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Synthesis and Characterization of Chitosan/Urea-Formaldehyde Hollow Resin for Metal Ion Removal

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In the current study, a series of hollow resins has been synthesized by using chitosan succinate and urea-formaldehyde resin as a cage resin to prepare new polychelates for different metal ions. Resins were characterized by FT-IR spectroscopy, thermal analysis and scanning electron microscopy. Resins have also been investigated for the removal of metal ions from their aqueous solutions through the formation of polychelates of the metal ions and their sorption capacity of such metal ions was determined. The hollow resin exhibited higher surface area than its separate components which facilitates higher ion uptake of metal ions from aqueous solutions.

Keywords: Urea-formaldehyde, Chitosan, Modification, SEM, Hollow resin.

INTRODUCTION

It is well known that the high polymers containing functional groups have attracted much attention since the beginning of the polymer chemistry on both academic and commercial levels. Also, numerous natural or naturally occurring polymers such as cellulose, starch, chitin and alginate have been chemically modified either through introduction of new functionalities or through chemical transformation of the present functional groups¹⁻⁵. Such chemical modifications were aiming to modification of their mechanical and/or physical properties of polymers to be suitable for certain applications^{6,7}. Among the most attention-attracting applications of the polymers is the application of the modified polymers in the wastewater treatment as well as for the isolation and separation of heavy metal ions from their aqueous solutions. Such polymers with certain functional groups are very important in the environmental applications⁸⁻¹⁰.

Ion-exchangers are usually used for separation and pre-concentration of species of different properties. Ions to be separated are often present in an aqueous solution, occasionally in aqueous-organic mixed solvents and rarely in pure organic solvents. The ion-exchanger is usually a polymer with a low solubility in the liquid phase and must have ionized groups chemically bonded to the polymer matrix. Such ionized groups are called ionogenic groups which are responsible for the ion exchange properties and the subsequent separation of ions.

The ionogenic groups are associated with ions of opposite charge (counter-ions) in just sufficient number to secure overall electrical neutrality. When the ion-exchanger is brought into contact with a solution containing ions of the same charge, ions in the solution may exchange with those in the ion-exchanger and equilibrium may set up. Hence, it is important to refer that the counter ions must not strongly bind to the ion-exchanger. Ions of opposite charge of the counter ions are called co-ions. Ion-exchange can remove traces of ionic impurities from water and gives out a product of ultra pure quality in a simple efficient and techno-feasible way. Ion-exchangers are commonly applied in water treatment and pollution control^{11,12}. Various hydroxybenzoic acid-formaldehyde and 4-hydroxy-acetophenone-biuret-formaldehyde copolymers have been reported as ion-exchangers^{13,14}.

Amino resins are often added during the processing of other materials to modify their properties^{15,16}. They are added to impart permanent press characteristics of textile fabrics, to improve the bonding of rubber to tire cord of automobile tires, to improve the tear strength of paper, especially of wet paper, and to improve the cure of alkyds and acrylics. Amino resins are also used for molding products, such as electrical devices, jar caps, buttons and dinnerware and in the production of countertops. It has been reported recently for the modification of urea-formaldehyde resin using different full generations of hyper-branched poly(amidoamine)s (PAMAM) as well as the corresponding ester-terminated half generations¹⁷.

Chitosan has been investigated due to its various advantages such as its environmental friendly nature and good ability to be dispersed in silicone oil¹⁸. Chitosan has polar amine and hydroxyl groups, thus, these polar groups may affect the electro-rheological behavior by acting as electron donors under the imposed electric field¹⁹. Therefore, chitosan shows good electro-rheological property without any treatment²⁰. Besides, there is a good possibility for those polar groups in chitosan to be attached to various functional groups. Due to these advantages, many researches are working in the field of electro-rheology of chitosan²¹⁻²³.

Our group has investigated the chemical modification of chitosan and urea-formaldehyde resins to be used in different applications such as removal of metal ions and *in-vitro* drug delivery systems. Chitosan has been modified with 5-fluorouracil to serve in the *in-vitro* antitumor drug delivery system^{1,2}. Chitosan has been modified also with different simple organic and polymeric materials as well as multi-walled carbon nanotubes (CNTs) to be used, for instance, in the ion-exchange applications^{6,8,9}. Also, both urea- and melamine-formaldehyde waste resins have been used as reinforcing materials within unsaturated polyester matrix⁷.

EXPERIMENTAL

All the employed chemicals have been purchased from Aldrich unless otherwise mentioned and used without further purification.

Preparation of urea-formaldehyde prepolymer: The pH of a 100 mL 38 % aqueous solution of formaldehyde was adjusted to 7-7.5 with aqueous solution of sodium hydroxide. The corresponding amount of urea was added at room temperature while stirring. After urea has been dissolved, the temperature of the reaction mixture was slowly increased to 90 °C for 1 h and to 95-98 °C for 1.5 h further. The reaction was terminated when the pH of the mixture reached about 5-5.5. A colourless sticky liquid product was obtained after adjusting the pH to 7-8. The experiment was conducted at 1:2; 1:1.5 and 1:1 molar ratios of urea : formaldehyde, respectively.

Synthesis of chitosan derivatives: 10 g of chitosan was mixed with 80 g succinic anhydride in a mixture of 400 mL dimethyl sulfoxide and 200 mL pyridine with stirring at 60 °C for 5 h. The modified Chitosan was washed with DMSO and deionized water before drying under vacuum at 40 °C.

Preparation of the hollow resin: 40 mL of 2 % aqueous solution of chitosan derivative was added to 1 mL of urea-formaldehyde solution and 0.215 g of ammonium chloride at 40-50 °C until a large quantity of gel formed. Then, the gel was isolated, dried under infrared light and finally ground and sieved to remove the coarse particles.

Synthesis of the metal polychelates: The polychelates of urea-formaldehyde resins with Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Cu²⁺ and Zn²⁺ were prepared by mixing aqueous solutions of 2.66, 1.97, 2.70, 2.37, 1.70 and 1.36 g, respectively, of the corresponding metal ions with 1.85 g of urea-formaldehyde resin in a 1:1.5 ratio. After stirring for 1 h, the mixture was left to stand and filtered. The solid product was dried overnight under vacuum at 40 °C. The ion uptake of the metal ions by the investigated resins is back-determined using ICP-AES spectroscopy (Table-1).

Characterization: FT-IR spectroscopic analysis was carried out by using a Perkin Elmer FT-IR Spectrophotometer. Thermal properties were investigated using Shimadzu Thermal Analyzer with a scan rate 10.0 °C/min in air atmosphere. Morphology of carbon nanotubes and composite was characterized by FEI-Field Emission Scanning Electron Microscope (FISEM) Quanta FEG 450, Netherlands. It has been achieved at the Electron Microscopy Unit in the Biology Department at KAU.

Surface area was determined from nitrogen adsorption/desorption isotherms measurements at 77 K by using a model NOVA 3200e automated gas sorption system (Quantachrome, USA). Samples were degassed for 6 h at 100 °C prior to measurement. The specific surface area was calculated by applying the Brunauer-Emmett-Teller (BET) equation.

RESULTS AND DISCUSSION

Prepolymer of urea-formaldehyde: The prepolymer samples of urea-formaldehyde (UF) with different composition of urea and formaldehyde were prepared in parallel to the method cited before²⁴ with some modification as described above in the experimental part. The obtained products were characterized by FT-IR spectroscopic analysis and shown in Fig. 1.

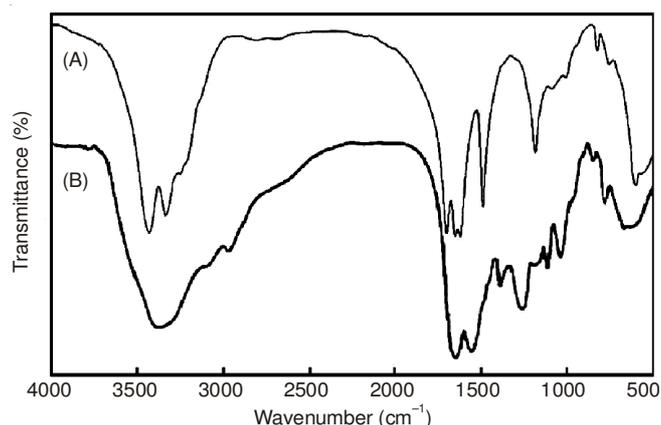


Fig. 1. FT-IR of (A): urea and (B): urea-formaldehyde resin

TABLE-1
ION UPTAKE OF THE DIFFERENT METAL IONS FROM THEIR
AQUEOUS SOLUTIONS BY THE INVESTIGATED RESINS

Sample	Ion uptake, mg/g polymer					
	Cu ²⁺	Cr ³⁺	Fe ³⁺	Co ²⁺	Mn ²⁺	Zn ²⁺
Urea-formaldehyde resin	1.90	1.96	1.64	1.58	1.42	1.38
Chitosan-succinate	2.6	2.2	1.82	1.9	1.86	1.74
Hollow resin	2.88	2.56	2.24	2.18	2.06	1.94

TABLE-2
FT-IR SPECTROSCOPIC DATA OF PURE UREA AND UF PREPOLYMER

Urea	UF resin	Assignment	Urea	UF resin	Assignment
3444s			1599s	1643	$\nu(\text{C}=\text{O})$
3347m	3422	$\nu(\text{N-H})$		1533	
3260s			1455m	1465	$\nu(\text{NH}_2)$
	3366	$\nu(\text{OH})$ and $\nu(\text{NH})$		1460	CH_2OH
	2946	$\nu(\text{CH})$ (sym.)		1298	$\nu(\text{CN})$
	2883	$\nu(\text{CH})$ (asym.)		1262	
	1880	CH_2OH		1085	$\nu(\text{C}=\text{O})$
1681 s	1635			1043	
1629s	1610	$\nu(\text{NH}_2)$	716w	720	$\nu(\text{NH}_2)$
	1643	Amide I & II		645	$\nu(\text{NH})$ bending
	1561		583m	590	$\nu(\text{CH})$

It is clear that the absorptions of N-H group at $\nu(\text{N-H})$ stretching frequencies are shifted to higher regions at 3422 cm^{-1} after the formation of UF prepolymer. Also, the characteristic absorptions of amide I, II, III are at 1635 , 1533 and 1465 cm^{-1} , respectively for urea. The main absorptions of urea and urea-formaldehyde resin are in Table-2.

Thermal analysis of urea-formaldehyde prepolymer:

Thermal analysis of the prepolymer of urea-formaldehyde shown in Fig. 2 proved that urea-formaldehyde prepolymer is stable up to about $360\text{ }^\circ\text{C}$ which accompanied by decomposition of about 75 wt. % and continued up to 82 wt. % decomposition at about $550\text{ }^\circ\text{C}$.

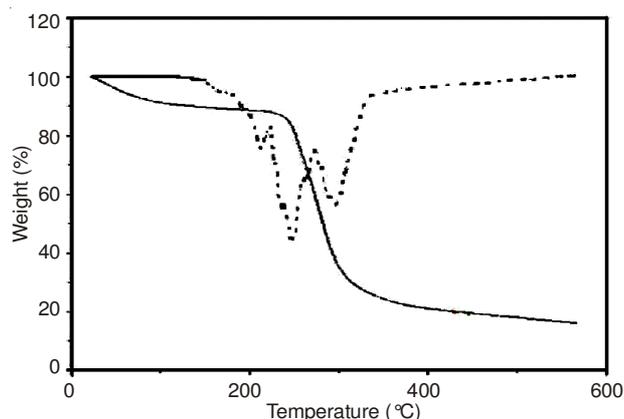


Fig. 2. TGA curves of urea-formaldehyde prepolymer

Scanning electron microscopy of urea-formaldehyde prepolymer:

Scanning electron microscopy of urea-formaldehyde prepolymer (Fig. 3) showed that the prepolymer is more or less homogenous in the particle size ranges from $3\text{-}5\text{ }\mu\text{m}$ which are not spherical in nature. Although the particles may look as loose particles and don't agglomerate to each other but actually they tend to agglomerate on standing for short time after preparation which lead to decreasing surface area.

Preparation of chitosan succinate: Chitosan succinate was obtained by reacting chitosan with succinic anhydride according to our previous work². The obtained product has been characterized by FT-IR spectroscopy. Fig. 4 shows the FT-IR spectra of chitosan (CS) and its succinate derivative (CS-succinate). The reaction of chitosan and succinic anhydride has been proved by the presence of the main characteristic bands of chitosan beside that for succinic acid at 1685 cm^{-1} .

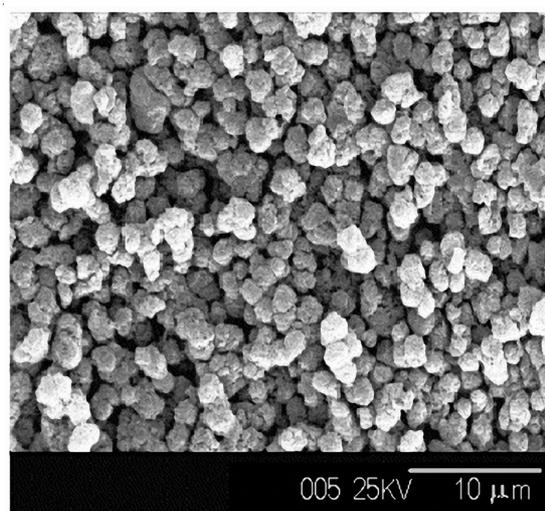


Fig. 3. SEM of urea-formaldehyde prepolymer

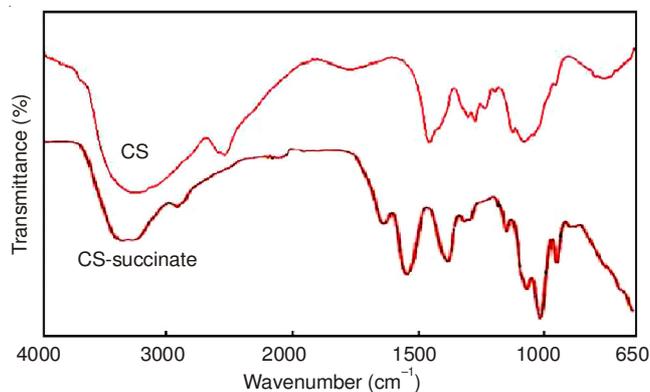


Fig. 4. FT-IR spectroscopic analysis of chitosan and chitosan-succinate

Thermal analysis of chitosan succinate: Thermal analysis of chitosan-succinate shown in Fig. 5 proves that chitosan-succinate is thermally stable up to $700\text{ }^\circ\text{C}$ where only 40 wt. % of chitosan-Succinate has been lost at about $220\text{ }^\circ\text{C}$. After that, there was no weight loss until the end of the measurement at $700\text{ }^\circ\text{C}$.

Scanning electron microscopy of chitosan succinate:

Scanning electron micrographs (SEM) of chitosan and chitosan-succinate are shown in Fig. 6 which shows that chitosan is neither crystalline nor fibrous material with any definite morphology as shown in Fig. 6A. After chemical modification of

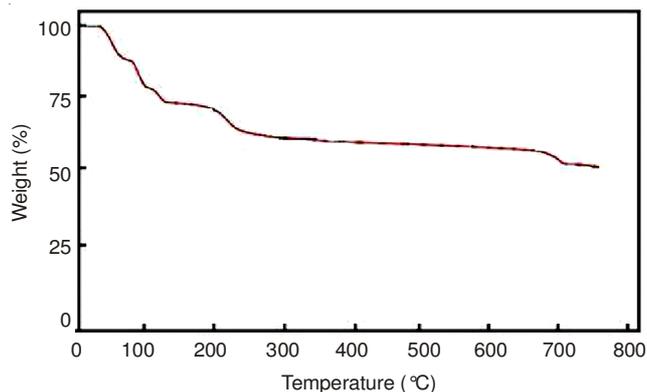


Fig. 5. TGA of CS-Succinate at heating rate of 10 °C/min

chitosan with succinic anhydride, the obtained chitosan-succinate has granular form with some inhomogeneous nature as shown in Fig. 6B.

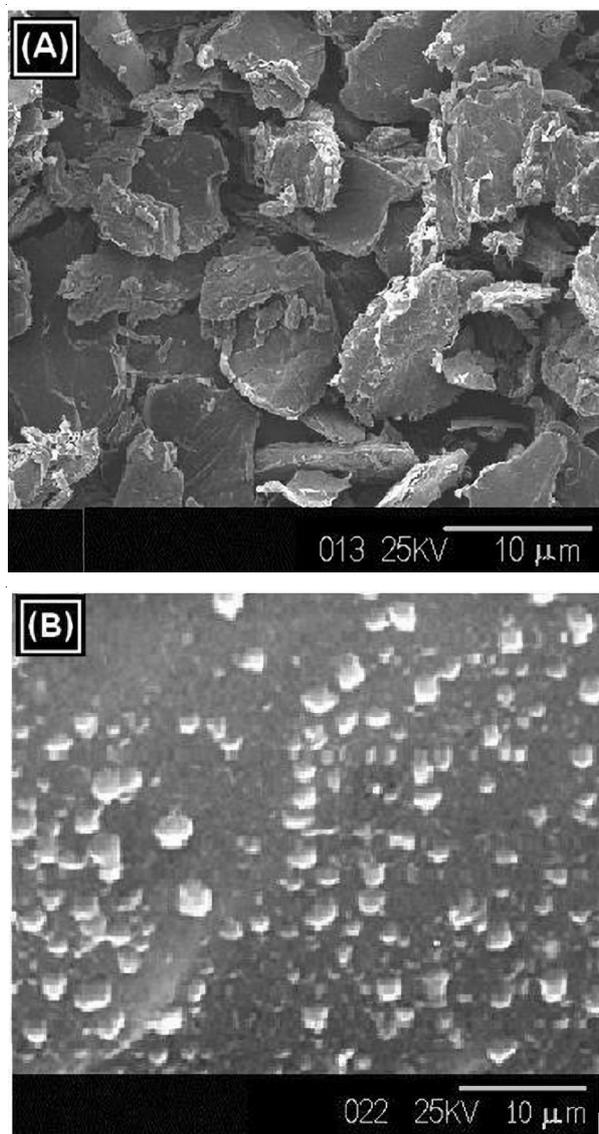


Fig. 6. SEM of (A): chitosan and (B) chitosan succinate

Chitosan succinate-urea-formaldehyde hollow resin: Chitosan succinate-urea-formaldehyde hollow resin has been

prepared as a gel material by mixing of aqueous solution of Chitosan succinate with urea-formaldehyde prepolymer in presence of NH_4Cl in parallel to the method cited before²⁴ with some modification as described in the experimental part. Fig. 7 shows the FT-IR spectrum of the chitosan succinate-urea-formaldehyde hollow resin.

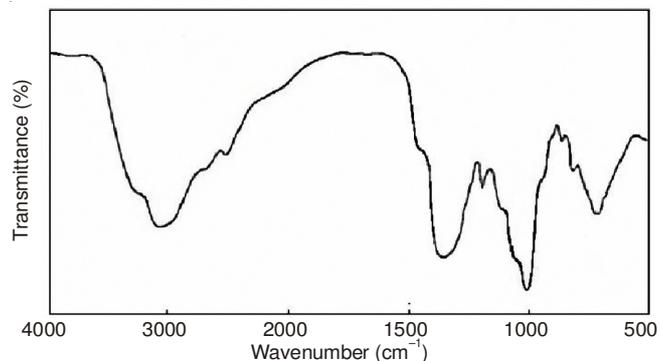


Fig. 7. FT-IR spectrum of chitosan succinate-urea-formaldehyde hollow resin

Recalling the FT-IR spectra of both chitosan succinate and UF prepolymer it is obvious that all the main characteristic bands of each component are shown in Fig. 7. This reveals that the hollow resin is composed of physically mixed components without chemical interaction between them.

Thermal analysis of chitosan succinate-urea-formaldehyde hollow resin: Thermo-gravimetric analysis of the hollow resin is shown in Fig. 8. It shows that chitosan succinate-UF hollow resin is thermally stable up to about 320 °C where about 60 wt. % of the sample remained unchanged up to around 700 °C. The TGA curve shows also that the sample has thermal behavior similar to the separate components of the hollow resin.

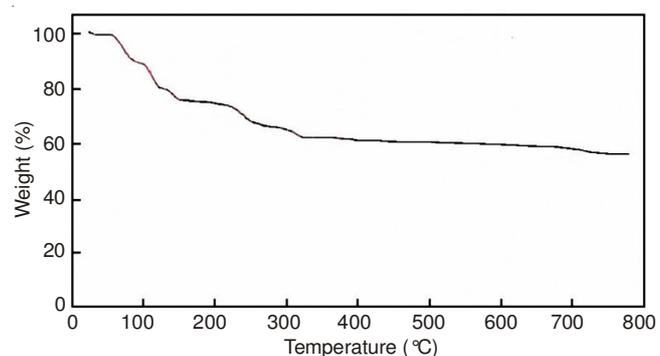


Fig. 8. TGA curves of chitosan succinate-urea-formaldehyde hollow resin

Scanning electron microscopy of the hollow resin: The hollow resin has been imaged by using scanning electron microscopy (SEM). Fig. 9 shows the micrograph of the hollow resin and it is obvious that the particles are not homogeneous in the particle size. In comparison to the micrographs of chitosan succinate and UF prepolymer one can notice that the ability of the hollow resin particles to aggregate is higher than that of the particles of the separate components. However, the hollow resin particles showed better characteristics in the light of their surface area and consequently their ion uptake of metal ions from their aqueous solutions.

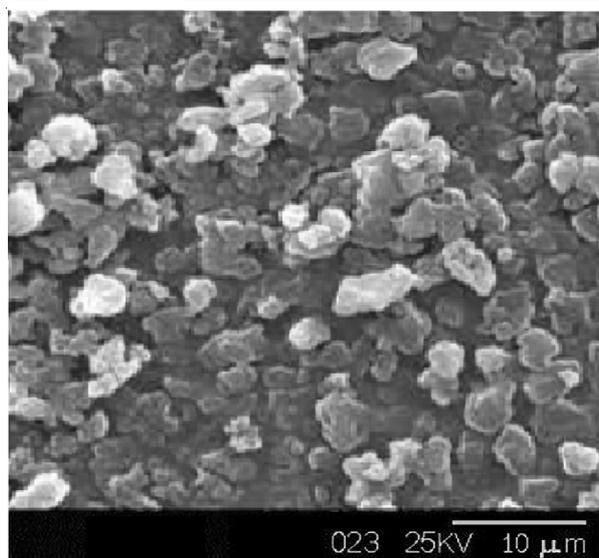


Fig. 9. Scanning electron micrograph of chitosan-Succinate/urea-formaldehyde hollow resin

Surface area measurements: The surface area of the particles of the hollow resin was determined using BET technique. The surface area measurements revealed that the modification process lead to higher surface area for the hollow resin than that for both of urea-formaldehyde prepolymer and chitosan succinate. The surface area was $140 \text{ m}^2/\text{g}$ for the hollow resin while it was 52 and $34 \text{ m}^2/\text{g}$ for urea-formaldehyde prepolymer and chitosan succinate, respectively.

The small surface area of urea-formaldehyde prepolymer and chitosan succinate can be attributed to the weak hydrophilic nature of urea-formaldehyde prepolymer and to the non-porous and non-fibrous nature of chitosan succinate. The modification process converted chitosan succinate gel material into thin films around the urea-formaldehyde prepolymer which was reflected on the surface area of the modification product.

Metal polychelates: The polychelates of urea-formaldehyde resins with Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Cu^{2+} and Zn^{2+} ions were prepared as described in the experimental part by mixing the suitable amounts of the corresponding metal ions with Urea-formaldehyde resin. The ion uptake of the investigated metals by urea-formaldehyde resin was determined by back determination of the remaining amount of metal ions using a Perkin Elmer ICP-AES spectrometer and shown in Fig. 10 where Cu^{2+} was the highest ion uptake while Zn^{2+} was the lowest one among the investigated metal ions. Chitosan succinate showed higher ion uptake than that for urea-formaldehyde resin as shown in Fig. 10. This can be attributed to the high ability of chitosan succinate to absorb water and consequently absorb high amount of metal ions.

On the other hand, chitosan succinate-urea-formaldehyde hollow resin showed ion uptake of the metal ion higher than both of urea-formaldehyde resin and chitosan succinate. The most acceptable justification to this result is the enhancement of the surface area of the hollow resin comparing with its separate components. Hence the enhancement of the surface area would more contributing than synergism due to presence of both components together.

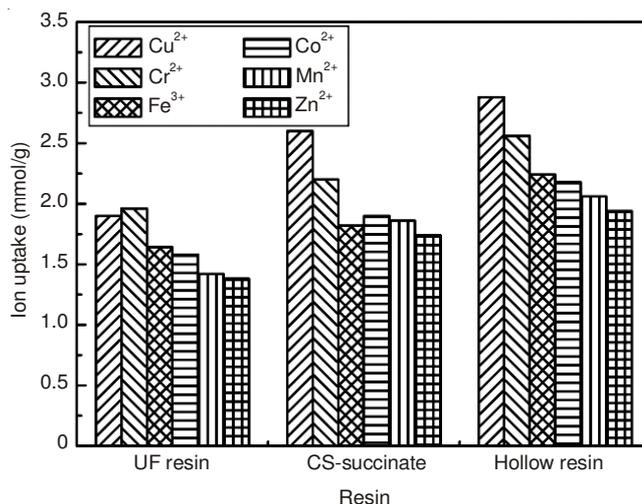


Fig. 10. Ion uptake of different metal ions by the investigated resins

Conclusion

Chitosan succinate and urea-formaldehyde prepolymer can be converted easily into hollow resin. The hollow resin showed good thermal stability and good ability to uptake metal ions from their aqueous solutions. It showed also reasonable exchange capacity to be used in ion exchange applications. The hollow resin obtained in a physical form suitable for application on a large scale which can help for mass production.

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