



Metal complexes of chitosan of *bombyx mori* with ions Co^{2+} , Cu^{2+} and features of their formation

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ABSTRACT

Influence of conditions of synthesis to a complex formation of a chitosan of *Bombyx mori* with Co^{2+} and Cu^{2+} has been investigated. It was revealed that at a complex formation of chitosan the factor pH has basic value during varying it, it is possible to receive polymer metal complex of various structure and type. Morphological and sorption researches of metal complexes of a chitosan were accomplished.

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KEYWORDS

Chitosan *Bombyx mori*;
Polymer metal complex;
Ions Co^{2+} and Cu^{2+} ;
Nanostructure.

INTRODUCTION

Research of physical and chemical properties and structure of macroligands, in particular, of biopolymers represents one of the most perspective approaches to a solution of the problem of the directed synthesis of polymer metal complex (PMC) with the given properties. Quite large amount of PMC containing almost any types of metals was synthesized, the kinetics of processes of a complex formation with the participation of polymeric ligands were researched, the main structural features of their structure taking into account polymeric effect as well as theoretical aspects of stereochemistry of coordination connections were revealed.

Purposeful selection of polymeric ligands carriers and right choice of methods of an immobilization allow constructing the fixed complexes of given structure using various synthetic methods of metal organic chemistry^[1].

It is established that the complex formation of ligands with metals increases their therapeutic activity, reduces toxicity of ions of metals and gives new specific properties^[2-4]. In this occasion the enormous numbers of researches on studying of a complex formation of biopolymers are implemented^[5].

EXPERIMENTAL

The examples of chitosan (CS) with molecular weight of $30-40 \times 10^3$ and degree of deacetylation (DD) of 75-80 % were given with deacetylation of chitin *Bombyx mori*, according to the technique described in the work^[6]. Chlorides of cobalt (II) and copper (II) of brand ch.p. were used as sources of ions of metals. Viscosity of CS solutions and its PMC were determined in acetum-water solution at 25 °C by viscosity method^[7]. The morphology of the examples was studied by electronic and microscopic methods – on nuclear and power microscope of

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AFM-5500 (Germany) and an optical microscope of BA-210 Motic (China).

RESULTS AND DISCUSSION

Synthesis of PMC of chitosan with ions Cu^{2+} and Co^{2+} was conducted taking into account the received results on influence pH to the reaction of chitosan. 1% solution of chitosan *Bombyx mori* in the diluted acetic acid is titrated by 0.1 M solution NaOH until the demanded value pH. Then estimate amount of ions of metals (1 mol of an ion of metal on 1 mol of amino groups of a chitosan) is added during intensive intermixing. Reactionary mixture is mixed up within 0.5-1 hours and it is besieged in acetone. The received powder is washed out by ethanol and dried up under vacuum up to the constant weight to allocate of not-reacted ions of metals from the complex.

As the complex formation of chitosan with ions of d-metals depends on a number of factors, influence of some factors (concentration of reagents, pH factor, temperature and etc.) was studied by us. Samples with various content of metals were synthesized to research of influence of initial concentration of Cu^{2+} and Co^{2+} to structure of PMC (Figure 1).

As it would be necessary to expect, with increase of concentration of ions of metals (R) in system their contents in PMC is increased naturally at pH = 4 - 5 and 6 accordingly. However change of pH factor has various impact on structure of PMC $CS-Cu^{2+}$

and $CS-Co^{2+}$. Possibly, it is connected with chemical nature of ions of cobalt (II) and copper (II). As it is established, at pH =4 interaction of ions of copper with the chitosan leads to formation of PMC of structure $CS-Cu^{2+}=2:1$ when at pH =6 structures $CS-Cu^{2+}=1:1$ and $CS-Cu^{2+}=4:1$ are prevailing. Perhaps, it is connected with that at pH=4 PMC are formed at the expense of a chemical bond as well as sorption of ions of copper (II) on the CS functional groups (primary and secondary hydroxyl groups, free amino groups and acetamide group of the chitinous residuum). When at higher values of pH coordinate connection is generally formed by interaction of ions of copper (II) with an amino group CS, it leads to reduction of the content of ions of copper (II) in complexes.

Proportional increase of the content of ions of cobalt (II) in PMC with increase of pH factor, probably, it is connected with that irrespective of pH, ions of cobalt (II) are interacting with atom of carbohydrate cycle of chitosan.

Influence of time of synthesis to the structure of PMC $CS-Cu^{2+}$ and $CS-Co^{2+}$ in the range of time of 5; 40; 80 and 120 min. is researched (Figure 2).

For $CS-Me^{2+}$ system the reproduced analytical facts were obtained after mixture of reagents as well as after keeping of reactionary mixes during defined time (till 120 min). It is obvious that time faintly influences to the content of ions of metals in complexes and it testifies that the complex is formed quickly

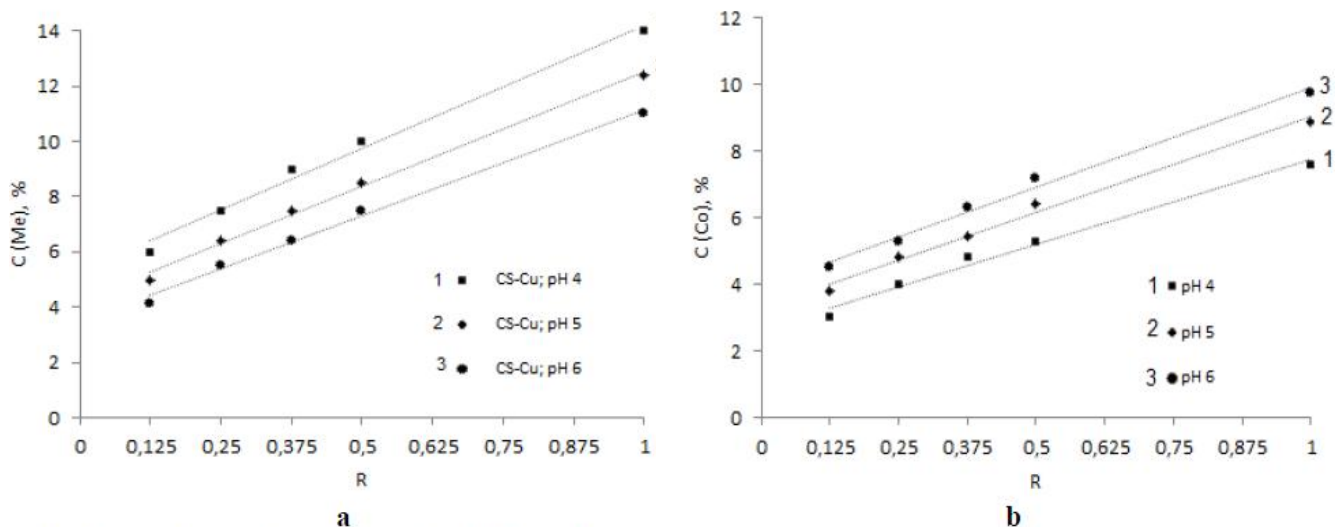


Figure 1 : Dependence of structure of metal complexes on correlation of reagents R (Me^{2+} /a monosection CS); CS (MM=40 000, DD=75%, $N_a = 7.62\%$) at various values $\delta \bar{i}$; $t = 25^\circ C$, = 40 min.

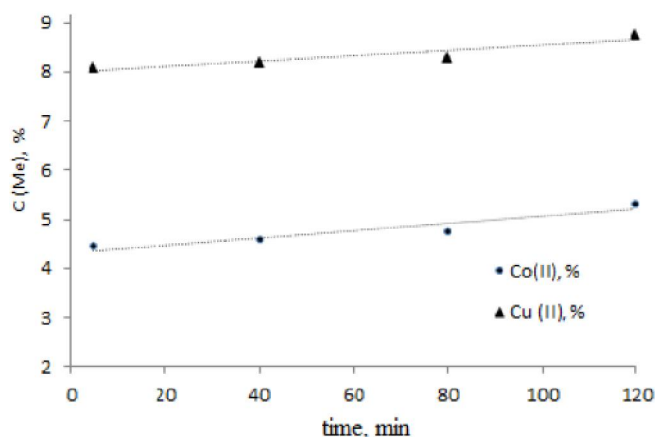
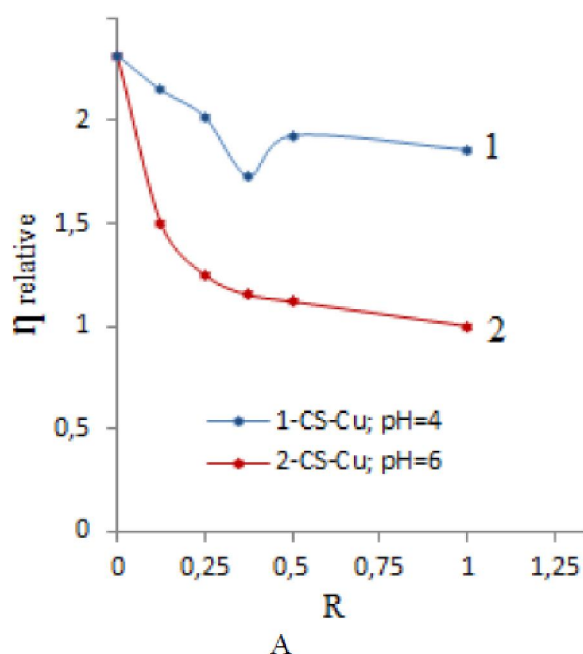


Figure 2 : Dependence of structure of metal complexes



relative viscosity of chitosan at presence and lack of ions of metals shows that initial values of viscosity of polymer – in lack of ions of metals have rather high values. There is a sharp falling of viscosity at addition of insignificant amount ($R=0.125$) of salt of metals. It should be noted that for PMC CS- Co^{2+} and CS- Cu^{2+} , synthesized at $\text{pH}=6$, with increase R relative viscosity naturally is decreased. However, for samples of CS- Co^{2+} , synthesized at $R=0.5$ and $\text{pH}=4$, sharp decrease of relative viscosity of solution which is caused by linking of ions of metal with polyelectrolyte is observed and it reduces the sizes of chain.

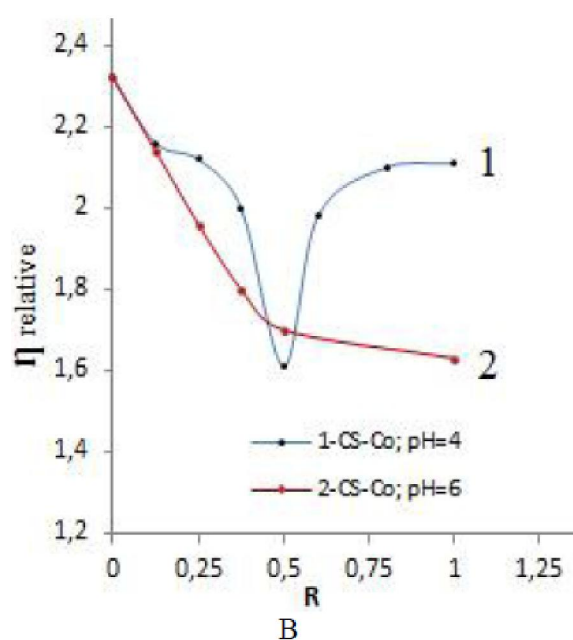


Figure 3 : Dependence of relative viscosity (η_{rel}) of solutions of metal complexes with ions of copper (II) and cobalt (II) from R reagents; concentration of solutions 0.5%; η_{rel} (0.5% CS) = 2.32

and its structure almost does not change by time.

Also we note that solubility of PMC of chitosan with copper and cobalt in acetic acid is equaled 98.5%. Increase of concentration of the CS initial solution to 2% promotes intermolecular interaction of ions of copper (II) with chitosan as a result of it partially sewed PMC CS- Cu^{2+} with solubility of 20-50% are formed.

It is well-known that the complex formation is defined, first of all, by the chemical nature of an ion of metal. It is also known that in fixing Me^{2+} in macroligands configuration and conformational effects are important. Influence of ions of Cu^{2+} and

Co^{2+} to conformational effects was researched through a viscosity method which is one of specific methods of research of polymers and complexes. Viscosity of the samples synthesized at various ratios of macroligand: Me^{2+} and pH reactions is researched. It is obvious that emergence of metal in the system of ions stabilizes conformational obstacles and it leads to reduction of viscosity of solutions according to the content of metal in PMC (Figure 3).

The results show that with increase both R and pH factor, the content of ions of Co^{2+} and Cu^{2+} in PMC is raised that leads to proportional reduction of relative viscosity of their solutions. The curve of

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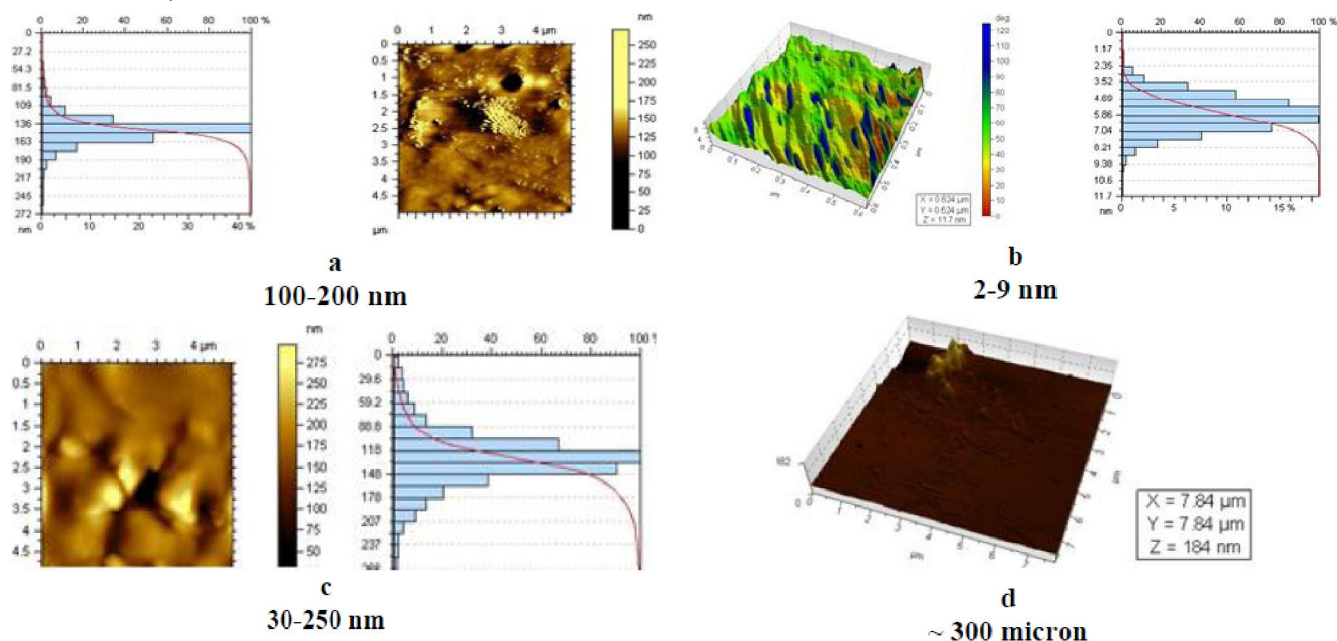


Figure 4 : AFM-pictures of nanoparticles CS- Co^{2+} and histograms of their distribution in a polymeric matrix. Conditions of synthesis of PMC: a – pH=4 and R=0.375; b- pH=4 and R=0.5; c - pH=5 and R=0.5; d - pH=6 and R=0.375

In similar conditions the reaction of molecules of PMC of chitosan with ions of copper (II) differs from the behavior CS- Co^{2+} , probably, it is explained by structure and content of the formed complexes. Apparently, in this case in decrease of relative viscosity of PMC solutions the structure of these connections takes the dominating role irrespective of the content of metal. Reducing of viscosity in case of PMC CS with ions of copper (II) at pH=4 and R=0.375 is explained with formation of the compact structures stabilized by the intra chain and inter chain “stitchings” significantly changing the hydrodynamic sizes of macromolecule where the role of the sewing agent is played by ions of metals. Possibly, it is explained with streamlining of a macromolecule CS at the expense of implementation of ions of metals to its structure and their interaction with functional groups of macroligand. It is established that pH systems are one of important factors to receive PMC of given content and various structure. The morphology of samples is researched to clarify of anomalous behavior of solutions CS- Cu^{2+} and CS- Co^{2+} , synthesized at pH=4 and R=0.5 and 0.375 accordingly. Morphological researches of samples of PMC received at various values of pH factor show a variety of their surface (Figure 4).

Morphological researches of surfaces of the films received on the basis of PMC CS- Co^{2+} testify that nanostructures are formed at pH=4 irrespective of R ratio in system. AFM-pictures, histograms of distribution of NP show that nanostructures in the range of 100-200 nanometers, with narrow distribution are formed in the samples of PMC CS- Co^{2+} , synthesized at pH=4 and R=0.375. We note that under constant conditions of synthesis increase pH to 5 leads to reduction of the sizes of the formed NP to 2-9 nanometers. According to the histogram NP are evenly distributed on all matrix and their average size is 5-7 nanometers. It should be noted that at R=0.5 increase pH to 5 leads to raising of the size of particles to 30-250 nanometers as well as degree of their polydispersion raises. Research of a surface of films CS- Co^{2+} , synthesized at pH=6 and R=0.375 by AFM method, testifies that there are particles of the size ~ 300 microns, i.e. there is no NP in the structure of films.

As results of AFM researches testify, CS, interacting with Cu^{2+} in the ratio $Cu^{2+}/CS=0.375$ at pH=4, 25°C, t=40 min, formes PMC which have nanostructure. Monodisperse nanoparticles have the size of 30-50 nanometers and a spherical form and they are also evenly distributed on a polymeric ma-

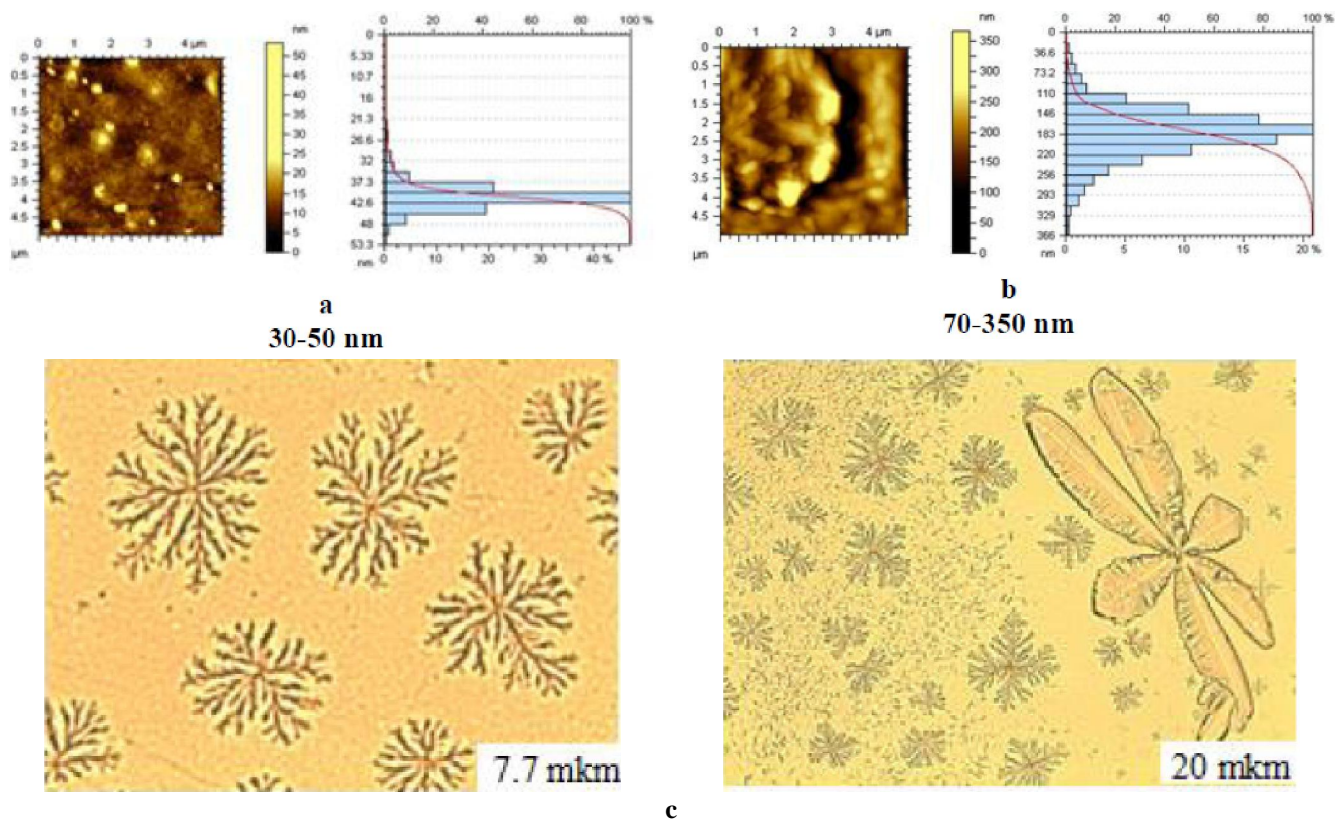


Figure 5 : AFM-pictures and histograms of distribution of nanoparticles CS-Cu²⁺ in a polymeric matrix. Conditions of synthesis of PMC: a – pH=4 and R=0.375; b- pH=4 and R=0.5; c – an optical picture of PMCCS-Cu²⁺, synthesized at pH=6 and R=1

trix. The increase of ratio of R to 0.5 leads to raise of the NP size to 350 nanometers and to expansion of an interval of distribution of NP on a matrix.

It is visible from the results that the average size of NP is 164 nanometers, i.e. 20% of total number of NP. PMC CS-Cu²⁺, synthesized in similar conditions at pH=6, has absolutely another architecture. It was not succeeded to investigate film by AFM method. The results of optical researches show that the complex has super branched structure.

Thus, research of morphology of PMC CS with ions Cu²⁺ and Co²⁺, synthesized at pH=4-6, showed that $\delta \hat{I}$ factors is an important factor regulating architecture (structure) of complexes. the spherical nanostructural monodisperse CS-Me²⁺ complexes with narrow distribution of the size are formed at pH=4. It is revealed that nanostructures are formed in the researched CS-Me²⁺ systems at pH=4-5 irrespective of a ratio macroligand: Me²⁺ in system where structural unit is the complex consisting of macromolecules and Me²⁺ are formed. It is estab-

lished that increase of pH from 4 to 5 leads to NP integration. It is revealed that PMC CS-Cu²⁺, synthesized at pH=4 and R=0.375, and also CS-Co²⁺ received at pH=4 and R=0.5 are nanostructured steady complexes. It should be noted that the variation of content and structure of PMC is connected with behavior of macromolecules of CS depending on pH factor.

It is known that a method of microencapsulation essence of which consists of giving of particles of Me²⁺ in cover from polymers as well as for regulation of dispersion of Me²⁺ on a matrix and creation of polymeric cover around the isolated ions^[1, 8, 9, 10, 11] issued receiving the polymer immobilized of catalysts. Accordingly to^[1, P.227], the transformations leading to emergence of polymeric cover around Me²⁺ is lying on the basis of chemical methods of microencapsulation are the cornerstone. The immobilization has essential impact on molecular design of polymers, formation in the process of polymerization of particles of a given size and form, appearance of



Preliminary scheme of microencapsulation of ions of metals by polymers^[1]

protective layers on surfaces of polymers, etc^[11].

Thus, proceeding from the analysis of literature and also on the basis of the obtained data, it is possible to assume that PMC received at pH=4-5 irrespective of a ratio of macroligand: Me^{2+} at the expense of microencapsulation form nanostructures, and the size of the microencapsulated particles varies with change of R and pH factor. Possibly, formation of nanostructural PMC is connected with behavior of macromolecules CS depending on pH factors. It should be noted that metals are in an ionic form in the synthesized systems, results of UV-researches testify to it as there are intensive strips of absorption of ions of copper (II) at 700-900 nanometers and cobalt (II) at 500 nanometers on ranges. It should be noted that viscosity of these solutions decreases that and it is peculiar to coordinate connections, besides, color of the formed PMC as well as an indicator of a condition of metals in a complex. In samples of PMC synthesized at pH=4-5 ions of metals in out of restored form as PMC CS- Cu^{2+} and CS- Co^{2+} have blue and light pink color. Usually nanosystems with NP of Cu^0 have color from red to brown depending on the size, and NP of Co^0 - brown color.

CONCLUSIONS

Thus, proceeding from the analysis of literatures and also on the basis of the obtained data, it is possible to assume that PMC received at pH =4-5 irrespective of ratio of macroligand: Me^{2+} at the expense of microencapsulation form nanostructures that the size of the microencapsulated particles increases with increase pH factor.

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