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Green synthesis of graphene-coated sand (GCS) using low-grade dates for evaluation and modeling of the pH-dependent permeable barrier for remediation of groundwater contaminated with copper

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ABSTRACT

In this study, a green method of synthesizing graphene-coated sand (GCS) employing low-grade Iraqi dates was elucidated. The GCS was used as a cost-effective and efficient reactive material in a pH-dependent reactive barrier. Besides, this study also endeavored to construct a Freundlich-based adsorption isotherm, to mimic the adsorption effects induced by the pH. It was utilized as a correlation between the Freundlich isotherm constants (K_F & N) and the values of initial pH of the aqueous solution and then combined with the advection–dispersion equation to mimic the influence exerted by the initial pH on the different possibilities of pollutant transport.

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GCS; copper; transport; modeling; Freundlich model

Introduction

There has been, over the recent past, an increasing apprehension concerning heavy metal pollution, produced as a backlash from the development of industries involving metal processing, tanneries, and electroplating.^[1] Heavy metal ions pose a great threat to human health and the environment, even at very low concentrations, as they are very toxic, biologically accumulated, non-biodegradable, stable, and persistent.^[2] Besides, in nature, heavy metal ions can occur in several chemical forms, and because they often co-exist in a variety of forms, it becomes even harder to get rid of them.^[3] Therefore, permeable reactive barriers (PRBs) have assumed great significance in the *in situ* polluted groundwater treatment systems. This is an effective passive process by which the contaminants present in an aquifer are removed simply by making them flow through a reactive material-loaded reactive barrier.^[4] This technology includes the following benefits, viz., subsurface contaminant treatment, plume capture completion, cost-effective operation and maintenance, and affordable long-term performance-monitoring expenditure. The permeable barriers, however, must include reactive material that is compatible with the subsurface environment, with no type of unfavorable chemical reactions, no potential of being a contaminant source, as well as not being expensive.^[5] Despite having the option of a substantial number of naturally present and low-cost reactive materials suitable for PRB, attempts

are still being made to design an absorbent, which is efficient, economically affordable and possessing strong removal characteristics.^[6] In this work, graphene-coated sand (GCS) was used as the effective, renewable and inexpensive reactive material for the PRB. Several research works dealing with GCS are available^[7–11], but this study differs from the others because it utilizes, for the first time, the low-grade Iraqi dates as a cheap carbon source, chiefly composed of carbohydrates (glucose and fructose). These dates considered high carbon sources, decompose naturally and exert no toxic effect on either humans or the environment; neither do they exert any side effects nor cause allergies. As it is cheap and plentifully available, sand makes an ideal constituent when combined with the date juice.^[12] In the groundwater, the mobility of the heavy metals is subjected to several reactions, during which the metals are either adsorbed or precipitated. The heavy metals are also subjected to chemical reactions that cause them to be associated with the solid phase.^[13] The main factor that influences and directs these reactions is the feed solution pH. It affects the sorbent capacity for ionic sorption from the aqueous solution, as it exerts an effect upon its surface properties and the ionic forms of the pollutants within the solutions. Therefore, the pH is found to significantly affect the metal ions retardation by the PRB and its longevity.^[14] Several trials that were done to randomly force fit the isotherms models (such as the Langmuir) to a variety of datasets, which gave various values for the adsorption capacity at

various pH levels.^[15,16] Thus, the modified Langmuir–Freundlich isotherm, the analytical isotherm model, was finally developed. This model can imitate the effect the pH exerts on the adsorption process in the set of experiments performed, using the linear correlation that exists between the pH and affinity coefficient values. It is substantiated by its prediction of arsenic adsorption onto pure goethite and goethite-coated sand, which were the two different sorbent types used.^[17] Chunying et al. developed a way to compare the Langmuir and Freundlich adsorption equations within the SWAT-K model to quantify the daily depletion of the K and budget, on a watershed level. Both the Langmuir and Freundlich adsorption equations were utilized and matched in the SWAT-K model to forecast the K adsorption in the soil, and the K losses in the volcanic Shibetsu River Watershed (672 km², Hokkaido, Japan).^[18] Sisca *et al.*, endeavors to briefly summarize the way the biomass works in the removal of heavy metals from aqueous solutions. They also discuss the equilibria and kinetic aspects of the biosorption. Per the literature survey, the Langmuir and Freundlich isotherms are the most popular models employed to reflect the biosorption equilibrium, while the pseudo-first and second-order kinetic models have gained greater popularity in kinetic studies, as they are quite simple.^[19] The way the pH affected the performance of the reactive barrier was studied utilizing olive pits to observe the copper migration in contaminated groundwater and then developing a Langmuir model-based adsorption isotherm, simulating the effects of the pH-dependent adsorption. This was derived from the findings drawn from a batch of experiments involving a copper-contaminated solution, using olive pits as the effective bio-sorbent, performed under favorable conditions.^[20] At present, most of the available models managing the solute transport in the underground, fail to show the pH effect on the PRB performance. Hence, we require an adsorption isotherm that can explain the adsorption effects dependent upon the pH levels. If this type of model is constructed, it can be potentially integrated into a widely pollutant transport model expressed by the advection-dispersion equation to mimic the transport outlines dependent upon the pH values. Keeping these facts in mind, this study aims at achieving the objectives listed below: (a) to synthesize a novel graphenized sand (graphene coated sand, GCS), made from sand and low-grade Iraqi dates that can act as an inexpensive reactive material in the PRB, to remove copper ions from contaminated groundwater, (b) to construct an integrated model which includes pollutant transmit, as well as simultaneously covers the pH-controlled adsorption effects. The integrated

model was confirmed using experimental datasets, which deposit the Cu²⁺ onto reactive material (GCS). This method of assessing the pH-dependent adsorption effects on the retardation factor and GCS reactive barrier longevity was found to be effective.

Materials and methods

Materials

To synthesize graphene coated sand (GCS) for use as a reactive media for PRB, the raw materials including low-grade (cheap) Iraqi dates and locally sourced sand were used. High-grade purity sulfuric acid (activating reagent) and CuSO₄·5H₂O (adsorbate) were the other chemicals employed. In all the experiments, only double distilled water was used.

Instrumentation for characterization

Before using the prepared reactive media (GCS) in the experiments, the reactive media was typified by applying the procedure mentioned below:

Fourier-transform infrared (FTIR) spectroscopy

A Shimadzu FTIR (Japan), 800 series spectrophotometer was used to record the FTIR spectra of the prepared reactive media. Samples for the spectral analysis were prepared by mixing GCS with KBr for use as the reference, and the spectra obtained fell within the range of 4000–400 cm⁻¹.

SEM/EDX analysis

The surface morphological and constituent analysis of the sand and GCS were examined under a scanning electron microscope using an energy dispersive X-ray spectrometer (SEM/EDX, TESCAN, Vega III, Czech Republic).

Specific surface area

The surface area of the GCS was established by applying the nitrogen adsorption method using the Quantachrome NovaWin software for data acquisition and reduction for the NOVA instruments at 77.3 K.

Preparation of graphene coated sand (GCS)

Three steps were involved in the preparation of graphene-coated sand (GCS) which involve the use of sand and low-grade Iraqi dates as a cheap and natural carbon source. In the first step, the date flesh (without date pits) was weighed and boiled for 20 min, using an adequate quantity of water, and then blended. The slurry thus produced

was filtered through a cloth in a hand press. The raw date juice collected was then centrifuged at 7,000 rpm for 30 min and the clear extract was then concentrated in a rotary evaporator apparatus, under vacuum, at 70°C. The date juice thus collected was mixed with the required quantity of sand, and this mixture was stirred and heated at 90° C in hot air oven until the date juice hardened on the sand grains. In the second step, the sample was burned for three hours, in a furnace under N₂ gas atmosphere (to avert oxidation) at 750° C. When the temperature reached (185° C), the melting point of hardened date juice, the sample changed color to dark brown and then transformed into carbon. The last step involved activation, which was performed by using a strong acid (H₂SO₄) to remove the ashes covering the surface. The GCS was then filtered, distilled water-washed, and oven-dried at 110°

C for 2 hours.^[21] The final material was cooled at room temperature and sieved through a mesh (63 µm–0.71 mm diameter). The geometric mean diameter is expressed by $d_{gm} = (d_1 d_2)^{1/2}$ where d_1 is the diameter of the lower sieve, where the particles were retained, and d_2 is the diameter of the upper sieve, which the particles passed through.^[22] The GCS revealed bulk density and porosity of 1.55 g/cm³ and 0.41, respectively.

Preparation of synthetic contaminated groundwater

An appropriate amount (3.9202g) of CuSO₄ · 5H₂O (manufactured by BDH, England) has been dissolved in 1 L of distilled water to prepare 1000 mg/L of the stock solution of standard copper (Cu²⁺). Further dilution of

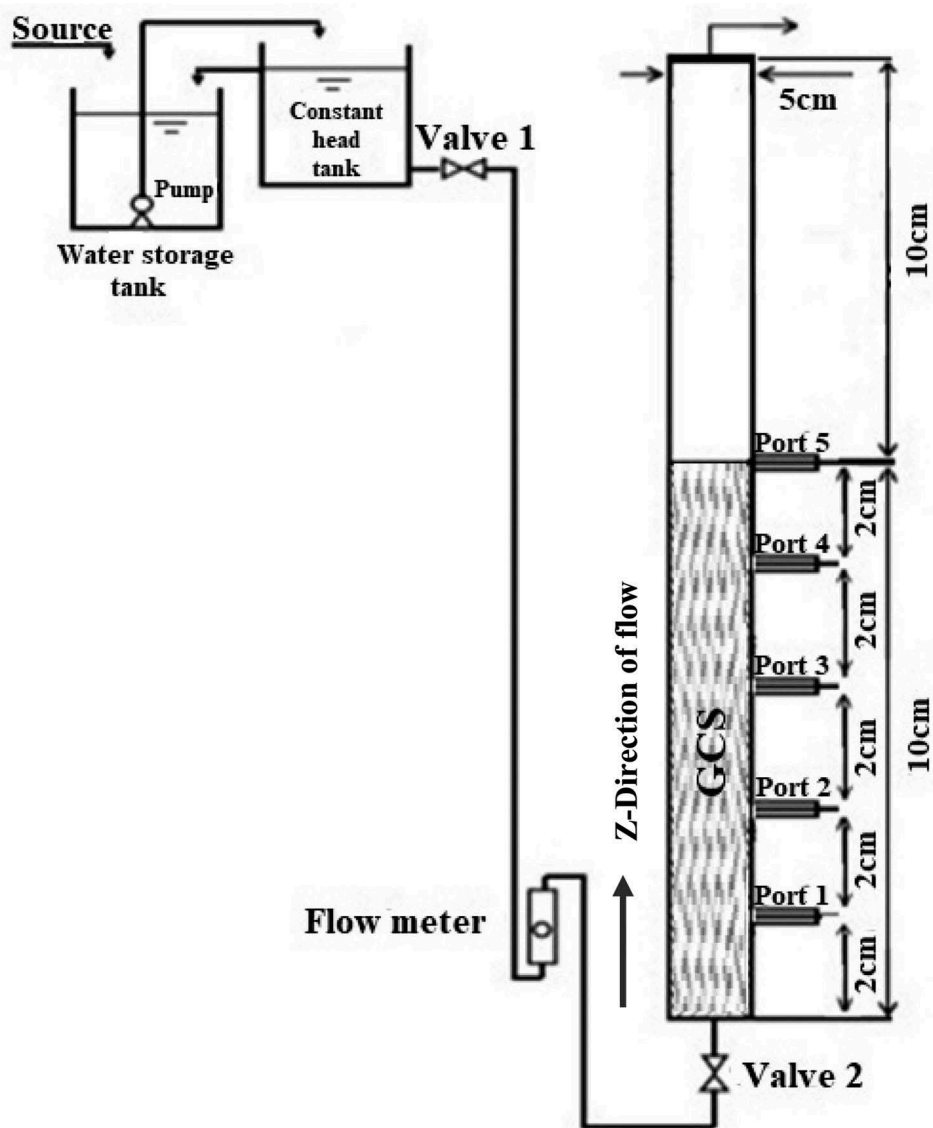


Figure 1. Schematic diagram of the laboratory-scale column.

this stock solution was done by adding deionized water to make up the solutions to the concentrations prescribed for the subsequent experiments.

Batch experiments

A series of batch bio-sorption tests were performed using different initial pH values (2.5–8.5) for the solution, with 180 min contact time, and initial copper concentration of 5, 10, 20, 30, 50, 60, 75, 85, 100 mg/L. The first involved the addition of 2 g of the GCS to 100 mL of the polluted solution, with continuous stirring in the shaker at 200 rpm, maintaining the temperature at a constant 25°C. While the equilibration times were identified at 90 min, for experimental causes the adsorption experiments were conducted for 180 min. Once each experiment reached completion, a sample bottle was used, into which the solution was decanted. The solution was analyzed to check for remain metal ions, using the atomic absorption spectrophotometer (AAS) (Shimadzu, Japan). The quantity of metal ions sorbed using GCS, q_e in (mg/g), was estimated, as illustrated in Equation 1^[23]:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where C_o refers to the initial Cu^{+2} concentration in the solution (mg/L), V indicates the volume of the solution (L), and m implies the mass of GCS (g).

Column experiments

Figure 1 depicts a schematic representation of the laboratory-scale column utilized in this study. This setup was constructed using a 20-cm high perspex cylinder, of 5 cm diameter. The column was provided with sampling ports 1 to 5, respectively, at 2, 4, 6, 8, and 10 cm distance from the bottom of the column. Samples were drawn from these ports to monitor the Cu^{+2} concentration variations in the effluent, during the period. Sampling was regularly performed and AAS was used for the analysis. The GCS, as the reactive material specimen, was packed into the column up to a height of 10 cm in the configuration and alignment, as shown in Fig. 1. At the commencement of the experiment, distilled water was slowly introduced into the column from the bottom end and flowed up through the effective material (GCS), displacing the air above it. This procedure thus circumvented any problem with entrapped air.^[24,25] The solution contaminated with the copper, which was reflective of the polluted groundwater, was then poured into the column from a reservoir placed at a height. Valves 1 and 2,

plus a flow meter helped to control the flow rate out of this reservoir. In this study, three contaminated water flow rate values (5, 10, and 15 mL/min) and three initial pH values for the introduced solution (2.5, 5.5, and 8.5) were selected for the experiments. The values of flow rate matched to the real velocities (0.565, 1.131, and 1.695 cm/min, respectively) to conserve Reynolds number <1–10 and validate Darcy's law.^[26] A tracer experiment was conducted, using the identical procedure of Ujfaludi (1986), to estimate the longitudinal dispersion coefficient for the GCS.^[27]

Modeling application

Pollutant transport in a porous medium was found to occur via the advection-dispersion processes. So that, for a one-dimensional system, the dissolved copper mass balance equation may be expressed, as cited by Ayad and Ziad^[28]:

$$D_z \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} = \frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial q}{\partial t} \quad (2)$$

where, D_z refers to the dispersion coefficient in direction z (cm/s); V represents the flow velocity (cm/s); C refers to the copper mass concentration in the aqueous solution (mg/L); q indicates the amount of copper adsorbed on the solid phase (mg/g); θ is the medium porosity (GCS); and ρ_b is the bulk density of GCS (g/cm³). Under isotherm conditions, the q in the second term on the right side of Eq.2 can be replaced with one of the isotherm models. The Langmuir or Freundlich isotherm model is the most suitable for one constituent processes when temperature is constant.^[29] In this work, however, we used the Freundlich isotherm model to explain the copper sorption onto the GCS. While this model was originally empirical in nature, it was explained as the sorption onto heterogeneous surfaces or surfaces that support sites possessing a variety of attractions. The stronger binding sites are assumed to become occupied initially, and the binding strength will decline in proportion to the increasing intensity of site occupation. This model can be represented by the following equation^[30]:

$$q_e = K_F C_e^{1/N} \quad N > 1 \quad (3)$$

where q_e refers to the equilibrium concentration of the copper on the GCS (mg/g), K_F (mg/g)(L/mg)^{1/N} is the Freundlich sorption coefficient, N indicates an empirical coefficient indicative of the adsorption intensity, and C_e is the equilibrium concentration of the copper in the aqueous solution (mg/L).

In this study, the q value was used as the main factor, to introduce the influence exerted by the initial pH of the

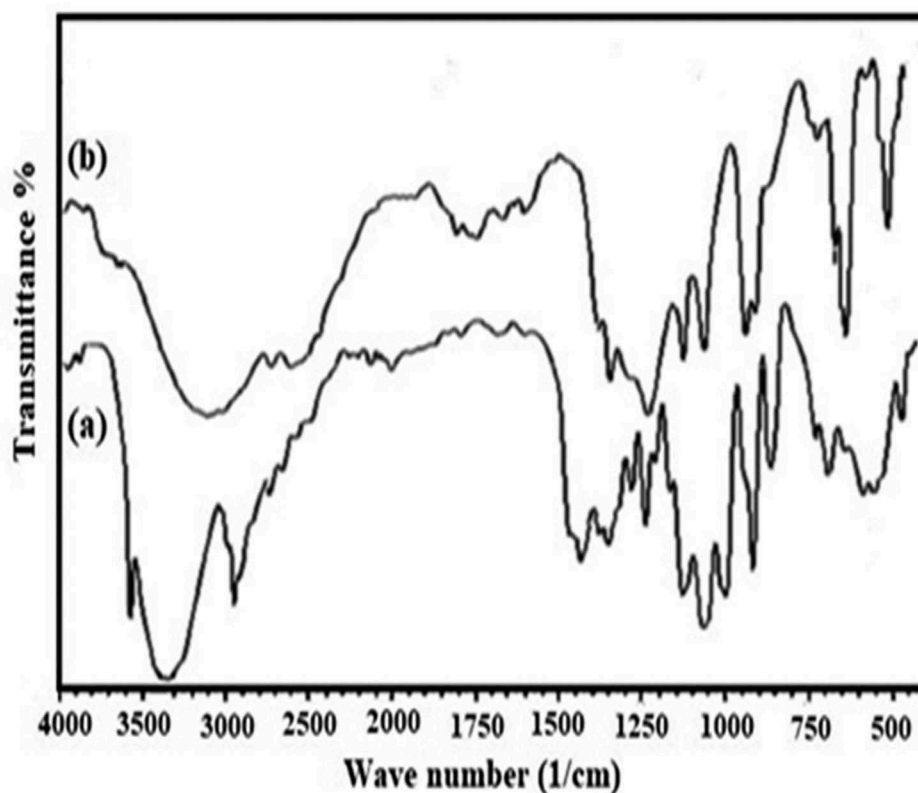


Figure 2. FTIR spectra of sand and sugar mixture (a) before and (b) after burning.

introduced aqueous solution on the transport of the pollutant via the effective barrier. This is indicative that the Freundlich model was compatible with the experimental data, and the K_F and N parameters were linked to the different levels of the pH. In fact, Equation 3 can be subrogated in Equation 2, and the equation consequently formed can be numerically constructed, as given below, employing the implicit (forward in “center in space and time”) finite difference method^[31]:

$$C_i^n = \left(-\frac{D_z \Delta t}{R(\Delta z)^2} - \frac{V_z \Delta t}{R \Delta z} \right) C_{i-1}^{n+1} + \left(\frac{2D_z \Delta t}{R(\Delta z)^2} + 1 \right) C_i^{n+1} + \left(-\frac{D_z \Delta t}{R(\Delta z)^2} + \frac{V_z \Delta t}{R \Delta z} \right) C_{i+1}^{n+1} \quad (4)$$

where R refers to the retardation factor (Equation 5), $n + 1$ and n superscripts are, respectively, the second and present time step, $\Delta t = t^{n+1} - t^n$ indicates the time step size, and i , $i + 1$, $i - 1$ indicate the grid, in the z -direction. This numerical model was solved employing a computer algorithm capable of integrating the constructed isotherm expression modeling framework, within the reactive transport code written in MATLAB R2009b (version 7.9).

$$R = 1 + \frac{\rho_b K_F}{\theta N} C^{[1-N]} \quad (5)$$

Results and discussion

Characterization of the GCS

Fourier transform infrared analysis

Prior to and post the burning, the FTIR spectra of the sand and date juice mixture were recorded, as listed in Fig. 2. However, Table 1 shows the contribution of each functional group. Figure 2(a) reveals strong peaks around 914 cm^{-1} , 995 cm^{-1} , 1064 cm^{-1} and 1126 cm^{-1} that could be attributed to the sucrose structure of the date juice. The adsorption bands at 1346 cm^{-1} , 2721 cm^{-1} , 2937 cm^{-1} , and

Table 1. Functional groups of sand and date juice mixture, before and after the heating.

(a) Before burning		(b) After burning	
Wave No. (cm^{-1})	Type of bond	Wave No. (cm^{-1})	Type of bond
472	SiO_2	1600	C-C
914	C-H	1685	C = C
995	C-O	1749	C-O
1064	C-OH	3525	O-H
1126	C-O-C		
1346	C-O		
2721	C-H-O		
2937	C-H		
3336	O-H		

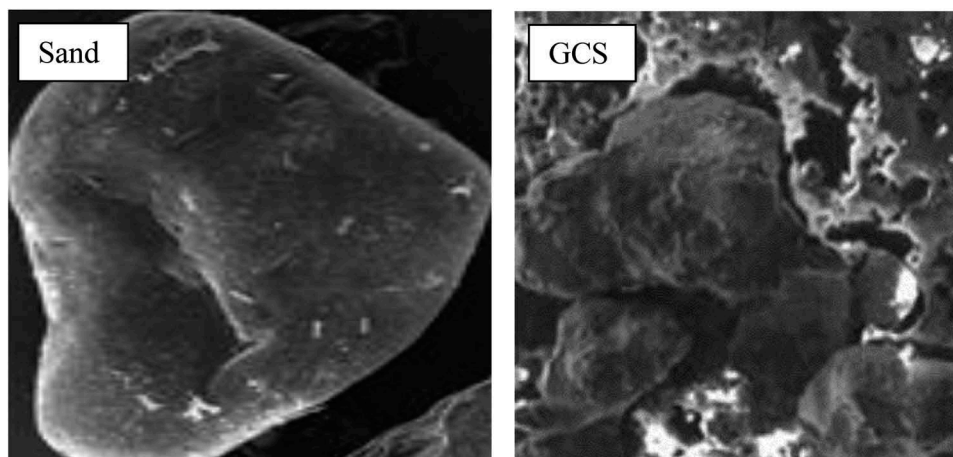


Figure 3. SEM images of sand and GCS.

3336 cm^{-1} represent the chemical functional groups of the sucrose present in the date juice. At 472 cm^{-1} the sharp peak observed is found to be caused by the SiO_2 group of the sand.^[32] Figure 2(b) depicts the distinctive graphene peaks at 1600 cm^{-1} , 1685 cm^{-1} , 1749 cm^{-1} , and 3525 cm^{-1} , which clearly show the graphitization of the hardened date juice.^[33]

SEM and EDX analysis

The morphology of the GCS was examined using the SEM image. In Fig. 3, we can observe the SEM images of the sand and GCS, where the carbon formed around the sand is obvious. Using the EDX analyzer, elementary mapping was done, which revealed that the surface was composed mainly of the elements C (76.15%) and O (20.5%),

Table 2. Percent weight of element on the surface of sand and GCS (EDX analysis).

Element	Weight%	
	Sand	GCS
C	-	76.15
O	45.2	20.5
Al	1	0.85
Si	52.3	0.9
S	0.8	0.7
Ca	0.7	0.9
Total	100	100

respectively, with traces of other elements like aluminum, silicon, and calcium, as shown in Table 2.

Specific surface area

Prior to and post the activation, specific surface areas of the GCS were estimated, respectively, at $113\text{ m}^2/\text{g}$ and

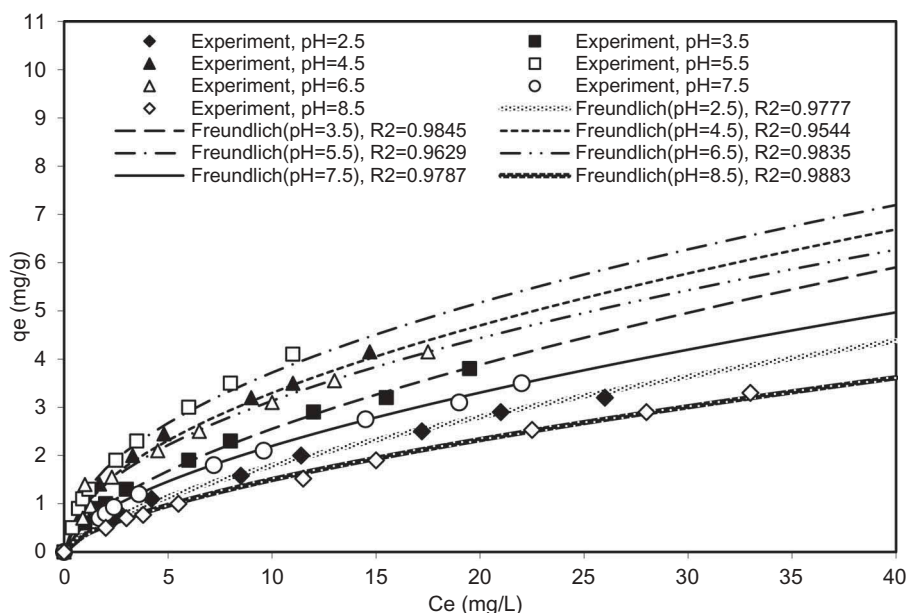


Figure 4. Effect of initial pH on sorption of copper ions onto GCS reactive material.

Table 3. Values of Freundlich isotherm constants as a function of initial pH of the feed solution.

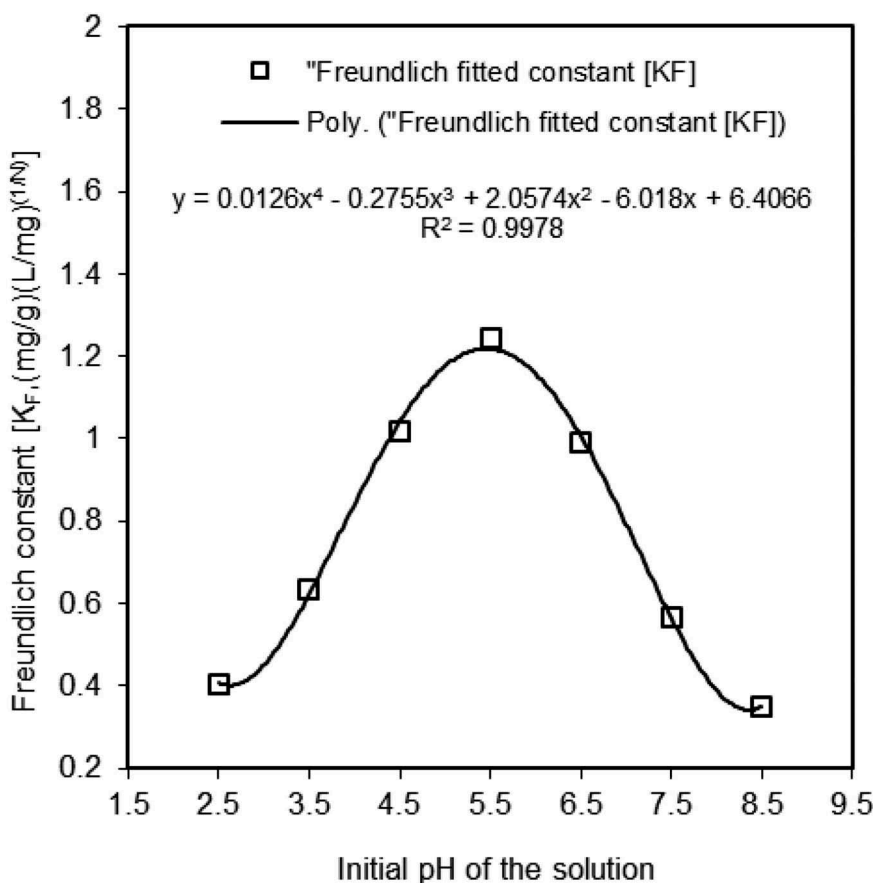
pH	K_F , (mg/g)(L/mg) ^{1/N}	N
2.5	0.4055	1.550
3.5	0.6342	1.653
4.5	1.0186	1.960
5.5	1.2423	2.100
6.5	0.9911	2.000
7.5	0.5674	1.700
8.5	0.3499	1.590

175 m²/g. It is noteworthy that although the GCS surface area is not large when compared with that of the other sorbents, it still has strong ability to remove the copper ions. This irregularity is most likely because of the existence of the graphene sheets on the surfaces of sand, which provide several active sites for adsorption, facilitating the high percentage of copper removal.^[8]

Development of Freundlich isotherm to the pH-dependent sorption model

In Fig. 4, the experimental dataset was assessed at different pH values, in the 2.5 to 8.5 range. The prepared GCS reveals the good sorption power that enables the

removal of the copper ions from aqueous solutions. The results indicate that the highest efficiency of removal occurred at pH = 5.5, where the GCS was able to remove a minimum of 90% of the copper ions from the solutions containing concentrations ranging from 5–100 mg/L. Each isotherm dataset that corresponded to each pH level was fitted to the Freundlich model (Eq.2). From the intercept and slope of the linear plot, the constants were identified employing Microsoft Excel 2003 software (Table 3). The values of K_F and N clearly varied with the initial pH value of the feed solution. Therefore, to appreciate the relationship between the two isotherm constant pairs [(K_F & pH) and (N & pH)], the fitted values of these parameters were plotted versus the pH, as illustrated in Figs. 5 and 6. This suggests that the K_F and N values, fitted with the polynomial (order 4) relationship, rise corresponding to the escalation of the pH value until the pH touches the 5.5 mark. After this point, these parameters show a decline with similar fitted relationships, in response to the rising pH values. The protonation and deprotonation of the basic and acidic groups of the sorbent influence the sorption behavior of the metal ions in a way that they are affected by the value of pH. This effects on the structure of the surface of the reactive

**Figure 5.** Effect of initial pH on K_F estimated by Freundlich model for copper adsorption onto GCS reactive material.

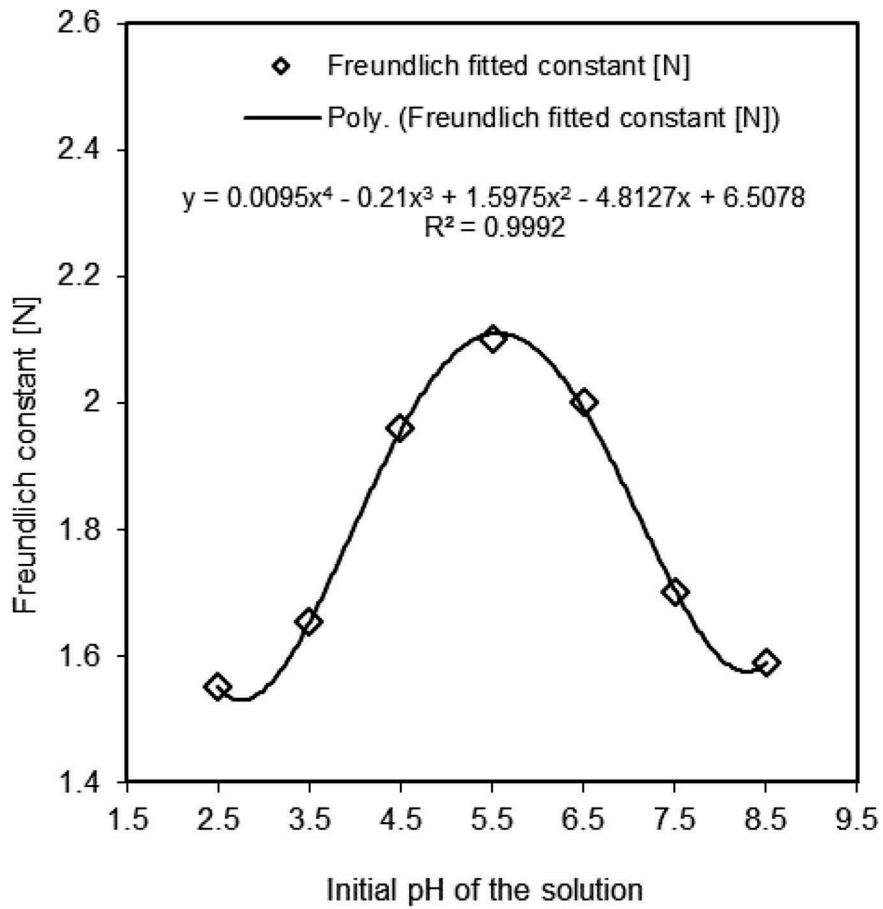


Figure 6. Effect of initial pH on N estimated by Freundlich model for copper adsorption onto GCS reactive material.

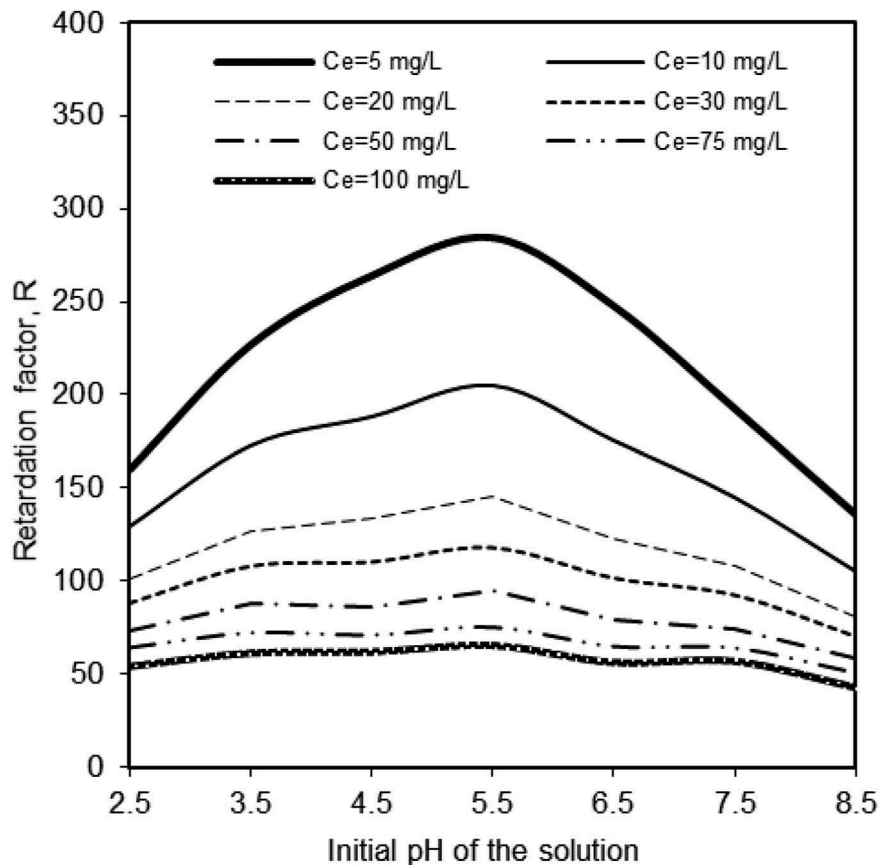


Figure 7. Retardation of copper ions onto GCS reactive material as a function of initial pH of the feed solution.

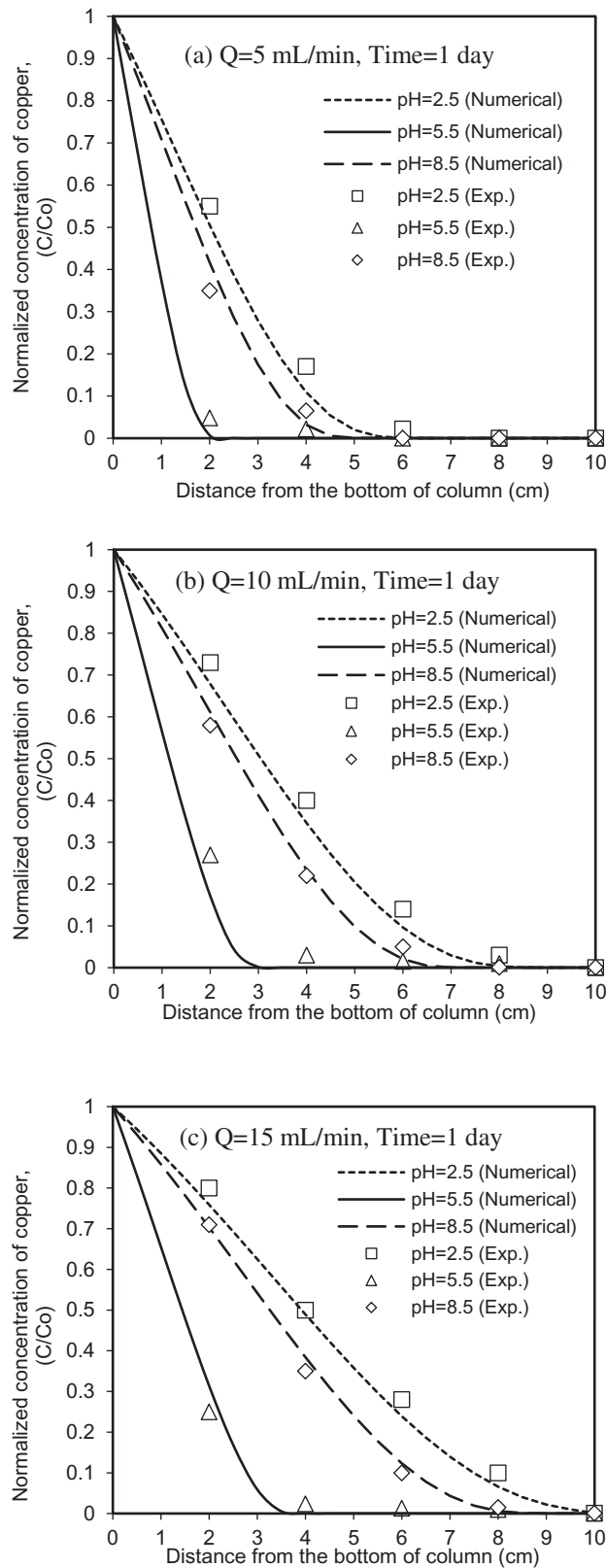


Figure 8. Comparison between numerical solution and experimental results of copper concentrations at different values of flow rate and pH.

material (sorbent, GCS), induces the formation of metal hydroxide and causes the reactive material to interact with the metal ions.^[34] This means that either the rise or drop in the pH from its most suitable value (5.5) lowered the affinity for the sites of surface. This may be because of the competition by the cations and protons, at low pH values, for the binding sites. When the pH values are higher (>6.5), the copper ion removal is also low, compared to the best pH value. This can imply that under basic pH conditions the binding sites may not be activated.^[35] Figures 5 and 6 list the relationships describing the K_F and N values, which can be explained using the following general polynomial expressions.

$$K_F = \alpha_1 pH^4 - \alpha_2 pH^3 + \alpha_3 pH^2 - \alpha_4 pH + \alpha_5 \quad (6)$$

$$N = \alpha_6 pH^4 - \alpha_7 pH^3 + \alpha_8 pH^2 - \alpha_9 pH + \alpha_{10} \quad (7)$$

When the above expressions are inserted in Equation 2, the result is as given below:

$$q_e = \left(\frac{\alpha_1 pH^4 - \alpha_2 pH^3 + \alpha_3 pH^2 - \alpha_4 pH + \alpha_5}{\alpha_6 pH^4 - \alpha_7 pH^3 + \alpha_8 pH^2 - \alpha_9 pH + \alpha_{10}} \right) C_e \quad (8)$$

This equation is a flexible configuration, which can explain the different degrees of sorption at various pH values, employing a stable set of isotherm parameters. In addition, Equation 8 is incorporated with Equation 2. It can produce an integrated model, which can facilitate the prediction of the pH-determined sorption outcomes on the way the GCS permeable reactive barrier performs (PRB), in terms of its retardation factor and longevity.

Performance of pH-dependent PRB

The developed integrated model described thus far can be solved, in which the initial and boundary conditions indicate the condition of the column experiments performed in this work. The initial concentrations of the liquid and solid copper ions are reckoned as zero during the entire flow domain and boundary conditions of Equation 9:

Lower boundary (@ $z = 0$): $C_{Cu} = 50 \text{ mg/L}$

Upper boundary (@ $z = 10\text{cm}$): advective flux (i.e. $\frac{\partial C_{Cu}}{\partial z} = 0$)

The sorption processes caused the dissolved metal ions to pass very slowly through the GCS, even slower than the inlet solution carrying them, a process termed

retardation.^[36] In Fig. 7, the retardation factor is observed to directly depend upon the concentration of the hydrogen ions present in the initial copper solution. It is evident that this factor escalates corresponding to the increase in the pH values until it reaches the 5.5 value, the point at which the GCS achieves the highest retardation factor, irrespective of the initial or equilibrium metal concentration. After this point, this factor decreased with increasing pH values. This behavior is logical and it concurs with the influence exerted by the adsorption (affinity), consequent to the initial pH of the inlet solution, as explained above.^[20] Figure 8 shows the predicted (numerical solution) and experimental results, which are compared in terms of the copper ion concentrations during the contaminant plume migration at the three flow rate values of the contaminated water (5, 10, and 15 mL/min) and the three initial pH values of the inlet solution (2.5, 5.5, and 8.5), after one day, along with the GCS reactive medium. This Figure demonstrates the crucial part the barrier plays in limiting the contaminant plume propagation. It appears that the escalated flow rate value will raise the flow velocity, and thus increase the pollutant front propagation, for any specified initial pH value of the solution. Therefore, the time needed for the column

effluent to achieve the steady-state concentration decreases as the flow rate value increases. In addition, the time required to reach the normalized copper concentration (C/C_0) to 1 (saturation state) in the effluent column ($z = 10$ cm) was related to the lowering or raising of the initial pH of the copper solution from its best value. These results show good concurrence, and this was recognized with the root mean square error (RMSE), which did not exceed the 0.038 value.^[37] The correspondence existing between the PRB longevity and initial pH of the inlet solution was examined using the integrated model developed in this study. Longevity implies the time needed to maintain the effluent pollutant concentration from the barrier to a level below the quality limit stipulated for drinking or surface waters. According to USEPA, the copper contaminant in drinking water has a stipulated maximum permissible level of less than 1.3 mg/L.^[38] In Fig. 9, the barrier longevity varies with the initial pH of the inlet solution for copper transport in a nonlinear manner, at the different flow rate values selected in this work. It can be noticed that the longevity of the barrier increased with increasing the pH values up to 5.5 and then start to decrease for three different values of flow rate. This behavior

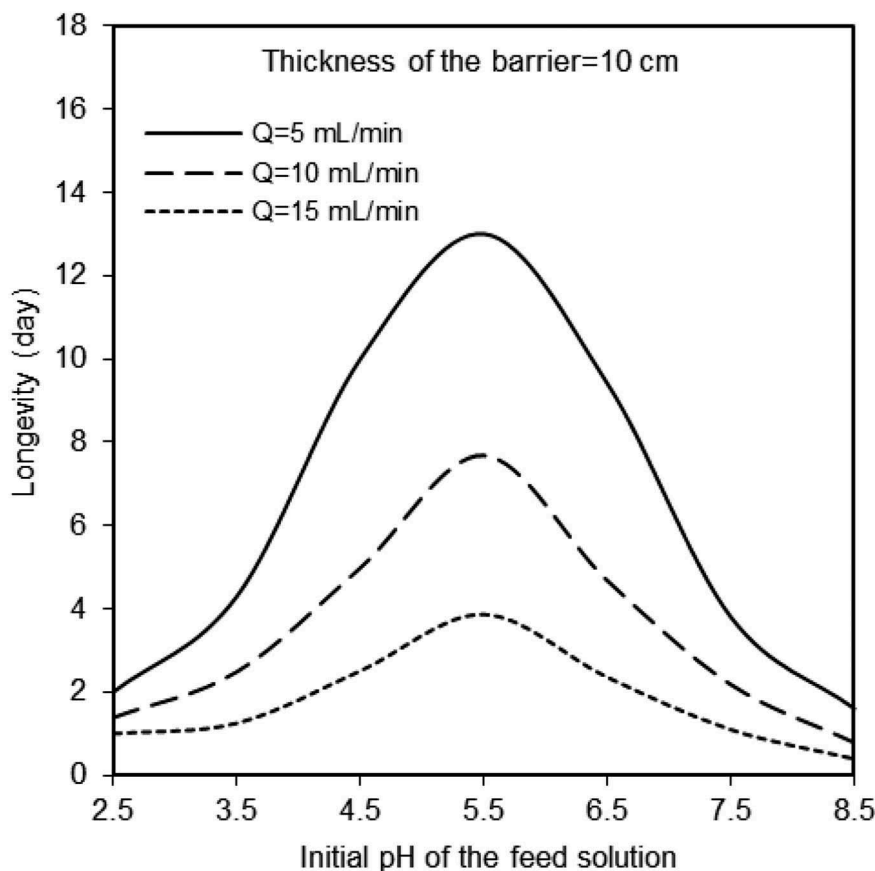


Figure 9. Effect of initial pH of the feed solution on the longevity of the barrier for different values of flow rate as predicted by present developed integrated model.

confirms the existence of a relationship between the longevity of the barrier and pH value of the contaminated groundwater. So, can conclude that controlling the pH of the contaminated groundwater can prolong the operation life for the reactive barrier.

Conclusions

- (1) The use of low-grade Iraqi date juice and sand enabled the production of inexpensive and effective reactive media composed of sand particles coated with graphene sheets, termed graphene coated sand (GCS). It can be used in PRB for the remediation of copper-contaminated groundwater. The FTIR spectra confirm the graphene deposited on the sand surface. The SEM/EDX examination shows the rather heterogeneous and porous character of the GCS surface that consider one of the reasons for effective copper removal
- (2) The GCS thus prepared has a good sorption capacity for copper ion removal from aqueous solutions. The highest removal efficiency (90%) was observed at pH = 5.5, at which the GCS was able to remove the copper ions from the solutions with concentrations of 5–100 mg/L.
- (3) An isotherm expression was developed to simulate the adsorption effects dependent upon the pH of the solution. Freundlich isotherm model was used as the base model, later modifying the expression by permitting the Freundlich isotherm constants (K_F & N) to vary with the pH values.
- (4) A computer algorithm that can illustrate the isotherm expression modeling framework within the effective transport was designated using MATLAB R2009b (version 7.9). With the help of this model, the GCS barrier was confirmed to be a good method of limiting the copper contaminant plume, and the initial pH appreciably influenced the retardation factor and longevity (operation life) of the GCS barrier, implying a nonlinear relationship trend.
- (5) The developed model predictions (numerical solution) and experimental results showed good concurrence between them, with the root mean square error (RMSE) did not exceed the 0.038 limit.

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