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STARCH CITRATE AS AN ION EXCHANGE MATERIAL – PREPARATION AND INVESTIGATION

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Waxy starch was allowed to react thermochemically with citric acid to yield starch citrate of high ion binding capacity. Purpose of the work was to prepare biodegradable ion exchange material of highest ion binding capacity. Reaction variables studied were: reaction time (15min–24h), reaction temperature (135-160 ºC), citric acid/starch ratio (0.3/1-5/1). Optimal reaction time vs. reaction temperature and optimal citric acid/starch ratio were determined. Best ion binding capacities were around 5 meqv/g (155-160 mg Cu^{2+}/g). Preparation of starch-citric acid granules proved to be possible in a batch mixer when saturated aqueous citric acid solution was sprayed on the stirred starch. The desired citric acid content was reached gradually. Samples were evaluated by ion binding capacity at pH 4.5 in aqueous Cu^{2+} solution. In further experiments the effect of bead size and the effect of the pH of solution on ion binding capacity was examined and preliminary column experiments were carried out to see how binding and regeneration steps work out in a glass column. Finally some tests were made to prove and investigate the biodegradability of Starch Citrate.

Keywords: ion exchange resin, environmental friendly chemicals, biodegradability

Introduction

Ion exchange resins of petrochemical origin have been used for the last few decades to remove heavy metal ions from industrial effluents. These resins are expensive, nonbiodegradable and produced from nonrenewable raw materials.

Using renewable resources is gaining ever greater importance in the European Community as well as in most countries of the world. Starch and citric acid are both produced in large quantity, they are inexpensive, environmental friendly, biodegradable and renewable. Obtained by their thermochemical reaction, starch citrate, the subject material of present study, is inexpensive and biodegradable, too.

Agriculturally produced materials can be derivatized to yield ion exchange resins [1,2]. These materials can be used for binding bivalent heavy metal ions like Cd, Cu, Pb, Ni, Zn.[4].

Among these modified materials starch citrate attracts attention with its high ion exchange capacities.

Several types of starch (waxy, corn, potato, wheat) were investigated from the aspect of ion binding capacity and durability against regeneration and starch citrate prepared from waxy corn starch proved to be of best properties among them [5].

The purpose of the present work was to prepare a biodegradable ion exchange material through modification of waxy starch by citric acid and investigate its properties as for further use in ion exchange columns.

Experimental

Materials

Waxy starch was supplied by Hungrana Ltd., Hungary, citric acid (CA) was supplied by Interkémia, Hungary. All other chemicals were reagent grade.

Reaction procedure

Laboratory scale: 200g of powdered CA was thoroughly mixed with 100g of waxy starch, then water was added and the mixture was rubbed till earth-damp.

Pilot scale: 1000g of waxy starch was placed in a batch mixer. While stirred, saturated aqueous CA solution was sprayed on it. When water content blocked mixing the product was dried and smashed through a 16 mesh screen; then it was put again into the mixer for further spraying. This process was repeated till desired CA content was reached.

Both the samples prepared by laboratory scale and pilot scale method were placed in forced air oven to dehydrate at 60 ºC for 24h. That way all surface moisture has been removed and the starch particles were sheathed with CA. Oven temperature was adjusted to 135-160 ºC and the mixtures were allowed to react for the reaction pre-determined time.

The resulting material was slurried in water for 10 min, then filtered, washed and air dried overnight.

Determination of copper binding capacity

1.000 g of each sample was slurried in 100 ml water containing 190 mg of Cu^{2+}. The Cu^{2+} solution was prepared from $Cu(SO_4)$. The pH was adjusted to 4.5 with 0.5 N NaOH and maintained at that level till the end of binding procedure. After filtration, copper was removed from the matrix with 50 m/m % HNO_3, and after filtration it was diluted for analysis with GBC Integra XM ICP spectrophotometer.

At laboratory scale experiments time of copper binding was 24h, while at the pilot scale experiment only 1h binding time was applied. This shorter time allowed faster determination of copper binding capacity and better control of factors (e.g. pH level) of the ion binding procedure.

Determination of biodegradability

10 g of each sample was put on a clock glass and exposed to the experimental conditions (kept wet; kept in a humid atmosphere). After about three months (101 days) the samples were investigated and the found results were evaluated.

Results and discussion

The purpose of the present study was to examine that at which values of the reaction variables (reaction time, reaction temperature, citric acid/starch ratio) will the thermochemical reaction of starch and CA result in starch citrate of possibly best ion binding capacity and to examine some features of the product in the light of further use in ion exchange columns.

When CA is heated it dehydrates and yields citric acid anhydride which can react with starch forming starch citrate adduct:

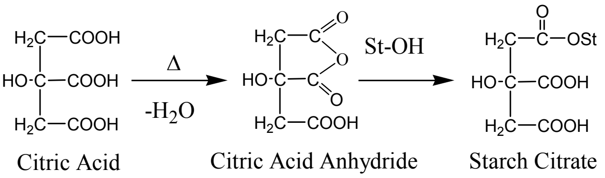

Figure 1 Thermochemical reaction of citric acid with starch resulting in starch citrate

If heated beyond an optimal reaction time, starch citrate dehydrates again and crosslinking can take place which results in drop of the ion exchange capacity of the matrix.

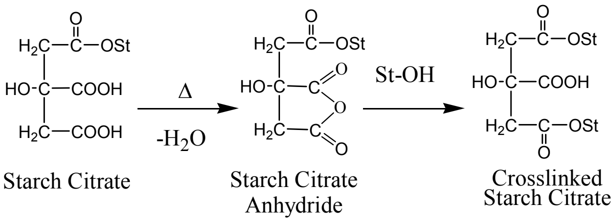

Figure 2 Further thermochemical reaction of starch citrate with starch: cross-linking

So determining the optimal reaction times at relevant reaction temperatures is essential.
The reaction variables studied were:

- Reaction temperature: 135-160 ºC
- Reaction time: 15 min-24 h
- Citric acid/starch ratio: 0.3/1-5/1

Laboratory scale experiments

At the first set of experiments the temperature range examined was 135-150 ºC by 5 ºC steps and at a range of reaction times 30-120 min by 30 min steps *(Fig. 3)*.

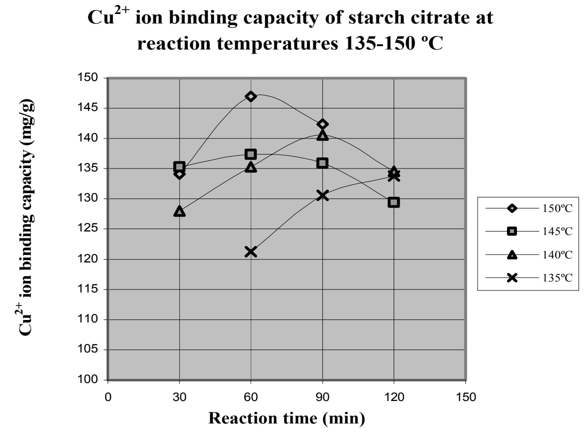

Figure 3 Results of experiment No.1.

Examining the curves the conclusions can be drawn that the optimal reaction time at 135 ºC is >120 min, at 140 ºC about 90 min, at 150 ºC approx. 60 min, while at 145 ºC it can be found between 60 and 90 min. Data in Table I. sums up these findings.

Table I Optimal reaction times at reaction temperatures 135-150 ºC

Reaction temperature (°C)	Optimal reaction time (min)
150	60
145	75
140	90
135	>120

At the second set of experiments the temperature range examined was 150-160 ºC by 5 ºC steps and at a range of reaction times 30-90 min by 15 min steps *(Fig. 4.)* and at 135 ºC the reaction times were 120 min, 360 min, 540 min, 720 min and 1440 min *(Fig. 5)*.

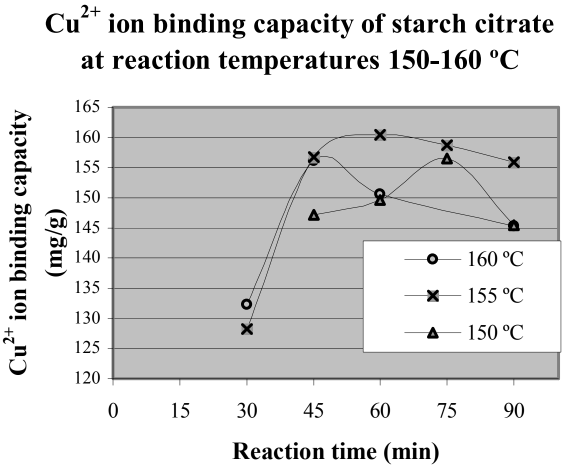

Figure 4: Results of experiment No.2.

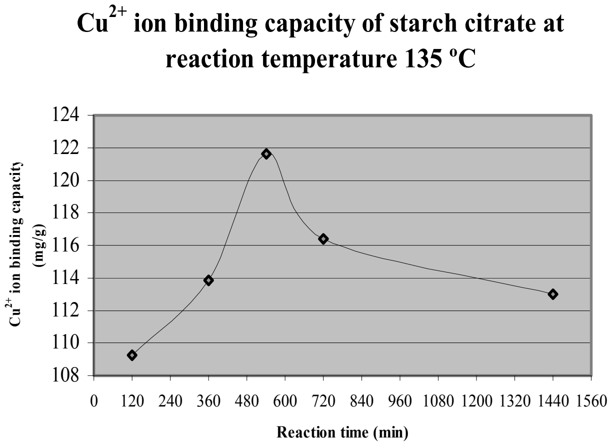

Figure 5 Results of experiment No.2.

From the figures it can be seen that the optimal reaction time at 135 ºC is around 540 min, at 150 ºC 75 min, at 155 ºC 60 min and at 160 ºC 45 min *(Table II)*.

Table II: Optimal reaction times at reaction temperatures 135 ºC and 150-160 ºC

Reaction temperature (°C)	Optimal reaction time (min)
160	45
155	60
150	75
135	540

The above results can be summarized in a graph showing the dependence of optimal reaction times on reaction temperature:

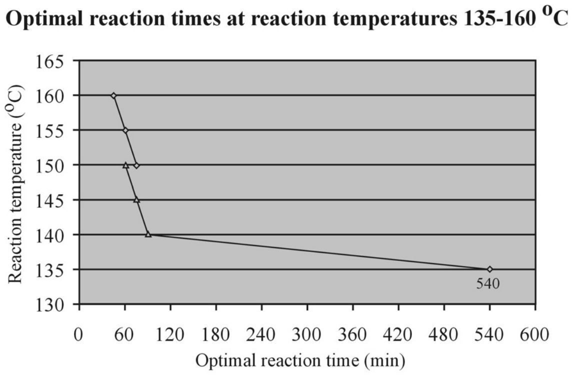

Figure 6: Optimal reaction times at reaction temperatures 135-160 ºC

Pilot scale experiments

Pilot scale experiments were carried out to examine the possibility of preparation of starch-citric acid granules in a batch mixer, the ion binding capacity of the starch citrate made out of the granules and at the same time the optimal citric acid-starch ratio.

The batch mixer used in the experiments has the dimensions shown in *Fig. 7*.

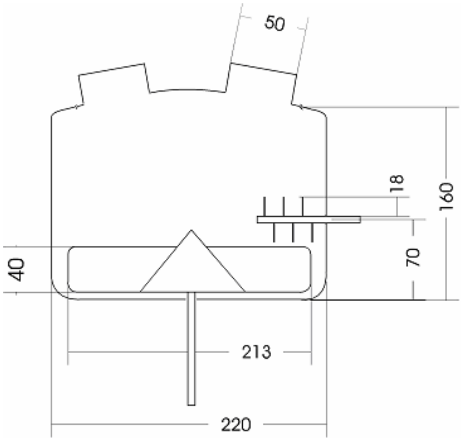

Figure 7 The dimensions of the batch mixer (mm)

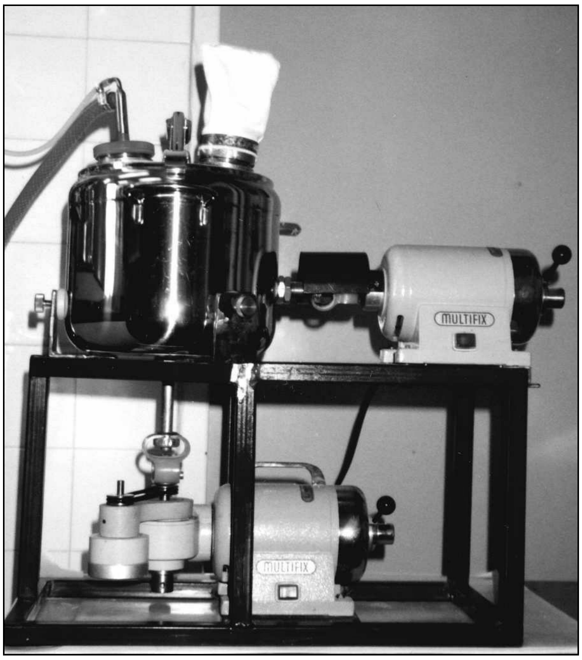

Figure 8 The batch mixer used at the experiments

The main impeller (100-350 rpm) of the mixer imparts a 3 dimensional tumbling action to the mixture and the side mounted breaker impeller (1800-2300 rpm) chops the larger granules into smaller ones.

Into one of the openings on the top of the mixer a spraying head is fitted while the other opening - mounted with a filter bag - is for the outlet air.

The mix was prepared as described before.

The samples taken out at each step were allowed to react at 140 ºC for 90 min.

The ion binding capacities were determined at 1h exposition time in Cu^{2+} solution *(Fig. 9)*.

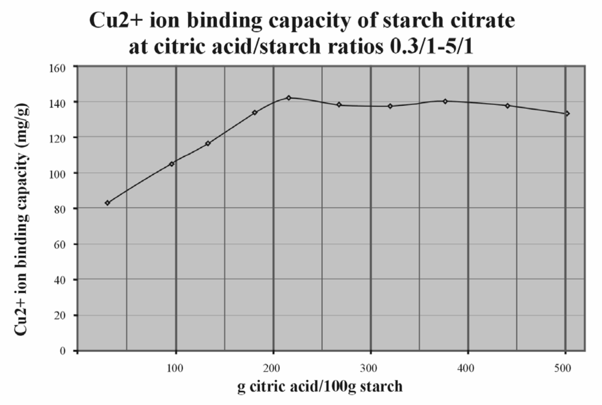

Figure 9 Cu^{2+} binding vs. CA/starch ratio

It can be made out from the graph that approx. 2/1 CA/starch ratio can be considered as an optimal mix composition beyond which no increase in ion binding capacity was experienced.

Ion binding vs. particle size

The particle size of an ion exchange resin influences the time required to establish equilibrium conditions. There are two types of diffusion that must be considered in an ion exchange equilibrium. The first is called film diffusion or the movement of ions from a surrounding solution to the surface of an ion exchange particle. The second is called internal diffusion and is the movement of ions from the surface to the interior of an ion exchange particle. The particle size of an ion exchange resin affects both film diffusion and internal diffusion. A small particle presents more surface area for film diffusion and also contains less internal volume through which an ion must diffuse. A decrease in particle size thus shortens the time required for equilibration.

Ion exchange processes are usually carried out in columns with resins filled in a column. The spherical particles of ion exchange resins resist the flowing of a liquid through or around them. The smaller the particle size, the greater will be this resistance and thus the pressure drop in the column. This resistance goes up very rapidly when particles smaller than Ø ~0.15 mm are used.

The starch-citrate granules were fractionated by sieves to <0.2 mm, 0.2-0.4 mm, 0.4-0.63 mm, 0.63-0.8 mm, 0.8-1.0 mm and 1.0-1.6 mm fractions. We have examined the amount of Cu^{2+} ions bound after 1h binding time.

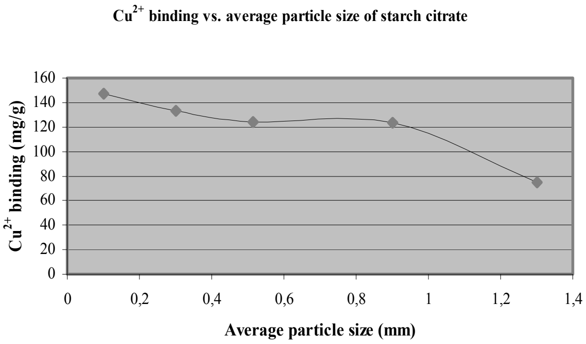

Figure 10 Cu^{2+} binding vs. average particle size of Starch-Citrate (Reaction temperature: 140 ºC, Reaction time: 1,5h, Cu2+ binding time:1h)

The figure shows well that fractions with smaller particle size can bind greater amount of Cu^{2+} ions within a short exposition time.

When using the material in an ion exchange column the pressure drop of the package is of much importance. According to the measurement results the diffusion at 0.2-0.4 mm particle diameter is still quick enough and pressure drop is expected to fall also into an acceptable range.

Ion binding vs. pH

Being a weakly acidic cation exchange material, ion binding capacity of Starch Citrate is greatly depending on the pH of the liquid processed. The tipical performance of a weakly acidic cation exchange resin is as seen on *Figure 11.*

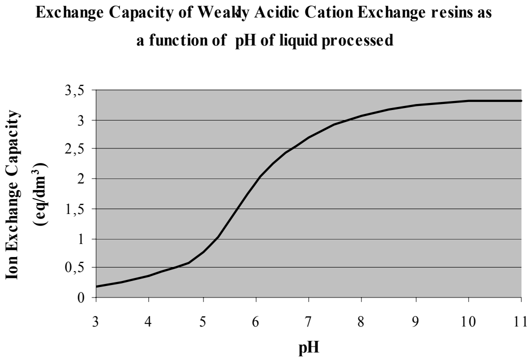

Figure 11 Exchange Capacity of a Weakly Acidic Cation Exchange resin as a function of the solution pH

If the pH is by 2 values less then the pK_a value of the carboxilic group then the ion exchange capacity practically becomes zero, while a maximum capacity is reached when the pH value is at least by 2 values higher than the pK_a value.

As in the case of Starch Citrate there are two carboxilic groups out of three that are still free and the corresponding pKa values are close to each other, the two exchange curves are overlapping and thus no such a characteristic curve can be detected.

The pKa values of the Citric Acid are: 3.1, 4.75 and 5.4 but in case of the Starch-Citrate we have to consider only the two greater value as the third carboxilic group is engaged in building the connection to the starch molecule.

pH<2,75 (=4,75-2) → 'zero' exchange capacity

pH>7,4 (=5,4+2) → maximal exchange capacity

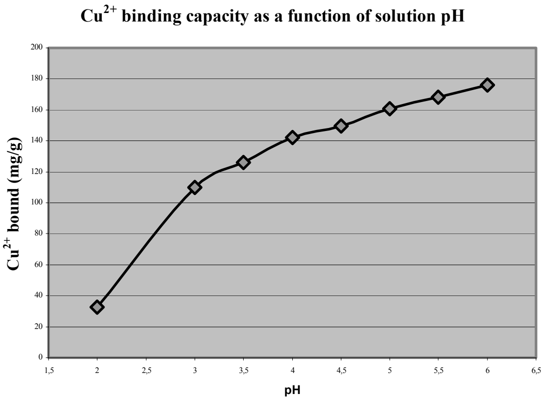

Figure 12 Ion Exchange Capacity as a function of the solution pH
(Starch Citrate reaction temperature: 140 ºC, Reaction time: 1.5h, binding time:1h)

As the measurements were carried out with Cu^{2+} solutions, at pH values higher than 6.0 the $Cu(OH)_2$ precipitation hindered the measurements.

Ion exchange in a column

Ion exchange processes are usually carried out with ion exchange resins filled into columns. So we made some preliminary experiments to see how Starch Citrate behaves when used in this way.

A glass column of 15 mm diameter was filled with 120 mm high Starch Citrate packing. $Cu(SO_4)$ solution of 10 g/dm^3 concentration was let to flow through the column by force of gravity. After the binding step the column was regenerated with 3 % m/m HNO_3.

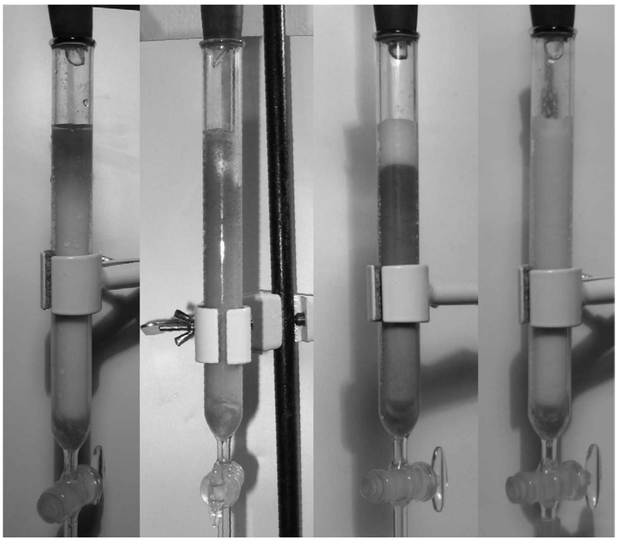

Figure 13 Ion Exchange process in a laboratory size glass column.
(a: ion exchange in process; b: starch citrate packing reached equilibrium; c: regeneration in process; d: fully regenerated)

When binding the Cu^{2+} ions the ion exchange front could be seen well, and while regeneration a sharp front could be detected by sight also. After the regeneration step was complete, no Cu^{2+} ion residue was left on the packing.

Both HNO_3 and HCl of 2-3 % m/m concentration was good regenerating agent for the Starch Citrate packing. Using HCl beyond 7 % m/m, $CuCl_2$ formation occured that can be seen from the yellowish green color appearance.

Some phisical properties of the packing:

Particle size:	0.2-0.4 mm (adjusted by mashing through sieves and screening)
Swelling (dry to wet):	2.2x
Wet density:	1.08 kg/dm^3
Dry density:	0.473 kg/dm^3

Measurements of further property values are in progress.

Investigation of biodegradability

One great advantage of starch citrate is its biodegradability. Some experiments were made to test this quality also.

Samples were kept in a wet condition for about three months. To quicken the degradation yeast infection was applied. Results can be seen on *Figure 14.*

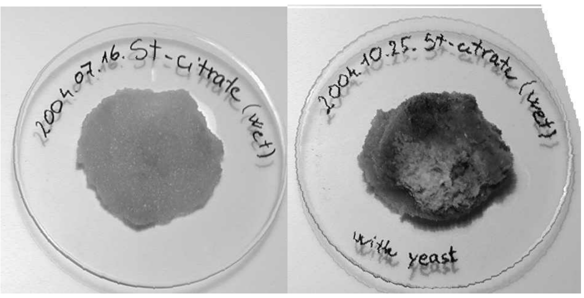

Figure 14 Samples of Starch Citrate kept in a wet condition for three months (a: before; b: after)

Other samples of Starch Citrate were kept in an atmosphere of high relative humidity for three months. The ones of H^+ form started to degrade properly while the ones of Cu^{2+} form kept their original condition even after this long exposition time.

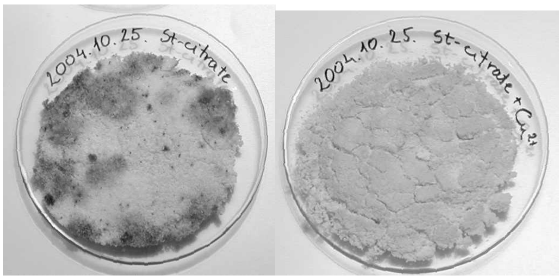

Figure 15 Samples of Starch Citrate kept in a humid atmosphere for three months (a: H+ form; b: Cu2+ form)

On *Figure 15*.a can be seen the well-developed microbial fundaments, while the Cu^{2+} content of the material impeded the degradation of the matrix.

Conclusions

The thermochemical reaction of starch-citric acid mix yielded starch citrate of high ion binding capacity.

Above 135 ºC optimal reaction times were found beyond which reaction times the ion binding capacity decreased, probably due to additional cross-linking.

An optimal citric acid/starch ratio was found (approx. 2/1 CA/starch) beyond which no increase in ion binding capacity was experienced.

With the pilot scale experiments using on-spraying technique we could prepare starch citrate of high ion binding capacity comparable to that of synthetic weakly acidic ion exchange resins. The best samples performed ~5 meqv/g (155-160 mg Cu^{2+}/g) ion binding capacity.

Starch citrate like traditional ion exchange resins can be used as packing in columns. It responses to the pH of the solution like other weakly acidic cation exchange resins, and the bead size of Starch Citrate can be adjusted to the desired average size by mashing through sieves and screening. Both binding and regeneration steps can be carried out in the usual way. For regeneration either HNO_3 or HCl of 1-3 % m/m concentration can be used properly.

The exhausted matrix after being regenerated can be deposed to an open field and the material will degrade in some months. Degradation can be quickened with application of degrading microbial infection. If heavy metal (e.g. Cu^{2+}) ions are bound on the matrix no considerable degradation could be detected.

Its low raw material and production costs together with its outstanding environmental friendly properties can make starch citrate a competitive alternative for traditional ion exchange resins.

Acknowledgement

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