

Novel biodegradable flocculating agents prepared by phosphate modification of Konjac

Chenxin Xie^{a,b}, Yujun Feng^{a,*}, Weiping Cao^a, Yu Xia^a, Zhiyong Lu^a

^a Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, No. 9, Section 4, Ren Min South Avenue, Chengdu 610041, Sichuan, PR China

^b Graduate University of the Chinese Academy of Sciences, Beijing 10039, PR China

Received 8 March 2006; received in revised form 31 May 2006; accepted 23 June 2006

Available online 23 August 2006

Abstract

A series of phosphate-modified Konjac was synthesized by esterification of natural polysaccharide Konjac, and comparative studies were conducted to examine the flocculation efficiency and biodegradability for the modified and unmodified products. It is found that both modified derivatives and the unmodified parent show flocculation ability and biodegradability. However, within the polymer concentration studied, the higher the phosphoric content, the better the flocculation efficiency is, and the modified analogues show superior biodegradability to that of the parent polymer. The degradation mechanism was confirmed by IR spectrum that the P–O–P bond was cut during the aging process at 30 °C.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Konjac; Phosphate esterification; Flocculant; Biodegradation

1. Introduction

Flocculant is an important family of components which cause flocculation by adding minute quantities of chemicals, and has played an important role in portable water purification, sewage and wastewater treatment (Bratby, 1980), etc. The flocculants can be conveniently classified into inorganic and organic categories. The inorganic flocculants with multivalent metals like aluminum and iron are mostly used. In general, organic flocculants are acrylamide-based polymers and more effective because they possess the advantages such as low dose, ease in handling, no interference with pH of the suspensions and larger floc forming capability (Bratby, 1980). However, the associated unreacted acrylamide monomers remained in synthetic polymers have been proved to be carcinogenic (Rice, 2005), though the synthetic polymers themselves are nontoxic. In addition, the unbiodegradable property presents another

major drawback of the polymeric flocculants, which will result in “secondary pollution” for environment.

To obviate these deficiencies of polymeric flocculants, “green” flocculants have been shown attractiveness in water treatment industry. These materials are normally prepared by modification of polysaccharide, which combined the merits of high flocculation efficiency from synthetic polymers and self-degradability from natural macromolecules. Singh group has successively investigated various biodegradable flocculants by grafting acrylamide onto natural polysaccharides such as guar gum (Nayak & Singh, 2001), xanthan gum (Adhikary & Singh, 2004), sodium alginate (Tripathy & Singh, 2001), carboxymethyl cellulose (Biswal & Singh, 2004a) and amylose (Karmakar & Singh, 1997), etc, and Khalil et al. (Khalil & Aly, 2001; Khalil & Abdel-Halim, 2001; Khalil & Farag, 1998; Khalil & Aly, 2002) developed a series of starch derivatives used as flocculants and chelating agents to remove heavy metals.

An attempt has been made in our laboratory to develop novel biodegradable flocculants based on Konjac glucomannan (KGM). KGM is a natural polysaccharide extracted from tubers of *Amorphophallus Konjac* plants

* Corresponding author. Tel.: +86 28 8523 6874; fax: +86 28 8523 6874.
E-mail address: yjfeng@cioc.ac.cn (Y. Feng).

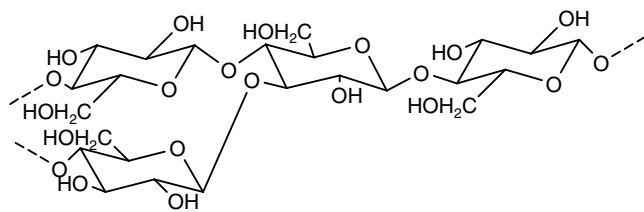


Fig. 1. The structural representation of Konjac glucomannan.

which grow in mountain or hilly areas mainly in the south-east Asia. Traditionally, it has been used as food and food additives in China and Japan. And now KGM has been extensively applied in pharmaceutical (Du, Sun, & Xiong, 2004), biotechnology, and chemical industries and some other areas (Zhang & Xie, 2005) because of its particular physical and chemical properties. As shown in Fig. 1, KGM consists of β -(1 \rightarrow 4)-linked-D-mannose and D-glucose residues as the main chain with branches through β -(1 \rightarrow 6)-glucose units (Katsuraya & Okuyama, 2003; Li & Xie, 2006). In a molar ratio of 1.6:1 (Kato & Matsuda, 1969) with branching of 8% degree, it has an average molecular weight of 0.67 to 1.9 million (Maeda & Shimahara, 1980; Maekaji, 1974).

Because of its high molecular weight and biodegradability (Chen, Liu, & Zhuo, 2005), it is possible to modify KGM through the O-H bond in its molecule architecture by esterification or graft functionality to a novel class of flocculants. Reported in this paper are the preliminary results of synthesis, flocculation performance and biodegradability of a series of phosphate-modified Konjac (PMKonjac).

2. Experimental

2.1. Materials

Fine powder (40~120 mesh) of purified Konjac was used as purchased from Root Ltd. (Chengdu, China) without further treatment. The effective KGM content in the powder is approximate to 75%.

Sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) and disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$), urea, hydrochloric acid, acetone, kaolin were commercial chemicals with analytical grade. All the chemicals were used as received without further purification.

2.2. Synthesis

The series of PMKonjac was prepared by modification of Konjac with phosphate followed the process reported in previous reports (Hu & Hu, 1990; Zhang & Yang, 1994), but with revision in this work. A typical procedure is as follows: appropriate amount of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ with 2 g urea were put into a beaker and were dissolved in 60 ml distilled water. pH of the final solution was adjusted to 2 by HCl. Konjac powder was then

added into the solution under magnetic stirring and the reaction was lasted for 5 min followed by transferring the reaction system into an oven to age at 60 °C for 2 h. Afterwards, the product was dissolved in distilled water and precipitated in excess of acetone. The obtained polymer was filtered and washed several times with acetone to remove unreacted Konjac and phosphate. The final product was dried under vacuum at 40 °C for 48 h prior to being stored in a desiccator. The feed ratio of the series of PMKonjac was summarized in Table 1.

2.3. Structural elucidation and phosphorous content determination

To confirm if phosphoric was introduced into the Konjac backbone, comparative FTIR analysis was performed with a Nicolet MX-1E Infrared spectrophotometer (KBr pellet) for the unmodified Konjac and the modified derivative PMKonjac-2.

A standard spectrophotometric method (ISO 3946, 1982) was employed to determine phosphoric content in the modified and unmodified Konjacs and the final results have been depicted in Table 1.

2.4. Flocculation test

Aqueous solutions (0.1%) of modified and unmodified Konjacs were prepared by dissolving designed amount of purified polymer powders into distilled water with mild agitation for 24 h. The stock solutions were then filtrated through stainless steel screen (200 meshes) to remove the undissolved microgel.

Flocculation performance of the polymers was examined using jar tests (Bratby, 1980): six beakers of 1% kaolin suspension prepared by mixing 1 g in 100 ml of distilled water were used for flocculation studies. Immediately after the addition of the polymer flocculants, all the suspensions were stirred with magnetic bars at a constant speed of 75 rpm for 2 min, followed by a slow agitation at 25 rpm for 5 min. The flocs were then allowed to settle down for 2 min. At the end of the settling period, the transmittance of supernatant liquid at 670 nm was measured using a UV-VIS spectrometer (HITACHI-U2010). The dose of flocculants was varied in the range of 0.1~3 ppm.

The flocculation characteristics were also measured by the column settling method (Biswal & Singh, 2004b). The

Table 1
Feed ratio and final phosphoric content in the series of Konjac products

Sample code	Feed ratio			Phosphoric content ^a (%)
	Phosphate (g)	Urea (g)	Konjac (g)	
Konjac	/	/	/	0.20
PMKonjac-1	4.0	2.0	6.0	1.73
PMKonjac-2	6.0	2.0	6.0	3.47
PMKonjac-3	9.0	2.0	6.0	4.98

^a Determined with spectrophotometric method (ISO 3946, 1982).

flocculation studies were carried out in 1 wt% kaolin suspension with the help of a 100 ml stoppered graduated cylinder. First, the kaolin suspension was put into the cylinder and then the polymer solution was added. The final polymer concentration in the suspension was kept at 1 ppm. The cylinder was then inverted 10 times for thorough mixing. After the cylinder was set upright, the height of sediment was measured over time interval.

2.5. Biodegradation study

Biodegradability of the polymer solutions was evaluated by monitoring the viscosity decay at a certain intervals of time with glass Ubbelohde capillary viscometers (ID: 0.5~0.6 mm). Viscosity measurement was conducted at 30 °C when bacterial activity is at a maximum (Singh & Karmakar, 2000a). The concentration of all polymer solutions was fixed at 0.1% and the pH of the aqueous solution was neutral.

To further examine the degradation mechanism of the modified Konjac, an FTIR spectral analysis was performed for the degraded PMKonjac-2: after 8 days of degradation at 30 °C, PMKonjac-2 was precipitated with acetone and dried in a vacuum oven at 40 °C for 48 h, followed by subjecting to FTIR analysis with KBr pellet method.

3. Results and discussions

3.1. Synthesis

Table 1 shows the synthesis parameters of the phosphate modification process of Konjac. The ratio of phosphate to Konjac was varied in order to examine the influence of phosphoric content on the flocculation efficiency. The added urea and acidity environment can fasten the esterification reaction. It is found that the final phosphoric content in the products increases with increasing the phosphate level in the feed ratio. Trace phosphor has also been

detected in the unmodified Konjac polymer. This is probably due to trace element resided in the natural Konjac (Kato & Matsuda, 1969).

Compared in Fig. 2 are the IR spectra of unmodified (Fig. 2(a)) and modified Konjacs (Fig. 2(b)). The peaks at 895 and 810 cm^{-1} are the characteristic absorption bands of mannose residues in the polysaccharides (Xiao & Liu, 2004). The broadband at 3381 cm^{-1} is due to the stretching mode of the O–H groups. An intense band at 1725 cm^{-1} is assigned to the first overtone of the O–H bending vibration and is considered as the absorption band of carbonyl of acetyl groups (Chiu, Hsiue, & Chen, 2004). The absorption band at 1636 cm^{-1} and 1151 cm^{-1} are corresponding to the intra-molecular hydrogen bonds and C–O stretching, respectively. The band at 1248 cm^{-1} is the fragment of CH_2OH , and the bands at 1060, 1305, 1383, 2890 and 2928 cm^{-1} are resulted from C–H stretching. The small smooth band at 1025 cm^{-1} contributes to the stretching vibration of C–O bond (Zhang & Nisinari, 2001).

The only difference between the IR spectra of unmodified Konjac and that of modified product PMKonjac-2 is that a peak appeared at 942 cm^{-1} in the spectrum of the latter, which is due to the P–O–P stretching. This clearly indicates that the phosphorous group has been well introduced into the Konjac molecule by esterification.

3.2. Flocculation

The flocculation performance can be explained in terms of the transmittance of the supernatant liquid. The higher the transmittance, the better the flocculating agent is. Plotted in Fig. 3 are the comparative studies on the transmittance of supernatant liquid of the unmodified and modified Konjac products carried out in 1% kaolin suspensions. Obviously, the transmittance of the supernatant, i.e., the flocculation efficiency of unmodified Konjac is much lower than those of modified analogues.

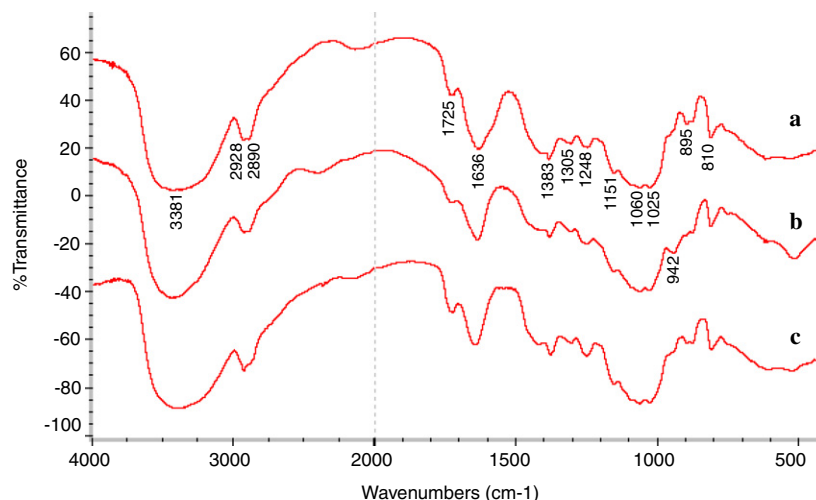


Fig. 2. IR spectra of (a) Konjac, (b) PMKonjac-2, (c) PMKonjac-2 after biodegradation.

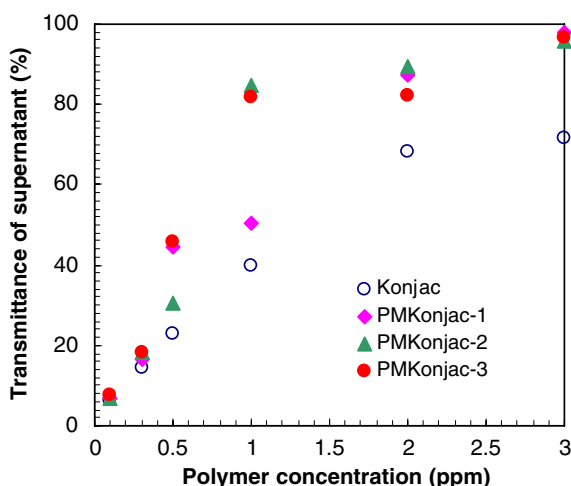


Fig. 3. Supernatant transmittance varies with flocculants dose in kaolin suspension (1%) for the modified and unmodified Konjacs.

Compared with the unmodified Konjac, the modified polymers show higher transmittance, indicating the latter has better flocculation performance. For all the polymers, initially the transmittance of the supernatant liquid is quite low as flocculation is at low doses of the flocculants and the efficiency of all the modified products is more or less similar when polymer concentration is lower than 0.3 ppm. When increasing polymer concentration, the small aggregates form big flocs, and then precipitated, which increases the transmittance of the supernatant accordingly. For the modified products, faster uptrend of transmittance for PMKonjac-2 and PMKonjac-3 was evidenced. This suggests that the higher the charge density, the better the flocculability is.

The flocculation performance of the series of products was further compared with column settling test (Fig. 4). The larger the settling velocity of the floc-containing contaminants, the greater the flocculation performance is. It is evident from Fig. 4 that the flocculation performance of all

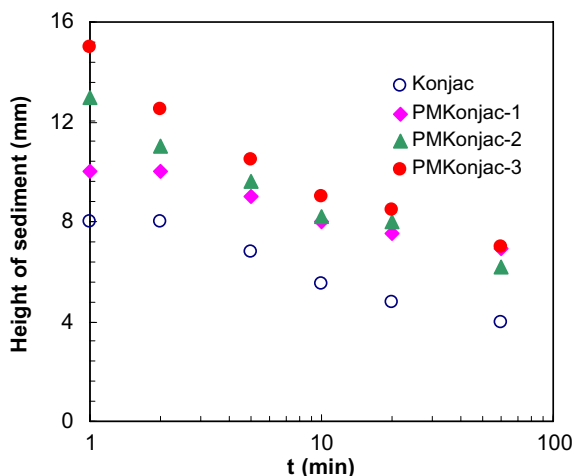


Fig. 4. Variation of the sediment height with time for kaolin suspensions (1%) flocculated by modified or unmodified Konjacs at 1 ppm.

the modified Konjacs is much better than that of unmodified Konjac, which has a good agreement with the jar test results appeared in Fig. 3.

The difference of the flocculability between the parent Konjac and the modified derivatives can be interpreted by their neutral and polyelectrolyte characteristics: there are no ionic groups in the unmodified Konjac while anionic phosphate moieties were incorporated into the unmodified products.

It is well-known that bridging and surface-charge neutralization are the two major flocculation mechanisms of polymeric flocculants depending on the nature of the polymer. Bridging occurs as a result of adsorption of polymer molecules onto the surface of different particles, thus linking them together to form flocs. Undoubtedly, bridging function operates with both the neutral and charged polymers. In bridging flocculation, macromolecule configurations and lengths play important roles (Stoll & Buffle, 1996). When the long-chain polymer molecules are adsorbed on the particles' surface, they tend to form loops and extend some distance from the particle surface into the aqueous phase (Singh, Tripathy, & Karmakar, 2000b). Their ends also dangle and get adsorbed on the surface of another particle, forming a bridge between the particles. As there are no ionic groups in the unmodified Konjac, its flocculability apparently arrives from bridging mechanism.

For the modified Konjac, the bridging also plays an important role although surface-charge neutralization is always attributed to the flocculation of polyelectrolytes. However, this is not the case in this work where modified Konjacs bear the same charge as that on Kaolin surface. Because of high surface area to edge area ratio, the Kaolin is known chemically carrying an overall net negative charge in the surface (Besra, Sengupta, & Roy, 2006; Williams & Williams, 1978). Thus, electrostatic repulsion predominates the interaction between phosphate-modified Konjac and Kaolin, while electrostatic attraction is always reported the main mechanism to coagulate kaolin particles by cationic polymers (Besra et al., 2006). Nevertheless, the anionic phosphorous groups placed along the modified Konjac backbone expand and the polymer coils, thus bridging more fine particles than the unmodified polymer. This is why the modified derivatives show superior flocculation efficiency to the parent Konjac (Fig. 3) over the polymer concentration examined in this work.

1 ppm in Fig. 3 was regarded as the optimal dose which can account for the flocculation effect at this flocculant comparison. Exhibited in Fig. 5 is the interrelation between phosphoric content and flocculation effect at 1 ppm polymer dosage. From this result it is apparently that flocculation efficiency increases upon increasing phosphoric content. When the phosphoric content reaches to a certain value, for example, 3 wt%, the transmittance of the supernatant becomes nearly unchanged. The more phosphate causes the more repulsion of negative charge from each other, which expands the polymer coils. The extend chain will make more bridging function. However, the repulsive

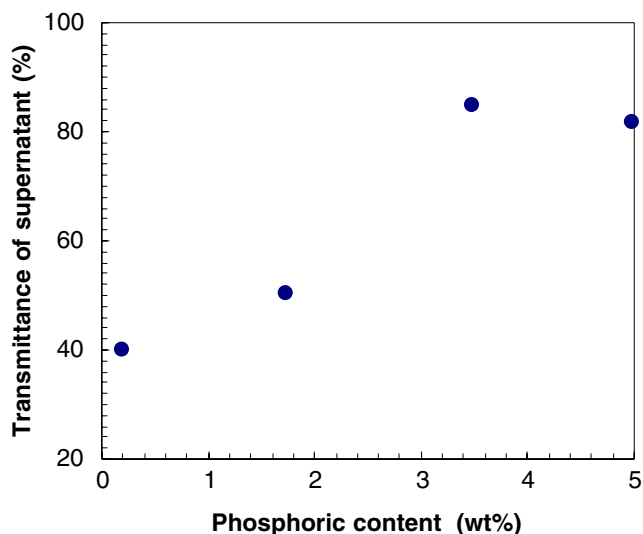


Fig. 5. The relation between phosphoric content and flocculation effect at 1 ppm.

operation arrives at the peak when phosphoric content reaches to a certain value at which the polymer chain stiffens at a maximum.

3.3. Biodegradability

The biodegradation of polysaccharide proceeds mainly through hydrolysis and oxidation. There are many factors influence biodegradability such as temperature, UV, moisture level, oxygen, nutrients etc (Jayasekara & Harding, 2005). In this test, the factors which influence biodegradability were controlled: the test temperature was controlled at 30 °C, UV, moisture level, oxygen and nutrients were also controlled in the common room condition. Hydroxy, hydroperoxide and carboxyl groups formed during degradation and they may lead to increased hydrophobicity, which can cause biodegradation. As reported by Singh et al. (Singh & Karmakar, 2000a), polymers which contain ester and anhydride group are prone to hydrolysis and biodegradation. The esterified products solution can be biodegraded in 5–7 days until it turned turbidity finally.

Biodegradation can be examined by monitoring the decay of relative viscosities (η_r , the ratio of viscosity of polymer solution to that of solvent, water) at certain intervals of time over the entire test. Normally, it took one day of time to completely dissolve the polymer powder in water, so the viscosity measurement was performed after 24 h of dissolution. Fig. 6 compares the relative viscosities of three modified PMKonjac products and the unmodified Konjac.

At the very beginning, the relative viscosities of the esterified PMKonjac products are higher than that of unmodified Konjac, and increase with increasing phosphoric level. As discussed above, incorporation of the anionic phosphate groups extends the polymer chains, i.e., expanding the polymer coils, and thus the relative viscosity of the polymers.

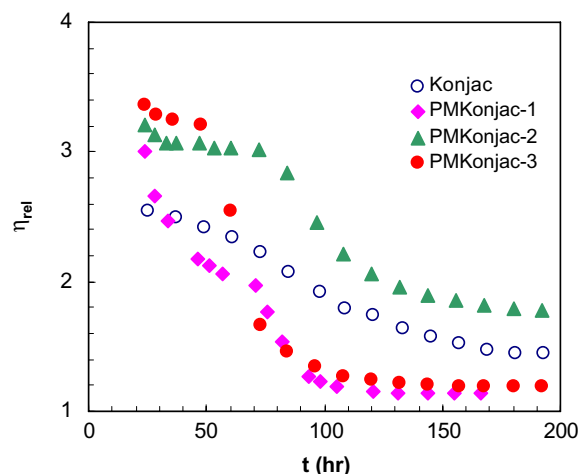


Fig. 6. η_r versus time to study the biodegradation of Konjac and its esterified products.

As shown in Fig. 6, after several days, biodegradation has been observed for all the polymers. The viscosity of the unmodified Konjac decreases smoothly, implying the breakdown of the polysaccharide chain. However, faster biodegradation is evidenced for all the modified PMKonjac products as there are inflexions in the viscosity curves (Fig. 6). The turning point of the curves indicates the P-O-P bonds have been cut, which can be confirmed from Fig. 2 where a band at 942 cm^{-1} disappeared in the IR spectra of the modified product PMKonjac-2 after biodegradation.

With the biodegradation process goes on, the relative viscosities of both modified and unmodified Konjac step down to a flat zone. The biodegradation test was terminated at about 190 h when the relative viscosities nearly unchanged further and fermentation residues found in the solution.

From what observed in Fig. 6, it seems there are two biodegradation processes for the modified products: breakdown of the main chain and elimination of the phosphorous groups. And these two processes are preceded simultaneously, while only rupture occurred in the unmodified Konjac. Interestingly, the final relative viscosities of PMKonjac-1 and PMKonjac-3 are close to 1, while those of Konjac and PMKonjac-2 stay around 2. This implies PMKonjac-1 and PMKonjac-3 have been degraded completely, whereas the degradation process for Konjac and PMKonjac-2 is still under way. However, all the polymer solutions were fermented when the experiments lasted for 190 h at 30 °C, which impedes our further test.

4. Conclusions

“Green” flocculants with both good flocculation efficiency and biodegradability are the pursuit of the water treatment industry. These products inherit the good performance but overcome the drawbacks such as toxicity and “secondary pollution” of traditional flocculants.

This paper is one part of our series work focusing on biodegradable flocculants. Incorporation of phosphate improves both flocculation efficiency and biodegradability, and the flocculation efficiency increases with increasing phosphoric content. The biodegradability was assured from the breakage of P-O-P bond along backbone of the esterified Konjac.

Ongoing work in our team is to get novel “green” flocculants by grafting acrylamide or cationic monomers onto the Konjac main chain.

References

- Adhikary, P., & Singh, R. P. (2004). Synthesis, characterization, and flocculation characteristics of hydrolyzed and unhydrolyzed polyacrylamide grafted xanthan gum. *Journal of Applied Polymer Science*, 94, 1411–1419.
- Besra, L., Sengupta, D. K., & Roy, S. K. (2006). Influence of unadsorbed and weakly adsorbed flocculants on separation properties of kaolin suspensions. *International Journal of Mineral Processing*, 78, 101–109.
- Biswal, D. R., & Singh, R. P. (2004a). Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. *Carbohydrate Polymers*, 57, 379–387.
- Biswal, D. R., & Singh, R. P. (2004b). The flocculation and rheological characteristics of hydrolyzed and unhydrolyzed grafted sodium alginate in aqueous solutions. *Journal of Applied Polymer Science*, 94, 1480–1488.
- Bratby, J. (1980). *Coagulation and flocculation*, London, England: Uplands Press Ltd.
- Chen, L. G., Liu, Z. L., & Zhuo, R. X. (2005). Synthesis and properties of degradable hydrogels of Konjac glucomannan grafted acrylic acid for colon-specific drug delivery. *Polymer*, 46, 6274–6281.
- Chiu, H. C., Hsiue, T., & Chen, W. Y. (2004). FTIR-ATR measurements of the ionization extent of acrylic acid within copolymerized methacrylated dextran/acrylic acid networks and its relation with pH/salt concentration-induced equilibrium swelling. *Polymer*, 45, 1627–1636.
- Du, J., Sun, R., & Xiong, C. D. (2004). Novel polyelectrolyte complex carboxymethyl Konjac Glucomannan-Chitosan nanoparticles as drug matrix. *Macromolecular Rapid Communications*, 25, 954–958.
- Hu, M., & Hu, M. W. (1990). Studies on esterification of phosphate onto Konjac glucomannan. *Tianran Chanwu Yanjiu Yu Kaifa*, 2(2), 8–14 (in Chinese).
- ISO 3946: (1982) (EN). Starches and derived products – Determination of total phosphorus content – Spectrophotometric method.
- Jayasekara, R., & Harding, I. (2005). Biodegradability of a selected range of polymers and polymer blends and standard methods for assessment of biodegradation. *Journal of Polymers and the Environment*, 13, 231–251.
- Karmakar, N. C., & Singh, R. P. (1997). Flocculation studies using amylase-grafted polyacrylamide. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 133, 119–124.
- Kato, K., & Matsuda, K. (1969). Studies on chemical structure of Konjac Mannan. *Agricultural and Biological Chemistry*, 33, 1446–1453.
- Katsuraya, K., & Okuyama, K. (2003). Constitution of Konjac Glucomannan: chemical analysis and C-13 NMR spectroscopy. *Carbohydrate Polymers*, 53, 183–189.
- Khalil, M. I., & Abdel-Halim (2001). Preparation of anionic starch containing carboxyl groups and its utilization as chelating agent. *Starch/Stärke*, 53, 35–41.
- Khalil, M. I., & Aly, A. A. (2001). Preparation and evaluation of some cationic starch derivatives as flocculants. *Starch/Stärke*, 53, 84–89.
- Khalil, M. I., & Aly, A. A. (2002). Preparation and evaluation of some anionic starch derivatives as flocculants. *Starch/Stärke*, 54, 132–139.
- Khalil, M. I., & Farag, S. (1998). Utilization of some starch derivatives in heavy metal ions removal. *Journal of Applied Polymer Science*, 69, 45–50.
- Li, B., & Xie, B. J. (2006). Studies on the molecular chain morphology of Konjac glucomannan. *Carbohydrate Polymers*, 64, 510–515.
- Maeda, M., & Shimahara, H. (1980). Detailed examination of the branched structure of Konjac Glucomannan. *Agricultural and Biological Chemistry*, 44, 245–252.
- Maekaji, K. (1974). The mechanism of gelation of Konjac mannan. *Agricultural and Biological Chemistry*, 38, 315–321.
- Nayak, B. R., & Singh, R. P. (2001). Comparative studies on the flocculation characteristics of polyacrylamide grafted guar gum and hydroxypropyl guar gum. *Polymer International*, 50, 875–884.
- Rice, J. M. (2005). The carcinogenicity of acrylamide. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*, 580, 3–20.
- Singh, R. P., & Karmakar, G. P. (2000a). Biodegradable drag reducing agents and flocculants based on polysaccharides: materials and applications. *Polymer Engineering and Science*, 40, 46–60.
- Singh, R. P., Tripathy, T., & Karmakar, G. P. (2000b). Novel biodegradable flocculants based on polysaccharides. *Current Science*, 78(7), 798–803.
- Stoll, S., & Buffle, J. (1996). Computer simulation of bridging flocculation processes: the role of colloid to polymer concentration ratio on aggregation kinetics. *Journal of Colloid and Interface Science*, 180, 548–563.
- Tripathy, T., & Singh, R. P. (2001). Characterization of polyacrylamide-grafted sodium alginate: a novel polymeric flocculant. *Journal of Applied Polymer Science*, 81, 3296–3308.
- Williams, D. J. A., & Williams, K. P. (1978). Electrophoresis and zeta potential of kaolinite. *Journal of Colloid and Interface Science*, 65(1), 79–87.
- Xiao, C. B., & Liu, C. H. (2004). Characterization of Konjac glucomannan-quaternized poly(4-vinyl-N-butyl) pyridine blend films and their preservation effect. *Journal of Applied Polymer Science*, 93, 1868–1875.
- Zhang, H., & Nisinari, K. (2001). Gelation behaviour of Konjac glucomannan with different molecular weights. *Biopolymers*, 59, 38–50.
- Zhang, Y. Q., & Xie, B. J. (2005). Advance in the application of Konjac glucomannan and its derivatives. *Carbohydrate Polymers*, 60, 27–31.
- Zhang, C. J., & Yang, Z. X. (1994). Synthesis and application of a new flocculating agent – Konjac. *HuaXue Shijie*, 35(2), 83–84 (in Chinese).