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Studying synthesis of a chelate-forming sorbent based on urea-formaldehyde and diphenylcarbazone

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In this research work, the synthesis of a new type of chelating sorbent based on the cross-polycondensation reaction of urea, and formaldehyde with diphenylcarbazone in an alkaline medium and the study of its various properties have been studied. When the effect of temperature on the synthesis of this new chelating sorbent has been studied, the optimal temperature is 90°C, the duration of time is 1.5-2 h, and the molar ratio of the starting materials is respectively: urea, formaldehyde (2:5) and diphenylcarbazone. It is obtained in 0.1:0.2:0.3 mol ratios. The static exchange capacity of the chelating sorbent is 4.3 mg/eq. for 0.1 N NaOH solution. In addition, the sorption levels of ions such as Cu(II), Zn(II), and Ni(II) have also been determined. The influence of the environment on the sorption process of this synthesized chelating sorbent with Cu(II) ions has been observed. The structure of the newly synthesized sorbent and the sorption of Zn (II) and Cu (II) ions in the solution with the help of the sorbent have been studied, and the formation of complex compounds in the sorbent phase is based on the change of vibration frequencies according to the results of IR-spectrum analysis. The IR results confirm that this sorbent contains OH groups, primary amides (attached melamine ring), and R-O-H group. The surface morphology of this sorbent has been studied by SEM analysis. The Langmuir and Freundlich isotherms of the sorption process of the chelating sorbent for Cu (II) ions have been studied and analyzed. The obtained results also confirm that the possibility of using KF-DK as a sorbent for the sorption of d-metals from metallurgical wastewater.

Keywords: Urea, Formaldehyde, Diphenylcarbazole, Sorbent, SEM analysis, IR-spectrum analysis

Nowadays, the cleaning and processing of industrial waste remains one of the urgent problems. There is an increasing need for chelating sorbents in the detoxification of waste solutions containing heavy metal ions. Currently, new derivatives of ion-exchange, complex-forming polymers have been developed[1]. It is of great importance to develop efficient and selective sorbents from high-tech devices for the processing of precious and heavy metals from secondary resources[2,3].

The following work studied the synthesis of sorbents based on urea, formaldehyde, and 2,4 dinitrophenylhydrazine which contain functional amino groups and their ion-exchange properties complex with heavy metal ions (Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, and Co^{2+})[4,5]. In this article, metal ion sorption with polymer-forming sorbents obtained from the interaction of metal complexes Cu(II) chloride with copolymers of 2-acrylamido-2-methylpropane sulfonic acid, AMPS and sodium salt of dodecyl methacrylate[6], and their level of sorption properties[7].

In an earlier study[8], the sorption isotherms of nickel and manganese were observed in mono- and bicomponent systems and experimental model results showed that chelation or complex interactions between Pb (II) and surface functional groups are responsible for the strong adsorption of heavy metal ions in microspheres[9]. Pseudo-second-order sorption kinetics is characterized by the mechanism of action on Cu^{2+} ions, structural features, respectively, DSC and TG analysis[10].

Effect of adsorption conditions, the molar ratio of chitosan on the sorption of four metals (Cu(II), Zn(II), Ni(II), and Pb(II)) on the matrix of chitosan with metal complexes linked by chemical bonds and glutaraldehyde as a binder and *p*H changes were studied. Adsorption of non-ferrous metals Cu(II), Zn(II), Ni(II), and Pb(II) ions in solutions[11], their IR spectra, SDRs, thermal analysis, and thermal stability were studied[12].

Jadhao M. M. *et al.* studied 2, 2-dihydroxy biphenyl was synthesized by condensation of urea and formaldehyde in the presence of a 2 M HCl catalyst, and its sorption properties of this polymer were studied for the several metal ions (Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+})[13]. The obtained results showed that the ion exchange polymer showed higher selectivity for Fe^{3+}, Cu^{2+}, and Ni^{2+} ions than Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions[13,14].

A new adsorbent was synthesized by modifying poly(glycidyl methacrylate) microspheres with 2-aminothiazole and the sorption of Au(I) ions from solutions, Zn(II), Mg(II), Cu(II), and Ge(IV). The results showed that the maximum adsorption capacity of Au(I) ions is 440.54 mg/g, and the equilibrium adsorption time is 3 hours when the *p*H of the soluble medium is 4 hours[15].

In this work, a bidentate chelating ligand based on 2-thiophenecarboxaldehyde and 3-aminopropyltrimethoxysilane was studied for sorption of Pb(II) ions in aqueous solutions using an organic-inorganic hybrid sorbent[16-18]. By means of sorption, it is possible to extract metals in the lowest concentration or to purify water[19]. The sorption capacity of the sorbents known to us today mainly depends on the functional groups in their composition[20]. From the above literature, it can be seen that the research of sorbents that form complex sorbing divalent d-metals, coordination compounds formed by metals, and sorbents have not been fully studied.

Materials and Methods

Substances such as urea, formaldehyde and diphenylcarbazone were used in the synthesis of this complex-forming sorbent. The obtained results were studied and analyzed using SEM EVOMA 10 scanning electron microscope (Carl Zeiss) and EMC-30PC-UV and IRTracer-100 SHIMADZU infrared Fourier IR spectrometer (Japan) (range 400–4000 cm^{-1}). Practical experiments were carried out in 0.05 *p*H units using the P25 *p*H-meter.

Experimental Section

Synthesis of sorbent based on urea, formaldehyde and diphenylcarbazone

To create a sorbent containing nitrogen and oxygen: a reflux condenser with an automatic stirrer was installed in a three-necked flask. Then, adding 12 g (0.2 mol) of urea to 38 mL (0.5 mol) of formaldehyde, the heating process was carried out at 40°C. By adding 5 mL of buffer solution (NH_4Cl+NH_4OH) to the solution, the environment was brought to *p*H = 9-10 and a weak alkaline environment was monitored during the experiment.

A solution of 4.8 g (0.02 mol) of diphenylcarbazone in benzene was added dropwise to the resulting mass, and the reaction mixture was heated to a temperature of 80-90°C and stirred at the same rate. As a result, after 1.5-2 hours, a tar-like compound was formed.

The synthesized resinous product was placed in a porcelain bowl for drying and left in a drying cabinet for 24 hours. The dried polymers were crushed in a mortar and the lower molecular compounds were washed several times first with 5% NaOH solution and then with distilled water. The resulting product is a fine, porous, brown solid sorbent insoluble in water and benzene. The yield of the reaction is 89%.

In the above experimental method, sorbents were synthesized based on 0.1, 0.2, and 0.3 mol ratios of diphenylcarbazone, taking urea and formaldehyde in a 2:5 mol ratio. According to the synthesis result and IR spectrum analysis, the chemical formula of urea, formaldehyde, and diphenylcarbazone (KF-DK) can be given as shown in Fig. 1.

Scanning electron microscope analysis of the sorbent

Studying the surface morphological (a scanning electron microscope (SEM) structure of KF-DK, and its sorption ability with some d-metals. It can be concluded that: the newly synthesized sorbent has a very high sorption capacity. Scanning electron microscopic photographs of KF-DK sorbent are shown below (Fig. 2).

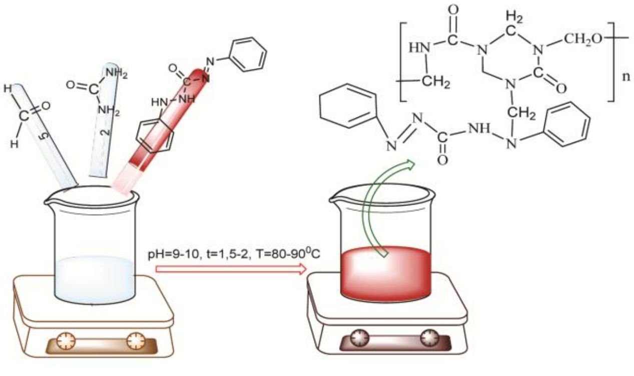

Fig. 1 — KF-DK brand complex formation scheme

A 10-μm photo of the complex-forming sorbent was studied and analyzed, and it was found that the sorbent has a microporous structure.

IR spectrum analysis of the sorbent

IR-spectrum analysis was carried out to determine the functional groups in the obtained sorbent, the areas where they are located, and the chemical formula of the sorbent. The IR spectra of KF-DK (Fig. 3) contain lines in the 3309 cm^{-1} region corresponding to the vibrational frequencies of the CONHR secondary amide and bonded OH groups (bonded -NH$_2$ groups, in one domain).

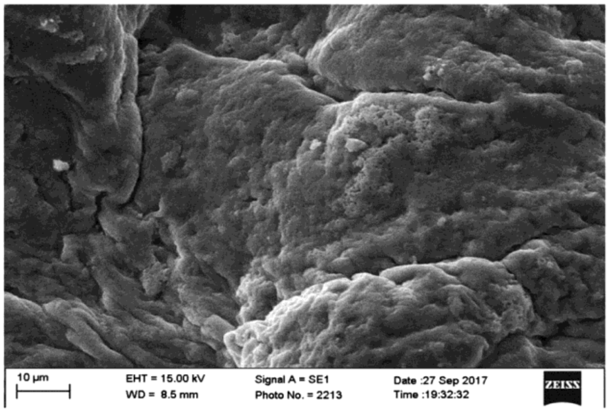

Fig. 2 — Image of the UF-DC electron microscope

The appearance of the 1616 cm^{-1} region indicates the presence of a –C=O bond group and a C=N group bond, and in the 1440 cm^{-1} region, we observe N=N variable bands. At the same time, the extended vibrations of the aromatic ring appeared in the 1616-1440 cm^{-1} range. In the region of 1389.49 cm^{-1} - CH$_2$, in the region of 829 cm^{-1} -S-H= group vibrations were observed.

Temperature effects were also investigated in making this new chelating sorbent. In this, the polycondensation process was studied at different temperatures of 348, 358, 363, and 373 K. In addition, the time duration of the reaction on the polycondensation process, the specific volume of the sorbent in water, and the influence factors of static exchange values for 0.1 m NaOH solution were also studied. According to the obtained results, the temperature for the optimal conditions of the polycondensation reaction is 363 K, the concentration of the medium is 0.1 n NaOH, the time duration is 1.5-2 hours, and the ion exchange capacity is equal to 3.4 mg/eq based on the experiments was determined (Table 1).

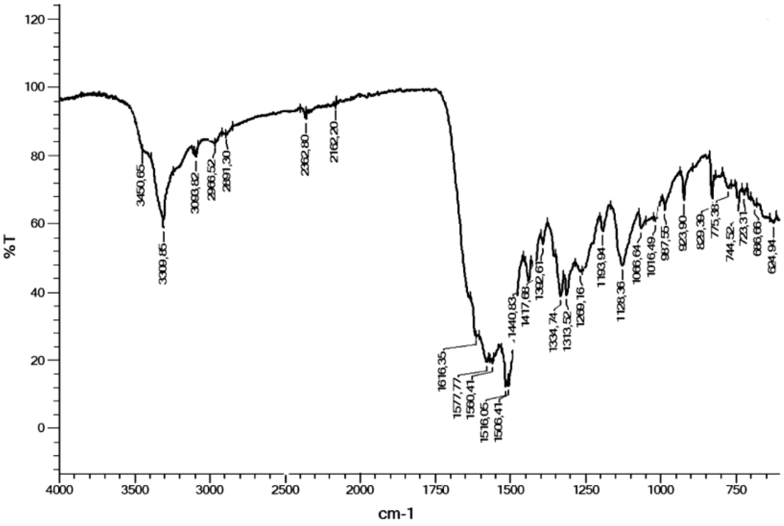

Fig. 3 — IR-spectrum of the sorbent

Table 1 — Factors affecting the polycondensation process

№	Reaction temperature t, K	Reaction time t, hour	Special volume of H-form sorbent swollen in water, mL/g	Ion exchange capacity for 0.1 n NaOH H solutions, mg/eq
1.	348	2.5-3	1.6	2.2
2.	358	2-2.5	1.66	3
3.	363	1.5-2	1.42	3.4
4.	373	1-1.5	1.20	2.8

Results and Discussion

In the research aimed at studying the dependence of the sorption and physico-chemical properties of the synthesized chelating sorbent on the concentration of substances in the sorbent, the increase in the sorption level of Cu^{2+}, Ni^{2+}, Zn^{2+} ions (Table 2) with the increase in the amount of reactive substances: urea, formaldehyde 2:5 and diphenylcarbazone changes detected[21].

It can be observed that the ion exchange capacity of the sorbent gradually decreases as the amount of diphenylcarbazone added to the urea formaldehyde resin as the main complexing agent increases. The available functional groups in the sorbent in the amount of KF-DK 2:5:0.3 mol come closer to each other and reduce the pore radius.

As a result, it becomes difficult for the sorbent to bind metal ions and be sorbed. According to the observed studies, the ratio of urea, formaldehyde, and diphenylcarbazone of KF-DK sorbent with the best sorption index is 2: 5: 0.2 mol. The dependence of the sorption of d-metals on KF-DK synthesized during the research (diphenylcarbazone exposed to urea-formaldehyde resin in a 2:5 mol ratio) studied, and results were depicted graphically (Fig. 4).

It can be seen from the Fig. 4 that the level of sorption of metal ions in KF-DK is higher in a weakly acidic environment. It was observed that the level of sorption decreases as the environment changes from neutral to alkaline. It can be seen that in a weakly acidic environment, metal ions form acidocomplexes of different composition and form ion associates with protonated active functional groups of ionite.

It was found that the static exchange capacity of KF-DK at a ratio of 0.2 mol has the maximum value when the sorption capacity is 2.6 mg-eq/g for Cu(II) in the range of the optimal medium *p*H=6[22]. Adsorption

The concentration of the components was determined spectrophotometrically based on the difference in the optical density of the initial and post-sorption solutions, and the sorption efficiency, *i.e.*, the amount of ions absorbed into the ionite q (mol/g) was determined by the amount of the component in the ionite phase from the following formula:

$$q = \frac{V}{m} \cdot (C_1 - C_2)$$

where,

C_1-the initial concentration of the solution in mol/l;

S_2 is the concentration of the solution after sorption, mol/l;

V – volume of solution taken for sorption, mL;

m - mass of dry sorbent, g.

The sorption process was carried out for each ionite at temperatures of 20, 40, 60, and 80°C, and according to the results of the analysis, the optimal sorption temperature of Cu (II) ions was determined to be 40°C (Fig. 5)

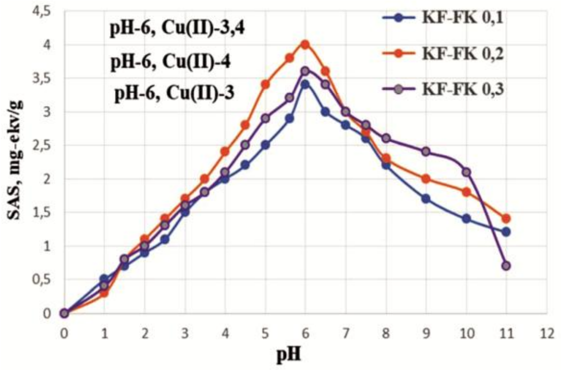

Fig. 4 — *p*H dependence of KF-FK Cu (II) sorption in different mole ratios

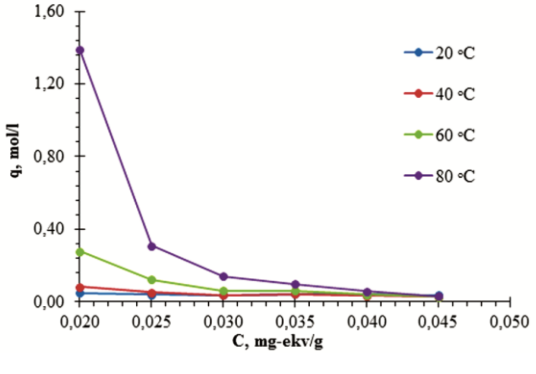

Fig. 5 — Sorption isotherms of linear Cu(II) ions with UF-DC according to the Langmuir model

Table 2 — Dependence of sorption properties of UF-DC on the ratio of reagents

The name of indicators		In molar ratio: urea, formaldehyde, diphenylcarbazone		
		2:5:0.1	2:5:0.2	2:5:0.3
Spray weight, g/mL		0.71	0.55	0.52
Static exchange capacity for 0.1 N solutions, mg-eq/g:	Cu^{2+}	3.1	3.6	3.5
	Zn^{2+}	3.7	3.7	3.4
	Ni^{2+}	3.4	3.3	3.6

In adsorption isotherms, the sorption process is widely used to investigate the relationship between the sorbates (at equilibrium) using the Langmuir and Freundlich equations. The Langmuir and Freundlich model was also used to determine the quantitative sorption equilibrium of Cu (II) ions (Table 3).

In the equations presented in the table, K_l and K_f are equilibrium constants in the Langmuir and Freindlich equations, q_{max} is the maximum capacity of ionite, mol/g; C– the equilibrium concentration of components in the solution, mol/l; n is a constant of the Freundlich isotherm indicating the intensity of sorption. Calculations of the values of the constants resulting from the Langmuir and Freundlich isotherm equations were carried out using the LINEYN function in the Microsoft Excel 2013 office package by the method of small squares.

The results obtained from the sorption isotherm of Cu (II) ions in the synthesized chelating sorbent are shown graphically in Fig. 5 and 6. The results obtained in the experiments are repeated according to the Langmuir and Freundlich models worked.

The Table 4 shows the constants of the sorption isotherms of Cu (II) ions according to the Langmuir and Freundlich models of the KF-DK sorbent. It can be seen that the sorption isotherm of Cu (II) ions in KF-DK obeys the Freundlich model. An increase in the maximum sorption capacity of the sorbent at a temperature of 40°C indicates the strength of coordination bonds in the sorbent. That is, as a result of the increase in the viscosity of the sorbent at 40°C, the sorbed ions penetrate deeper into the ligand and are sorbed.

Table 3 — Sorption isotherm model

Model	The equation
Langmuir	$q = q_{max}\dfrac{Kl * C}{1 + Kl * C}$
Freindlich	$q = K_f * C^{1/n}$ $lgq = lgK_f + 1/n * lgC$

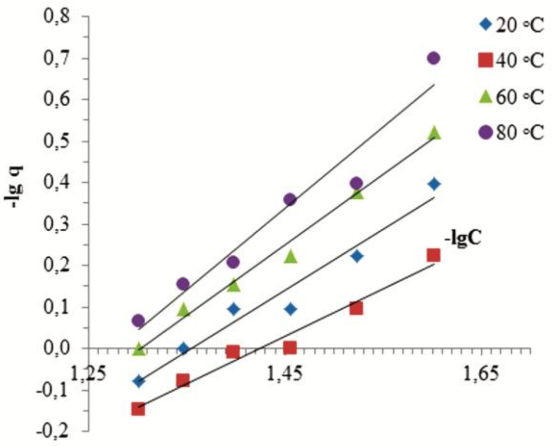

Fig. 6 — Sorption isotherms of linear form of Cu (II) ions with UF-DC according to the Freundlich model

The light absorption frequencies in the IR spectrum of the coordination compound formed by the zinc (II) ion of the KF-DK sorbent were analyzed, and changes in the following areas were observed (Fig. 7).

Vibrations corresponding to vibration frequencies of secondary amide and bound OH groups appeared in the valence vibration of 3307 cm^{-1}. The appearance of the 1616 cm^{-1} region indicates the presence of –C=O group and C=N group bonds. The valence vibration 1438 cm^{-1} region, the variable bands of the N=N group were observed, and at the same time, the stretching vibrations of the aromatic ring were observed in the 1616-1436 cm^{-1} the valence vibrations. In the region of 1336 cm^{-1} – CH_2, the valence vibration of 829 cm^{-1} –S-N group deformational vibrational signals were observed.

Table 4 — Absorption isotherm of Cu (II) ions

№	Isotherm parameters	Values
	Langmuir isotherm	model
1	Q_{max}	1.962
2	K_L	10.05
3	R_L	0.002
4	R^2	0.967
	Freundlich isotherm	model
1	1/n	1.405
2	n	0.711
3	K_F	4.078
4	R^2	0.982

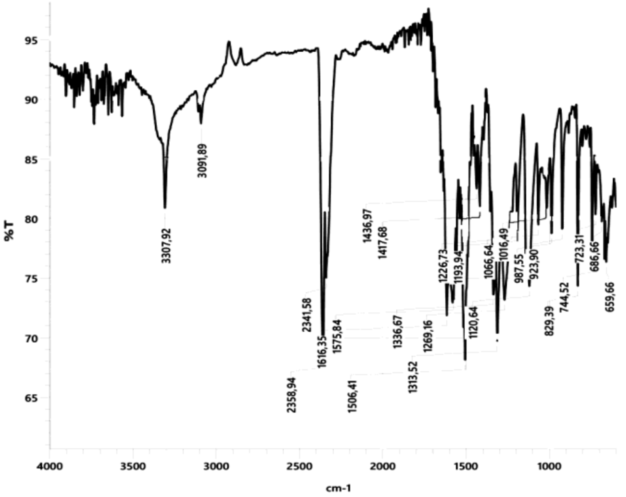

Fig. 7 — UF-DC IR spectrum of Zn (II) sorbent and complex compounds with them. IR spectrum frequency shifts of MK-DK and MK-DK+Zn (II)

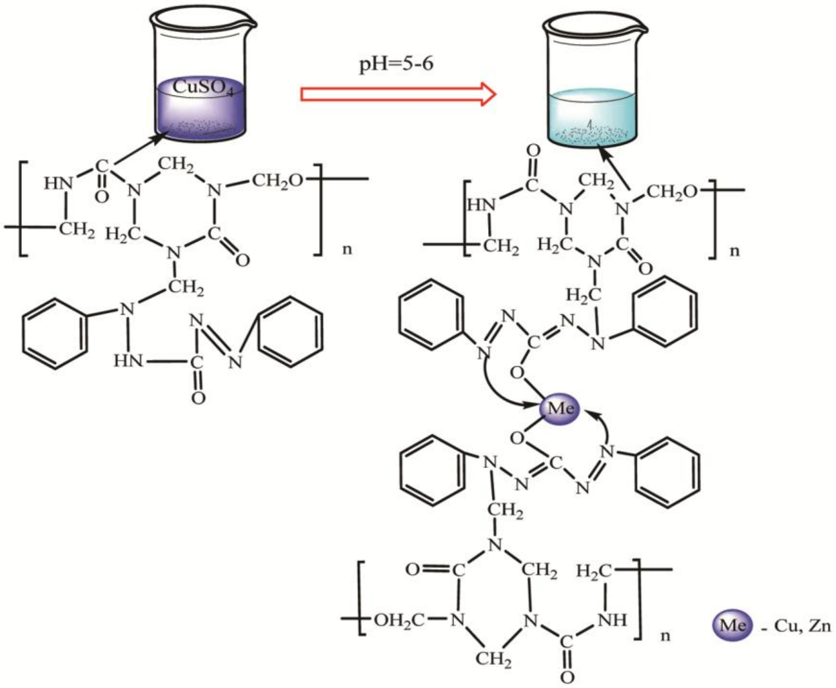

Fig. 8 — Complex structure of KF-FK sorbent with Cu and Zn

Table 5 — The IQ-spectrum frequency shifts of MK-DK and MK-DK-Zn (II)

Classification vibration	ν(NH)	$\nu_s(CH_2)$	$\delta(CH_2)+\delta(CN)$	(N=N)	ν(C-N)	ν(C-OH)
KF–FK	3309	2891	1616	1440	829	775
KF–FK+Zn (II)	3307	2885	1616	1417	829	744

According to Table 5, the amino groups in the sorbent provide coordination of the metal ion, forming a four-membered chelate ring.

Complex combinations of KF-DK with divalent d-metals can be expressed as shown in Fig. 8.

Conclusions

According to the results of the research, the process of polycondensation in the synthesis of a chelating sorbent based on urea, formaldehyde, and diphenylcarbazone, the effect of temperature, molar ratios of starting materials, and the effect of *p*H during the process were studied. The various properties of this sorbent were identified, and the following main points were found:

(i) It was determined that the polycondensation process was carried out at 40°C and 80-90°C temperatures and the reaction was carried out in an environment with a *p*H of 9-10. IR spectra of the sorbent were also analyzed and the estimated formula of the sorbent was proposed.

(ii) The sorption properties of the sorbent towards Cu (II) ions depend on different mole ratios (2:5:0.1; 2:5:0.3; 2:5:0.2) of urea, formaldehyde, and diphenylcarbazone, and the environment studied. In this case, urea, formaldehyde, and diphenylcarbazone in a 2:5:0.2 mol ratio showed the highest sorption index in a weakly acidic environment.

(iii) The obtained sorbent was analyzed using a scanning electron microscope. Due to the large number of mesopores in this sorbent, it shows that the sorbent has a high sorption capacity.

Overall, the present study confirmed that the chelating sorbent synthesized in this work has a high selectivity for Cu(II) ions.

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