SORPTION OF Pb(II) IONS OF A POLYCOMPLEXONE CONTAINING AMINO AND SULFOGROUP

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Abstract

In this article, a new polyampholyte containing amino and sulfo groups was obtained by adding polyethylenpoliamine to a sulfocation exchanger resin obtained from polyvinyl chloride. The absorption patterns of Pb^{2+} ions from artificial solutions into a new polyampholyte based on polyvinyl chloride containing amino and sulfo groups were studied. As a result, an isotherm of the sorption process was constructed, and the equilibrium constant of adsorption, and thermodynamic parameters were found: the values of the isobaric-isothermal potential (ΔG), enthalpy (ΔH) and entropy (ΔS).

Keywords: PVC ompound. polyampholyte, sorption, ion exchanger, lead ion. kinetics. pseudofirst and pseudosecond kinetic models.

1. INTRODUCTION

On a global scale, environmental pollution with toxic metals occurs as a result of the activities of many industrial enterprises, the hydrometallurgical industry, the production of paint products, military operations, and agricultural emissions. Additionally, in the hydrometallurgical method, technological solutions formed during the extraction of metals contain ions of nonferrous and heavy metals, such as copper, nickel, lead, and mercury [1]. Almost all different heavy metals can be found in wastewater from many industries [2]

In particular, an increase in the concentrations of ions such as Pb^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+} and Zn^{2+} in such waters has a harmful effect on the environment [3, 4].

Currently, ion exchangers are widely used for the desalination of water used in industrial enterprises [5]. Among the methods for softening water hardness, especially those involving calcium and magnesium ions in natural water, the most common method involves ion exchange with the participation of ion exchangers [6]. The areas of application of ion exchangers and ion exchange processes are continuously expanding. In particular, at present, synthetic, granular ion exchange materials are used for the desalination of water used in the chemical industry. for the purification of wastewater from various harmful-ions and for concentrating ions of nonferrous, rare and precious metals in process solutions in hydrometallurgy. Ion exchangers containing nitrogen and sulfur, especially-in- granular-ion-exchange sorbents, are distinguished by their selectivity toward ions of precious, rare and nonferrous metals [7, 8].

The functional groups in certain types of ion exchange materials vary depending on the type: strongly acidic sulfonate groups ($-SO_3H$) weakly acidic carboxyl groups (-COOH), strong-basic-quaternary amines ($-N-R_3$) and weakly basic tertiary and secondary amino groups ($-N^+R_2H$ and $-N^+RH_2$) [9]. Sorbents used in various industries must meet a number of requirements [10]. In this article, a new polyampholyte-containing amino and sulfo groups was obtained by adding polyethylenpoliamine to a sulfocation exchanger resin obtained from polyvinyl chloride. Therefore, one of the pressing issues is the synthesis of new ion-exchange ion exchangers with a high sorption capacity for metal ions. Considering similar problems, the law of absorption of Pb^{2+} ions from artificial solutions into an ion exchange resin under static conditions by polycomplexone containing nitrogen and sulfur in a polyvinyl chloride-based plasticizer was studied [11].

There are many theories for describing ion exchange processes [12, 13]. Over the years, when modeling the rate constants of various ion exchange reactions, Lagergren's equations and others have mainly focused on changes in the kinetic analysis process. [14, 15, 16]. Research has established isotherms of the sorption process. as well as the adsorption equilibrium constant and thermodynamic parameters, such as the isobaric-isothermal potential (ΔG). enthalpy (ΔH) and entropy (ΔS) [17].

Therefore, polycomplexes containing amino and sulfo groups help to remove heavy metal ions and lead ions from wastewater.

Materials and methods

Modifications of polyvinyl chloride (PVC) with sulfur to obtain such polymers have been studied. A sulfocation-exchange resin can be obtained by oxidizing the sulfur in PVC to a cation-exchange sulfonate group. The physicochemical properties of many of these ion exchangers have been studied. To date, the sorption properties of ion exchange resins based on polyvinyl chloride have been studied. In the experiment, the sorption of Pb^{2+} ions from artificial solutions into a polyampholyte obtained on the basis of PVC was studied. To do this, using $Pb(NO_3)_2$ salt, we prepared solutions of Pb ions with concentrations of 0.025, 0.05, 0.075, and 0.1 mol L-1. and studied the duration of metal ion sorption from prepared artificial solutions for 2, 4, 6, and 8 hours, as well as sorption isotherms at temperatures of 293, 303 and 313-K. For this purpose, a dry sorbent with a static exchange capacity of 4.5 mg-eq.g 1-for-HCl-and-3.5 mg-eq-g-1 for NaOH was measured on an analytical balance (0.3 g each) and placed in conical flasks with a volume of 250 mL filled with 100 mL of saline solution. The change in the concentration of metal ions in solution before and after sorption was detected using a UV-1900i spectrophotometer (Shimazu, Japan) (wavelength 295 nm for Pb^{2+}) [18].

The amount of metal ions absorbed by the sorbent was calculated using the following equation:

$$q_e = \frac{\left(C_0 - C_p\right)}{m} \times V$$

In this case, qe is the amount of absorbed metal ions in the ion exchanger in mol/g, Co is the initial concentration of metal ions in mol/L, Cp is the equilibrium concentration of metal ions in mol/L, V is the solution volume L, and m is the mass of dry sorbent (g) [19].

The results obtained and their discussion

To study the dependence of the time of absorption of Pb(II) ions by polyampholytes from artificial solutions and from water-soluble lead salts, solutions with different concentrations were prepared, and the absorption rate was determined at different times [20]. The results obtained are shown in Figure 3.1

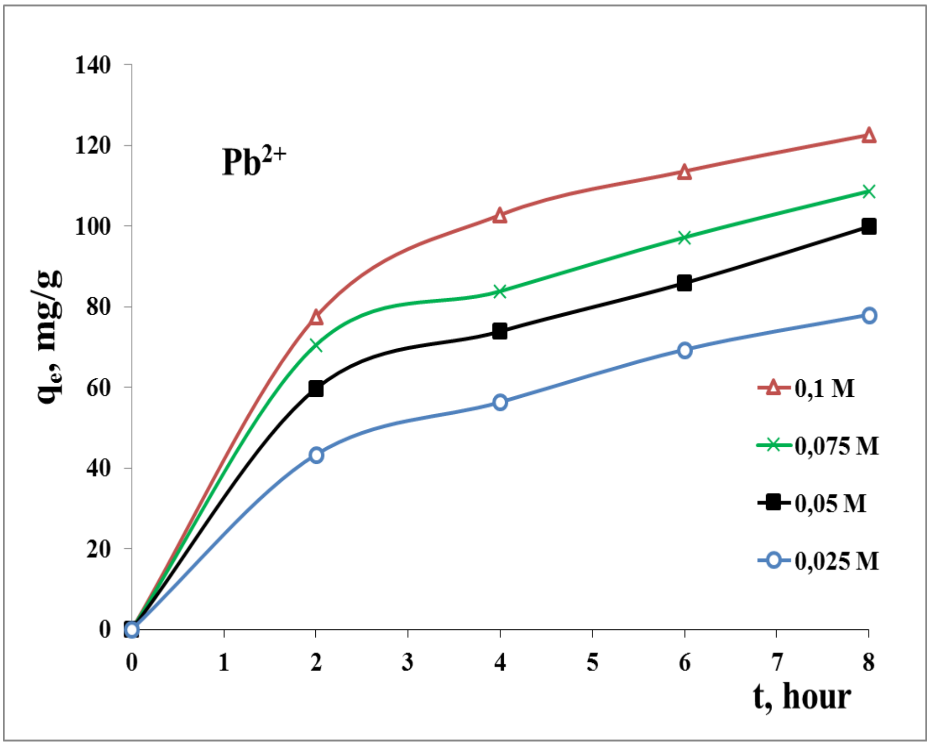
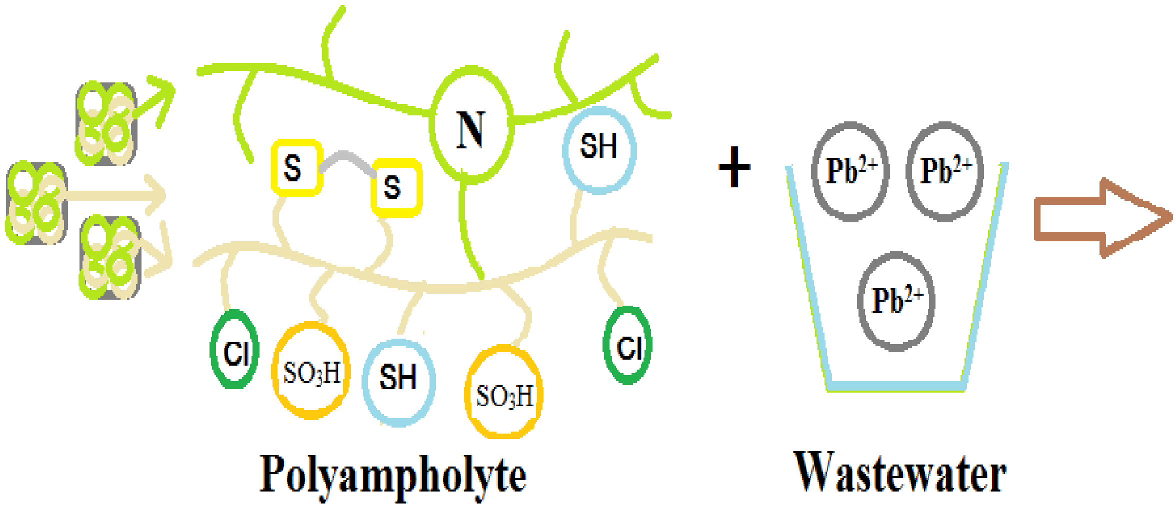


Figure 1. Kinetics of sorption of Pb^{2+} ions in the resulting polyampholyte



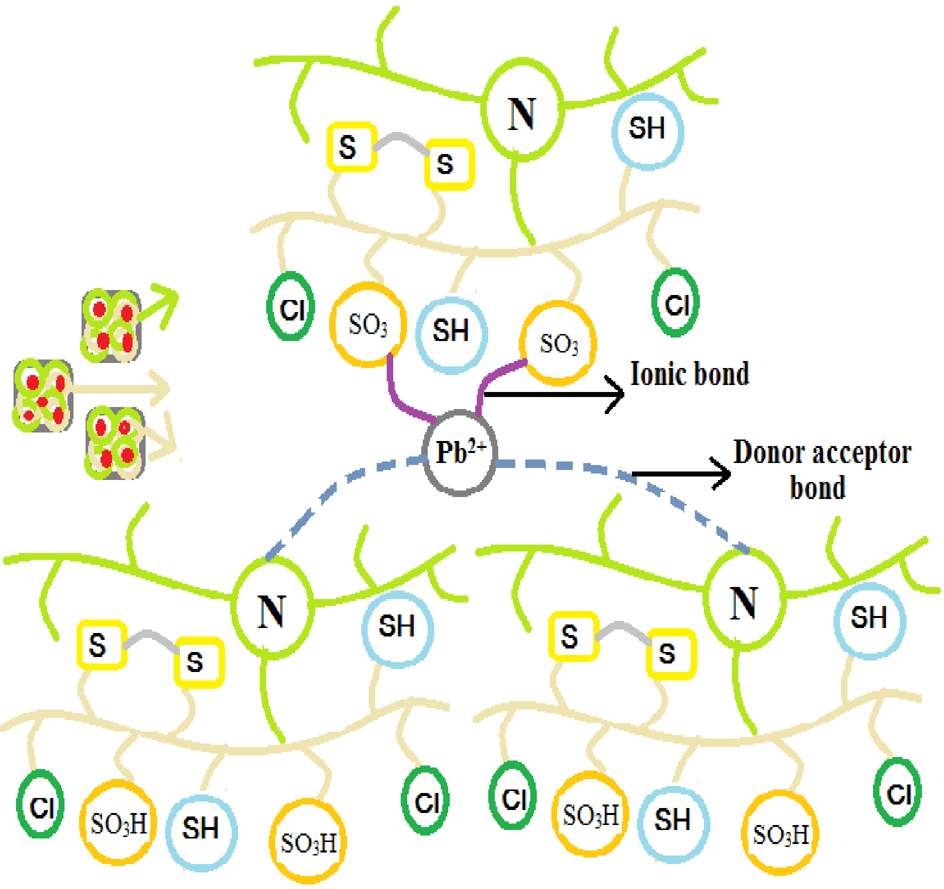


Figure 2. Ion exchange and complexation of metal ions on the polyampholyte

From the above figure, it can be seen that the degree of absorption of Pb(II) ions by the polyampholyte increases with increasing time. The sorption of metal ions occurs on the basis of electrostatic interactions between metal cations and their groups on the surface of the ion exchanger, as well as on the basis of the coordination bond between the >NH groups in the ion exchanger. This indicates that the process involved chemical-sorption.

Adsorption isotherms are the most important tools for analyzing equilibrium processes. To express equilibrium processes in liquid and solid systems, the Langmuir model, which is the most widely used and convenient model, is widely used.

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

where qe is the amount of metal absorbed by a sorbent of known mass (mg/g), Cp is the equilibrium concentration of the solution (mg/L), and qmax'is the maximum amount of metal absorbed by a sorbent of known mass (mg/g) [21].

To determine the Langmuir constant (KL), the linear form of the Langmuir equation shown below is used

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

The values of q_{max} and K_L are determined from the graph of C_p/q_e versus C_p.

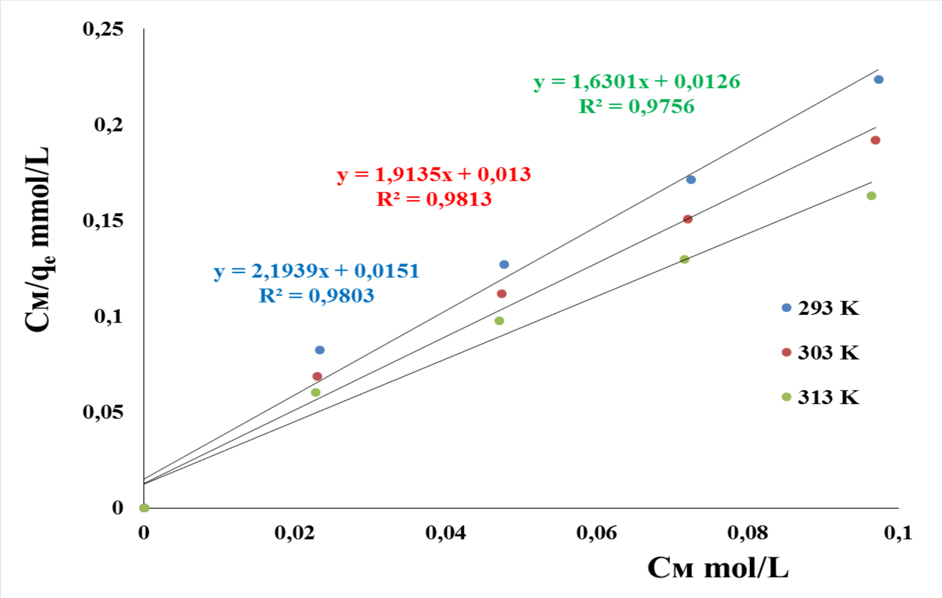


Figure 3. Langmuir isotherm for Pb^{2+} ions on the polyampholyte

As shown in Figure 3.3, Langmuir constants were calculated for the sorption of Pb^{2+} ions from solutions at temperatures ranging from 293-K-to 313 K-into the PVC-based polyampholyte. Based on the results obtained, the infinite equilibrium constant of adsorption and sorption was calculated using the Langmuir equation.

Table 1.

Equilibrium constant for the reaction of Pb(II) ions to polyampholyte and changes in thermodynamic functions

Metal ions	T, K	q_∞, mmol/g	K, L/mol	$-\Delta G^0$, J/mol	$-\Delta H^0$, J/mol	ΔS^0, J/mol•K
Pb(II)	293	90,125	145,29	3441	4369	26,66
	303	104,55	146,07	3708		
	313	122,57	129,37	3974		

From the table below, it can be seen that the value of qmax calculated from the Langmuir equilibrium constant increased at temperatures-of-293, 303-and-313- K. The ΔH values shown in this table are positive, and the adsorption process is endothermic. Additionally, an increase in the entropy of the system indicates the occurrence of an ion exchange reaction between Nations on the surface of the sorbent and Pb(II) ions in the erythema. The decrease in free energy indicates that the sorption of Pb(II) ions in the polyampholyte occurs on its own.

Conclusion

A new polyampholyte was obtained as a result of the addition of the sulpho- cation exchanger obtained on the basis of PVC in this study. Physicochemical- analysis revealed that the obtained polyampholyte contains S and N, as well as S and N. that bind to the PVC chain, forming sulfonate and amine groups, respectively. Adsorption of the obtained polyampholyte in artificial solutions containing Pb(II) ions at different initial concentrations and temperatures. Moreover, the changes in thermodynamic parameters during the sorption process are exothermic. This indicates that the s indicates that the metal ions are chemically absorbed into the polyampholyte. These results revealed the complex sorption of polyampholyte Pb(II). Modified PVC, containing S and N, shows that a polyampholyte can be used as an effective ion exchange agent for the purification of Pb(II) ions from wastewater.

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