

Sorption of Ca^{2+} and Mg^{2+} ions of sulphocationite obtained by S modification of polyvinyl chloride using CaS_x solution.

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Abstract

In this work, $-\text{SO}_3\text{H}$ groups in the material obtained from polyvinyl chloride, a new ion-exchange resin for purifying water from metal ions, were proven and their physicochemical parameters were determined. Kinetics and isotherms of sorption of Ca^{2+} and Mg^{2+} ions from aqueous solutions in PVC-SC were studied. The results showed that the adsorption of Ca^{2+} and Mg^{2+} ions from aqueous solutions on PVC-SC was consistent with Langmuir's monomolecular theory. This indicated that PVC-SC was chemisorbed by absorbing Ca^{2+} and Mg^{2+} ions from aqueous solutions.

Keywords: polyvinyl chloride, sulphur, sorption, cationite, calcium and magnesium, isotherm.

1. Introduction

Many countries are facing environmental problems due to improper disposal of waste generated as a result of industrial activities. Pollutants formed in water bodies have a harmful effect on the environment even at low concentrations. Recently, there are some methods of water purification such as chemical precipitation, solvent extraction, oxidation, reduction, dialysis, electro dialysis, electrolytic extraction, reverse osmosis, ion-exchange, evaporation, cementation, dilution, adsorption, filtration, flotation, air stripping, steam stripping, flocculation, sedimentation and soil flushing/washing chelation which ion exchange resins are widely used to purify Ca^{2+} and Mg^{2+} ions, which cause water hardness [3-5]. The most common reason for the purification of water from contaminants by the adsorption method is its technological simplicity, ease of process, repeated recycling of ion exchange material by recycling, and cost-effectiveness.

Water hardness is caused by metal ions such as iron, manganese, calcium, and magnesium, especially calcium and magnesium ions. The sorption of Ca^{2+} and Mg^{2+} ions for water purification in the food industry from existing ion exchange resins on a weak acidic resin PC200FD was studied [5]. The adsorption equilibrium of calcium to an aqueous solution of synthetic ion exchange resin Purolite C100E was also studied, and the Langmuir and Freundlich isothermal models were used [6]. The authors [7] determined the structure of the ion exchange resin by modifying the cellulose with amines by IR spectroscopy. The absorption rate and equilibrium of Ca^{2+} and Mg^{2+} ions from aqueous solutions to the obtained ion exchange resins were studied, with the maximum sorption rate for the Langmuir isotherm model being 54.1 mg/g for Ca^{2+} and 42.6 mg/g for Mg^{2+} . New anion exchange material obtained by modification of polyvinyl chloride has been studied in water treatment for industrial use [8]. The pseudo-first and pseudo-second models of the sorption kinetics of Ca^{2+} and Mg^{2+} ions from aqueous solutions to the sulpho-cation exchange resin obtained on the basis of PVC were studied and the sorption amounts were $55 \text{ mg} \cdot \text{g}^{-1}$ and $31.2 \text{ mg} \cdot \text{g}^{-1}$, respectively [9]. Researchers are working on creating low-cost adsorbents for industrial wastewater treatment. One of the most important tools for studying the mechanism of the adsorption process of ion-exchange materials is the organization of the adsorption isotherm. In recent years, the isotherm models of Langmuir, Freundlich, Temkin, Dubinin-Radushkevich have been analyzed in the study of ion sorption from solutions [10]. From the above literature, it is clear that ion exchange resins were obtained by modifying natural and synthetic polymers, and the adsorption of various metals was studied using isothermal models.

In this paper, the absorption isotherms of Ca^{2+} and Mg^{2+} ions for PVC-based ion exchange resins were studied.

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2. Materials and methods of research

Analytical pure substances were used in the preparation, oxidation of calcium polysulfide solution and the sorption of Ca^{2+} and Mg^{2+} ions to cation exchange resins for the modification of sulphur in polyvinyl chloride plastic.

2.1. Synthesis of a cation exchange resin on the basis of PVC

2.1.1. Process of obtaining a solution of CaS_x

As a result of many experiments, the optimal conditions for obtaining a solution of CaS_x are the reaction in a flask with a mass ratio $\text{CaO}:\text{S}:\text{H}_2\text{O}$ of 1.0: 3.0: 16.8, respectively, at a temperature of 358-368 K for 70-90 minutes [11]. Additional substances such as H_2S , $\text{Ca}(\text{SH})_2$, CaS_2O_3 can be formed during the reaction. The result of the reaction is a dark red solution, which is filtered off. The mass fraction of CaS_x in the solution was found to be 28-34%. The residue can be used for re-synthesis or buried in the ground as fertilizer. An increase in the reaction time can lead to an increase in the amount of thiosulfate ions, but this has a positive effect on the production of a cation exchange resin containing sulphydro-groups from PVC. This is because thiosulfate ions or ion radicals, such as sulfide groups, are more likely to oxidize to sulphur groups during the oxidation process after being bonded to a PVC chain.

2.1.2. Modification of sulphur to PVC and extraction of cation exchange resins

Various experiments have been performed to modify sulphur to PVC [12]. Granular plastic PVC (grade I-40-13A) was extracted in ethyl acetate for 2 h. The goal is to increase the porosity of plastic by producing a plasticizer (dibutyl phthalate) from PVC. The PVC is filtered and poured into a vessel, on which is poured a boiling solution of CaS_x , the vessel is hermetically sealed and heated in an oven at 423 K for 4 hours. In the next stage, the reaction is carried out in a water bath with a concentrated solution of HNO_3 for 3-4 hours to oxidize the - S_x -, -S-H groups of sulphur-modified polymer to the $-\text{SO}_3\text{H}$ group.

The gained ion exchange resin was washed and the NaOH static exchange capacity (SEC) was determined, SEC value of 3.5 mg·eq/g.

2.2. Study of adsorbent properties

The physicochemical properties of synthesized sulphydro-cation exchange resins were studied and element analysis and FTIR spectroscopy. The amount of elements contained in the samples obtained was determined using the Euro EA Elemental Analyzer. The spectra of the samples are taken with the help of the IR-Fourier spectrometer IRTracer-100 complete with a single NIP prefix with a prism diamond/ZnSe MIRacle 10. It is designed for the analysis of solid, liquid, pasty, gel-like and hard-to-process substances in the scanning range: 4000-400 cm^{-1} . The study of the physicochemical parameters of the obtained cation exchanging material showed that it meets the requirements of GOST 20298-74 for use in the separation of ions available on an industrial scale. The ion exchange resin obtained on the basis of PVC plastic is registered by the Scientific Research Institute of Standardization, Certification and Technical Regulation of the Agency of the Republic of Uzbekistan "UZSTANDART" under the number Ts 02072392-00: 2020.

2.3. Experiments of sorption

2.3.1 Preparation and sorption conditions of metal solutions

CaCl_2 and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were used to study the sorption of metal ions that cause water hardness to PVC-based cation exchange resins. Solutions of Ca^{2+} and Mg^{2+} ions with concentrations of 0.1 to 0.025 $\text{mol} \cdot \text{L}^{-1}$ were prepared by diluting with distilled water. The sorption process was studied in solutions at temperatures of 293, 303 and 313 K. To do this, 100 ml of a cation exchange resin 2g·L⁻¹ with a SEC value of 3.5 mg·eq·g⁻¹ was studied in conical flasks at a speed of 100 rpm that is, at a time interval of up to 12 hours until sorption reaches equilibrium. Initial and post-

sorption solution concentrations were determined in the way of EDTA. The amount of metal ion absorbed in the sorbent is calculated by the following equation (1)

$$Q_e = \frac{(C_0 - C_e)}{m} \cdot V \quad (1)$$

In this equation: Q_e - the amount of metal ion absorbed into the ion exchange resin $\text{mg} \cdot \text{g}^{-1}$, C_0 and C_e initial and equilibrium concentrations of metal ions $\text{mg} \cdot \text{L}^{-1}$, V – volume of solution L; m - mass of dry sorbent g.

2.3.2. Isothermal models

In the analysis of equilibrium processes, one of the most important tools is the adsorption isotherm. Therefore, in this work, the adsorption mechanism was analyzed using the isotherm models of Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R), which are widely used in liquid-solid systems.

3. Results and discussion

3.1. Identification of a cation exchange resin obtained on the basis of PVC.

The functional groups in the polymer were studied by elemental analysis and IR spectroscopy of the cation exchanging composition obtained by oxidation of a polymer gained by modifying CaS_x to PVC.

3.1.1. IR spectroscopy of a cation exchange resin based on PVC

IR spectrum analysis was performed to identify the cation of the oxidized cation exchange resin using HNO_3 , the product of the reaction of sulphur modified by CaS_x to PVC.

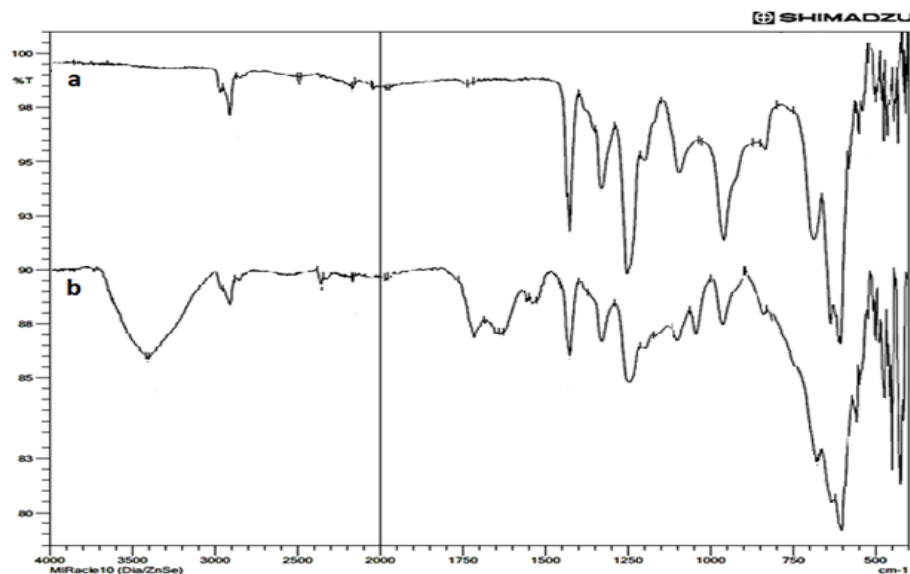


Fig 1. IR spectroscopy of a cation exchange resin (b) obtained on the basis of PVC (a) and PVC.

Comparative analysis of infrared spectroscopy data shows that the cation exchange resin contains a sulphur group. In the infrared spectrum in Figure 1- (b) above, the intensive absorption regions characterizing the monovalent - SO_3H bonds in the 1714 and 1210 cm^{-1} areas, as well as the valence oscillations of the $\text{S}=\text{O}$ bond in the $1220\text{-}1080 \text{ cm}^{-1}$ area, around 3400 cm^{-1} characterizing the $-\text{OH}$ groups wide absorption areas have emerged. This indicates that the sulfide, polysulfide, and hydrosulfide groups in the sulphurized polymer were oxidized by oxidative action and converted to sulphur groups. Figure 1 (a, b) of the samples shows the lines of accelerated absorption in the IR spectra in the regions of 700 and 605 cm^{-1} , which, in turn, are characteristic of the S-Cl valence

oscillations. This means that a certain part of the chlorine atoms in PVC is exchanged for sulphur groups. Absorption lines were observed in 2966, 2922 and 2862 2933 cm⁻¹ areas for all studied samples, which are characteristic of C-C, C-N and CH₂ valence oscillations in the polymer chain and deformation oscillations of absorption-CH₂- groups in 1420 cm⁻¹ area [12, 13]. This means that the polymer base chain is preserved during the stages of obtaining a sulpho-cation exchange resin by modifying PVC.

3.1.2. Elemental analysis of the cation exchange resin obtained on the basis of PVC

The results of elemental analysis of the composition of the sulphur-modified PVC polymer and its CaS_x and cationic oxidized sulphur with HNO₃ are shown in Table 1 below.

Table 1. Content of elements of PVC, sulphur modified PVC and a cation exchange resin

Sample	PVX			PVX-S			PVX-SO ₃ H		
Element	C	H	S	C	H	S	C	H	S
Quantity(m,%)	36,4	5,2	0	29,2	4,2	14,3	22,4	4,1	10,4

Table 1 shows that after sulphurization, PVC was found to contain 14.3% sulphur. This means that the chlorine atoms in the PVC are not completely replaced by sulphur. The oxidation of the sulphur-containing polymer showed that the polymer contains 10.4% sulphur, which may be due to the amount of oxygen in the sulphur groups.

Elemental analysis, IR spectroscopy, and other physicochemical parameters confirm the addition of sulphur to PVC and the oxidation of sulfite-containing cation exchange resins. The isotherms of sorption of Ca²⁺ and Mg²⁺ ions from aqueous solutions by PVC-based cation exchange resin with sulphur group were studied.

3.2. Adsorption isotherms

3.2.1. Langmuir isotherm model

Langmuir The Langmuir adsorption isotherm states that the binding of the adsorbate on the surface of the adsorbent occurs only in the active centers, and that the binding energy is the same, the adsorbate molecules are adsorbed, forming a monomolecular layer, without interacting with each other. The Langmuir equation is represented by the following equation.

Langmuir's theory of isotherms states that the binding of the adsorbate on the surface of the adsorbent occurs only at the active centers, and that the binding energy is the same, the adsorbate molecules are adsorbed to form a monomolecular layer without interacting with each other. The Langmuir equation is represented by the following equation (2).

$$Q_e = \frac{Q_{max} \cdot (K_L \cdot C_e)}{1 + K_L \cdot C_e} \quad (2)$$

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} \cdot K_L} + \frac{1}{Q_{max}} \cdot C_e \quad (3)$$

In this equation: Q_e and Q_{max} – the amount of metal ions absorbed by the sorbent of a given mass and the maximum amount of metal ions absorbed by the sorbent surface (mg·g⁻¹), C_e- equilibrium concentration of the solution (mg·L⁻¹), 2-3- K_L is the adsorption equilibrium constant of Langmuir in the equation L·mg⁻¹. To find the Langmuir constant, the linear view of the Langmuir equation (3) above is used. The values of Q_{max} and K_L are determined from the C_e dependence graph of C_e/Q_e. The relationship between the adsorbent and the adsorbate can be derived using the separation coefficient “R_L”, which is an important characteristic of the parameters of the Langmuir isotherm.

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

According to (4), the adsorption process $0 < R_L < 1$ is favorable, $R_L > 1$ is inconvenient, the adsorption isotherm $R_L = 1$ is considered linear, and $R_L = 0$ means that the adsorption is irreversible [6].

Based on the results obtained in this study, a C_e/Q_e dependence graph of C_e/Q_e was constructed in Figure 2 (a) to calculate the Langmuir isotherm constants. The Langmuir constants calculated on the basis of this graph are given in Table 2. According to him, the maximum monolayer sorption amount (Q_{max}) for Ca^{2+} and Mg^{2+} ions is 55.3 mg/g and 37.5 mg/g, respectively, the K_L values are 0.00162 and 0.00116, as well as the separation factor (R_L) 0.134 and 0.264 due to the convenience of the sorption process. The fact that the sorption isotherm of Ca^{2+} and Mg^{2+} ions to a PVC-based cation exchange resin obeys the Langmuir model proves that the value of R^2 is 0.995 and 0.991, respectively.

3.2.2. Freundlich isotherm model

The equation of the Freundlich isotherm model, which is widely used to theoretically evaluate the adsorption process in heterogeneous systems, is represented by the following equations (5) and (6) [14]:

$$Q_e = K_F \cdot C_e^{1/n} \quad (5)$$

$$\log Q_e = \log K_F + \frac{1}{n} \cdot \log C_e \quad (6)$$

In the equations (5) and (6) The values of the Freundlich constant K_F ($(mg \cdot g^{-1}) (L \cdot g^{-1})^n$) and the sorption intensity $1/n$ ($n = 1-10$ represent the sorption ease) are found by the angular value of the intersection slope of the $\log C_e$ correlation graph with $\log Q_e$. Based on the data in Figure 2 (b), the Freundlich parameters were calculated. For the sorption of Ca^{2+} and Mg^{2+} ions with the Freundlich constants shown in Table 2 below, the K_F values are 8.15 and 1.14, respectively, and the sorption intensity (n) is 4.56 and 2.43, respectively, which means that the sorption process is favorable.

3.2.3. Temkin isotherm model.

In this isotherm, we can make theoretical assumptions about the adsorbent-adsorbate interactions, that is, about the binding energy. The change in temperature during adsorption reduces the sorption of particles linearly. From equation (7) given below, equation (8) is reduced to a linear form for calculating the parameters of the Temkin isotherm and plotted on the dependence graph of Q_e on $\ln C_e$.

$$Q_e = \frac{RT}{b} \cdot \ln (K_T C_e) \quad (7)$$

$$Q_e = \frac{RT}{b_T} \cdot \ln K_T + \frac{RT}{b_T} \cdot \ln C_e \quad (8)$$

$$B = \frac{RT}{b_T}$$

$$Q_e = B \ln K_T + B \ln C_e$$

Here, K_T – Temkin equilibrium constant $L \cdot g^{-1}$, B - Temkin isotherm constant $J \cdot mol^{-1}$, R - gas constant ($J \cdot mol^{-1} \cdot K^{-1}$), T - temperature K . A high value of B indicates rapid absorption of the adsorbate at the initial stage. Similarly, the low value of K_T is related to the weak binding of the adsorbate to the sorbent [15]. In this work, to find the Temkin constants, Q_e and $\ln C_e$ in Figure 2 (b) were calculated from the slope of the dependence graph and the cross section of this curve. The values of the Temkin constants K_T given in Table 2 were found to be 0.0364 at sorption Ca^{2+} and 0.0137 $L \cdot g^{-1}$ (-73.2) at sorption Mg^{2+} and values R^2 (0.977 and 0.986), respectively. The sorption heat parameter (B) for Ca^{2+} and Mg^{2+} was found to be 9.7 and 8.6 $J \cdot mol^{-1}$, respectively.

3.2.4 Dubinin-Radushkevich (D-R) isotherm model

In heterogeneous systems, information about the adsorption energy can be obtained in accordance with the characteristic porosity of the adsorbent. The Dubinin-Radushkevich isotherm model is commonly used to represent

the adsorption mechanism using a Gaussian energy distribution. The equation of the D-R isotherm model is expressed as follows (9).

$$Q_e = Q_{D-R} \exp(-\beta \varepsilon^2) \quad (9)$$

In this equation: Q_{D-R} – Absorbed amount of adsorbate (ions) according to D-R model ($\text{mg} \cdot \text{g}^{-1}$), β – constant depending on adsorption energy ($\text{mol}^2 \cdot (\text{kJ}^2)^{-1}$), ε – The Dubinin-Rudushkevich isotherm constant (Polanyi potential), ie the adsorption energy ($\text{kJ} \cdot \text{mol}^{-1}$), is calculated as follows. (10).

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (10)$$

Here: R – gas constant $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, T – temperature (K). To calculate the Dubinin-Radushkevich isotherm constants, the equation is reduced to a linear form (11).

$$\ln Q_e = \ln Q_{D-R} - \beta \varepsilon^2 \quad (11)$$

The value of the average free energy of sorption E_{ads} ($\text{kJ} \cdot \text{mol}^{-1}$) can be calculated from the following equation (12)

$$E_{\text{ads}} = \frac{1}{\sqrt{2\beta}} \quad (12)$$

In this equation, E_{ads} gives information about the adsorption mechanism. In this regard, $E_{\text{ads}} < 8 \text{ kJ} \cdot \text{mol}^{-1}$ indicates the predominance of physical adsorption, while $8 \text{ kJ/mol} < E_{\text{ads}} < 16 \text{ kJ/mol}$ and $E_{\text{ads}} > 16 \text{ kJ/mol}$ represent the occurrence of ion exchange reactions and diffusion, respectively [16]. In this research work, a graph dependence ε^2 of $\ln Q_e$ in Figure 2 (d) was formulated to calculate the Dubinin-Radushkevich isotherm constants in the absorption of Ca^{2+} and Mg^{2+} ions into a PVC-based cation exchange resin. The isotherm constants calculated on the basis of this graph are given in Table 2. According to the Dubinin-Radushkevich isotherm model, the maximum sorption capacity Q_{D-R} of Ca^{2+} and Mg^{2+} ions of a cation exchange resin was calculated as $46.9 \text{ mg} \cdot \text{g}^{-1}$ and $26.3 \text{ mg} \cdot \text{g}^{-1}$, respectively, and the R^2 value was 0.927 and 0.885, respectively. The adsorption free energy E_{ads} calculated according to the D-R isotherm model in Ca^{2+} and Mg^{2+} ions is possible that the absorption of metal ions into PVC-based ions equal to $10.5 \text{ kJ} \cdot \text{mol}^{-1}$ and $8.2 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, was accompanied by an ion exchange reaction under the influence of minimal chemical forces.

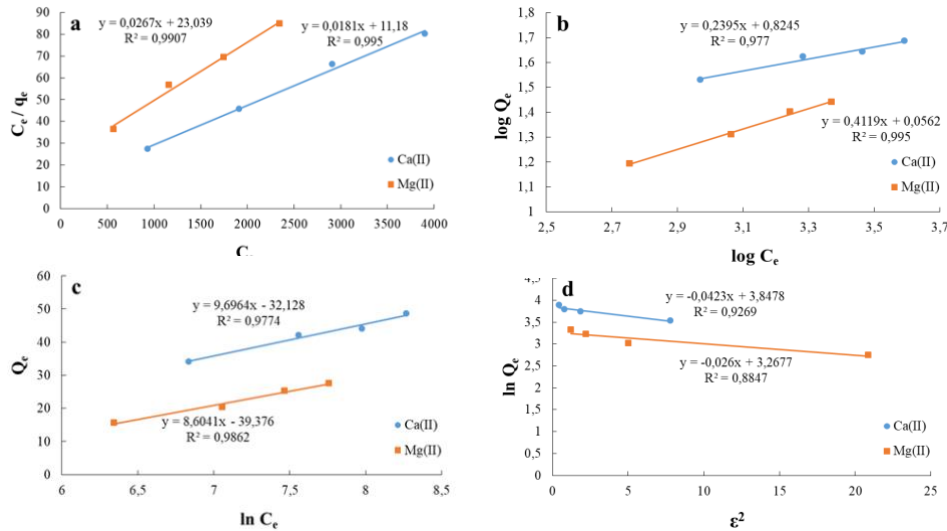


Fig 2. Expression of adsorption of Ca^{2+} and Mg^{2+} ions on PVC-based cation exchange resins in (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Temkin isotherm and (d) Dubinin-Radushkevich isotherms.

Table 2. Isothermal constants in the adsorption of metal ions on PVC-based cation exchange resins

Metal ions	Langmuir constants				Freundlich constants			Temkin constants			D–R constants		
	$Q_{\max}$	K_L	R_L	R^2	n	K_F	R^2	$-K_T$	B	R^2	Q_{D-R}	E_{ads}	R^2
Ca^{2+}	55.3	0.00162	0.134	0.995	4.56	8.15	0.977	27.7	9.7	0.977	46.9	10.1	0.927
Mg^{2+}	37.5	0.00116	0.264	0.991	2.43	1.14	0.995	73.2	8.6	0.986	26.3	8.1	0.885

4. Conclusion

- The solution CaS_x was originally used in the modification of PVC with sulphur to produce a cation exchange material containing sulphur-groups. A solution of HNO_3 was used to oxidize the sulphur groups in the resulting polymer to sulphur groups. The ion exchange content in the resulting ion exchange resin was determined by elemental analysis at 14.3%, and the formation of sulphur groups was confirmed by IR spectroscopy. The solution CaS_x was originally used in the modification of PVC with sulphur to produce a cation exchange material containing sulphur groups. A solution of HNO_3 was used to oxidize the sulphur groups in the resulting polymer to sulphur groups. The ion exchange content in the resulting ion exchange resin was determined by elemental analysis at 14.3%, and the formation of sulphur groups was confirmed by IR spectroscopy.

- Sorption isotherms of Ca^{2+} and Mg^{2+} ions are formed on the PVC-based cation exchange resin. The results showed that the sorption process with $R^2 > 0.88$ in the Langmuir isotherm, Freundlich isotherm, Temkin isotherm, and Dubinin-Radushkevich isotherm models is suitable for these models. According to Langmuir's monomolecular theory, the high sorption capacity $Q_{\max}$ is equal to $55.3 \text{ mg} \cdot \text{g}^{-1}$ (Ca^{2+}) and $37.5 \text{ mg} \cdot \text{g}^{-1}$ (Mg^{2+}) and the R_L value (in the range of 0-1 at all concentrations of Ca^{2+} and Mg^{2+}) and the value n of Freundlich constant of 4.56 (Ca^{2+}) and 2.43 (Mg^{2+}) indicate that the sorption process is convenient. In the Temkin isotherm, the adsorption energy was found to be $0.268 \text{ kJ} \cdot \text{mol}^{-1}$ and $0.303 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, for Ca^{2+} and Mg^{2+} ions. The adsorption process calculated by the D-R model indicates that the free energy E_{ads} in the Ca^{2+} and Mg^{2+} ions are chemically sorbed at $10.5 \text{ kJ} \cdot \text{mol}^{-1}$ and $8.2 \text{ kJ} \cdot \text{mol}^{-1}$, respectively.

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