite for post-treatment management with the recovery post decontamination, it is less feasible to utilize simple graphene nanosheets in water treatment. Further, large quantities need to be placed in the water as they reveal large α-µl interactions and strong van der waal forces (Khan et al. 2019). In order to cope with such engineering issues, the graphene needs to be established on an inorganic substrate, which is both cost-effective and stable, like sand. Apart from the complete presentation of the graphene adsorption sites, the creation of these graphene sand hybrids will contribute the required vital separation from the water. In recent times, several synthetic techniques for graphene-coated sand (GSHs) have been proposed, from various carbon sources, such as sugar, gelatin, palm sugar, asphalt, etc. It is anticipated that their structural and composite chemistry will go a long way in controlling the properties of the as-proposed GSH, considering that the chemical carbon sources vary from one another across the globe (Abd Ali 2021b). However, sustainable graphene-based nanomaterial manufacturers will inevitably encounter serious problems during mass production due to the limited supply of energy-saving and renewable raw materials (Abd Ali 2021a).

In the present study a single-step method was developed, composed largely of carbohydrates (glucose and fructose) from affordable sources, in this case low-grade date syrup, to create the Graphene Sand Hybrid (GSHs) which is effective and environmentally friendly. These dates are allegedly high in carbon and not detrimental either to human beings or the environment, and cause neither side effects nor allergies. During pyrolysis, the natural sucrose and fructose molecules present in abundance in the date syrup are apparently completely exfoliated to produce the graphene nanosheet on the surface of the sand. The principal finding from this study is the development of the graphene nanosheets on the green sand surface, produced from date syrup as a sustainable carbon source. These nanosheets find good use
in the technology of the Permeable Reactive Barrier (PRB) for the treatment of lead- and tetracycline-contaminated groundwater, as a cost-effective and ecofriendly substance.

2. Materials And Methods

2.1. Materials

In the manufacture of the graphene-sand hybrid (GSH) low-grade, (inexpensive) Iraqi dates were utilized as a cheap carbon source, and the quartz sand as the solid, inert and immobilized matrix. The initial porosity of the sand was 0.44, with particle size in the 1- 2 mm range, and specific gravity of 1.36. Two kinds of substances, chemically distinct and different, namely, Tetracycline (TC) and lead (Pb) were chosen with care to signify the organic and inorganic contaminants, respectively, and simulate the contamination in the groundwater under study. Aqueous solutions of lead, \((\text{Pb(NO}_3)_2 \cdot 4\text{H}_2\text{O})\), HiMEDIA, India) and TC (\(\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8\), Samarra drugs factory) were prepared to make the stock solutions, 1000 mg/L in concentration. The TC or Pb stock solution was stored and saved for later use in the preparation of necessary concentrations of the contaminant. The solution pH of the TC or Pb was adjusted by adding 0.1 M HCl or NaOH.

2.2. Preparation of graphene-sand hybrid (GSH)

The graphene-sand hybrid (GSH) preparation can be clarified as stated (Abd Ali 2021a):

The flesh of the dates (after extracting the date pips) was first weighed before boiling for about 20 minutes, in sufficient amount of water. The slurry composed of water and date juice mix was first filtered, and then concentrated at 70°C. The sand was then combined with the date juice thus collected (in the ratio of 2:5). After thorough mixing, it was heated in a hot air oven at 80° C until the date juice solidified on the sand grain surfaces. The dried and homogeneously mixed solid product was then placed in a ceramic boat and transferred to an \(\text{N}_2\) carbonized furnace at the rate of 100 mL/min. Heating was done progressively to 750° C for complete graphitization of the date syrup, adhering to the heating procedure described here. In the first step, the mixture was heated to 10° C for 0.5 hours at 2.5° C/min; next the temperature was boosted to 200° C at the rate of 3.3° C/min, until the fusion point was reached for dates; in the third step, when the sucrose and fructose molecules in the date juice were converted to the carbon material, the temperature was finally escalated to 750° C at the rate of 9.1° C/min for 3h. Then, the furnace was left undisturbed to cool down naturally, until ambient temperature was achieved, and the resultant carbonaceous and graphene-like substance was termed 'Graphene-Sand Hybrid' (GSH). The GSH thus produced was subjected to further analysis and used in the batch and continuous trials, to characterize the reactive medium required for the PRB technology.

2.3 Instrumentation for characterization

The manufactured reactive materials (GSH) were subjected to testing of their characteristics through several analyses conducted at the University of Tehran / Iran prior to their use in the experiments, as cited,
2.3.1 Raman spectroscopy analysis

The Raman spectroscope is a good tool, with high sensitivity and strong non-destructive capacity, and can provide a rapid and easy structural characterization of the material created (GSH). Such spectroscopy has been used in the study of the formation of graphene crystals, both ordered and disordered. The Raman spectra range of 0–4000 cm⁻¹ was measured.

2.3.2 X-ray diffraction analysis (XRD)

Using this analysis, the XRD patterns of the crystalline structure of the GSH were obtained, and collected in the range of 2θ from 20° to 80° C, having 0.02° step-width and 1° scan rate per second.

2.3.3 Surface area analyzer

The specific surface area was measured using the surface area analyzer, which takes into consideration one of the principal traits in assessing the adsorbent substances in terms of effectiveness. The BET method, based on the nitrogen adsorption at 77 K, was used to accomplish this.

2.3.4 Fourier-Transform Infrared spectroscopy (FTIR):

The FTIR spectra of the prepared reactive media (GSH) enables the spectrophotometric observation and identification of the functional groups on the surface of the sorbent (Khan et al. 2019). The GSH sample combines with the KBr sample, and from the spectrum analysis of this sample, the spectra were visible in the 4000-400 cm⁻¹ region.

2.3.5 SEM/EDX analysis

The investigation was done of the GSH surface morphology and its components with the help of a scanning electron microscope and an energy dispersive X-ray spectrometer.

2.3.6 Transmission Electron Microscopy (TEM)

The morphology of the GSH and native sand were evaluated via TEM, performed with a Morgagni-270-D transmission electron microscope, at a speed voltage of 80.0 kV. The samples were drawn by placing a drop of the sample solution on the C grids coated with Formvar to estimate the TEM.

2.4 Batch and Experiments

Through the performance of batch studies, the single TC and Pb sorption equilibrium data were collected and the optimal batch conditions for the pollutant removal were determined. Factors including contact time, initial solution pH, agitation speed, concentration of the initial contaminants, and quantity of the GSH dosage were included in these conditions. The procedure adopted in the experimental work is as cited: First, 100 ml of the TC and Pb solutions were added to each 250 ml flask, in concentrations of 50 mg/L, after which 0.1 g of the GSH was added. All the flasks containing both the adsorbent, as well as the TC and Pb pollutant solutions were agitated for 3 hours at 200 rpm speed. Filtering of the contaminated solution was done next, to separate the clear contaminant solution from the residual solid
material, after thorough mixing was done. Using a pipette, the residual untreated quantity of the TC and Pb present in the solution was specified using 10 mL samples drawn from the filtered solution. Employing Atomic Adsorption Spectroscopy (AAS) the Pb was analyzed; however, UV-Visible Spectroscopy was utilized to assess the TC. At different values of pH (for TC pH = 2 to 12 and for Pb pH = 2 to 7), and using a variety of dosages (0.05–1 g/100 ml), in a time span of 0 to 180 minutes, the sorption was determined based on the different initial concentrations of the contaminants (Co, 50-250 mg/L). In fact, Eq. 1 was used to calculate the quantity of the contaminants retained in solid phase (qe) to adopt the best experimental findings (Sulaymon et al. 2015; Ali and Abd Ali 2020).

\[ q_e = \left( C_o - C_e \right) \frac{V}{m} \]

1 Where Co and Ce represent the initial and equilibrium of the TC or Pb concentrations (mg/L) in the flask, V refers to the volume of the solution in the flask (L), and m is the mass of GSH with the flask (g).

2.5 Isotherm models

The sorption data were represented by employing two isotherm models, as given below: (Abd Ali 2016; Mhawesh and Abd Ali 2020):

1) **Freundlich model**: Applicable for non-homogeneous surfaces showing multi-layer sorption, and having the following formula,

\[ q_e = K_F C_e^{1/n} \]  

(2)

where \( K_F \) is the Freundlich constant and \( 1/n \) (< 1) indicates the sorption intensity (Gheju and Miulescu 2007).

2) **Langmuir model**: This is used for homogeneous surfaces and monolayer sorption; the relationship given below was developed by Langmuir (Foo and Hameed 2010; Abd Ali and Ismail 2020).

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

3 where \( q_{max} \) refers to the maximum adsorption capacity (mg/g) and \( b \) implies the intensity of the contaminant onto the solid phase.

2.6 Kinetic models

The rate of transfer of the dissolved contaminant to the solid phase is essential for the design of an accurate sorption process (Puranik et al. 1999; Ibrahim and Ali 2020). This rate can be calculated using the following models
1) **Pseudo first order model:** The sorption rate with time can be calculated, using the following expression (Lagergren 1989; Faisal and Abd Ali 2016),

\[
\frac{dq}{dt} = k_1 (q_e - q_t)
\]

It is possible to integrate Eq. 4 to obtain the equations given below, in the nonlinear forms,

\[
q_t = q_e (1 - e^{-k_1 t})
\]

Where the quantities of the contaminants sorbed in the period interval and time of equilibrium are represented as \(q_t\) and \(q_e\) (mg/g), and \(k_1\) is the rate of the contaminant sorbed in this model (L/min).

2) **Pseudo second order model:**

The assumptions to derive this model include the contaminant monolayer fixed onto the sorbent surface, identical sorption energy for the sorbent, and absence of interaction between the contaminant sorbed molecules, and they can be expressed in the ordinary differential equation, as stated below (Ho and McKay 1999; Ali and Abd Ali 2020),

\[
\frac{dq}{dt} = k_2 (q_e - q_t)^2
\]

where \(k_2\) is the rate constant of the 2nd model (g/mg min).

To obtain the 2nd equation in nonlinear forms, Eq. 6 is integrated, as shown below (Ho and McKay 1999; Ali and Abd Ali 2020),

\[
q_t = \frac{t}{\left(\frac{1}{k_2 q_e^2} + \frac{t}{q_e}\right)^{0.5}}
\]

Therefore, because the pseudo first and second order models are inadequate to provide an explanation for the dominating processes, the intra-particle diffusion given below has been employed:

3) **Intra-particle diffusion:**

\[
q_t = k_{int} t^{0.5} + C
\]
where \( k_{int} \) refers to the sorption rate constant (slope) of the diffusion model (mg/g min\(^{0.5}\)) and \( C \) indicates the intercept and reveals the thickness of the boundary layer.

## 2.7 Column experiments

The hydraulic behavior and degree of reactivity of the reactive material were investigated through column tests for the removal of TC and Pb from the simulated contaminated groundwater, employing the indicators of the percentage of contaminant removal and coefficient of hydraulic conductivity. As schematically revealed in Fig. 1, the column setup included an acrylic cylinder 50 cm in height and 2.5 cm in diameter, provided with the sampling ports, placed from the bottom of the column, at a distance of 10, 20 and 35 cm for the P1, P2, and P3, respectively. Along the column length these ports were provided with plastic valves. Inside the column, the sorbent material (GSH) was well packed. First, distilled water was added until the GSH was progressively saturated, and the feeding was done slowly, beginning with the lowest part of the column, and forcing it upward and through the sorbent material, with the help of a peristaltic pump. The upward flow propels the air above it, thus averting the formation of entrapped air between the particles of the sorbent material. At room temperature, the column tests were conducted, with assessments of the concentrations of the TC or Pb in the effluent water being done once every 120 hours. The water samples were then immediately taken in a test tube and analysis was done using UV-Visible spectroscopy for the TC and Atomic Adsorption Spectroscopy (AAS) for the Pb.

## 2.8 Modeling of TC & Pb transport in GSH as reactive porous media:

Characterization of the TC or Pb propagation in the GSH as a reactive porous medium was done using the advection-dispersion equation (one-dimensional) (Eq. 9). According to this equation, this movement is ascertained by dispersion and advection, the two principal mechanisms. Dispersion indicates the propagation of the contamination through a concentration gradient and by several pathways, while advection implies migration of the contaminant induced by moving water, as shown (Abd Ali et al. 2019; Abd Ali 2019):

\[
D \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} \pm \frac{r}{n} = \frac{\partial C}{\partial t} \tag{9}
\]

Where, \( r \) indicates the reaction term which may refer to either source (+) or sink (-) for the contaminant, \( n \) refers to the porous medium porosity, \( V \) represents the pore water velocity, \( C \) implies the concentrations of the effluent, and \( D \) is the hydrodynamic dispersion coefficient.

The form of Eq. 9 depends on the processes of mass transfer through \( r \). Sorption is one of the major techniques of mass transfer during mass movement. Incorporating the sorption process can be achieved by using one of the isotherm models \( (q=f(C)) \) used in this study, which achieves the best fit (higher \( R^2 \)) with the experimental results in batch mode. The rate expression \( r \) is equal to the product of the time
derivative of the sorbed amount of the contaminant onto the sorbent substance (GSH) \( q \), and bulk density, \( \rho_b \). Thus,

\[
r = \rho_b \frac{\partial q}{\partial t}
\]

Eq. 10 and Eq. 9 can be incorporated as follows:

\[
D_z \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} = \frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial (q)}{\partial t}
\]

As the term \( \frac{\rho_b}{n} \frac{\partial (q)}{\partial t} \) refers to the rate of change in the concentration of the solution by the sorption processes, it can be expressed as follows:

\[
\frac{\rho_b}{n} \frac{\partial (q)}{\partial t} = \frac{\rho_b}{n} \left( \frac{dq}{dc} \frac{\partial C}{\partial t} \right)
\]

Hence, the typical form of the 1D advection-dispersion equation, considering the sorption for the equilibrium case of the contaminant transport can be given as,

\[
D_z \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} = R \frac{\partial C}{\partial t}
\]

where \( R \) is the retardation factor and can be defined as:

\[
R = 1 + \frac{\rho_b}{n} \frac{\partial q}{\partial C}
\]

It is possible to numerically resolve Eq. 13 plus plot the temporally and spatially calculated value of \( C \) for the flow domain, which will take a curve of S shape. From this curve, it is evident that the pollutant concentration at a given position in the flux area is dependent upon time. This is termed the ‘breakthrough curve’ (Masood and Abd Ali 2019; Abd Ali et al. 2020). In order to provide a numerical solution in this study, Eq. 13 was resolved numerically, employing the COMSOL Multiphysics 3.5a software on the basis of the finite element technique, together with the initial and boundary conditions. The initial concentrations of the liquids and contaminants in the entire flow domain are assumed to be zero, while the boundary conditions employed are expressed as cited here,

Lower boundary \((z = 0): C = \text{initial contaminant concentration} (C_o)\)
Upper boundary (z = L): advective flux (i.e. $\frac{\alpha C}{\alpha z} = 0$) (15)

3 Results And Discussion

3.1 Characterization of the prepared reactive material (GSH)

3.1.1 Raman spectroscopy analysis

In Fig. 2A the Raman spectrum of the sand is shown. In the literature, the range can be categorized under three areas, from 700–800 cm$^{-1}$ (S-O modes), from 350–500 cm$^{-1}$ (O–Si–O bending modes), and from < 300 cm$^{-1}$ (S-O-Si bending modes). Thus, it is evident that the Raman spectrum of the sand sample possesses three distinct peaks at 113, 203, and 471 cm$^{-1}$ for the vibrational mode, representative of quartz (Ami et al. 2013). Hence, these peaks are indicative that the sand sample employed is composed of quartz (Malard et al. 2009). On the other hand, the Raman spectrum of the GSH samples revealed three well-defined peaks, which are the D (defects and disorder), G (graphic) and 2D bands (number of graphic layers), at 1,1110 cm$^{-1}$, 1632 cm$^{-1}$, and 2529 cm$^{-1}$, respectively. From these results it becomes evident that the GSH possesses a substantial part of the material of the Sp2 graphene carbon frame created from the transformation of the sucrose and fructose molecules in the date syrup. The ID/IG ratio of 5.69 reveals the presence of a structural disorder in the GSH, identical to that of the graphene oxide; however, the I2D/IG ratio was 8.65 because the GSH is multi-layered (Lavin-Lopez et al. 2014). These GSH spectra reveal the occurrence of the sharp band at 1110 cm$^{-1}$ and implies the presence of the sites necessary for the adsorption to accomplish complete graphitization, and the band at 1632 cm$^{-1}$ (Dubey et al. 2015).

3.1.2 XRD analysis

The powdered GSH under X-ray diffraction (XRD) showed a distinctive peak of about 20.4° (2θ), with 3.81 Å spacing and a diffraction pattern of the graphene structures in multi-layers at the GSH surface. From the spectrum, many other small and medium peaks of a variety of 2θ are evident, which can be used for this work and which relate to the crystalline sand support employed and the distinct quartz and silica diffraction patterns (Fig. 2B). In this study, the very crystalline desert sand support employed shows peaks which conform most likely to the diffraction patterns typical of the quartz and silica; the symbols ‘o’ and ‘+,’ are used to represent them, as shown in Fig. 2B. The GSH diffraction pattern is much lower than that of the sand support, as the graphene sheets show distribution throughout the particles of sand. Besides, a few more peaks of 2θ relating to 15° and 32.5° of the Fe3O4 particles, are visible in the XRD spectrum of the GSH. These peaks suggest the presence of iron particles in the date syrup. Both the Raman and XRD imply that the GSH prepared shows a close relationship to the graphene material, as mentioned in the literature (Gao et al. 2012; Khan et al. 2019).

3.1.3 Surface area analyzer
The specific surface area determined employing the Brunauer–Emmett–Teller (BET) theory was found to be 19.1 m$^2$/g. While a large potential surface area of pure graphene sheets (2630 m$^2$/g), is present, the surface area of the GSH is quite modest. In fact, the surface area of the GSH is dependent fundamentally upon the sand particles present when it gets coated with graphene. The result of this test was compatible with the result of other researchers such as Yang et al. (2015) where the pure graphene sheets are layered with SiO$_2$ particles, the specific surface of these sheets significantly decreases.

### 3.1.4 Fourier-Transform Infrared spectroscopy (FTIR):

From Fig. 2C the sand, fresh-GSH, GSH-Pb, and GSH-TC infrared absorption spectra and the functional groups of GSH responsible for the adsorption of TC and Pb were illustrated. The Si–O–Si bond is clearly seen on a distinct 1021 cm$^{-1}$ absorption band, and the Si–O vibration bending occurring at 1415 cm$^{-1}$ and 1621 cm$^{-1}$ reveals the presence of quartz in the sand (Krivoshein et al. 2020). In the case of the GSH, the C-O distribution of the -COOH groups and C-H spread of the vibratory vibrations that appeared were possibly due to the peaks at 1284 and 1523 cm$^{-1}$, respectively. The data offer proof that the sucrose and fructose fragments on the surface of the sand may be fully graphitized. From these observations it is clear that carbonaceous adsorption has taken place, which becomes binding sites for the TC and Pb with several functional oxygen groups (such as the –OH, –COOH, etc.). Besides, a significant drop was seen in the band intensity after the sorption of the TC and Pb which occurred at 1284 cm$^{-1}$ and 1523 cm$^{-1}$, as well as a shift to the lower wavelengths (of 1272 and 1268 cm$^{-1}$) and (1505 and 1515 cm$^{-1}$), respectively, for the TC and Pb. The removal of the TC and Pb from the aqueous solution through these bands is confirmed by the transmission of these bands.

### 3.1.5 SEM/EDS analysis

From the SEM images the morphological properties of the sand, fresh-GSH, GSH-Pb, and GSH-TC were clearly evident, as displayed in Fig. 3. The sand revealed a morphologically heterogeneous surface with appreciable rod particles, despite the disorderly appearance of the surface of the structure. Although the sand was present, no surface roughness was noticeable. In Fig. 3B it is clear that the GSH is composed of interconnected, multi-layered graphene, caused by the alteration of its morphology by the hybridization of the sand surface. Due to the many macropores, making the surface appear very rough and wrinkled, the highly active surface was preserved, together with the multi-layered structure. From the theoretical viewpoint, the active adsorption sites of the Pb and TC, seen in Figs. 3C and D are considered to contribute significantly in providing crucial morphological changes, particularly in the surface because of the adsorption of the agglomerated pollutants across the surface. These characteristics are known to play a vital part in providing the active adsorption sites for the Pb and TC, as shown in Figs. 3C and D; here, a dramatic morphological change occurred and the surface became irregular because of the pollutant particles getting agglomerated and adsorbed throughout the surface of the sand. Next, the EDS analysis was done to investigate the elements of which the sand was composed, before and after the graphene was coated, as evident from Fig. 3. This clearly shows that in the structure of sand, silica was the principal constituent. Besides, this test confirms that the carbon showed the highest percentage in terms of content in the GSH among all the other constituents, implying that the graphene nanoparticles
were successful in coating the sand. Furthermore, the presence of N (as an indicator for TC) as well as the Pb elements were confirmed by the EDS as the constituents of the GSH after sorption had occurred, implying the successful loading of the Pb and TC onto the surface of the GSH.

3.1.6 Transmission Electron Microscopy (TEM)

In Figs. 3E and F are shown, respectively, the TEM images of the sand and GSH. From Fig. 3E (sand) it is evident that the sand is composed of a single piece (particle) without smaller constituent parts, indicating that no material has coated the sand surface. Although Fig. 3F (GSH) reveals that small intermittent pieces were formed (discrete particles) quite different from those displayed in Fig. 3E, the presence of these pieces suggests that it was the graphene coating the sand surface. Thus, the TEM images confirmed that the sand surface was coated successfully by the graphene nanoparticles.

3.2 Influence of operational conditions in batch mode

3.2.1 Contact time

In the batch tests, the time equilibrium is a crucial step, meaning the time needed for the Pb and TC to be redistributed from an aqueous solution to GSH. Therefore, during the contact time not exceeding 180 minutes, the transference of the Pb and TC from an aqueous solution to GSH was measured, as revealed in Fig. 4A. The substantial rise in the Pb and TC removal percent with time is probably due to the available GSH sites assigned for the sorption of Pb and TC; however, the reduction in these sites was marked by a decline in the sorption rate, particularly after 90 minutes. Therefore, no significant variations were noticed in the elimination percentage up to 180 minutes, prior to achieving the equilibrium time.

3.2.2 Initial pH of the solution

Another factor that must be considered is the pH of an aqueous domain, which influences the elimination of Pb and TC. This necessitates performing experiments with two fixed initial pH ranges namely, 3 to 12 for TC and 3 to 7 for Pb, with parameters as expressed in Fig. 4B. The rise in pH obviously resulted in a marked improvement in the TC and Pb removal percentage, up to a pH value of 6; once this pH value was crossed, the removal percentage was observed to become relatively stable without any change for Pb, although it was reduced for TC. The explanation for this behavior is given: For Pb, the removal was accomplished by the functional groups available on the GSH surface, which were ion-chelating and negatively charged and which showed a rise in the density as the neutral state (pH = 7) was approaching (Gao et al. 2012). Although the removal percentage for the TC was low at pH of 3.0, due to the TC and H+ competing for the adsorption sites present on the GSH surface at the low pH, when there was a rise in the pH value, the removal percent also started to escalate, until it touched maximum value, at pH 6. In this neutral state, the TC shows lowered ionization and hydration, a result of the adsorption induced by the hydrogen bonding and the π–π stacking action. The adsorption capacity of GSH, however, reveals a tendency to slightly decline with a corresponding rise in the pH, resulting in slowed-down hydrogen bonding caused by the formation of OH- (Khan et al. 2019).
3.2.3 Agitation Speed

The effect of the agitation speed on the removal of the Pb and TC was assessed by altering the speed from 0 to 250 rpm, while the other parameters were maintained equal to the best achieved in the prior step. From Fig. 4C, it was clear that about 24% and 12% of the Pb and TC, respectively, were removed prior to being shaken, and that there was a rise in the absorption as the rate of shaking increased. The adsorption of the contaminant escalated from zero to 250 rpm, when about 73% of the Pb and 45% of TC were removed. The uptake of the contaminant showed improvement, although the outcomes could be related to the fact that any rise in the agitation speed caused an escalation in the pollutant distribution on the GSH surface. Therefore, there was adequate contact between the solution of the sorbates and the sites, which boosted the successful transfer of the sorbates onto the sorbent sites (Gao et al. 2012).

3.2.4 Initial concentration

In this series of experiments, an investigation was done on the influence exerted by the values of the Initial Concentration ($C_0$) on the removal efficiency of the Pb and TC when specific values were selected at the optimal pH levels and specified times, in the range 50 to 250 mg/L. In fact, Fig. 4D clearly shows the significant drop in the removal of Pb and TC (to 48% and 23.8% of Pb and TC, respectively), when the initial concentration ($C_0$) increased to 250 mg/L. The principal cause for such a reduction in the removal rates was related to the sites of the adsorbent becoming saturated with the molecules of the Pb and TC.

3.2.5 GSH dosage

Additionally, the importance of the removal of the Pb and TC through the different dosages of GSH was investigated in the 0.1-1g range, as seen in Fig. 4E. These findings show that only 73% of the Pb and 45% of the TC were sorbed, when 0.1 g of a manufactured sorbent was used; however, an increased GSH dosage of 0.5 and 0.7 g per 100 mL of the Pb and TC, respectively, can be combined to induce a significant improvement in the removal rate of 98% caused by the raised amount of the sorbent, which provides more numbers of sites for the contaminant molecules to be adsorbed (Amarasinghe and Williams 2007). From Fig. 4E, it is also evident that an increased dose exceeding 0.5 and 0.7 g/100 mL respectively, of the Pb and TC, does not significantly affect the percentage of removal because of the stabilization of the contaminant concentration that remaining in the fluid-phase (Unuabonah et al. 2008).

3.3 Sorption isotherms

The models of the adsorption isotherms described earlier are employed to explain the equilibrium results of the sorption test for the interaction of the GSH with Pb and TC. A list of the parameters of these models is given in Table 1. The models are examined with the experimental data, as shown in Fig. 5. The Langmuir model is seen to fit well and adequately represent the sorption process, with a higher R-squared value. The adsorption capacity of the Pb or TC at its maximum to the manufactured sorbent is found to be equal to 55.4 mg and 46.40 mg/g, respectively.
Table 1
Estimated parameters for sorption isotherm models

| Model      | Parameter               | Pb   | TC   |
|------------|-------------------------|------|------|
| Freundlich | $K_F \text{ (mg/g)}(L/mg)^{1/n}$ | 9.76 | 7.812|
|            | $n$                     | 2.12 | 2.122|
|            | $R^2$                   | 0.97 | 0.958|
| Langmuir   | $q_m \text{ (mg/g)}$    | 55.4 | 46.40|
|            | $b \text{ (L/mg)}$      | 0.14 | 0.1334|
|            | $R^2$                   | 0.99 | 0.986|

### 3.4 Sorption kinetics

The kinetic models were constructed using the first- and second-order Pseudo kinetic models, as shown in Fig. 6. For kinetic models with experimental results, non-linear regression was applied, employing Microsoft Excel 2016. A list of the parameters of the kinetic models ($R^2$) and sum of the values of the squares errors (SSE) is shown in Table 2. From this Table, it is also evident that the kinetic sorption data of the Pb and TC are well suited to the second-order pseudo model because it is in this model that the highest $R^2$ values and the lowest SSE values are seen. Therefore, by monitoring the kinetic sorption, the retention of the Pb and TC sorbed onto the GSH was noted to be chemisorption. The measurements of the kinetic model were further examined by the application of the intra-particle diffusion models, after which it became clear that in the linear relationships, the $t^{0.5}$ can relate to the $q_t$, with acceptable $R^2$, as given in Fig. 7. In the intra-particle diffusion model, the lines are intercepted with the y-axis at specific values, indicating that the intra-particle diffusion takes place in the Pb and TC sorbents, although this step is not rate-controlling. Further, the plotted lines represent the three linearity sections, while the sorption is induced by two or more processes. The slopes of the plotted lines are represented by the rate constant ($k$), and for 'portion 1' its values are higher than those for 'portions 2 and 3' as revealed in Table 2. Hence, it is possible to regulate the first portion by instantaneous or external surface sorption (Cheung et al. 2007). From the data collected, it appears that the sorption processes of Pb and TC in the composite sorbent comprise three main steps, implying that the limiting rate for the entire reaction is not the intraparticle diffusion. The different steps involved include bulk diffusion, which is the initial part (portion 1), the linear phase (portion 2) represented by intra-particle diffusion, and the equilibrium stage (portion 3). The $k_1$, $k_2$, and $k_3$ values are ascertained from the slopes of the straight lines, as shown in Table 2. The diffusion of the pores and film was proposed to play a significant part in the sorbent because the macro pore diffusion was greater than that of the micro pore (Rajoriya et al. 2007; Wasewar 2010). The parameters of the models were calculated by Linear Regression using Microsoft Excel. The sorption process for the contaminants was governed apparently, mostly by the external mass transfer,
while the rate was limited by diffusion because the lines were not passing at the origin point (Kalavathy et al. 2005).

### Table 2
Parameters resulted from fitting of kinetic measurements for sorption of Pb and TC onto GSH.

| Model                     | Parameter | Pb   | TC   |
|---------------------------|-----------|------|------|
| Pseudo-first order        | $q_e$     | 35.443 | 31.195 |
|                           | $k_1$     | 0.075 | 0.052 |
|                           | $R^2$     | 0.987 | 0.989 |
|                           | SSE       | 21.378 | 14.988 |
| Pseudo-second-order       | $q_e$     | 39.227 | 35.817 |
|                           | $k_2$     | 0.003 | 0.002 |
|                           | $R^2$     | 0.995 | 0.996 |
|                           | SSE       | 6.579 | 4.891 |
| Intra-particle diffusion  | Portion 1 | $k_{int}$ (mg/g min$^{0.5}$) | 5.068 | 4.356 |
|                           |           | $R^2$ | 0.980 | 0.980 |
|                           | Portion 2 | $k_{int}$ (mg/g min$^{0.5}$) | 1.435 | 1.480 |
|                           |           | $R^2$ | 0.959 | 0.967 |
|                           | Portion 3 | $k_{int}$ (mg/g min$^{0.5}$) | 0.8639 | 0.6001 |
|                           |           | $R^2$ | 0.8908 | 0.9808 |

#### 3.5 Continuous Column Experiments

The schematic representation in Fig. 1 shows a series of column experiments performed using the perspex column, having three sampling ports. These experiments were done utilizing GSH as the reactive material for PRB with Pb, and the TC solution as the simulated contaminated groundwater. From the batch tests for each contaminant, the best conditions identified were applied. Significantly, the sand used
to synthesize the GSH has been studied alone, by employing it as the bed in the packed column, to assess its capacity for the removal of Pb and TC and to ascertain that the principal removal process takes place exclusively through the graphene. The results confirmed that the sand clearly exerts no effect in eliminating the Pb and TC throughout the test period, not extending beyond three days. However, the results drawn from the column experiments were discussed as given:

### 3.5.1 Effect of inlet concentration

In Figs. 8 and 9, respectively, an explanation is offered regarding the influence exerted by the inlet concentration of the Pb and TC via the GSH reactive medium, at a 5 mL/min flow rate. At the higher concentrations of the contaminants, it is obvious that the reactive medium starts to saturate, resulting in the breakthrough curves beginning to rise earlier, indicative of a decrease in the removal efficiency; at lower concentrations of the contaminants, however, the breakthrough curves start rising much later, implying that the reactive medium is effective, and it stays active for a lengthier time period, until it gets exhausted. An explanation for this behavior is as follows: the low concentration gradient causes the Pb and TC to slowly propagate through the pores because of a decrease in the mass transfer coefficient, which lengthens the time to achieve bed saturation, and *vice versa*. Several other researchers reported results similar to the ones reported in this work (Maged et al. 2020). Besides, as the reactive medium possesses a fixed number of effective sites, any rise in the initial concentrations of the contaminants, meaning an increase in the quantity of the contaminants, will cause a drop in the removal efficiency because the effective sites get filled up with the contaminants to a point that no extra sites are available to remove any more contaminants.

### 3.5.2 Effect of flow rate

In this section, the column experiments were performed for three different flow rates (5, 10, and 15 mL/min), as seen in Figs. 10 and 11. In these Figures, the levels of normalized concentrations are shown, which rapidly increased and touched saturation point (C/Co=1) as the flow rates increased. This phenomenon can be explained as the period of residence of the pollutants (Pb and TC) in the bed column, with a corresponding rise in the flow rate, resulting in a reduction in the residence time and a decline in the removal efficiency. As there was no contact time between the Pb & TC and the GSH, there is a decrease in the number of available sites, thus restricting the number of pollutants that can be removed. Besides, the rapid flow rate can induce a breakdown of the weak ionic bonds that present between the pollutants and the binding sites of the reactive material (Faisal and Abd Ali 2017b, a).

### 3.5.3 Effect of bed height

From Fig. 12 the normalized concentrations of Pb and TC are clearly shown throughout the column bed length, at a flow rate of 5 mL/min and at different time intervals. This figure reveals that any increase in the reactive bed material, in terms of thickness, enhances the efficiency of the treatment. This may have some bearing on the fact that a thicker bed implies the availability of more numbers of sites for sorption,
resulting in improved sorption capacity and more time to reach the point of getting exhausted or saturated, and therefore, causing an improved process of adsorption. However, apparently, the bed starts to get saturated with the increase in both travel time and flow rate.

### 3.5.4 Variations in hydraulic conductivity with time

The current study revealed that monitoring the variations in the hydraulic conductivity of the column bed at port 3 at specific time periods was one of the most significant aspects, as is obvious from Fig. 13. The calculation was done using Darcy’s law which was dependent upon the accumulated volume of the treated water. In this experiment, the starting value was 0.027 cm/s, which refers to the initial value of the hydraulic conductivity of the reactive medium (GSH). After a brief time of operation, this value began to slowly drop and then stabilize at a particular level. From the findings, the GSH was found appropriate for preservation of the bed reactivity and maintenance of the hydraulic conductivity of the bed, so that any decrease in the quantity of the effluent water can be averted. The presence of the sand which aids in producing large-sized voids can relate to it, and thus remove any restriction in the flow channels (Alakayleh et al. 2018).

### 3.5.5 Comparison between the COMSOL and column experimental results

From Figures 8-11a a clear comparison is drawn between the COMSOL predicted and experimental data for the concentrations of Pb and TC right through the migration of the pollutant plume, at different time intervals, inlet concentrations, and flow rate. This clarifies that the reactive medium plays a crucial part in limiting the contaminant plume propagation. However, this influence clearly reduces with time, due to the decline in the function of the bed in the slowing down (retardation) of the contaminants. Further, an appropriate correspondence is observed between the outcomes of the predictions of the COMSOL model and the experimental measurements. This is probably due to the sorption of the Pb and TC onto the reactive medium (GSH), which was considered in the COMSOL model, meaning the retardation factor of the contaminants on the GSH had exceeded 1. However, any negligible differences may have arisen because of an experimental error related to the nature of the sampling and measurement, which significantly influenced these differences. Besides, it was the statistical measures that could specify the level of concurrence between the predicted and experimental values by using the Sum Square Error (SSE). Calculations were performed by applying the equation given below (Guyo et al. 2015):

\[
SSE = \sum [(C/Co) \text{ experimental} – (C/Co) \text{ predicted}]^2
\]

From the calculations, using equation (16), it can be proven that good agreement is present between the experimental results and the COMSOL predicted ones, with the SSE value below 0.15; this indicates that the COMSOL model can be used successfully for simulating the remediation of contaminated groundwater.

**Conclusion**
1. In this study, the GSH was synthesized using date syrup, adopting the one-step pyrolysis. The GSH was employed in PRB technology as a cost-effective and eco-friendly reactive material, without any negative effects, to remedy simulated Pb- and TC-contaminated groundwater, through batch and continuous experiments. From the experimental results, the synthesized GSH showed that it can be a promise reactive material in treating contaminated groundwater by removing the contaminants, Pb and TC.

2. The parameters investigated in the batch mode included the initial pH, contact time, agitation speed, GSH dosage, and initial concentration, the factors that influenced the removal of Pb and TC. The effective values of these parameters were 90 min, 6, 200 rpm, 50 mg/L, and 0.5 and 0.7 g/50 mL/min, at which the maximum removal efficiency of Pb (98%) and TC (97%), was noted.

3. The sorption data of Pb and TC, according to the Langmuir isotherm model with a minimum R2 value of 0.98, was evident from the batch experimental data. Besides, the pseudo-second-order model showed a better fit kinetically with the experimental data than did the pseudo-first-order model.

4. From the continuous column experiments, the GSH can be proven to play a significant part in curtailing the migration of the Pb and TC plume; this curtailment was more pertinent for the Pb than for the TC.

5. When the predicted COMSOL was compared with the experimental findings during the propagation of the Pb and TC plume, the COMSOL model predictions and experimental results showed good agreement, where the SSE was below 0.15.

Declarations

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The authors confirm that the article has been subject to the ethics of your journal

Consent to Publish

The authors confirm their agreement to publish the article according to the journal’s instructions if the article is accepted for publication

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**Author Contributions**

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**Availability of data and materials**

All data and materials were available in the manuscript

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**Figures**

**Figure 1**

Schematic diagram of the laboratory-scale column.
Figure 2

Characteristics of GSH: (A) Raman Spectroscopy for sand and GSH, (B) XRD of sand and GSH, (C) FTIR analysis of sand, GSH, GSH-Pb, and GSH-TC,
Figure 3

Characteristics of GSH: SEM/EDS test for (A) sand, (B) GSH, (C) GSH-Pb, (D) GSH-TC, and TEM test for (E) sand, (F) GSH.
Figure 4

TC and Pb removal percent at different (A) contact time, (B) pH, (C) agitation speed, (D) Initial concentration, and (E) GSH dosage.
Figure 5

Concurrence between equilibrium isotherms and sorption measurements for interaction of Pb and TC.

Figure 6
Kinetic models and experimental measurements for sorption of Pb and TC.

Figure 7

Intra-particle diffusion model and experimental measurements for sorption of Pb and TC.
Figure 8

Measured breakthrough curves in comparison with predictions of models for different inlet concentrations of Pb for P1, P2 and P3 at Q=5 mL/min.

Figure 9
Measured breakthrough curves in comparison with predictions of models for different inlet concentrations of TC for P1, P2 and P3 at Q=5 mL/min.

Figure 10

Measured breakthrough curves in comparison with predictions of models for different inlet flow rate of Pb for P1, P2 and P3 at Co=50 mg/L.

Figure 11

Measured breakthrough curves in comparison with predictions of models for different inlet flow rate of TC for P1, P2 and P3 at Co=50 mg/L.

Figure 12
The Pb and TC transport along the length of the column bed at different time intervals (Q=5mL/min and Co=50 mg/L)

Figure 13

Variation of hydraulic conductivity as a function of time at port 3 (Q= 5 mL/min)

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