

**Sorption of heavy metals from complex solutions using ion exchangers
obtained from peanut shells**

Karimova Dilfuza Eldor qizi

4th-year student of Chirchik State Pedagogical University

Izatillayeva Charos Baxrom qizi

4th-year student of Chirchik State Pedagogical University

Abdurashidova Guljahon Abdunazar qizi

4th-year student of Chirchik State Pedagogical University

Abstract

*This article analyzes the heavy metal sorption properties of ion exchangers obtained from peanut (*Arachis hypogaea*) shells using various chemical modification methods in complex (multi-component) solutions. The research focuses on studying the influence of different modification techniques (H_3PO_4 , KOH, , mercaptoacetic acid, iron oxides) on sorption capacity, inter-ionic competition mechanisms, and selectivity characteristics. The results indicate that the modified ion exchangers exhibit high selectivity in complex solutions, with Pb^{2+} ions predominating over other metals in most cases*

Keywords: *peanut shell, ion exchanger, biosorbent, heavy metals, complex solutions, selectivity.*

Yeryong'oq po'stlog'idan olingan ionitlar yordamida murakkab eritmalarda og'ir metallarni sorbsiyalash

**Сорбция тяжелых металлов из сложных растворов с помощью ионитов,
полученных из шелухи арахиса**

Annotatsiya

*Ushbu maqolada yeryong'oq (*Arachis hypogaea*) po'stlog'idan turli kimyoviy modifikatsiya usullari yordamida olingan ionitlarning murakkab (ko'p komponentli)*

eritmalarda og'ir metallarni sorbsiyalash xususiyatlari tahlil qilingan. Tadqiqot turli modifikatsiya usullarining (H_3PO_4 , KOH, merkapto-asetik kislota, temir oksidlari) sorbsiya sig'imiga ta'sirini, ionlararo raqobat mexanizmlarini va selektivlik xususiyatlarini o'rganishga qaratilgan. Natijalar shuni ko'rsatadiki, modifikatsiyalangan ionitlar murakkab eritmalarda yuqori selektivlik namoyon etadi va Pb^{2+} ionlari ko'pchilik hollarda boshqa metallar ustidan ustunlik qiladi.

Аннотация

*В данной статье анализируются сорбционные свойства ионитов, полученных из шелухи арахиса (*Arachis hypogaea*) с помощью различных методов химической модификации, по отношению к тяжелым металлам в сложных (многокомпонентных) растворах. Исследование направлено на изучение влияния различных методов модификации (H_3PO_4 , KOH, меркаптоуксусная кислота, оксиды железа) на сорбционную емкость, механизмы меж-ионной конкуренции и характеристики селективности. Результаты показывают, что модифицированные иониты проявляют высокую селективность в сложных растворах, причем ионы Pb^{2+} в большинстве случаев преобладают над другими металлами.*

Kalit so'zlar: *yeryong'oq po'stlog'i, ionit, biosorbent, og'ir metallar, murakkab eritmalar, selektivlik*

Ключевые слова: *шелуха арахиса, ионит, биосорбент, тяжелые металлы, сложные растворы, селективность.*

Introduction

The release of heavy metals (lead, copper, cadmium, nickel, chromium) into aquatic environments as a result of industrial and agricultural activities represents a global environmental concern. These metals exhibit high toxicity and pose significant risks to human health and ecosystems [1], [2]. Conventional purification methods

(chemical precipitation, membrane filtration, electrochemical methods) are costly and can produce secondary pollution [3]. Consequently, recent years have seen rapid progress in research focused on developing inexpensive, environmentally friendly, and effective biosorbents.

Agricultural residues, particularly peanut shells, have attracted considerable attention as biosorbents. Peanut shell is a lignocellulosic material consisting of cellulose, hemicellulose, and lignin [4]. These compounds contain hydroxyl, carboxyl, and phenolic groups, which are capable of forming complexes with metal ions [5], [6]. Furthermore, peanut shell is produced in large quantities across many regions of the world and is typically discarded as waste, rendering its use as a biosorbent economically feasible [7].

However, the sorption capacity of raw peanut shell may be relatively low. Consequently, various chemical and physical modification methods—including activation with acids or bases, modification with organic functional groups, and biosorbent preparation via pyrolysis—are employed [8], [9]. These modifications increase the sorbent's comparative surface area, introduce new functional groups, and improve the adsorption of metal ions [10].

In practical settings, wastewater typically contains several heavy metals. Therefore, it is important to investigate the sorption process in complex (binary or multicomponent) solutions. In multicomponent systems, a competitive adsorption process is observed, wherein different metal cations compete with each other to form coordination bonds with the active sites (functional groups) on the sorbent surface. [11], [12]. In this context, the selectivity of the sorbent—namely, its high thermodynamic affinity for a specific metal cation and its preferential adsorption capacity in the presence of other competing ions—is of fundamental importance. [13]

The objective of this article is to analyze the sorption properties of ion exchangers derived from peanut shells in complex solutions for the removal of heavy metals, mechanisms of interionic competition, and selectivity factors. The article provides a detailed review of various modification methods, sorption kinetics and isotherms, as well as the mechanisms of interionic interactions in complex solutions.

Composition and Structure of Peanut Shell

The peanut shell is primarily a lignocellulosic material, containing 35–45% cellulose, 18–25% hemicellulose, and 30–40% lignin [14]. Cellulose and hemicellulose contain numerous hydroxyl (-OH) groups, while lignin contains phenolic and methoxyl groups. These functional groups interact with metal ions via complex formation, ion

$$q_i = \frac{q_{max,i} K_{EL,i} C_i}{1 + \sum_{j=1}^n K_{EL,j} C_j}$$

exchange, and electrostatic attraction [15].

The specific surface area of raw peanut shell is typically around 1–5 m²/g, which limits its sorption capacity [16]. Therefore, modification methods are employed. Treatment with acid or alkali partially degrades the lignocellulosic structure, increases porosity, and exposes new functional groups [17]. The production of biosorbent by pyrolysis (300–700°C) yields a carbonaceous material with a high specific surface area (100–500 m²/g) [18].

Interionic competition in complex solutions

In complex solutions, multiple metal ions compete for the same active sites on the sorbent surface. As a result of competition, the sorption capacity of each metal decreases compared to the mono-component system [24]. The Extended Langmuir Model is used to characterize interionic competition.

q_i (Equilibrium sorption capacity): This is the amount of a specific i -metal (for example, only lead) adsorbed by the Sorbent.

$q_{max,i}$ (**Maximum sorption capacity**): The theoretical maximum amount that can be adsorbed when all active sites of the Sorbent are saturated exclusively with this metal. This indicator represents the 'capacity' of the Sorbent.

$K_{EL,i}$ (Extended Langmuir constant): This parameter is referred to as the affinity coefficient. It indicates the strength of binding between the metal ion and the active sites on the sorbent surface. The higher this parameter, the more strongly the metal adheres to the sorbent.

C_i (**Equilibrium concentration**): After the sorption process is complete, the amount of i -metal ions remaining in the solution.

Selectivity coefficient ($\alpha_{i/j}$)

This parameter determines the ability (selectivity) of the sorbent to preferentially bind one metal over another:

i and j metals: **For example**, i — lead (Pb^{2+}), j — copper (Cu^{2+}).

$\alpha_{i/j} > 1$: The sorbent has a higher affinity for the metal. That is, the peanut shell exhibits greater selectivity for lead over copper.

$\alpha_{i/j} = 1$: The sorbent shows no preference between the two metals and removes both equally.

$\alpha_{i/j} < 1$: The sorbent prefers the other metal (copper).

Chemical modification methods

Various reagents are utilized for the chemical modification of peanut shell. The most widely used methods are as follows:

Modification with H_3PO_4 : In the study by Santos et al., peanut shells were treated with a $\alpha_{i/j} = \frac{K_{EL,i}}{K_{EL,j}}$ 1 M H_3PO_4 solution to obtain the activated peanut shell (AQps) sorbent [1]. This method partially decomposes the lignocellulosic structure, increases the specific surface area, and exposes carboxyl groups. The AQps sorbent effectively removed Cd^{2+} and Pb^{2+} ions from solution.

Modification with KOH: Alkaline modification is also considered an effective method. Treatment with KOH partially dissolves lignin and hemicellulose, resulting in the formation of macro- and micropores [27]. Studies indicate that KOH-modified sorbents demonstrate high selectivity toward Pb^{2+} ions.

Modification with $ZnCl_2$: Modification with zinc chloride is also applied. This method results in the formation of a porous structure with a high specific surface area [28].

Pyrolysis– is the thermal decomposition of peanut shell at high temperatures (300–700°C) in an oxygen-free environment. As a result, a biosorbent with high carbon content, porous structure, and chemical stability is obtained [29].

In the study by Taşar and colleagues, a biosorbent was obtained from peanut shell and used for the sorption of Pb^{2+} ions [8]. The maximum sorption capacity of the biosorbent reached 56.5 mg/g, and the Langmuir model fit the experimental data well [8].

Modification with iron and manganese oxides

Impregnation with iron (Fe) and manganese (Mn) oxides imparts magnetic properties to the sorbent and enhances selectivity. In the study by Chen and colleagues, peanut shell biochar was modified with $FeCl_3$ to obtain Fe-modified biosorbent (FeBC) [3]. This sorbent exhibited high selectivity for Pb^{2+} in mixed solutions of Pb^{2+} , Cu^{2+} , and Ni^{2+} [3].

An increase in specific surface area and the appearance of new functional groups significantly enhance the sorption capacity.

Kinetic models

Various kinetic models are employed to describe the rate of the sorption process. The most commonly used models are the pseudo-first order and pseudo-second order models.

Pseudo-first order model (Lagergren model):

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where q_e – equilibrium sorption capacity (mg/g), q_t – sorption capacity at time t , k_1 – pseudo-first order rate constant (min^{-1}) [31].

Pseudo-second order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where k_2 is the pseudo-second order rate constant ($\text{g}/(\text{mg}\cdot\text{min})$) [32].

Most studies indicate that the pseudo-second order model provides a better fit to experimental data for peanut shell-based sorbents [2], [5], [6], [8]. This demonstrates the predominance of a chemical sorption (chemisorption) mechanism, whereby metal ions form chemical bonds with functional groups on the sorbent surface.

For example, in Xiaoshan's study, the sorption of Pb^{2+} , Cu^{2+} , Cr^{3+} , Cd^{2+} , and Ni^{2+} ions using raw peanut shell was characterized by the pseudo-second order model [2]. In the study by Tashar and colleagues, the pseudo-second order model also provided the best fit for the biosorbent [8].

Isotherm models characterize the relationship between sorption capacity and solution concentration at equilibrium. The most widely used are the Langmuir and Freundlich models.

Langmuir model:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$$

where q_{max} – maximum sorption capacity (mg/g), K_L – Langmuir constant (L/mg), and C_e – equilibrium concentration (mg/L) [33].

Freundlich model:

$$q_e = K_F C_e^{1/n}$$

where K_F – Freundlich constant, and n – sorption intensity parameter [34]. The Freundlich model suggests multilayer sorption and the energetic heterogeneity of active sites.

Thermodynamic parameters

The thermodynamic parameters of the sorption process (Gibbs energy ΔG° , enthalpy ΔH° , entropy ΔS°) describe the degree of spontaneity and the thermal effect of

$$\Delta G^\circ = -RT \ln K_d$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

the process:

where K_d is the distribution coefficient, R is the universal gas constant, and T is the absolute temperature [35].

Various results have been reported in the literature. In some studies, the sorption process is exothermic ($\Delta H^\circ < 0$), and the sorption capacity decreases with increasing temperature [6]. In other studies, endothermic ($\Delta H^\circ > 0$) results have been obtained [8]. These differences are associated with the sorbent preparation method, the type of metal, and experimental conditions.

In all cases, $\Delta G^\circ < 0$, indicating that the sorption process is spontaneous [2], [8].

Interionic competition and selectivity in complex solutions

Competition in binary component solutions

When multiple metal ions are simultaneously present in complex solutions, they compete for the active sites on the sorbent surface. As a result of this competition, the sorption capacity of each metal decreases relative to the mono-component system.

In the study by Santos and colleagues, the sorption of Cd^{2+} and Pb^{2+} ions from a binary solution was investigated using H_3PO_4 -activated peanut shell (AQPs) [1]. The extended Langmuir model was applied, and the following parameters were obtained:

- For Pb^{2+} : $q_{max} = 0.7 \pm 0.1$ mmol/g (144.9 mg/g), $K_{EL} = 40.5 \pm 14.9$ L/mmol

- For Cd^{2+} : $q_{max} = 0.7 \pm 0.3$ mmol/g (78.4 mg/g), $K_{EL} = 5.0 \pm 3.6$ L/mmol

Selectivity coefficient:

$$\alpha_{Pb/Cd} = \frac{K_{EL,Pb}}{K_{EL,Cd}} = \frac{40.5}{5.0} = 8.1$$

This result demonstrates that the AQPs sorbent adsorbs Pb^{2+} ions eight times more than Cd^{2+} ions [1]. This can be attributed to the larger ionic radius of Pb^{2+} and its greater propensity to form covalent bonds.

In the study by Gama and colleagues, the sorption of Cd^{2+} and Cu^{2+} ions in mono- and binary-component solutions was investigated using peanut shell biosorbent (BPS) [4]. In binary-component solutions, the sorption capacity of both metals decreased, confirming the effect of interionic competition [4].

Competition in multicomponent solutions

In Xiaoshan's study, the sorption of five different metal ions (Pb^{2+} , Cu^{2+} , Cr^{3+} , Cd^{2+} , Ni^{2+}) from a multicomponent solution using raw peanut shell was investigated [2]. According to the Langmuir model, the maximum sorption capacities are as follows:

- Pb^{2+} : 32.25 mg/g
- Cu^{2+} : 7.09 mg/g
- Cr^{3+} : 3.82 mg/g
- Cd^{2+} : 2.95 mg/g
- Ni^{2+} : 2.22 mg/g

These results indicate that the sorption capacity decreases in the following order: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cr}^{3+} > \text{Cd}^{2+} > \text{Ni}^{2+}$ [2]. This sequence is associated with the chemical properties of the metals.

In the study by Chen and colleagues, the sorption of Pb^{2+} , Cu^{2+} , and Ni^{2+} from complex solutions using Fe-modified biosorbent was investigated [3]. The results indicated that the biosorbent exhibits high selectivity toward Pb^{2+} [3]. This is attributed to the strong complex formation ability of iron oxides with Pb^{2+} .

Factors determining selectivity

In complex solutions, the selectivity of the sorbent depends on several factors:

1. Chemical properties of the metal ion:

- *Ionic radius*: A higher ionic radius (Pb^{2+} : 1.19 Å) demonstrates greater selectivity compared to metals with a lower ionic radius (Ni^{2+} : 0.69 Å) [36].

2. Functional groups on the sorbent surface:

- Carboxyl (-COOH) and hydroxyl (-OH) groups form complexes with a broad range of metals, but the selectivity is lower [40].

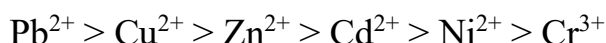
- Iron and manganese oxides exhibit higher selectivity towards Pb^{2+} and Cd^{2+} [3], [30].

3. Solution conditions:

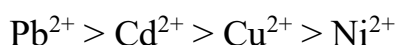
- *pH*: Changes in pH affect the degree of protonation of functional groups and the hydrolysis of metal ions [41]. Typically, a pH of 5–6 is considered optimal.

Based on literature analysis, the general selectivity order for peanut shell-based sorbents is as follows:

Raw and acid/alkali-modified sorbents:



Sorbents modified with iron/manganese oxides:



These experiments depend on the modification method and the nature of the functional groups. However, in all cases, Pb^{2+} demonstrates the highest selectivity, which can be attributed to its chemical properties (large ionic radius) [2], [3], [5], [14].

Comparative analysis of modification methods

The following criteria are important for comparing the efficiency of different modification methods:

1. *Selectivity*: Modification with iron oxides provides high selectivity toward Pb^{2+} [3].

2. *Economic efficiency*: Modification with H_3PO_4 and KOH is relatively inexpensive and straightforward [1].
3. *Regeneration capability*: Biosorbent and modified sorbents can be effectively utilized over multiple cycles [4], [9].
4. *Environmental safety*: Raw peanut shells and biosorbents do not require chemical reagents and are easy to dispose of [8].

In practical applications, it is necessary to balance these factors. For example, for industrial wastewater containing high concentrations of Pb^{2+} , iron-modified sorbents are preferable. In cases where an inexpensive and environmentally friendly solution is required, H_3PO_4 modification or biosorbent use is appropriate.

Conclusion

In this article, the sorption properties of ion exchangers derived from peanut shells in the removal of heavy metals from complex solutions, mechanisms of interionic competition, and factors influencing selectivity were analyzed. The main conclusions are as follows:

1. *Modification methods significantly increase the sorption capacity*. Modification with H_3PO_4 and KOH is economically efficient [1], while modification with iron oxides imparts high selectivity [3].
2. *The sorption process is primarily characterized by pseudo-second-order kinetics and the Langmuir isotherm*. This demonstrates the superiority of the chemical sorption mechanism and indicates monolayer sorption [2], [5], [6], [8].
3. *In complex solutions, interionic competition decreases the sorption capacity*. The extended Langmuir model is an effective tool for characterizing binary and multicomponent solutions [1], [4].

4. *The order of selectivity is primarily as follows: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$. This order is explained by the chemical properties (ionic radius) of the metal ions [2], [3], [5], [14].*
5. *The modification method alters selectivity. Iron oxides provide high selectivity for Pb^{2+} [3], [5].*
6. *pH, ionic strength, and the initial concentration ratio significantly influence sorption efficiency. The optimal pH is typically in the range of 5–6 [1], [2], [8].*
7. *Peanut shell-based ion exchangers can be practically applied in industry, agriculture, and drinking water purification. They are considered inexpensive, environmentally friendly, and effective biosorbents [7], [46].*

Further experimental and theoretical studies are required to obtain a deeper understanding of interionic competition and selectivity in complex solutions.

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