Synthesis and study sorption properties oligo(poly)-mer sorbents based on urea-formaldehyde and cyanuric acid

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Abstract: Using the Chem3D Pro program, some empirical and semi-empirical orbital properties of urea, formaldehyde, urea-formaldehyde and 1,1',1''-((2,4,6-trioxo-1,3,5-triazinan-1,3,5-tri)-tris(methylene))triurea The length and angular relationships of the bonds, optimization and calculation of the energy of the molecule, quantum chemical calculations of the studied compounds using the MM2 method are shown. The resulting samples were examined using IR spectroscopy and X-ray phase analysis. Also, in this article, the dependence of the sorption of some d-metals on the sorbent based on cyanuric acid on the pH environment was studied and the results were presented. In sorption, the optimal pH size corresponds to the pH size of the formation of the acidocomplexes of the respective metals. Accordingly, the level of sorbation of the ions of the metals studied (SA+MFO (III)) in the sorbent increases in the following series: Mn (II) < Fe (II) < Co (II) < Ni (II) < Zn (II) < Pb (II) < Hg (II) < Cd (II) < Cu (II) < Ag (I).

1 Introduction

The reaction of urea and formaldehyde is an important synthetic chemical process used in the production of various industrially produced resins, including wood adhesives and polymer powders. The reactions of urea and formaldehyde that produce powder or resin can also be used to extract potassium from minerals and to produce coupling agents for CAVP (colloidal aggregation induced polymerization), which produces inorganic materials with various functions [1].

The polymer powder produced by the reactions of urea and formaldehyde can be used in a variety of products, including paper, pigments, varnishes, fillers and additives in plastic products. There are numerous reports on their synthesis [2, 3]. It is expected that polymer powders obtained from reactions of urea and formaldehyde can be used as lightweight fillers and other additives. Such polymer powders, although lightweight, would have wider applications if their low heat resistance, chemical resistance and mechanical strength were improved. Particularly in the case of powdered fillers, they must be of controlled particle types and sizes. However, no studies have been carried out on the specific physical or

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chemical properties of powders obtained from reactions of urea with formaldehyde. These powders have several critical disadvantages due to the inherent properties of urea and formaldehyde precursors. For example, manufactured polymer powders continually release formaldehyde, and creating sub-micrometer particles is difficult because the reaction is a condensation polymerization of formaldehyde. Therefore, these powders require further development for use as nanoscale fillers or additives that are environmentally friendly.

Previously, the authors studied oligomers based on aminoaldehyde compounds for leather fillings [4-10]. Studying trends in the world of application of oligo(poly)mers based on urea-formaldehyde, we concluded that it is possible to synthesize nano-sized polymer powders with increased functionality that do not have a cross-linked structure.

In addition, fundamental physical data for nanoscale urea-formaldehyde particles are reported to develop their functionality as porous materials. Formaldehyde-based resins are still being used as adhesives for the manufacturing of wood-based composite panels such as particleboards (PB), oriented strand board (OSB), plywood, and medium-density fiberboard (MDF). Among these resins, amino resins such as urea-formaldehyde (UF) resins and melamine-urea-formaldehyde (MUF) resins are mainly used for the production of plywood, PB, or MDF panels. These resins are dominantly used as adhesives, owing to their low cost, high reactivity, fast curing time, colorlessness, and good adhesion [11]. In spite of these advantages, there are two drawbacks for UF and MUF resins: low water resistance and formaldehyde emission. In particular, the formaldehyde emission from wood-based composite panels bonded with these resins has been a serious issue of these amino resins [12].

Also, the authors obtained new complexing sorbents based on nitrogen-containing reactive compounds [13, 14] and new chelating sorbents with phosphinate, arbamoylmethylphosphinate and methylene diphosphine; dioxide functional groups are synthesized by chemical and non-covalent binding of the ligature [15]. Use in wastewater treatment has been tested in several industrial enterprises [14-18].

Melamine-urea-formaldehyde (MUF) resins are used in the production of waterproof chipboards, paper, and laminates. The chemical reaction between melamine, formaldehyde, and urea-formaldehyde is well understood [19]. A monolithic resin with a molecular imprint has also been synthesized from MUF through in-situ polymerization [20], which shows good compatibility with water and excellent molecular recognition for plant growth regulators when used as a sorbent for TFE. MUF introduces a large number of hydrophilic groups, such as hydroxyl, carboxyl, imino and amino, into the polymer, improving its compatibility with aqueous solutions and promoting rapid mass transfer [21].

While studying the literature data, we synthesized a new oligopeptide composition based on urea-formaldehyde and cyanuric acid. From the first, we carried out a quantum chemical calculation and conformational analysis of the energies of the original and proposed compounds; after the conclusion of the quantum chemical calculation, we synthesized 1,1',1"-((2,4,6-trioxo-1,3,5-triazinan -1,3,5-triyl)tris(methylene))triurea.

The resulting samples were examined using IR spectroscopy and X-ray phase analysis. Also, in this article, the dependence of the sorption of some d-metals on the sorbent based on cyanuric acid on the pH environment was studied and the results were presented.

2 Materials and methods

2.1 Materials and preparations of sorbents

Cyanuric acid (2,4,6-trihydroxy-1,3,5 – triazine) is a heterocyclic acid, cyanuric acid consists of two tautomeric forms: lactim (cyanuric acid itself, formula I) and lactam

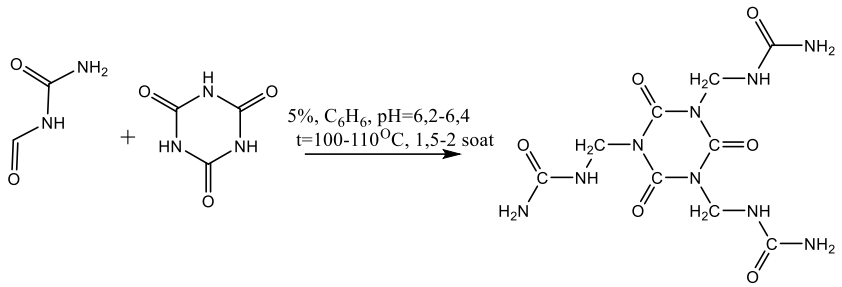
(isocyanuric acid, triazinotrion, formula II). Ionization constants in lactam form: $K_1=6.3\cdot10^{-7}$, $K_2=7.8\cdot10^{-11}$, $K_3=3.2\cdot10^{-14}$ (in aqueous 25°C solutions). Pure white powder-like substance with a specific smell. Liquefaction temperature 320-360 °C, density 1,758 g/sm^3. Boiling liquid at 160.5 °C. Soluble in water, alcohol and ether. Soluble in a number of solvents: in water – 2.7 g/l, in benzene – 67 g/l, in DMSO – 115 g/l. This reagent was synthesized by method [22] in our laboratory.

Formalin - CH2O (GOST 1625-75), colorless liquid. An aqueous solution of 40% formaldehyde was used. Good in water, alcohol, benzene, ether, slightly soluble in chloroform, insoluble in petroleum ether. The density of liquid formaldehyde at 80°C is 0.915 g/cm3. Water absorbs up to 50% CH2O.

Urea (carbamide, amide of carbonic acid) $(NH_2)_2CO$ – crystal. Ts=132.7°C, soluble in water, enters alcohols and liquid NH_3 and CO_2 according to the Bazarov reaction (saves 46% N).

2.1.1 Modification of cyanuric acid into the matrix by urea oligopeptide-formaldehyde

6 g (0.1 mol) of urea was placed in a three-neck flask equipped with a reverse cooler and an automatic stirrer, and dissolved at 40 ° C, adding 15.8 ml (0.2 mol) of formalin. After that, 5 g (0.1 mol) was added dropwise from a 5% solution of cyanuric acid in benzene and intensively mixed, heating the reaction mixture to a temperature of 100-110 ° C. As a result, a resinous mass formed after 1.5-2 hours. The resulting resinous mass was poured into a porcelain cup and dried in a drying cabinet for 24 hours at a temperature of 80-90 ° C. The dried polymer was crushed in a vegetable, and the low molecular weight compounds were first washed with a solution of NaOH 5% concentration, and then several times with distilled water. It was also washed with acetone and dehydrated. The resulting product consists of small, porous, light yellowish granules with a reaction yield of 65%.



These synthesis reaction equations involve tris-urea, which is a derivative of formaldehyde that is used as a sorbent. By adjusting the amounts of urea and formaldehyde, it is possible to create sorbents based on cyanuric acid with different compositions, including those with mono-, bi- and tris-urea-formaldehyde. The composition and properties of these sorbents have been confirmed through various physicochemical and quantum chemical analyses.

2.2 Methods

2.2.1 Quantum chemical calculations and theoretical computation

Optimization and calculation of the energy of the sorbent molecule and quantum chemical calculations of the studied compounds using the MM2 method were carried out using the ChemOffice software package [23-25].

2.2.2 FTIR analysis

FTIR spectroscopic analysis was determined using the infrared spectrometer "IR Tracer-100" Fure (Shimadzu, Japan), wavelengths of the spectral range 4000÷600 cm^{-1}, signal–to-noise sensitivity ratio - 60,000:1, scanning speed of 20 spectra per second.

2.2.3 XRD analysis

The investigation of the particle nature of the sorbent based on cyanuric acid was carried out on the basis of X-ray images obtained in a XRD-6100 (Shimadzu, Japan) powder diffractometer. X-ray diffraction analysis of sorbents was performed under the influence of CuKa radiation (b-filter, Ni, λ=1.54178Å, current and voltage in the X-ray tube 30 mA, 30 kV). In this case, the constant rotation speed of the detector was 4 degrees/min, in steps of 0.02o (ω/2th-link), and the scanning angle was taken from 4º to 80º. The samples were analyzed in a rotary chamber with a rotation speed of 30 rpm.

3 Results and discussion

3.1 Quantum chemical calculation results

The quantum chemistry method is used to study the photophysical properties of linear and angular oligo-peptides with conjugated external carbonyl compounds [24, 26-28]. The basis of our theoretical approach is the concepts and methods of quantum chemistry and the theory without radiative transitions in polyatomic organic molecules.

Empirical and semi-empirical orbital properties of the synthesized cyanuric acid derivative of mono-, bis- and tris-substituted urea-formaldehyde, condensed 1,1',1"-((2,4,6-trioxo-1,3,5-triazinan- 1,3,5-tri)tris(methylene))triurea was studied using an algorithm created by the authors of Bukhara State University [24]. As in the proposed algorithm, at the first stage a molecular structure is created in the "chemical editor" **ChemDraw Ultra 12.0.** When you activate the "Convert Structure to Name" item in the main "Structure" menu, the program displays the chemical name: 1,1',1"-((2,4,6-trioxo-1,3,5-triazinane-1,3, 5-triyl)tris(methylene))-triurea [24].

Using the ChemDraw Ultra 12.0 and Chem3D Pro 12.0 programs, molecular models of urea, formaldehyde, urea-formaldehyde and the resulting new compound 1,1',1"-((2,4,6-trioxo-1,3,5-triazinan- 1,3,5-triyl)tris(methylene))-triurea, which are presented in Fig. 1. This stage will be our second algorithm.

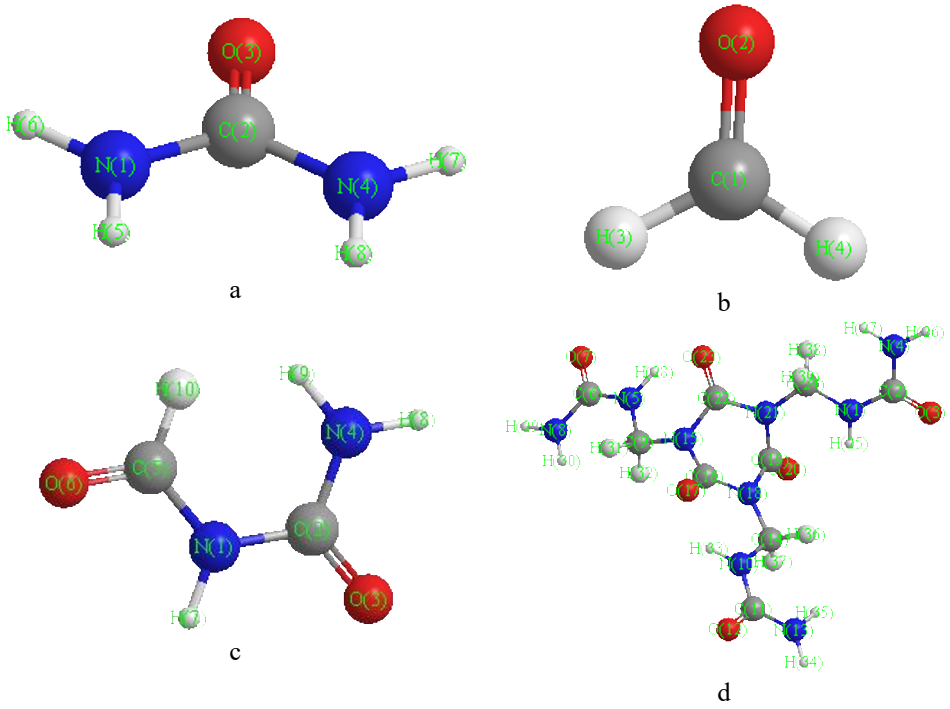


Fig. 1. Ball and stick model: a - urea; b - formaldehyde; c - urea-formaldehyde; d - 1,1',1"-((2,4,6-trioxo-1,3,5-triazinan-1,3,5-triyl)tris(methylene))triurea

Quantum chemical calculations allow us to make some estimates, which often reflect the real state of affairs. At the third stage of the algorithm, the molecule was constructed in **ChemDraw Ultra 12.0** and its nuclear magnetic resonance spectrum H^1 and C^{13} was evaluated (Fig. 2).

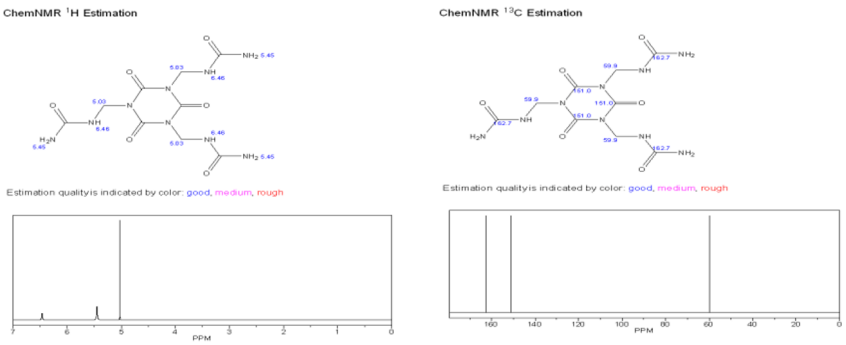


Fig. 2. Evaluation of the NMR H^1 and NMR C^{13} spectrum of the 1,1',1"-((2,4,6-trioxo-1,3,5-triazinan-1,3,5-triyl)tris(methylene))triurea molecule

In the Chem3D Pro 12.0 program, using an expanded and modified version of the MM2 force field using the molecular mechanics method, geometry optimization and conformational analysis of sorbent, a representative of the group of effective carbonyl and hydroxyl agents in the syntheses of hydrazone or dihydrazone ligands, were carried out.

For molecular mechanics and molecular dynamics calculations in Chem3D Pro 12.0 There is an item MM2 in the menu of the Calculations line, which contains the

corresponding items Minimize Energy for optimizing the geometry of the molecular system and Molecular Dynamics for running the molecular dynamics algorithm.

Theoretical calculations of bond lengths, bond and torsion angles, as well as the conformation of the molecule and the minimum energy were determined in the following fourth algorithm. To do this, select Molecular Dynamics from the Calculations menu bar in the MM2 menu item and run Run (Calculations → MM2 → Molecular Dynamics → Run). In the Dynamics tab, all the default options of the opened form were left unchanged: Step interval (Integration step size) – 2 fs (femtoseconds); Frame interval – 10 fs; Terminate After 10000 steps (Stop after 10000 steps); Heating/Cooling Rate – 1.000 Kcal/atom/ps (Heating/cooling rate, kcal/atom/ps); Target Temperature – 300 K. In the Job Type tab, turn off the Record Every Iteration item so that the molecular dynamics trajectory is not saved. The results of the algorithm show that with an increase in temperature from 22.66±2.09 to 292.51±44.51 K, the kinetic energy of the molecule decreases from 0.2353 to 0.0000 kJ/mol [29]. Next, we optimized the geometry of the molecule and calculated the geometric parameters using the empirical method of molecular mechanics by selecting "Minimize Energy" in item MM2 or sequentially using the molecular mechanics program (Calculations → MM2 → Minimize Energy → Run). The calculation results of the fifth algorithm are presented in Table 1.

Table 1. Minimize Energy Analysis Results

English language	Properties
Stretch:	1.4479
Bend:	8.2895
Stretch-Bend:	-0.0740
Torsion:	13.5663
Non-1,4 VDW:	-15.6071
1,4 VDW:	-0.3947
Dipole/Dipole:	-45.3682
Total Energy:	-38.1402 kcal/mol

We calculated geometric parameters (bond lengths, bond and torsion angles) and conformational analysis for H_2L^1 in the specialized application Chem3D Pro 12.0 of the ChemOffice software package [23] using an extended and modified version of the MM2 force field using the molecular mechanics method.

Using the method of molecular mechanics, we calculated the bond lengths, bond and torsion angles, as well as the conformation and minimum energy of the H_2L^1 molecule equal to –17.3859 kcal/mol.

3.2 IR spectroscopic study

In the IR-spectrum of SA+MFO - sorbent, absorption lines of medium intensity corresponding to the valence vibration frequency of symmetric N-H groups are visible in the areas of 3197.98 and 3049.46 cm^{-1}. Absorption lines of the (N-H) imide group correspond to valence vibrations in the 2883.58-2775 cm^{-1} area, while deformational vibrations of the N-H bond were observed in the 1398.39 cm-1 area. Absorption lines of medium intensity were seen in the region of 1795-1683.86 cm^{-1} for the bonded C=O group. Absorption spectra in the region of 1458.18 cm^{-1} correspond to the frequency of valence vibrations of the s-triazine ring (Fig. 3, 4).

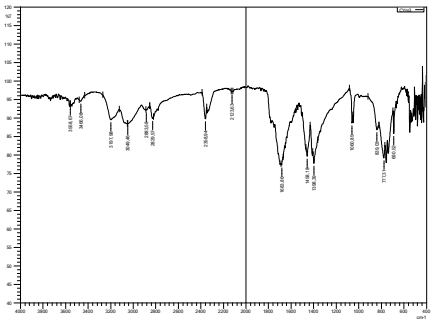


Fig. 3. IR spectrum of SA+MFO

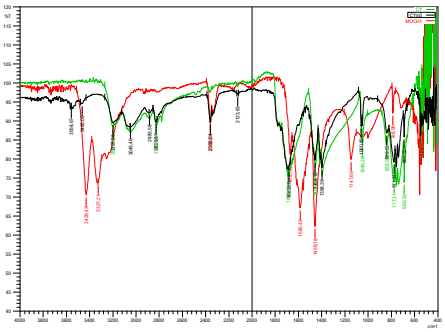


Fig. 4. Comparative spectra of SA+MFO and reagents

3.3 X-ray diffraction analysis of SA+MFO

Identification of oligopeptide derivatives based on cyanuric acid, i.e. individuality, was proved using X-ray phase analysis (powder diffractometry) method. For example, when comparing the X-ray image of the mono-urea-formaldehyde substituted cyanuric acid derivative with the X-ray values of the cyanuric acid and melamine cluster, it can be observed that the corresponding crystal beds are different. The observation of intense bands in areas 20.12, 27.22, 31.17, 43.23 of the SA+MFO sorbent confirms the individuality of the substance (Fig. 5, 6) [30].

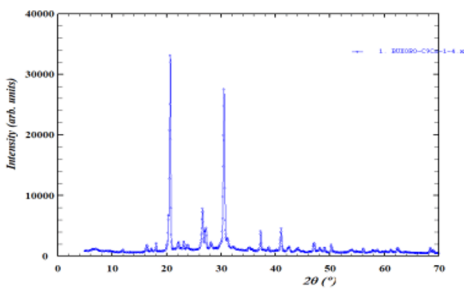


Fig. 5. Diffractogramm of the SA+MFO

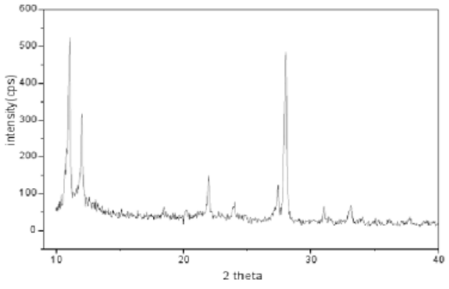


Fig. 6. Diffractogramm of the cyanuric acid and melamine cluster

3.4 The effect of the pH of the SA+MFO medium on the sorption of metals

A cyanuric acid-modified urea formaldehyde oligomer SA+MFO was studied to depend on the size of the pH environment of some D-metal sorption, and the results obtained were graphically illustrated (Fig.7).

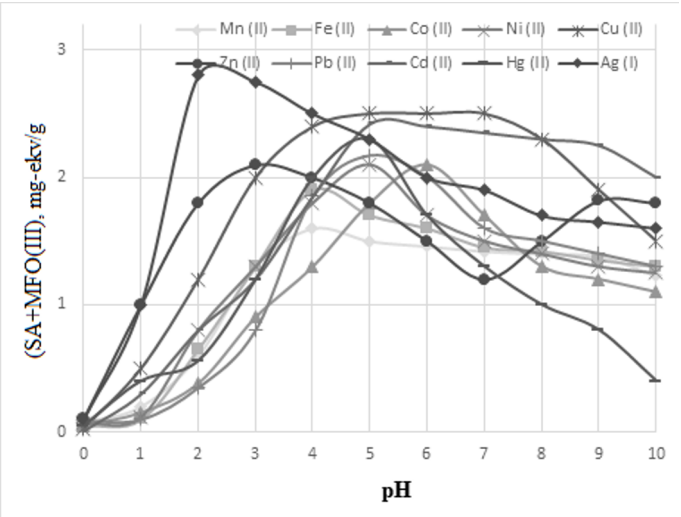


Fig. 7. Graph of the effect of pH on sorption of d-metals in SA+MFO medium (S_{Me}=0.1 n, m_{sorb}=0.1 g, τ=2 s, V=10 ml).

From graphs in synthesized complex-forming oligopeptides where metal sorption is described as dependent on ambient pH size, it is seen that the sorption of metal ions in ligands is relatively greater in weakly acidic environments. A study of metal sorbents in the (SA+MFO) sorbent found that the sorbent's static exchange capacity (mg-ekv/g) would be the following at the size of the optimal pH environment:

Mn (II) -1,6 (pH=4); Fe (II) – 1,85 (pH=5); Co (II) – 2,1 (pH=6); Ni (II) – 2,1 (pH=5); Hg (II) - 2,3 (pH=5), Cu (II) – 2,5 (pH=4); Cd (II) - 2,4 (pH=5); Zn (II) - 2,1 (pH=5); Pb (II) - 2,17 (pH=5); Ag (I) - 2,8 (pH=2). The graph in Figure 22 shows that as the pH of the solute medium increases, that is, the degree of sorption of ions of metals from pH=2 to pH=6 passes through the maximum. As the value of the ambient hydrogen indicator increases from 6 to more neutral to alkaline, there is a decrease in the level of sorption. This is evidenced by the fact that in an acidic environment, the ions of metals are sorbed by forming acidocomplexes with protonated active functional groups of the ligand, forming ion associations.

In sorption, the optimal pH size corresponds to the pH size of the formation of the acidocomplexes of the respective metals. Accordingly, the level of sorbation of the ions of the metals studied(SA+MFO (III)) in the sorbent increases in the following series:

Mn (II) < Fe (II) < Co (II) < Ni (II) < Zn (II) < Pb (II) < Hg (II) < Cd (II) < Cu (II) < Ag (I).

This sorbent contains amino -, imino-and carbonyl groups, and in weakly acidic environments these groups are protonated and activated. As a result, the ions of the metals are sorbed with the activated functional groups contained in the sorbent to form ion bonds. As the solute medium progresses to alkalinity, metal ions precipitate into the oligopepti sorbent phase, forming hydroxocomplexes in the corresponding hydroxides or strongly alkaline environments.

4 Conclusion

The oligomeric content of cyanuric acid has been found to be directly dependent on the acidity of the solution in which sopolicondensation occurs, and increased cyanuric acid coupling with decreased acidity.

The molecular mechanical method calculated bond lengths, valence and deflection angles, as well as the conformation and minimum energy of the SA+MFO(III) molecule equal to -17.3859 kcal/mol, and noted the donor atom properties to sorbate metal ions in itself as sorbents.

Sorbent contains amino -, imino-and carbonyl groups, and in weakly acidic environments these groups are protonated and activated. As a result, the ions of the metals are sorbed with the activated functional groups contained in the sorbent to form ion bonds. As the solute medium progresses to alkalinity, metal ions precipitate into the oligopepti sorbent phase, forming hydroxocomplexes in the corresponding hydroxides or strongly alkaline environments.

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