Adsorption of Cu²⁺, Zn²⁺ and Pb²⁺ ions on a novel graphene-containing nanocomposite: An isotherm study

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Abstract. The present research is dedicated to the problem of adsorption purification of aquatic media from toxic heavy metal ions. To extract some of these species (Cu²⁺, Zn²⁺, and Pb²⁺) from aqueous solutions, a novel material - polyhydroquinone/graphene nanocomposite – was used as adsorbent. Its adsorption/desorption performance was assessed through isotherm studies. The following process parameters were determined: equilibrium metal concentrations in solution, metal distribution coefficients, percentage desorption, and adjusted metal distribution coefficients. Besides, based on experimental data, adsorption isotherms were constructed, from which it was possible to determine the maximum adsorption capacity of the nanocomposite regarding each heavy metal ion (Pb²⁺ - 1350 mg⁻¹; Cu²⁺ - 800 mg g⁻¹, and Zn²⁺ - 300 mg g⁻¹). In order to elucidate adsorption-desorption mechanisms occurring in the considered adsorbate/adsorbent systems and the process nature, the data were fitted to different isotherm models: empirical (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich), and combined (single- and dual-site Langmuir-Freundlich). All the models provided satisfactory fits to the data, thereby making it possible to assume heterogeneity of adsorption sites on the adsorption surface, and the irreversibility of the adsorption process.

1. Introduction
Graphene, a single graphite layer, is a very interesting material. It possesses unique physical, chemical and mechanical properties, due to which it can be used in many application fields [1, 2]. As for water/wastewater purification area, high specific surface area of graphene, together with its pore size and volume, makes it possible to employ this material for adsorption of various species, including heavy metal ions [3, 4].

In the literature, several graphene-based materials and composites are reported for the adsorption of heavy metals such as Cu²⁺, Zn²⁺ and Pb²⁺ (table 1).
Table 1. Adsorption capacities of graphene oxide based materials.

| Material                          | Metal ions                      | pH   | $C_{\text{init}}$ | $Q_{\text{max}}, \text{mg L}^{-1}$ |
|----------------------------------|---------------------------------|------|-------------------|-----------------------------------|
| Graphene Oxide (GO) [5]          | Fe(III), Mn (II)                | 6    | 200 mg L$^{-1}$   | Fe (III) – 24, Mn (II) – 21        |
| Magnetic GO modified with a pyrrole-thiophene (mGO/SiO$_2$@coPPy-Th) [6] | Cu(II), Zn (II), Pb (II)      | 6    | 250               | Cu(II) – 201, Zn (II) – 125, Pb (II) – 230 |
| GO-TiO$_2$ [7]                   | Zn (II), Pb (II)                | 5.6  | 50                | Zn (II) – 89, Pb (II) – 65         |
| GO [8]                           | Pb (II)                         | 6    | 50-100            | 70                                |
| r-GO [9]                         | Pb (II)                         | 4.4  | 150               | 93                                |
| GO/Fe$_3$O$_4$ [10]              | Cd (II), Cu (II), Pb (II)       | 6    | 50-150            | Cd (II) – 164, Cu (II) – 156, Pb (II) – 179 |
| GO [11]                          | Cd (II)                         | 6.5  | ~100              | ~900                              |

Based on the tabular data, it can be established that graphene composites are actively used for the adsorption of heavy metals, exhibiting high sorption activity. It should be noted that the GO modification positively affects the adsorption capacity – it increases by 3-4 times.

However, the relevance and scientific novelty of activities on developing novel adsorption materials based on graphene and its derivatives are due to low elaboration and lack of systematics in studying processes of liquid-phase adsorption of heavy metals on the existing nanostructured graphene materials. In this regard, the development of directional methods for synthesizing these materials and the investigation of their physical and chemical characteristics is of undoubted scientific interest in the world community, since they provide the prospect of a significant improvement in the quality of fine adsorption purification of aquatic media [12].

Establishing patterns of the influence of the physical-chemical and structural parameters of graphene-based nanomaterials being developed on the selective adsorption of target pollutants (heavy metals) is an important trend. Besides, a comprehensive study on the mechanisms of extraction processes is required, which, in turn, will make it possible to predict the behavior of adsorption systems.

In this regard, studying the fundamentals of the heavy metal adsorption on graphene adsorbents based on empirical dependencies and mathematical models that take into account the availability of various adsorption sites on the adsorbent surface, as well as establishing the relationship between the structure of graphene adsorbent and adsorption mechanisms, appear to be important issues.

Considering the aforementioned, the aim of the present research was to propose a polyhydroquinone/graphene (PHQ/G) nanocomposite (synthesized by the authors of this paper) as a novel adsorbent for removing some heavy metal ions ($\text{Cu}^{2+}$, $\text{Zn}^{2+}$ and $\text{Pb}^{2+}$), and study its adsorption and desorption behavior under batch conditions using an isotherm approach and employing empirical and combined isotherm models to fit experimental data.

2. Experimental part

2.1. Material and reagents

The PHQ/G nanocomposite was developed by the authors at the Research Department “Technology and Methods of Nanoproducts Manufacturing” (Tambov State Technical University, Tambov, Russia) and produced by NanoTechCenter Ltd. (Tambov, Russia). The technology of its manufacturing is described elsewhere [13].
Heavy metal salts: Cu(NO₃)₂, Zn(NO₃)₂ and Pb(NO₃)₂ (all – analytical grade) were purchased from Laverna Lab Ltd. (Moscow, Russia). Heavy metal stock solutions (1,000 mg L⁻¹) were obtained by diluting certain amounts of the corresponding salts in deionized water. Before using in tests, the solutions were diluted to the required concentrations: 12, 25, 50, 100, 200, 250, 450, 650, and 900 mg L⁻¹.

2.2. Adsorption-desorption isotherm studies
For adsorption studies, 0.01 g of the PHQ/G material and 30 mL of 12-900-mg L⁻¹ metal solutions (pH=6.0) were separately placed into 50-mL conical tube sand then shaken at 100 rpm and ambient temperature for 1 h on BioRS-24 rotators (Biosan, Riga, Latvia). After that, the mixtures were centrifuged using a 5810 R centrifuge (Eppendorf, Hamburg, Germany) at 10 000 rpm for 10 min for phase separation, and supernatants were collected to measure the metal equilibrium concentrations on an MGA-915 MD atomic absorption spectrometer (Atompribor, Saint Petersburg, Russia).

For desorption tests, performed after the adsorption experiments, the solid phase (PHQ/G) was separated, dried at 45 °C for about 15 min to remove surface moisture, and placed to 50-mL conical tubes, to which 30 mL of metal-free buffering aqueous solutions (pH=6.0) were then separately added. Like in the adsorption tests, the tubes were also shaken at 100 rpm and ambient temperature for 1 h, the mixtures were centrifuged at 10 000 rpm for 10 min for phase separation, and supernatants were collected to measure the metal equilibrium desorption concentrations on the spectrometer.

2.3. Experimental data processing
The equilibrium adsorption capacity \( Q_e, \text{ mg g}^{-1} \) of the material was determined according to the following expression:

\[
Q_e = \frac{(C_{in} - C_e)V}{m}, \tag{1}
\]

where \( C_{in} \) is the initial metal concentration in solution (before adsorption), mg L⁻¹; \( C_e \) is the equilibrium metal concentration in solution (after adsorption), mg L⁻¹; \( V \) is the solution volume, L; \( m \) is the adsorbent weight, g.

Correspondingly, the equilibrium adsorption capacity for the desorption case \( Q_{e}^{des}, \text{ mg g}^{-1} \) was estimated as follows:

\[
Q_{e}^{des} = \frac{(C_{in} - C_{e}^{des})V}{m}, \tag{2}
\]

where \( C_{e}^{des} \) is the equilibrium metal concentration in solution (after desorption), mg L⁻¹.

Further, the coefficients of the distribution of the adsorbates between the phases were calculated for the adsorption (\( K_d, \text{ L g}^{-1} \)) and desorption (\( K_d^{des}, \text{ L g}^{-1} \)) cases according to the following equations:

\[
K_d = \frac{(C_{in} - C_e)V}{c_e m} = \frac{Q_e}{m^{*}}, \tag{3}
\]

\[
K_d^{des} = \frac{(C_{in} - C_e^{des})V}{c_e^{des} m} = \frac{Q_{e}^{des}}{m^{*}}. \tag{4}
\]

\( K_d^{des} \) provides information about the equilibrium displacement of the adsorbate between the adsorbent and the contact solution it is already incorporated into.

The percentage desorption \( R_{des}, \% \), which shows the adsorbate amount percent leached back into the aqueous phase, and the adjusted distribution coefficient \( K_d^{adj}, \text{ L g}^{-1} \), which corrects the adsorption (reversible)distribution coefficient \( K_d \) in the adsorbate fraction involved in the adsorption equilibrium, were assessed as follows:

\[
R_{des} = \frac{100C^{des}_{e}}{(C_{in} - C_e)}, \tag{5}
\]

\[
K_d^{adj} = \frac{100K_d}{R_{des}}. \tag{6}
\]
2.4. Experimental data fit

2.4.1. Empirical models. The metal adsorption data were fitted to the following empirical models: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (table 2).

| Empirical models implemented [14] |
|-----------------------------------|
| Langmuir | Freundlich | Temkin | Dubinin-Radushkevich |
| $Q_e = Q_{max} \frac{K_F C_0}{1 + K_F C_0}$ | $Q_e = K_F C_e^n$ | $Q_e = B_T \ln (k_T C_e)$ | $Q_e = Q_{max} \exp (-K_{DR} \varepsilon^2)$ |
| $E = \frac{1}{\sqrt{K_{DR}}}$ |

$Q_{max}$ – maximum adsorption capacity, mg g$^{-1}$; $K_F$ – Freundlich constant (adsorbate-adsorbent binding energy), L mg$^{-1}$; $n$ – indicator of heterogeneity of adsorption sites on the adsorbent surface, dimensionless; $B_T$ – constant related to the heat of adsorption, J mol$^{-1}$; $K_T$ – Temkin equilibrium constant (maximum binding energy), L g$^{-1}$; $K_{DR}$ – Dubinin-Radushkevich isotherm constant related to the mean free energy of adsorption, mol$^2$kJ$^{-2}$; $\varepsilon = RT \ln (1 + (1/C_e))$ – Polanyi potential, equal to kJ mol$^{-1}$; $E$ – mean free energy of adsorption, kJ mol$^{-1}$.

2.4.2. Combined models. Two modifications of the combined Langmuir-Freundlich (Sips) model were implemented – single- (equation (11)) and dual-site (equation (12)):

$$Q_e = \frac{Q_{max}(K_{LF1} C_0)^{n_1'}}{1 + (K_{LF1} C_0)^{n_1'}} + \frac{Q_{max}(K_{LF2} C_0)^{n_2'}}{1 + (K_{LF2} C_0)^{n_2'}}$$

where $K_{LF1}, K_{LF2}$ are the Langmuir-Freundlich constants (binding energy), L mg$^{-1}$; $n'$, $n_1'$, $n_2'$ are indicators of heterogeneity of adsorption sites; subindexes “1” and “2” stand for adsorption sites possessing different affinity (binding energy) for the adsorbate.

3. Result and discussion

3.1. Adsorption isotherms

The isotherms constructed for the heavy metal adsorption on the PHQ/G nanocomposite based on the experimental data obtained are presented in figure 1.

![Figure 1](image-url)  
**Figure 1.** Isotherm constructed for the metal adsorption on the PHQ/G material. Conditions: adsorbent weight – 0.01 g, solution volume – 0.03 L, contact time – 1 h, temperature – 298 K, and pH 6.0.

As can be seen, all the isotherms may be related to the $L$-type by their shape, according to the classification introduced by Giles and its colleagues [15]. This means that the adsorbates possess a relatively high affinity for the adsorbent surface at lower concentrations. When the surface is saturated, with an increase in the adsorbate concentration, the number of vacant adsorption sites located on the adsorbent surface decreases, and the adsorbate amount decreases as well – the maximum adsorption capacity is reached (for Pb$^{2+}$ ~1350 mg g$^{-1}$, for Cu$^{2+}$ ~800 mg g$^{-1}$, and for Zn$^{2+}$ ~300 mg g$^{-1}$).

3.2. Adsorption and desorption parameters

Table 3 presents the data obtained for the adsorption and desorption of Pb$^{2+}$ on the
PHQ/G nanocomposite (the data for Cu$^{2+}$ and Zn$^{2+}$ are not given herein, since all the ions showed the similar pattern; in this regard, Pb$^{2+}$, having the highest adsorption capacity, is taken as an example).

Table 3. Adsorption-desorption parameters obtained for the system Pb$^{2+}$-PHQ/G.

| $C_e$, mg L$^{-1}$ | $Q_e$, mg g$^{-1}$ | $K_{ds}$, L g$^{-1}$ | $C_{e_{des}}$, mg L$^{-1}$ | $Q_{e_{des}}$, mg g$^{-1}$ | $K_{d_{des}}$, L g$^{-1}$ | $K_{d_{des}}/K_d$ | $R_{des}$, % | $K_{d_{adj}}$, L g$^{-1}$ |
|------------------|------------------|-------------------|------------------|------------------|-------------------|----------------|------------|-------------------|
| 4.2              | 23.4             | 5.57              | 1.41             | 19.17            | 13.60             | 2.44           | 18.08      | 30.82             |
| 10.2             | 59.4             | 5.82              | 1.59             | 54.63            | 34.36             | 5.90           | 8.03       | 72.52             |
| 23.3             | 80.1             | 3.44              | 2.58             | 72.36            | 28.05             | 8.16           | 9.66       | 35.58             |
| 70               | 120              | 1.71              | 2.62             | 112.14           | 42.80             | 24.97          | 6.55       | 26.17             |
| 77.67            | 156.99           | 2.02              | 2.97             | 148.08           | 49.86             | 24.67          | 5.68       | 35.61             |
| 151              | 747              | 4.95              | 6.30             | 728.1            | 115.57            | 23.36          | 2.53       | 195.53            |
| 195.5            | 913.5            | 4.67              | 6.17             | 894.99           | 145.06            | 31.04          | 2.03       | 230.60            |
| 312.7            | 1311.9           | 4.20              | 5.52             | 1295.34          | 234.66            | 55.93          | 1.26       | 332.36            |
| 369.2            | 1292.4           | 3.50              | 6.27             | 1273.59          | 203.12            | 58.03          | 1.46       | 240.52            |
| 550.7            | 1347.9           | 2.45              | 6.36             | 1328.82          | 208.93            | 85.36          | 1.42       | 172.91            |

It can be observed that when increasing the initial $C_{in}$ (not shown) and, correspondingly, equilibrium $C_e$ concentration of the adsorbate, adsorption capacity $Q_e$ (equation (1)) progressively increases, the adsorption sites of the adsorbent surface become more and more saturated, and the coefficient of the adsorbate distribution between the solid and liquid phases $K_d$ (equation (3)) decreases.

For the desorption case, the capacity $Q_{e_{des}}$ (equation (2)) and the desorption distribution coefficient $K_{d_{des}}$ (equation (4)), giving information about the equilibrium displacement of the adsorbate between the adsorbent and the contact solution it is already incorporated into, increase with increasing the equilibrium desorption concentration $C_{e_{des}}$ (it directly depends on the equilibrium adsorption concentration $C_e$).

Comparing the $K_d$ and $K_{d_{des}}$ values, it can be seen that $K_{d_{des}}/K_d > 1$, thereby standing for the irreversibility of the Pb$^{2+}$ adsorption, which is a good factor for efficient wastewater purification (the pollutant is poorly lixiviated from the adsorbent). The percentage desorption $R_{des}$ (equation (5)) and the adjusted distribution coefficient $K_{d_{adj}}$ (equation (6)) confirm this assumption. From figure 6 and table 1, one can see that the $R_{des}$ decreases when increasing the $Q_{e_{des}}$ (and, correspondingly, the $C_e$ and $C_{e_{des}}$). The maximum percentage value was found to be only about 18.08 %, decreasing down to 1.42 %. Regarding the $K_{d_{adj}}$, which corrects the adsorption (reversible) distribution coefficient $K_d$ in the adsorbate fraction involved in the adsorption equilibrium, it provides almost the same information as the $K_{d_{des}}$ does; both the parameters were found to be satisfactorily correlated: $K_{d_{adj}} = 0.71 K_{d_{des}} + 10.66$ ($R^2 = 0.85$).

3.3. Adsorption and desorption data fit implementing isotherm models

First, the metal adsorption data were fitted to the following empirical models: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (table 4).

The Langmuir model (equation (7)) is based on the fact that the adsorbate is localized on the adsorbent surface by a single mechanism [16]. It is generally stated that a monomolecular layer of the adsorbate is formed on the adsorbent surface, and all the active sites possess equal energy and enthalpy.

The Freundlich model (equation (8)) is used to describe the adsorption process taking place on a heterogeneous surface. Since, according to this model, the adsorption sites have different energy values, the ones possessing maximum energies will be saturated first of all. However, the model does not consider maximum saturation.
According to the Temkin model (equation (9)), either the surface sites are not identical in activity and can be characterized by a certain distribution, or they are the same in activity, but the activity of each site decreases as a result of the appearance of chemisorbed molecules. The more the number of such molecules, the more the initial activity of this site changes, i.e. the activity of each site decreases when increasing the degree of surface coverage with the adsorbate [17].

To study the mechanisms of the adsorption process, the equilibrium data are processed using the Dubinin–Radushkevich isotherm model (equations (10)). It is more general than the Langmuir isotherm, since it does not imply a homogeneous surface and a constant adsorption potential [18]. This model makes it possible to establish the nature (physical or chemical) of the adsorption process on the adsorbent surface, and can be used to calculate the mean free energy of adsorption E (equation (10')). The mechanism of the adsorbate binding is judged by the value of this parameter. If $E < 8 \text{ kJ mol}^{-1}$, the adsorption process is physical, whereas if $8 < E < 16 \text{ kJ mol}^{-1}$, the process is governed by ion exchange, but if $16 < E < 40 \text{ kJ mol}^{-1}$, chemisorption takes place. The $Q_{\text{max}}$ value determines the porosity of the adsorbent: the larger this value, the more developed the porosity, and the smaller the pore diameter [16-19].

Figures 2 and 3 demonstrate the experimental data fitted to the above-mentioned models, and table 3 presents the model parameters obtained.

![Figure 2](image)

**Figure 2.** Isotherms of the metal adsorption on the PHQ/G material: Langmuir (a), and Freundlich (b).

![Figure 3](image)

**Figure 3.** Isotherms of the metal adsorption on the PHQ/G material: Dubinin-Radushkevich (a), and Temkin (b).
Table 4. Parameters of the adsorption isotherm models.

| Model                | Parameters | Model Parameters | Parameters | Parameters | Parameters |
|----------------------|------------|------------------|------------|------------|------------|
|                      |            | Cu²⁺              |            |            |
| Langmuir             | $K_L$      | $Q_{max}$         | $R^2$      |
|                      | 0.0007     | 2176              | 0.9848     |
| Freundlich           | $n$        | $K_F$             | $R^2$      |
|                      | 0.7663     | 4.85              | 0.9783     |
| Temkin               | $K_F$      | $B_T$             | $R^2$      |
|                      | 0.4633     | 257.23            | 0.8869     |
| Dubinin-Radushkevich | $K_D$      | $Q_{max}$         | $E$        | $R^2$      |
|                      | 0.0016     | 609.2             | 17.68      | 0.7354     |
|                      |            | Pb²⁺              |            |            |
| Langmuir             | $K_L$      | $Q_{max}$         | $R^2$      |
|                      | 0.0029     | 2211              | 0.9416     |
| Freundlich           | $n$        | $K_F$             | $R^2$      |
|                      | 0.5909     | 32.48             | 0.8945     |
| Temkin               | $K_F$      | $B_T$             | $R^2$      |
|                      | 0.6572     | 471.41            | 0.9006     |
| Dubinin-Radushkevich | $K_D$      | $Q_{max}$         | $E$        | $R^2$      |
|                      | 0.0021     | 1364.4            | 15.43      | 0.9954     |
|                      |            | Zn²⁺              |            |            |
| Langmuir             | $K_L$      | $Q_{max}$         | $R^2$      |
|                      | 0.0063     | 344               | 0.9329     |
| Freundlich           | $n$        | $K_F$             | $R^2$      |
|                      | 0.3285     | 31.36             | 0.8979     |
| Temkin               | $K_F$      | $B_T$             | $R^2$      |
|                      | 0.0651     | 71.433            | 0.8828     |
| Dubinin-Radushkevich | $K_D$      | $Q_{max}$         | $E$        | $R^2$      |
|                      | 0.0016     | 279.85            | 17.68      | 0.9509     |

The graphic description shows that, in general, all these models are highly fitted to the experimental data ($R^2$ ~0.89-0.98). According to the Langmuir equation, $Q_{max}$ varies in the following sequence: Zn²⁺ (344 mg g⁻¹) < Cu²⁺ (2176 mg g⁻¹) < Pb²⁺ (2211 mg g⁻¹). Comparing these values with those experimentally obtained (Zn²⁺ (300 mg g⁻¹) < Cu²⁺ (800 mg g⁻¹) < Pb²⁺ (1350 mg g⁻¹)), it can be seen that the model overestimates the adsorption capacity more than 2 times for Cu²⁺ and Pb²⁺, thereby implying the occurrence of the other process (e.g., precipitation) parallel to the adsorption. For Zn²⁺, the capacity values almost coincide, indicating the absence of precipitation.

The $E$ values obtained from the Dubinin-Radushkevich model are as follows: 15.43 kJ mol⁻¹, and 17.68 kJ mol⁻¹, (both – Cu²⁺ and Zn²⁺). This means that the ion exchange is the prevailing mechanism for the Pb²⁺ adsorption, whereas the chemisorption governs the Cu²⁺ and Zn²⁺ adsorption.

Judging by the $n$ values of the Freundlich model, it can be seen that Zn²⁺ presents the highest heterogeneity of the adsorption sites on the adsorbent surface (0.3285), followed by Pb²⁺ (0.5909) and Cu²⁺(0.7663). The assumption about the surface heterogeneity is confirmed by the Temkin model.

Using the combined sing- and dual-site Langmuir-Freundlich (or Sips) models (equations (11) and (12)) makes it possible to overcome some limitations of the Langmuir and Freundlich equations, and consider the effect of the heterogeneity of the adsorption sites on the adsorption process, since they contain more parameters and take into account energy changes from zero to infinity [20-22]. Moreover, the dual site model can separately describe the affinities of the sites possessing more or less
energy and estimate their contribution to the process. The graphical interpretation of these models is given in figure 4, and their parameters are presented in table 5.

Both these models fit the adsorption data successfully ($R^2$~0.94-1.00), and thus confirm the assumptions of the Langmuir model (e.g., the existence of the precipitation process for Cu$^{2+}$ and Pb$^{2+}$, and its absence for Zn$^{2+}$). Regarding the surface heterogeneity, based on the dual-site model, from the sum of $Q_{max1}+Q_{max2}$, the contribution of the adsorption sites with higher (H) and lower (L) binding energies (affinities) was determined (H/L, %): for Pb$^{2+}$ - 24/76, for Zn$^{2+}$ - 33/63, and for Cu$^{2+}$ - 60/40. Thus, in the case of the Cu$^{2+}$ adsorption, the process is controlled by higher-affinity surface sites responsible for complexation and chemical interaction, whereas in the case of the Pb$^{2+}$ and Zn$^{2+}$, the lower-affinity sites responsible for electrostatic interactions and ion exchange prevail.

![Figure 4. Langmuir-Freundlich isotherms of the metal adsorption on the PHQ/G material: single-site (a), and dual-site (b).](image)

![Table 5. Parameters of the Langmuir-Freundlich models.](table)

| Adsorbate | Single-site Langmuir-Freundlich | Dual-site Langmuir-Freundlich |
|-----------|---------------------------------|--------------------------------|
|           | $Q_{max}$ | $K_{LF}$ | $n'$ | $R^2$ | $Q_{max1}$ | $K_{LF1}$ | $n_{1'}$ | $Q_{max2}$ | $K_{LF2}$ | $n_{2'}$ | $R^2$ |
| Zn$^{2+}$ | 306       | 0.0075   | 1.563 | 0.9396 | 216       | 0.0056   | 4.020   | 71       | 0.952    | 1.546    | 0.9968 |
| Pb$^{2+}$ | 1372      | 0.0067   | 2.936 | 0.9964 | 5078      | 2.710     | 0.323   | 1214     | 0.007    | 3.473    | 0.9979 |
| Cu$^{2+}$ | 1185      | 0.0021   | 1.525 | 0.9888 | 369       | 0.0022   | 6.994   | 545      | 0.005    | 1.252    | 0.9989 |

Finally, table 6 shows the parameters obtained after fitting the Pb$^{2+}$ desorption data using the Langmuir, Freundlich and single- and dual-site Langmuir-Freundlich (Sips) models.
Table 6. Parameters of the isotherm models for the Pb\(^{2+}\) desorption from the PHQ/G material.

| Langmuir          | Freundlich          |
|-------------------|---------------------|
| \(Q_{\text{max}}\) | \(K_L\)  | \(R^2\) | \(K_F\) | \(n\) | \(R^2\) |
| 1.6 \times 10^6   | 0.0001             | 0.7177  | 23.51   | 2.11  | 0.8406 |

| Dual-site Langmuir-Freundlich | Single-site Langmuir-Freundlich |
|-------------------------------|---------------------------------|
| \(Q_{\text{max}}\) | \(K_{LF}\) | \(n'\) | \(R^2\) | \(Q_{\text{max}1}\) | \(K_{LF1}\) | \(n_1'\) | \(Q_{\text{max}2}\) | \(K_{LF2}\) | \(n_2'\) | \(R^2\) |
| 1107                      | 0.2893       | 10.71   | 0.8936  | 1188            | 0.1437       | 2.37   | 600             | 0.2639       | 9.32   | 0.8822 |

It can be seen that all the models rather adequately describe the process (\(R^2\approx0.72-0.89\)). Besides, the percent contribution of the higher-affinity sites to the Pb\(^{2+}\) desorption is about 34%. Moreover, in this system, the process is difficult to occur (\(n>1\) in the Freundlich equation), which is additionally a favorable factor of the adsorption irreversibility confirmed above by the experimental data.

4. Conclusion
The novel material, PHQ/G nanocomposite, was proposed and tested as an adsorbent to remove Pb\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\) from aqueous solutions. When using this adsorbent, rather high adsorption capacity was obtained, and the adsorption irreversibility was confirmed by the desorption studies and isotherm fitting (e.g., maximum 18 % of Pb\(^{2+}\) is desorbed from the adsorbent in to the aquatic medium). The isotherm studies were carried out implementing the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, as well as single- and dual-site Langmuir-Freundlich (Sips) models, all of which successfully fitted the experimental data. From the analysis of the results obtained, it was found that the adsorbent surface is heterogeneous – at least, two types of adsorption sites are available: higher-affinity (complexation and chemical interactions) and low-affinity (ion exchange and electrostatic interactions), as determined by the dual-site Langmuir-Freundlich equation. For the Cu\(^{2+}\) adsorption, the higher-affinity sites control the process, whereas for the other ions, the lower-affinity ones prevail. Thus, the PHQ/G material can be efficiently used to remove heavy metal ions for water/wastewater purification purposes.

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