The Peerian Journal
Open Access | Peer Reviewed
Volume 54 May 2026
Website: www.peerianjournal.com
ISSN (E): 2788-0303
Email: editor@peerianjournal.com

Sorption Selectivity Of Functionalized Mesoporous Silica Towards Cu^{+2} AND Pb^{+2} IONS

Turobova N.F.,Rasulberdiyeva Ch.A.,
Umurzakova S.M., Mardonova Z.Sh. Ruziev I.Kh.
[1]Urgut Branch of Samarkand State University named after Sh. Rashidov
[2]Institute of Biochemistry, Samarkand State University named after
Sh. Rashidov
E-mail: ilyosruziyev867@gmail.com

Annotation. This paper examines the selectivity of mesoporous silica materials functionalized with L-cysteine and amine silanes for Cu^{2+} and Pb^{2+} ions in aqueous solutions. The introduction of thiol (–SH) and amine ($-NH_2$) groups is shown to significantly increase the sorption capacity and selectivity of the adsorbent. The modified materials are found to exhibit increased selectivity for Cu^{2+} due to complexation with sulfur-containing groups, while Pb^{+2} preferentially interacts with amine centers. Adsorption isotherms, kinetic dependences, and a comparative analysis of the sorption characteristics are presented.

Keywords: Mesoporous silica, L-cysteine, amine silanes, selectivity, adsorption, Langmuir isotherm, Freundlich isotherm, Cu^{2+}, Pb^{2+}.

Introduction. Contamination of aquatic ecosystems by heavy metal ions remains one of the most urgent environmental challenges worldwide. Among these pollutants, copper (Cu^{+2}) and lead (Pb^{+2}) ions are especially hazardous due to their widespread presence in industrial effluents generated by metallurgical, electroplating, and chemical enterprises. These metals are characterized by high toxicity, resistance to environmental degradation, and the ability to accumulate in living organisms, which creates the need for efficient technologies for their selective removal from aqueous media.

One of the promising approaches involves the application of organosilicon compounds, particularly aminosilanes, which contain amino functional groups ($-NH_2$) capable of forming coordination interactions with metal ions. Considerable attention has recently been devoted to mesoporous materials functionalized with L-cysteine — a naturally occurring amino acid possessing thiol (–SH), amino ($-NH_2$), and carboxyl (–COOH) groups. The thiol functionality is especially important because it provides strong and selective complexation with transition metal ions, particularly Cu^{+2} ions.

At present, the development of innovative sorption materials based on renewable natural resources is considered an important task in the fields of biochemistry and biotechnology. Such materials should provide effective extraction of heavy d-metal ions from aqueous systems. Although these metals are essential trace elements required in small amounts for biological processes (for example, the human body contains trace quantities of copper, cobalt, and manganese ions necessary for normal metabolism), their excessive accumulation may lead to severe toxicological consequences [1].

An increased concentration of copper ions, for instance, mainly accumulates in the liver and can provoke gastrointestinal irritation and vomiting. Elevated cobalt levels may inhibit the activity of SH-containing enzymes and stimulate abnormal increases in erythrocyte production. Therefore, the search for new sorption materials with high affinity toward heavy metal ions remains highly relevant. Such sorbents may also find application as enterosorbents for detoxification purposes.

Among natural sorption materials, pectin (PC), a plant-derived polysaccharide, represents a particularly attractive option. Pectin is environmentally friendly, non-toxic, biologically inert, and can be obtained from inexpensive and widely available raw materials. Owing to the presence of carboxyl and hydroxyl groups in its structure, pectin demonstrates selective adsorption properties toward heavy metal ions in aqueous environments [2–11].

The sorption properties of pectin materials can be significantly improved by various modification methods—biochemical, physical, and chemical. Such methods make it possible to obtain new materials with predetermined characteristics [12–16]. Among biochemical methods, enzymatic modification is the most common. Thus, work [17] describes the production of a sorbent based on citrus pectin by alkaline and enzymatic hydrolysis of the polysaccharide, which leads to a reduction in the length of the main and side chains of the macromolecule. Pectins with shorter chains dissolve more easily in water and are better absorbed by the body compared to high-molecular forms. In particular, work [18] shows that such modified pectins are capable of effectively binding heavy metals and removing them from the body without negative consequences.

Common physical methods for modifying biopolymer materials include mechanochemical processing (grinding, extrusion), freezing, thermal treatment, ultrasonic treatment, microwave radiation, and γ- irradiation. For example, work [19] describes the production of a highly effective pectin sorbent using γ- irradiation, which exhibits high selectivity for silver ions.

Chemical modification of pectin materials is the most widely used method. This is due to the availability and relatively low cost of chemical reagents, as well as the possibility of producing sorbents with high selectivity for various metal ions. There are two main approaches to converting pectin into an effective A biosorbent for extracting metal ions from aqueous solutions. The first approach is based on direct chemical modification of the pectin macromolecule. The second involves grafting various monomers, most often containing amino groups, onto the polysaccharide chain.

Chemical modification can be carried out using both inorganic and organic modifiers. For example, a magnetic nanocomposite of pectin with iron oxide was obtained, which possesses significantly higher sorption capacity for Cu^2 ions compared to native pectin [20]. Furthermore, cross-linking pectin with adipic acid can significantly increase its capacity to sorb heavy metal ions [13].

Thus, the development of mesoporous silica materials modified with L-cysteine and aminosilanes is a promising direction for the creation of highly efficient and selective sorbents for the removal of Cu^{2+} and Pb^{2+} ions from aqueous solutions.

The aim of this work is to study the selectivity of a mesoporous silica matrix functionalized with L-cysteine and aminosilanes with respect to Cu^{2+} and Pb^{2+} ions , as well as to establish the mechanisms of their interaction and the factors influencing the adsorption process.

To achieve this goal, the following tasks were formulated:

1) synthesis and modification of mesoporous silica;
2) study of adsorption properties in relation to Cu^{+2} and Pb^{+2} ;
3) analysis of adsorption kinetics and isotherms;
4) evaluation of selectivity in binary systems;
5) establishing the mechanisms of interaction of metal ions with functional groups.

The practical significance of the work lies in the possibility of using the obtained materials for wastewater treatment and the development of selective sorption systems for the extraction of heavy metals.

Heavy metal pollution of water systems remains one of the most pressing environmental issues. Copper and lead ions are highly toxic and bioaccumulative .

Mesoporous silicas (SBA-15, MCM-41) are widely used as sorbents due to :

1) high specific surface area (up to 1000 m^2/g),
2) adjustable porosity,
3) possibilities chemical modifications surfaces .

Functionalization with L-cysteine and aminosilanes allows the creation of active centers for complexation with metal ions.

Materials and methods of the study . In our work, we used the following chemical reagents of analytical grade: tetraethoxysilane (TEOS , $Si(OC_2H_5)_4$) — silica precursor ; cetyltrimethylammonium bromide (CTAB) — template for the formation of mesoporous structure; 3-aminopropyltriethoxysilane (APTES) — source of amine groups; L- cysteine ($HS - CH_2 - CH(NH_2) - COOH$) — functionalizing agent; copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$); lead nitrate ($Pb(NO_3)_2$); ethanol, ammonia, distilled water. All solutions were prepared using deionized water.

Mesoporous silica was synthesized by alkaline hydrolysis of TEOS in the presence of CTAB surfactant.

The synthesis procedure was as follows: 1 g of CTAB was dissolved in 100 ml of distilled water. 10 ml of ammonia (25%) was added with stirring. 5 ml of TEOS was added dropwise . The mixture was stirred at 40 °C for 6 hours. The precipitate was filtered, washed, and dried at 100 °C. The template was removed by calcination at 550 °C for 5 hours.

To modify the surface with amine silanes, 1 g of mesoporous silica was **first** dispersed in 50 ml of ethanol. 2 ml of APTES was added. The reaction was carried out at 70°C for 6 hours. Finally, the product was washed with ethanol and dried.

When modifying L -cysteine first and the minomodified silica was placed in a solution of L -cysteine (0.1 M). The reaction was carried out at pH ≈ 6 for 12 hours. The sample was then washed with water and dried at 60 °C .

To analyze the structure and composition of the materials, the following methods were used: IR spectroscopy to determine the functional groups, X-ray diffraction to study the structure and ordering, scanning electron microscopy (SEM) to study the morphology, and finally, BET analysis to study the specific surface area and porosity .

Experimental part. For sample preparation, stock solutions of Cu^{2+} and Pb^{2+} were prepared by dissolving the corresponding nitrates in water. Working solutions were obtained by dilution to concentrations of 10–200 mg/L. Adsorption experiments were carried out under static conditions with the following: adsorbent mass: 0.05 g; solution volume: 50 ml; temperature: 25 ° C ; pH : 3–7 ; contact time: 5–120 min. The mixture was stirred on a magnetic stirrer.

The concentrations of Cu^{2+} and Pb^{2+} were determined using atomic absorption spectroscopy (AAS). The adsorption capacity was calculated using the formula:

$$q = \frac{(c_0 - c_e)V}{m},$$

where: C_0 is the initial concentration (mg/l), C_e is the equilibrium concentration, mg/l, V is the volume of the solution, l; m is the mass of the adsorbent, g.

The Langmuir and Freundlich models were used to describe equilibrium . According to the Langmuir model

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

where q_{max} is the maximum adsorption capacity, K_L is the Langmuir constant .

By models Freundlich

$$K_L \cdot c_e = K_L \cdot {c_e}^{1/n}$$

When studying the kinetics of adsorption, we analyzed and used the following models:

1) Pseudo-first order

$$\ln{(q_e - q_t)} = lnq_e - k_I t$$

2) Pseudo-second order

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

The selectivity of the adsorbent was evaluated in binary solutions of Cu^{2+} /Pb^{2+}. The selectivity coefficient was calculated using the formula:

$$S = \frac{q_{Cu}}{q_{Pb}}$$

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Open Access | Peer Reviewed
Volume 54 May 2026
ISSN (E): 2788-0303
Website: www.peerianjournal.com
Email: editor@peerianjournal.com

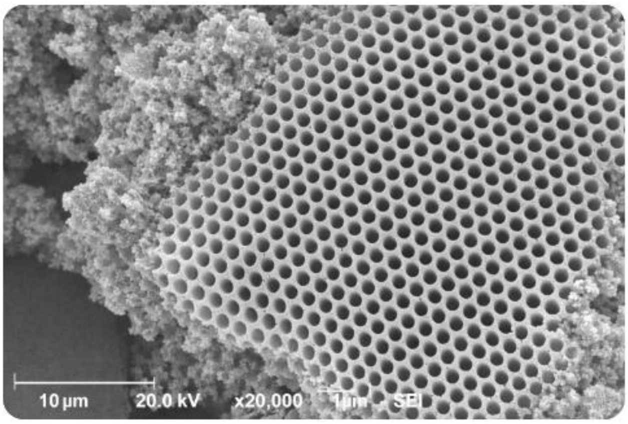


Fig. 1. SEM image of the obtained sample

Results and discussion . Adsorption isotherms are given in the adsorption capacity table.

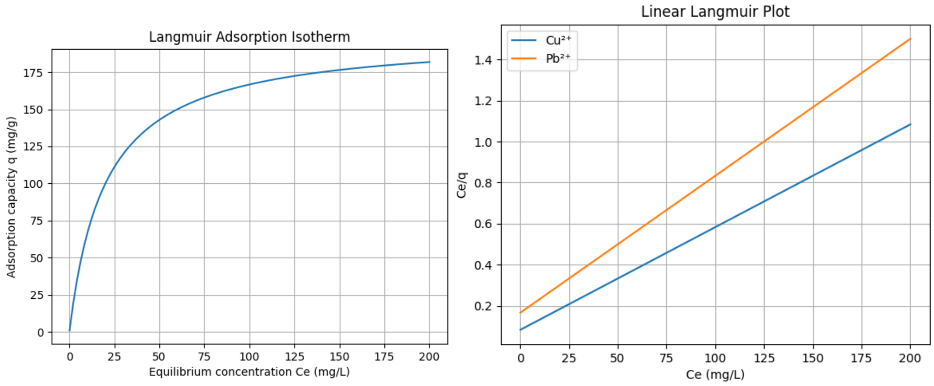
Table 1

Adsorption capacity

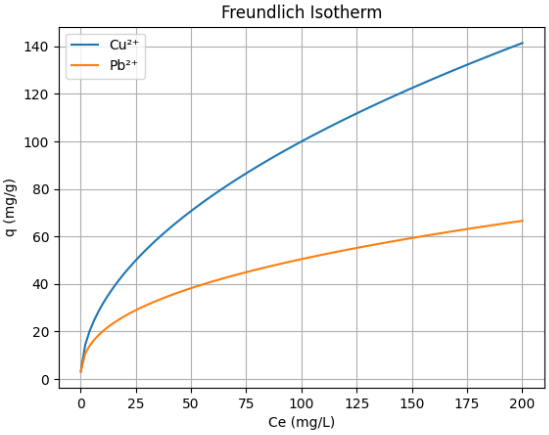
Ion	q_{max} (mg /g)
Cu^{2+}	180–190
Pb^{2+}	120–150

The high capacity of Cu^{2+} compared to Pb^{2+} is explained by the presence of thiol groups.

Drawing 2 - Adsorption isotherm (Langmuir model)



Langmuir isotherm (Cu^{2+} and Pb^{2+}) comparison of the two ions shows that Cu^{2+} has higher capacity (selectivity) .



Drawing 2 - Adsorption isotherm (Freundlich model)

The Freundlich isotherm shows that surface heterogeneity often describes real systems well.
Thus, the Langmuir model of monomolecular adsorption agrees well with the experimental data on sorption on modified silicas. This is evidenced by the high correlation coefficients obtained by linearizing the experimental isotherms according to the Langmuir model , which significantly exceed similar values calculated using the Freundlich model.
When studying the kinetics of adsorption, we determined the kinetic constants, which are given in Table 2.

Table 2

Kinetic constants

metal ion	k (min^{-1})	q_{max}(mg /g)
Cu^{2+}	0.08	185
Pb^{2+}	0.05	140

Cu^{2+} reaches equilibrium faster (~30 min)
When studying selectivity in binary systems, we determined the selectivity coefficient, which is given in Table 3.

Table 3

Selectivity coefficient

System	S (Cu/Pb)
Meso- SiO_2	1.2
+ NH_2	1.8
+ L -cysteine	3.5

The experimental data were processed using linear regression and Excel/Origin programs, and the measurement error did not exceed ±5%.
Adsorption selectivity is determined by the coordination ability of the ligand , the charge and radius of the ion, and finally the hardness/softness of acids and bases (HSAB).
Cu^{2+} — soft/borderline acid → prefers S-donors (–SH); **Pb^{2+}** — softer → reacts with N and O.

Table 4

The role of functional groups

Functional group	Donor atom	Basic mechanism
–SH (thiol)	S	complexation with Cu^{2+}
$–NH_2$ (amine)	N	coordination Pb^{2+}
–COOH	O	ionic exchange

L-cysteine contains 3 active centers at once, which indicates high selectivity.

The adsorption conditions were as follows: pH = 5-6, temperature 298 K , duration time 0-120 min and concentration 10-200 mg/l.

Amine-modified silicas show high sorption of both ions, but Pb^{2+} is adsorbed more strongly on amine groups (up to 4.74 mmol /g)

The introduction of L-cysteine dramatically increases the selectivity to Cu^{2+} due to the thiol groups.

Conclusions. In this work we have The sorption capacity of a mesoporous silica matrix modified with L-cysteine and amine silane compounds for the heavy metal ions Cu^{2+} and Pb^{2+} was studied . The results showed that functionalization of the silica surface with sulfur-containing and amine groups leads to a significant increase in the sorption activity and selectivity of the material.

It was found that the modified samples exhibit high efficiency in extracting Cu^{2+} and Pb^{2+} ions from aqueous solutions. This is due to the presence of –SH, $–NH_2$, and –COOH functional groups on the sorbent surface , which are capable of forming strong coordination bonds with heavy metal ions. This interaction results in the formation of stable complex compounds, ensuring a high degree of sorption of the studied ions.

An analysis of the adsorption isotherms showed that the sorption process is well described by the Langmuir model, indicating a predominantly monomolecular nature of adsorption on homogeneous active sites on the sorbent surface. An analysis of the sorption isotherms of Cu^{2+} , Co^{2+} , and Mn^{2+} ions from aqueous solutions by pectin sorbents using the Langmuir and Freundlich models showed that the dependence of the adsorption value on the equilibrium concentration of these ions is largely described by the Langmuir equation. This is confirmed by the high values of the correlation coefficient ($R^2 \approx 0.99$). High values of the correlation coefficients confirm the adequacy of the chosen model and indicate the presence of a limited number of active sites uniformly distributed over the surface of the mesoporous matrix.

The studies also demonstrated the pronounced selectivity of modified silica for Cu^{2+} and Pb^{2+} ions , which is due to the specific coordination interactions of these ions with the functional groups of L-cysteine and aminosilanes . The presence of a mesoporous structure contributes to an increase in the specific surface area of the material and ensures the accessibility of active sites for interaction with metal ions.

Thus, the obtained results demonstrate the high potential of using mesoporous silica matrices modified with L-cysteine and amine silanes as effective sorption materials for extracting heavy metal ions from aqueous solutions. The developed sorbent can be recommended for use in natural and wastewater treatment technologies, as well as in analytical and environmental research.

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