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Preparation and Characterization of Metal Complex Hydrogels Crosslinked with Hyperbranched Polyester

Ahmed A. Haroun*[1], O. A. Hakeim[2], Olga Trhlíková[3], Miroslav Šlouf[3], Miloš Netopilík[3]

[1]Chemical Industries Research Division, [2]Textile Division, National Research Centre 12622 Dokki, Giza, Egypt and [3]Institute of Macromolecular Chemistry, ASCR,v.v.i, Heyrovskho Sq.2, Prague 6,16206 Czech Republic.

THIS WORK deals with preparation and characterization of metal complex hydrogels based on crosslinked chitosan with hyperbranched polyester generation 2. These materials were prepared using miniemulsion technique with different ratios. Besides, the metal complexes using Co, Ni and Fe salts were investigated. All the prepared materials were characterized using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), particle size and zeta potential analysis using dynamic light scattering (DLS) technique. Moreover, XRF was also carried out. The results indicated that the successful network structures were obtained with particle size ranged between 118 and 148 nm. In addition, high performance metal complexes were prepared with metal percentages about 6.55, 7.01 and 6.56 (wt%), in the case of Co, Ni and Fe, respectively.Moreover, thermal analysis revealed that hydrogen bonds played an important role for hydrogel networks formation.

Keywords: Hyperbranched polyester,Chitosan, Miniemulsion, Metal complexes, Hydrogels.

Introduction

The grafted nanosurfaces using hyperbranched polymers have become an attractive research field because of their multifunctional properties [1-3]. Moreover, hyperbranched polyesters (HBPE) were previously used as crosslinking agents for polyurethane networks to explore novel polymeric materials in industry [4]. The high branching results in high solubility, low viscosity and could be used as initiator for ring opening polymerization of lactones. Chitosan is a biodegradable renewable polymer obtained by deacetylation of chitin. It has an excellent metals binding capacity by its physical or chemical modifications [5-12]. On the other hand, it has some disadvantages such as: acidic solubilization which prevents its use as insoluble sorbent in this medium. Consequently, it must be modified *via* crosslinking reaction. Some crosslinking agents could be used such as: epichlorohydrin (EPI), and glutaraldehyde [13, 14].

Nowadays, the water resources in the low-income countries suffer from the industrial effluents, which becomes a serious problem. Metal ion contamination has increased substantially because of the use of metal ions in many industrial applications.The functional polymeric composites have gained great importance in environmental applications for determining of toxic metal ions and their removal from aqueous media because of their high selectivity, excellent loading capacity and good recovery [15,16]. This work deals with preparation and characterization of metal complex hydrogels based on crosslinked chitosan with hyperbranched polyester generation 2 (HBPE) in the presence or in absence of acetate salts of cobalt, nickel and iron, separately. In other words, the study aims to enhance the hydrophilicity and metal binding ability of chitosan through incorporation of HBPE with 16-OH groups along chains using easy emulsion technique.

Experimental

Materials

Hyperbranched polyester generation 2 obtained from Sigma-Aldrich. Chitosan of low molecular

weight was obtained from Aldrich. All other chemicals and reagents were used as received.

Methods

Preparation of metal complex hydrogels using emulsion technique

Emulsion experiments [17] were carried out in tubes after homogenizing with high speed sonication. Chitosan (10 mg) was dissolved in aqueous acidic medium. The solution was mixed with different ratios (1:1 and 2:1) of HBPE in an aqueous solutions containing definite amounts of acetate salts of different metal salts (Co, Ni and Fe), separately and emulsified in presence of cetyltrimethylammonium bromide(CTAB) using an ultrasonifier (3 min at 200 W). In other experiments, the same ingredients were prepared without metal salts. The resulting hydrogels were separated using centrifuge, then collected and kept for further investigation, as shown in Table 1.

Characterization

All the prepared materials were characterized using different analytical tools:

1) Perkin-Elmer Fourier transform infrared spectroscopy (FTIR) under certain condition such as: scan resolution: 4 cm^{-1}, scan rate: 2 mm sec^{-1}, number of scan: 32, range: 600-3800 cm^{-1} and mode: transmission,

2) The shapes and morphologies of the preparations were examined by transmission electron microscopy using JEOL, JEM-1230 transmission electron microscope, Tokyo, Japan. Drops of the diluted preparations were deposited on a carbon-coated copper grid, then left to dry at room temperature for 10 min before investigation.

3) The particle size distribution and zeta potential analysis were recorded at: run time: 2 min, temperature: 23°C, solvent: water, concentration: 1mg/mL, using Gaussian/Nicomp distribution analysis, particle sizing systems Inc. Santa Barbara, California, USA.

4) The quantitative analysis of the metals was determined using XRF Instrument: Axios, Sequential WD_XRF Spectrometer, PANalytical 2005.

5) Thermogravimetric analysis (TGA) of the prepared samples was carried out on Perkin-Elmer thermogravimetric analyzer TGA 7. The dry samples were heated from room temperature to 700°C at 5°C/min.

Results and Discussion

Characterization of the crosslinked hydrogels

Figure 1 shows FTIR spectra of the prepared materials relative to chitosan and HBPE, separately. It was observed that the broad band at 3200-3500 cm^{-1} is attributed to OH stretching vibrations. In case of sample 2, HBPE crosslinked chitosan exhibited strong peaks at 2900 and 2850 cm^{-1} corresponding to CH$_3$ and CH$_2$ of HBPE. While, these peaks were decreased in case of samples 4, 5 and 6 due to the presence of metal complexes. The bands at 1652 and 1556 cm^{-1}are assigned to the carbonyl stretching of amide I bond and the N-H bending vibrations of amide II bond, respectively [18].The results indicated that crosslinking of chitosan by HBPE was occurred.

Figure 2 shows TGA diagrams of the prepared crosslinked chitosan with HBPE relative to chitosan and HBPE, respectively. It was observed that the chitosan and HBPE are found in the thermograms of the prepared hydrogels with ratios 1:1 and 1:2 (samples 2 and 3). It is worthy to mention that the weight loss at temperature range less than 200ºC is accomplished to the physically adsorbed water molecules. Moreover, in the case sample 2, at temperature region above 300ºC, the weight loss percentage of chitosan at 200-300ºC (33 %) is about nearly the same of HBPE at temperature region 300-400ºC(33.6%). While in the case of sample 3, the weight loss percentage of chitosan at 200-300ºC (24 %) is about two times higher than that of HBPE at temperature region 300-400ºC (40 %). This is proved that the obtaining HBPE crosslinking with different ratios typically as was mentioned in the experimental section. On the other hand, the presence of metals Co or Ni exhibited catalytic degradation of the prepared hydrogels [19].

Figure 3 A and B show SEM-micrographs and TEM images of the prepared hydrogels, respectively. When the metals (Co, Ni and Fe) were reacted with the composites, the surfaces exhibited high porosity and the particles became more stable and well dispersed in the matrices. In case of sample 1, the morphology showed rough surface. While in case of sample 2 (1:1), HBPE crosslinked chitosan exhibited smoother surface. When the concentration of HBPE was increased, small particulates were obtained and covered the surface. From TEM images, chitosan particles exhibited heterogeneous colloid shapes due to HBPE crosslinking reaction. While, in case of presence of metals, they adsorbed in between the
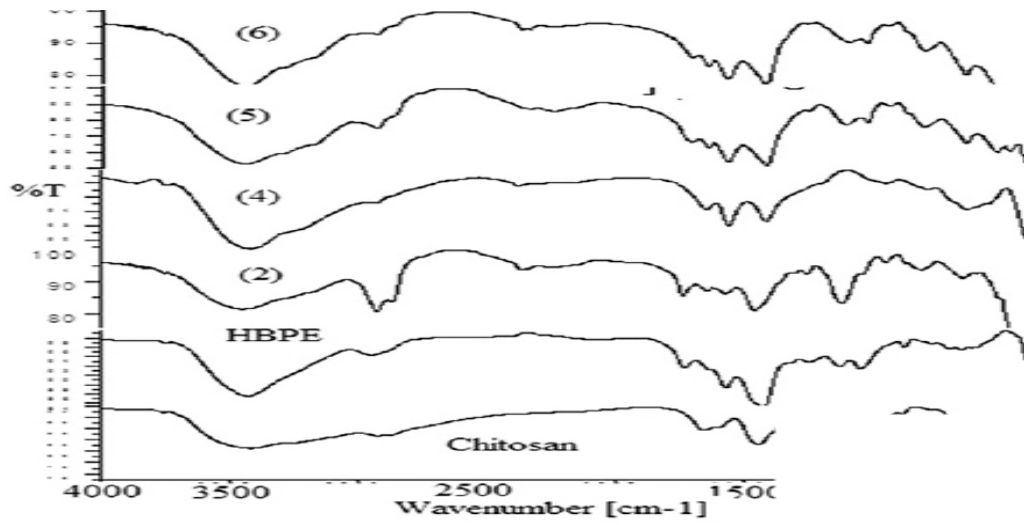
Fig 1. FTIR spectra of the prepared materials in comparison with chitosan and HBPE.
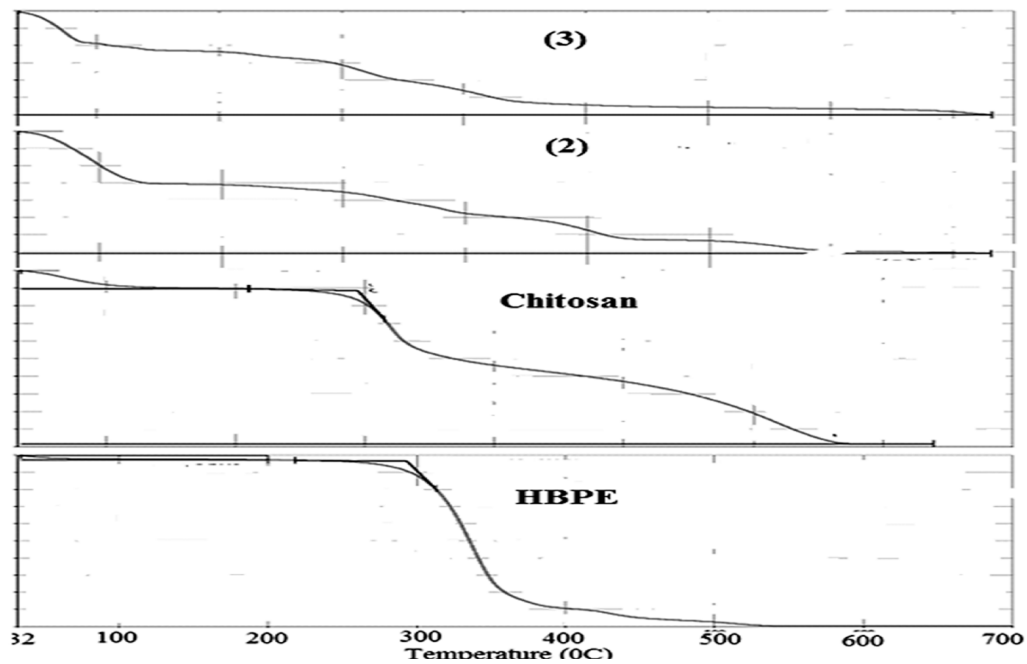

Fig 2. TGA diagrams of the prepared crosslinked chitosan with HBPE (2 and 3) relative to chitosan and HBPE, respectively.
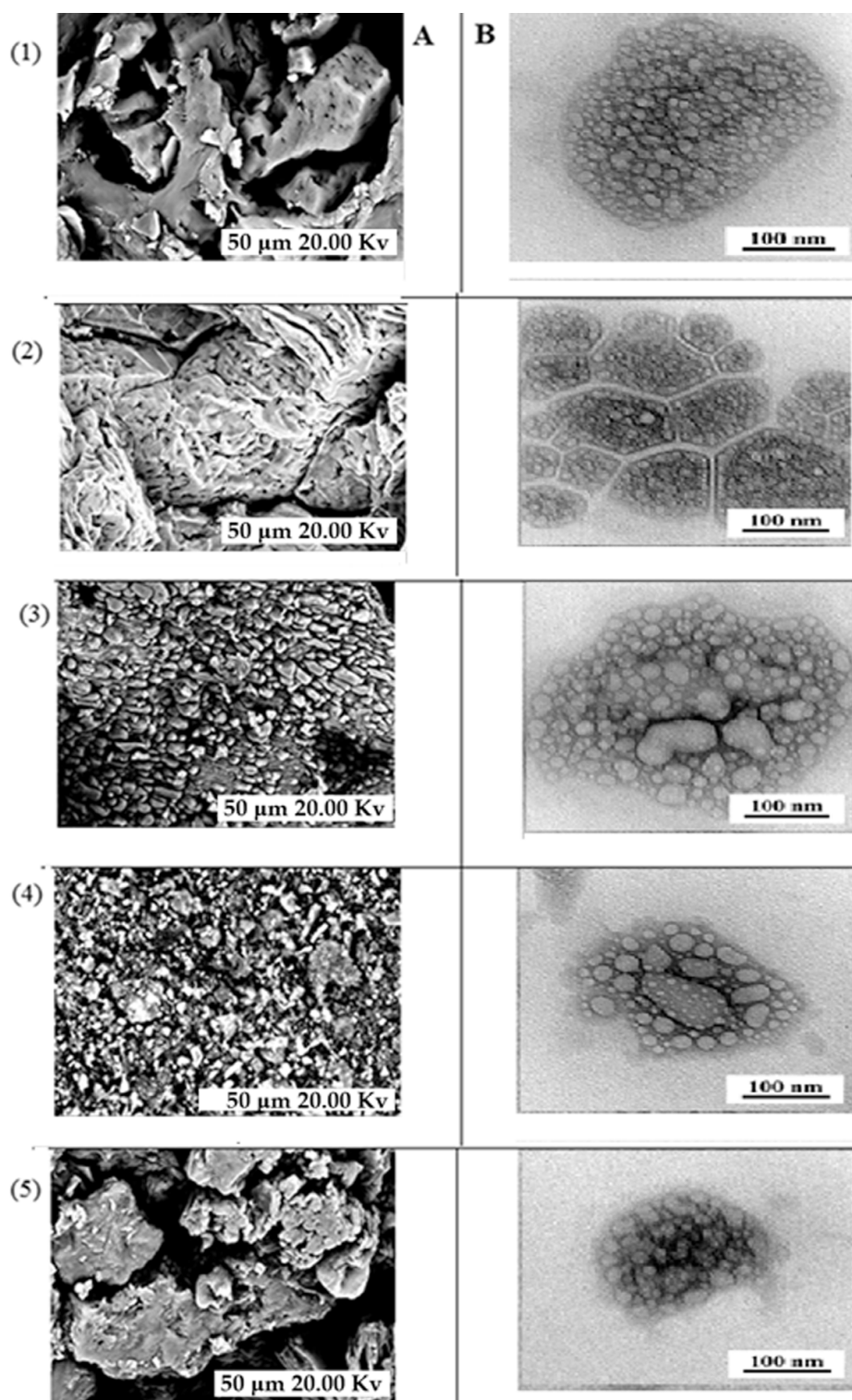
Fig 3. (A) SEM-micrographs and (B) TEM images of the prepared materials.

TABLE 1. Chemical composition of the prepared hydrogels

Sample Code	Chemical Composition (wt%)				
	Chitosan	HBPE	Co	Ni	Fe
(1)	20	10	-----	-----	-------
(2)	10	10	-------	------	-------
(3)	10	20	------	------	-------
(4)	10	10	10	------	-------
(5)	10	10	------	10	------
(6)	10	10	------	-------	10

TABLE 2. TGA data of the prepared hydrogels (2) chitosan/HBPE (1:1) and (3) chitosan/HBPE (1:2) relative to chitosan and HBPE separately.

Sample Code	Weight loss (wt%) at different temperature range			
	35-200ºC	200-300ºC	300-400ºC	400-700 ºC
Chitosan	12.2		58.0	
HBPE	---------		99.6	
(2)	33.0	33.0	33.6	---------
(3)	36.2	24.0	40.0	--------

individual stable colloidal shapes. It can be concluded that, the cobalt, nickel and iron metals were adsorbed at the surface and in between the network chains of the prepared hydrogels.

Figure 4 shows particle size and zeta potential analysis of the prepared samples 1, 2 and 7 using DLS technique. The particle size of the prepared hydrogels with ratios 2:1 and 1:1 are around 139 and 118 nm, respectively. While, the iron-complex has particle size around 136 nm. It is clear that the particle size distribution analysis exhibited narrow peaks one modal in case of chitosan/HBPE and iron metal complex (1:1). However, in case of 2:1 ratio, a bimodal of particle size distribution had been observed. This may be attributed to the increasing content of chitosan, which has an anionic –OH solubilizing groups with high PDI value (0.5) in comparison with that in case of the similar ratio (0.271). On the other hand, all zeta potential had negative values, which indicates that the prepared hydrogels were obtained with good stability particles. In other words, iron-complex hydrogel had high negative zeta potential value (-49 mv). It is assumed that the high zeta potential particles is more electrically stable than those lower values which tend to obtain flocculating and agglomerating particles with time. This assumption is arisen from the charged shell around the hydrogel particles, which is prohibited the particle-particle interaction and increased the dispersion stability. This was confirmed in terms of PDI values which are little changed in between 0.192 and 0.536 in case of iron-complex and uncomplexed hydrogel.

Metal-binding behaviour of the prepared hydrogels

According to the previous work [20], in case of using HBPE with low generation (16 –OH) as crosslinker agent, the metal ions could be easily diffused into the interior of the HBPE and to be adsorbed during the complex reaction. In spite of chitosan was not a suitable adsorbent because of the fact it was soluble in aqueous acidic solution and could not be recovered, crosslinked chitosan with HBPE could be used in acidic solution as well as its adsorption capability was improved.

Figure 5 and Table 3 show XRF data analysis of the prepared Co, Ni and Fe metal complex hydrogels. They demonstrated that the metal complex of the crosslinked chitosan with HBPE had been successful prepared. In other words, Co,

TABLE 3. XRF Analysis Results of the prepared metal complex hydrogels

Main Constituents in (wt%)	(4)	(5)	(6)
Fe	0.06	0.04	6.56
Ni	0.02	7.01	0.01
Ca	0.06	0.11	0.11
Na	15.10	19.85	17.67
K	0.02	0.02	0.01
Co	6.55	0.01	--
LOI	77.52	72.34	74.70

TABLE 4. Particle size and zeta potential measurements using DLS technique.

Sample code	Particle size (nm)	Zeta potential (mv)	PDI (Variance)
(1)	118±70	-6.88	0.536
(2)	139± 67.6	-11.8	0.271
(3)	582±430	17.17	0.554
(4)	679±495	29.71	0.531
(5)	509±330	-36.1	0.419
(6)	136±54.2	-49.3	0.192

hydrogel particles and the composites showed more
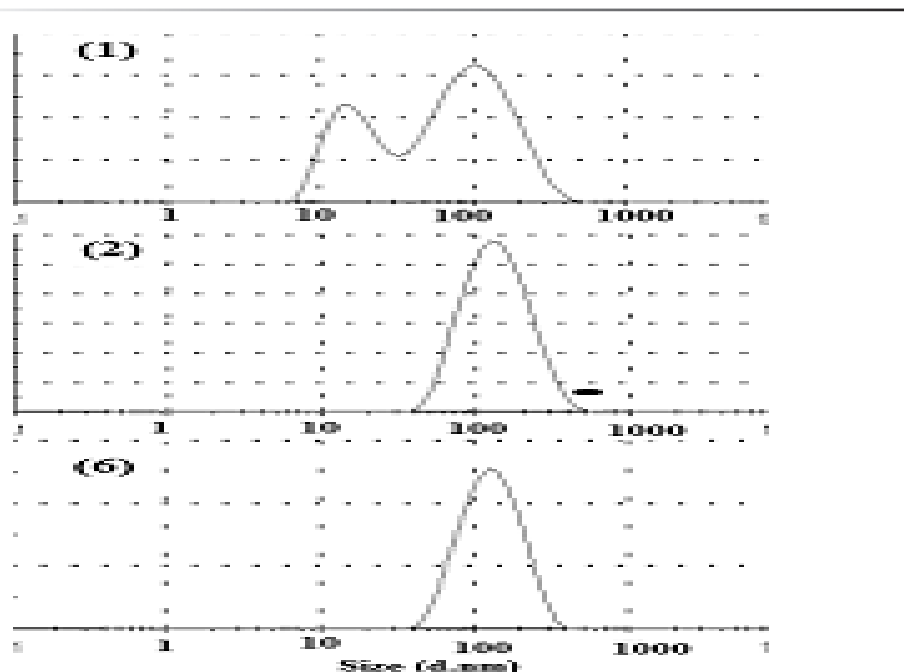
Fig 4. Particle size distribution and zeta potential analysis of the prepared materials using DLS technique.
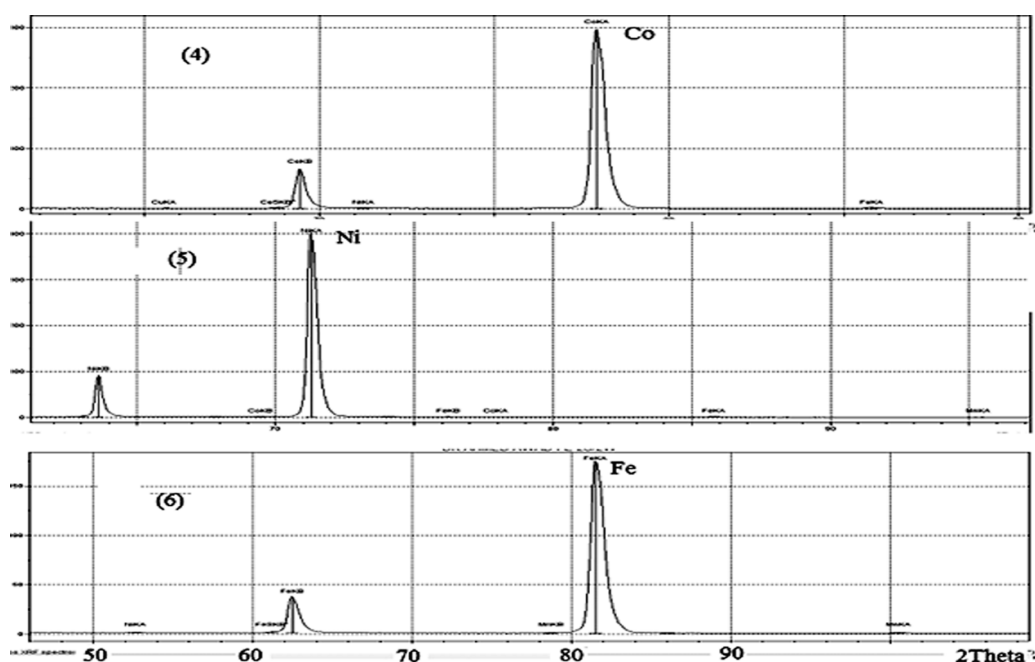
Fig 5 . XRF diagrams of the prepared metals complex hydrogels.

Ni and Fe percentages were decreased to 6.55, 7.01 and 6.56 (wt%) in the prepared samples relative to the initial metal concentrations (10 wt %), respectively.

Conclusions

Metal complex chitosan hydrogels crosslinked with HBPE generation 2, were successfully prepared in different ratios. The characterization gave supporting evidence for crosslinking of chitosan with typical ratios (1:1 and 1:2) as was mentioned in the experimental part. Moreover, the different metals Co, Ni and Fe were complexed with the hydrogels. The morphological observations indicated the presence of embedded metal ions. The prepared materials could be used as colour adsorbents. In other words, these complexed hydrogels have multifunctional application modes after further investigations.

Acknowledgment

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تحضير وتوصيف هيدروجيل معقد معدني متصلد شبكيا مع البوليستر عالي التفرع

أحمد عوض هارون١، أسامه عبد الحكيم علي٢، أولجا ترلكوفا٣، ميرسلاف سلوف٣، ميلوس نيتوبليك٣

١شعبة بحوث الصناعات الكيميائيه. ٢شعبة بحوث الصناعات النسجيه - المركز القومي للبحوث. شارع البحوث. ١٢٦٢٢ الدقي، الجيزه، مصر و٣معهد كيمياء جزيئات الماكرو - الاكاديميه التشيكيه للعلوم - براج - جمهورية التشيك.

يهدف هذا البحث إلي تحضير وتوصيف لهيدروجل معقد معدني مبني علي الكيتوزان ومتصلد شبكيا مع البوليستر عديد التفرع. تم تحضير هذه المواد بإستخدام تقنية الاستحلاب الدقيق بنسب مختلفه من املاح معادن الكوبلت والنيكل والحديد. تم توصيف جميع المواد المحضره بإستخدام الاشعه تحت الحمراء، التحليل الحراري الوزني، قياس حجم الجزيئات بإستخدام تقنية التشتت الضوئي الديناميكي، بالإضافه إلي قياس تركيزات المعادن.

أثبتت النتائج نجاح تكوين التركيب الشبكي المتصلد بحجم جزيئي يتراوح من ١١٨ إلي ١٤٨ نانوميتر. من ناحيه اخري تم تحضير متراكبات عالية الاداء تحتوي علي تركيزات ٦،٥٥، ٧،٠١، ٦،٥٦ للمعادن كوبلت ونيكل وحديد علي التوالي. أثبت التحليل الحراري أن الروابط الهيدروجينيه تلعب دورا هاما في التكوين الشبكي للهيدروجيل المحضر. يمكننا القول بأنه يمكن تطبيق الهيدروجيل المحضر في إمتصاص مختلف المعادن من الوسط المائي مما له من مردود إيجابي علي النواحي البيئيه.