

Preparation of Guar Gum Bonded with β -Cyclodextrin Microspheres and the Absorption on Basic Fuchsin

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ABSTRACT: β -Cyclodextrin microspheres (β -CDMs) were prepared and then bonded to guar gum (GG). The structures of the precursor material and product were characterized by X-ray diffraction and Fourier transform infrared spectroscopy. Phenolphthalein and spectrophotometry were used to determine the content of β -cyclodextrin (β -CD) in products. By changing environmental conditions and types of adsorbents, the adsorption capacities of polymers on basic fuchsin were studied. The results indicate that the absorption capacity was decreased accordingly when the pH value was reduced. The increase of temperature had no obvious influence on improving the absorption capacity from 40 to 60°C. When the mass ratio of chloropropyl hydroxyl GG to β -CDMs

to sodium carbonate was 0.6 : 0.8 : 1.0, with the reaction time of 2 h, the best adsorption capacity of 24 mg/g was achieved; this was in accordance with the results of the measurement of the content of β -CD in the products. The higher content of β -CDM was beneficial for improving the absorption capacity. By comparing its properties with the absorption capacity of traditional flocculating agents polyacrylamide and polyaluminum chloride, the best absorption results for GG bonded with β -CDMs were obtained. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2250–2256, 2012

Key words: carbohydrate synthesis; functionalization of polymers; high performance polymers

INTRODUCTION

Many industries (plastics, paper, textiles, and cosmetics) use dyes to color their products. With the growing use of a variety of dyes, the pollution from dye wastewater is becoming a major environmental problem. It is known that there are about 3000 types of dyes in the world market. Among them, synthetic dyes, having potential toxicity and low biodegradability, and in particular, some water-soluble cationic dyes could cause great damage to natural ecosystems when they are discharged with wastewater. In addition, many dyes are difficult to degrade because of their complex aromatic structure and, thus, tend to persist in the environment, creating serious water quality and public health problems. Therefore, it would be advantageous to develop technologies to eliminate them. Over the last few decades, adsorption has been recognized as an efficient process for the removal of dyes from industrial effluent.¹ Currently, the most common procedure involves the use of activated carbons as adsorbents because of their excellent adsorption abilities.² However, their use is limited by its high cost. For this reason, the use of clean methods with low-priced and biodegradable

adsorbents could be a good tool for minimizing the environmental impact caused by manufacturing and textile effluents.

In this study, we exploited biodegradable and effective adsorbents based on polysaccharides, in particular, starch and starch derivatives, for the removal of cationic dye from aqueous solutions. Guar gum (GG) is a natural galactomannan gum that is distilled from the endosperm of GG germ. It has great water-solubility and thickening performance and is usually used in paper making, food, oil drilling, and so on.^{3–5} A series of cationic GGs was developed by the incorporation of a cationic moiety, *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride, onto the backbone of GG by Singh et al.,⁶ who compared the flocculation performance of GG grafted polyacrylamide (PAM) with hydroxypropyl GG grafted PAM at the same time.⁷ Because of its special molecular structure and physicochemical properties, GG has potential usage in environmentally friendly auxiliaries, such as absorbing dyes and heavy metallic ions in dye wastewater, and in the reduction of suspended solids.^{8–11} β -Cyclodextrin (β -CD) is a kind of oligosaccharide with seven glucose units connected through α -1,4-glucosidic bond. It is well known that this structure gives rise to a remarkable capacity to form inclusion complexes with organic molecules through host–guest interactions.^{12–14} It is used in many fields, including pharmaceuticals, foods, cosmetics, and chemicals.^{15,16} β -Cyclodextrin

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microspheres (β -CDMs) can increase the surface area; accordingly, the adsorption capacity can be enhanced. Although GG and β -CDM have all been used as adsorbents for the removal of dye in wastewater, to the best of our knowledge, GG bonded with β -CDM and its adsorption properties have seldom been reported so far. In this study, β -CDM with a large surface area was prepared and then bonded to GG with epichlorohydrin and gave a series of natural polymeric adsorbents. Through changing experimental conditions, we also evaluate and discuss the adsorption capacity of the bonded products toward basic fuchsin.

EXPERIMENTAL

Materials

GG (food grade) was provided by Shanwang Chemical Co., Ltd., Dongying, China. β -CD was obtained from Bio Life Science & Technology Co., Ltd., Shanghai, China, and was recrystallized twice before use. Poly(aluminum chloride) was provided by Lanbo Chemical Industry Co., Ltd., Guangzhou, China. The content of alumina in poly(aluminum chloride) was more than 30%. PAM, a chemical reagent, was obtained from United Chemical Reagent Institute, Chengdu, China. The molecular weight was more than 3 million. Sodium carbonate (SC), acetone, ethanol, toluene, methanol, epichlorohydrin, perchloric acid, and dimethylformamide were analytical reagents and were provided by Chemical Reagent Factory, Guangzhou, China. Phenolphthalein was obtained from Chemical Reagent Co., Ltd., Tianjin, China. Basic fuchsin was provided by the Second Factory of Dye Chemistry, Tianjin, China. Polyoxyethylene (20), sorbitan monolaurate (Tween 20), and sorbitan monooleate (Span 80) were obtained from Runjie Chemical Reagent Co., Ltd., Shanghai, China. Phenolphthalein, basic fuchsin, Tween 20, and Span 80 were used as received.

Synthesis

Synthesis of β -CDMs

NaOH (4.0 g) was dissolved in 10 mL of extracted water; then, 6.0 g of β -CD was dissolved in the this solution. Then, 7.34 g of epichlorohydrin was added drop by drop. After the solution was stirred for 1.5 h, 40 g of kerosene and 0.8 g of emulsifier were added, and the mixture was stirred vigorously for 5 min. Kerosene was used as a solvent for the oil phase. The temperature was increased to 60°C and, at the same time, was cooled with a condenser pipe after 8 h of stirring. The product was washed thoroughly with dilute hydrochloric acid, methanol, distilled water, and acetone and then dried at 60°C *in vacuo*.

Synthesis of GG bonded with β -CDMs

Epichlorohydrin (16.0 mL), perchloric acid (0.32 mL), ethanol (2.0 mL), and distilled water (2.0 mL) were poured into a round-bottom flask. After stirring for a certain period of time, 4.0 g of GG and 40.0 mL of toluene were added to the solution. The mixture was stirred for 4 h at 90°C. The product chloropropyl hydroxyl guar gum (cl-GG) was washed by acetone and dried at 60°C. Then, β -CDM, cl-GG, SC, and distilled water were added and stirred in a round-bottom flask for 2 h at 90°C. Dilute hydrochloric acid was then added to adjust the pH of the mixture to less than 7. The residue was filtered and washed with dimethylformamide under ultrasound, further washed with ethanol and acetone, and then dried at 60°C *in vacuo*.

After GG bonded with β -CDMs was prepared, a series of bonded polymers were synthesized by alteration of the reaction time from 1 to 3 h while the mass ratio (M) of cl-GG to β -CDM to SC was kept constant at 0.6 : 0.8 : 1.0 or by alteration of M from 0.4 : 0.6 : 1.0 to 0.6 : 0.8 : 1.0 to 0.8 : 0.8 : 1.0 to 1.0 : 0.8 : 1.0 while the reaction time was kept constant at 2 h.

Characterization

The precursor materials and the bonded polymers were characterized by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. XRD was measured with a Rigaku D/MAX-2200 X-ray powder diffractometer (Japan). FTIR spectra were obtained with KBr pellets with a Bruker Equinox FTIR instrument (Germany). The spectra were recorded in the range 400–4000 cm^{-1} .

Measurement of the content of β -CD in the products

Phenolphthalein spectrophotometry was used to measure the amount of β -CD absorbed by the bonded polymers. Phenolphthalein was coupled with β -CD to form an inclusion complex. The solution turned red when basic buffer solution, such as SC, was added, and the absorbance of the solution was recorded. There was a direct relationship between the reduced absorbance and the content of β -CD when the concentration was below 30 $\mu\text{g}/\text{mL}$. Accordingly, the standard curve could be plotted versus absorbance, which was the absorbance difference between the absorbance of the phenolphthalein-SC solution and the chromogenic solution with the β -CD standard sample. The difference in the concentration of β -CD between the standard sample in the phenolphthalein colorimetric solution and the new samples were calculated by the curve. The

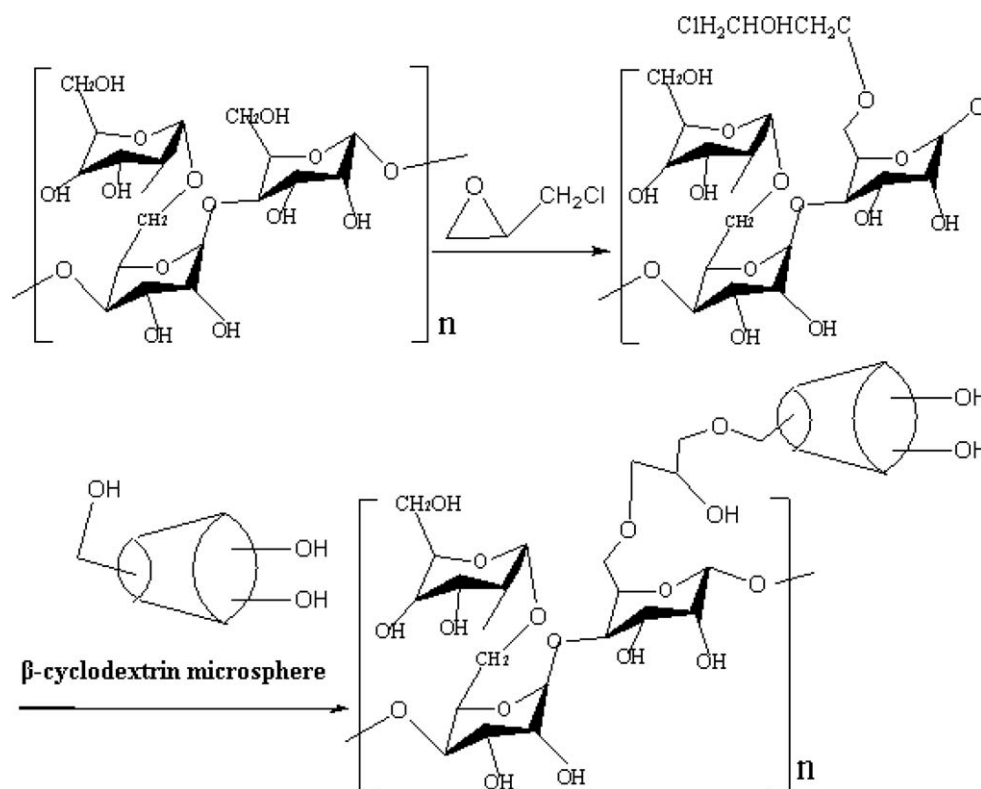


Figure 1 Synthetic route of GG bonded with β -CDMs.

maximum adsorption wavelength of the phenolphthalein-SC solution was 550 nm. As such, the absorbance in this study was determined at 550 nm. Details of the experiment have been published elsewhere.¹⁷

RESULTS AND DISCUSSION

Synthetic mechanism of GG bonded with β -CDMs

GG bonded with β -CDMs could be prepared in two steps, as follows (shown in Fig. 1):

1. In the GG molecules, there are large numbers of —OH groups, GG (GG-OH) can interact with epichlorohydrin in sodium hydroxide solution to generate epoxy GG. Because of the concentrated electron density in the oxygen atoms of epichlorohydrin molecules, oxygen atoms are very active in electrophilic reagents. Epichlorohydrin cationic intermediates are formed, but this intermediate is unstable and easily transformed into 3-chloro-2-hydroxypropyl cation. The carbon ions are replaced by H^+ derived from GG on cl-GG. Epoxidized GG is prepared through a ring-closing reaction.
2. Epoxidized GG interacts with hydroxyl groups in β -CDM with an epoxy-based crosslinking bridge in a sodium hydroxide alkali solution. Due to the higher acidity of the primary hydroxyl

group versus that of the secondary hydroxyl group and volume steric effects of the glucose pyran ring, the C6 primary hydroxyl group in β -CDMs is mainly involved in the reaction.

Determination of the absorption properties

The bonded polymers were added to the basic fuchsin solution. After stirring and centrifuging, its absorbance was determined. By changing stirring time, pH value, and temperature, we calculated the adsorption capacity of bonded polymers.

Structural characterization

The XRD patterns of the precursor materials and products are shown in Figure 2. M of cl-GG to β -CDM to SC was fixed at 0.6 : 0.8 : 1.0, whereas the reaction proceeded for times of 1 to 2 to 3 h and gave products GGCD1, GGCD2, and GGCD3 (When the reaction time was varied from 1 to 2 to 3 h, the products were named GGCD1, GGCD2, and GGCD3, respectively). In Figure 2, for samples a, c, d, and e, the three peaks were located near $2\theta = 21, 38, \text{ and } 44^\circ$, which were the characteristic positions of the reflections of cellulose II.¹⁸ The peak intensities of GG decreased after bonding with β -CDM;

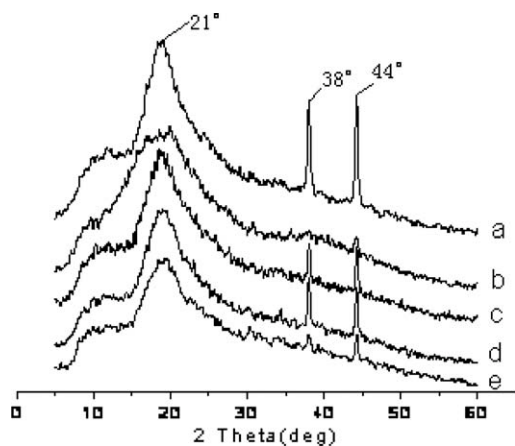


Figure 2 XRD spectra of (a) GG, (b) β -CDM, (c) GGCD2, (d) GGCD1, and (e) GGCD3. When M of cl-GG, β -CDM, and SC at 0.6 : 0.8 : 1.0 was fixed by alteration of the reaction time from 1 to 2 to 3 h, respectively, the products were named GGCD1, GGCD2, and GGCD3, respectively.

this indicated that the crystallinity and regularity of GG dropped.

The infrared spectra of the precursor materials, intermediates, and products are shown in Figure 3. The peaks at 2962 and 1080 cm^{-1} , shown in Figure 3(b), were associated with the C–H and C–O bonds, respectively. These two peaks are more intense in Figure 3(c) than in Figure 3(b) because of the bonding interaction between the chloride group of cl-GG and the hydroxyl group in GG; the peak at 1458 cm^{-1} in Figure 3(c) was assigned to the bend vibration of the C–H bond and corresponded to the peak at the same wavelength in Figure 3(a). In addition, the peak at 1083 cm^{-1} in Figure 3(a) was correlated to the peaks at 1082 and 1036 cm^{-1} in Figure 3(d) and the peak at 1080 cm^{-1} in Figure 3(c). There-

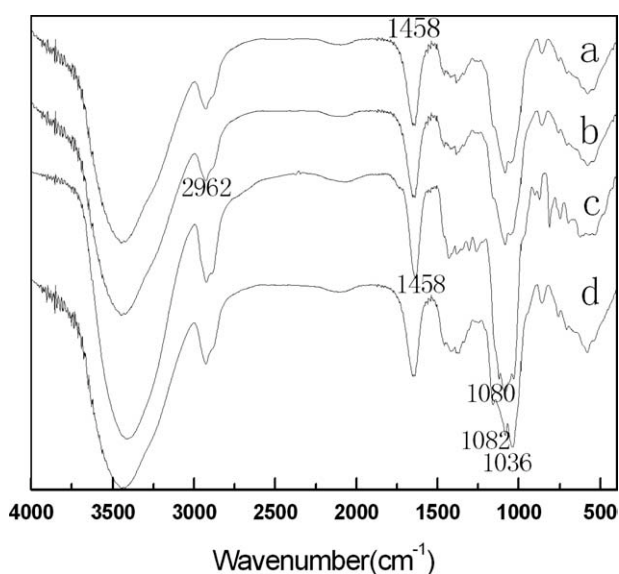


Figure 3 FTIR spectra of (a) guar-gum-bonded β -CDMs, (b) GG, (c) cl-GG, and (d) β -CDMs.

TABLE I
Content of β -CD in a Series of Bonded Polymers

Bonded polymer	Content of β -CD ($\mu\text{mol/g}$)
Reaction for 1 h, $M = 0.6 : 0.8 : 1.0$	9.53
Reaction for 2 h, $M = 0.6 : 0.8 : 1.0$	12.45
Reaction for 3 h, $M = 0.6 : 0.8 : 1.0$	10.88
Reaction for 2 h, $M = 0.4 : 0.8 : 1.0$	11.21
Reaction for 2 h, $M = 0.6 : 0.8 : 1.0$	12.45
Reaction for 2 h, $M = 0.8 : 0.8 : 1.0$	9.36
Reaction for 2 h, $M = 1.0 : 0.8 : 1.0$	9.71

fore, we concluded that the β -CDMs had bonded to the GG.

Measurement of the content of β -CD

According to the method described by other researchers, the standard curve was drawn as $y = 0.1099x$, $R = 0.9981$. On the basis of the relation between the absorbance and the concentration of β -CD, the content of β -CD in a series of bonded polymers was calculated (seen in Table I).

As shown in Table I, GGCD2 had the highest content of β -CD. Under fixed M , with the increase of reaction time, the content of β -CD in the bonded polymers could not be enhanced. This suggested that only with sufficient reaction time and a suitable M of raw material could the content of β -CD reach the high value of 12.45 $\mu\text{mol/g}$.

Absorption properties of the product

The maximum wavelength (544 nm) of basic fuch sine was determined by an ultraviolet spectrophotometer. The absorption experiment of GGCD2 was studied by changes in the experimental conditions.

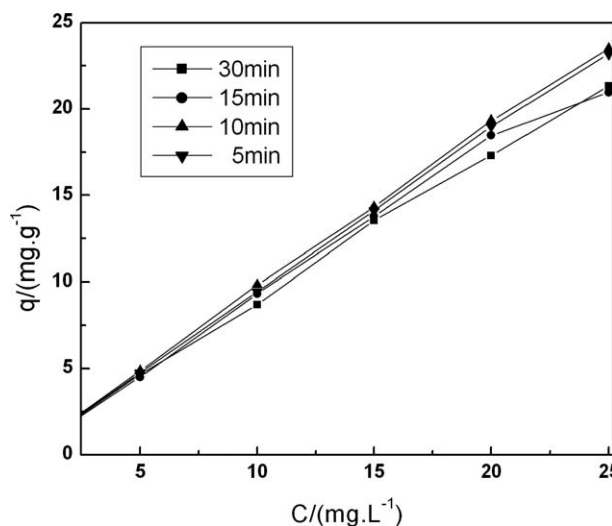


Figure 4 Effect of the stirring time on the absorption capacity of GGCD2. (X-axis C means the content of basic fuch sine solution, Y-axis q means the absorption capacity, the same definition in the following figures).

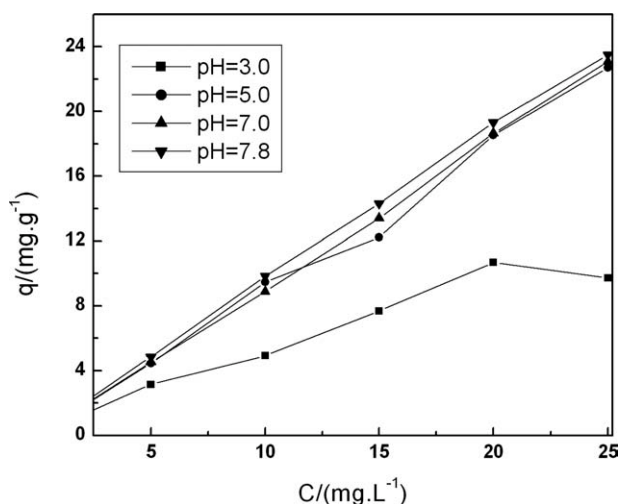


Figure 5 Effect of the pH value on the absorption capacity of GGCD2.

Effect of the experimental conditions on the absorption properties

The effect of stirring time on absorption properties of GGCD2 is shown in Figure 4. The absorption capacity reached the maximum value at 10 min. The absorption capacity could not be enhanced with increases in the stirring time. Therefore, the optimal stirring time was chosen as 10 min. The effects of pH value and temperature on the absorption capacity of GGCD2 are shown in Figures 5 and 6, respectively. When the pH values were reduced, the absorption capacity was decreased accordingly. Under strong acidic conditions, amino became NH_4^+ ion, which prohibited β -CD from having multiple hydroxyl groups from absorbing the basic fuchsine.

On the other hand, the effect of the temperature on the absorption capacity was studied in the range 40–60°C; the absorption capacity was increased slightly

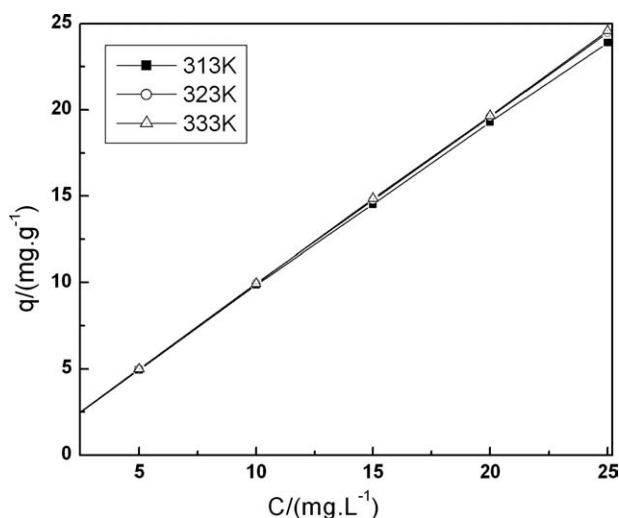


Figure 6 Effect of the temperature on the absorption capacity of GGCD2.

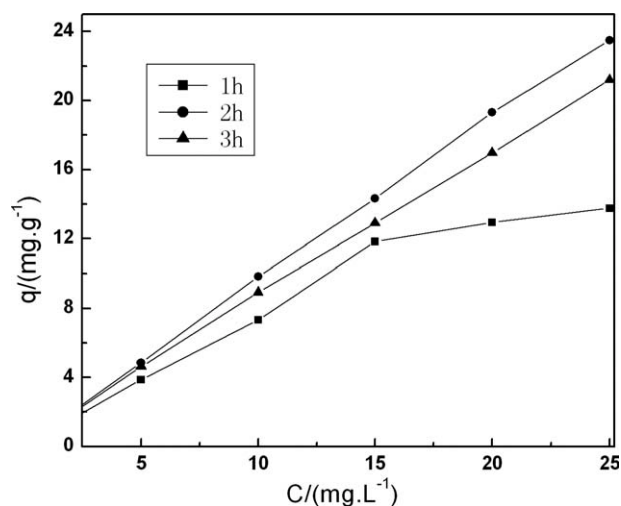


Figure 7 Absorption capacity of GGCD1, GGCD2, and GGCD3.

by increasing the temperature. It was indicated that the absorption was endothermic in nature. This phenomenon was attributed to the three following reasons. First, GG had the bridging effect. Second, a complex was formed between basic fuchsine and β -CD, which consisted of four types of force, including hydrophobic interaction, coulomb attraction, hydrogen bonding interaction, and van der Waal's forces.¹⁹ The third reason was that the absorption capacity was enhanced through the big surface area of β -CDM. So the absorption capacity was strongly dependent on the content of β -CDM. The increase of temperature had no obvious influence on improving the absorption capacity from 40 to 60°C.

Study of the absorption abilities in a series of bonded polymers

The absorption abilities of a series of bonded polymers (GGCD1, GGCD2, and GGCD3) were studied (Fig. 7). Basic fuchsine had optimal absorption capabilities on GGCD2; meanwhile, GGCD2 had the highest content of β -CD. It was proven that the absorption capacity increased as the content of β -CD increased.

The basic fuchsine was adsorbed best with the bonded polymer with M of 0.6 : 0.8 : 1.0 among all of the polymers shown in Figure 8. In addition, when the content of β -CD in M was increased, the content of β -CD in the product could not be enhanced (seen in Table I). To conclude, the content of β -CD in the product and the adsorption capacity did not increase under the condition of excess weight of β -CD in M of raw materials.

Absorption capacity comparison with traditional flocculating agents

In general, there were two types of flocculants, organic and inorganic. In the case of dye wastewater

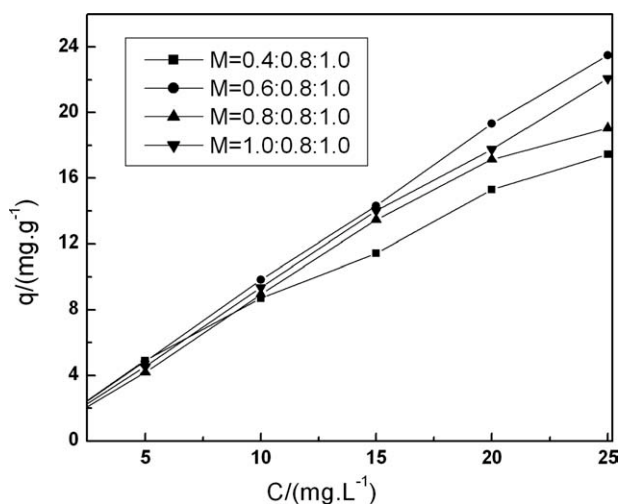


Figure 8 Absorption capacity of bonded polymers with different Ms.

treatment, a large amount of inorganic flocculating agent was needed, which caused sludge at the same time. On the other hand, suspended particles and colored materials could be absorbed efficiently by the organic flocculating agent. PAM is a soluble organic linear polymer that contains amino groups, which could be polymerized by acrylamide. Through electrical neutralization and bridging absorption, suspended particles were flocculated on the PAM. Polyaluminum chloride (PAC) contains multivalent anions. Due to the bridging action of hydroxide ion and the polymerization of multivalent anions, some pollutants, pigments, and turbidity could be removed efficiently. Their absorption capacities on basic fuchsin were studied.

Comparison with an individual flocculating agent

The absorption capacities of these flocculating agents were studied under the best absorption conditions, as

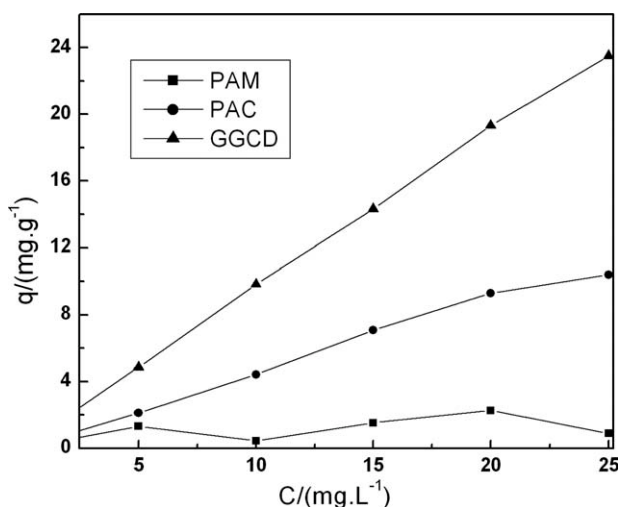


Figure 9 Absorption effect of PAM, PAC, and GGCD2 to basic fuchsin.

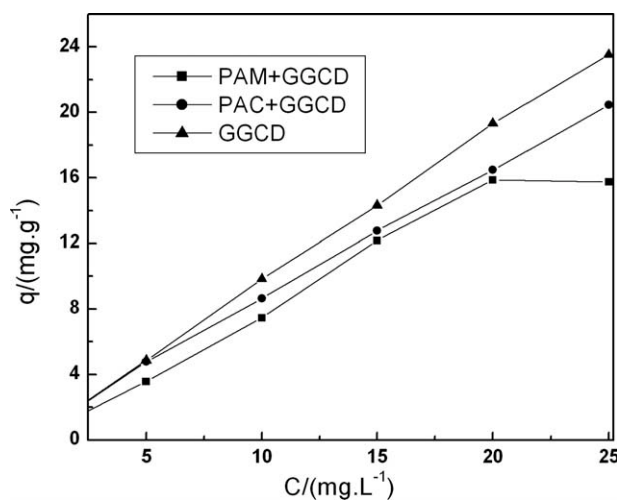


Figure 10 Absorption capacity of the combined use of PAM, PAC, and GGCD2.

discussed previously. As shown in Figures 9 and 10, less basic fuchsin was absorbed in PAC and PAM than in GGCD2. Because of the bridging action and the electrical neutralization of PAC and PAM toward the suspended particles, they were flocculating agents with good properties. However, basic fuchsin was soluble and electrically neutral; therefore, it could not be absorbed effectively by PAC and PAM. In contrast, both GG and β -CDM could absorb basic fuchsin with high absorbing capacities.

Comparison with a composite flocculating agent

To study the absorption capacities of composite flocculating agent, three types of flocculating agents, 10 mg of PAM and 10 mg of GGCD2, 10 mg of PAC and 10 mg of GGCD2, and 20 mg of GGCD2, were poured into the basic fuchsin solutions. The absorption process was carried out under the conditions described before.

As Figure 8 shows, with the same weight of flocculating agent, the absorption capacity of GGCD2 alone was higher than those of other combinations because of its higher β -CD content. The combined use of GG and PAC could enhance the positive charge through electrostatic attraction and bridging action, so the suspended materials, such as direct black and reduce red, could be congregated and subsided. Among three types of combination, basic fuchsin was absorbed most effectively by GGCD2.

CONCLUSIONS

β -CDMs were synthesized by emulsification and bonded to GG. By varying the reaction time and M of raw materials, we prepared a series of bonded polymers. The content of β -CD in a series of bonded polymers was determined through phenolphthalein spectrophotometry. Their absorption capacities on basic fuchsin were

studied. It was suggested that GGCD2, with a reaction time of 2 h and M of 0.6 : 0.8 : 1.0, was the most efficient flocculating agent among a series of bonded polymers. Its absorption capacity could reach 24 mg/g at normal temperature. Basic fuchsin was absorbed in GG bonded with β -CDM polymers by the bridging and sweeping action of GG and the hydrophobic association of β -CDMs. In addition, GGCD2 was combined with PAM and PAC, respectively, and their absorption capacity was also examined. It was observed that GGCD2, when used alone, gave the best absorption results compared to other traditional flocculating agents.

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