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Preparation of Crosslinked Grafted Modified Anionic Starch-Based Flocculants and Their Dye Removal Performance

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Abstract

This study addresses two critical limitations of conventional flocculants applied to textile dyeing and printing wastewater: their poor biodegradability and persistent toxic residues. It also tackles the suboptimal performance commonly observed with single-modified starch flocculants. To overcome these challenges, a novel cross-linked, graft-copolymerized anionic flocculant—termed CSPA—was synthesized using cassava starch (St) as the backbone polymer, acrylamide (AM) and sodium acrylate (AANa) as co-grafting monomers, N,N′-methylenebisacrylamide (MBA) as the cross-linker, and an ammonium persulfate/sodium bisulfite redox system as the initiator. The dye removal efficiency of a composite coagulant composed of CSPA and polyaluminium chloride (PAC) was evaluated under ambient conditions. Structural and compositional characteristics of CSPA were systematically elucidated via Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and solid-state ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectroscopy. Using Disperse Red FB and Disperse Yellow RGFL as model dyes, the effects of key synthesis parameters—including the St-to-monomer mass ratio, AM-to-AANa molar ratio, MBA dosage (wt% relative to total reactants), initiator dosage (wt% relative to total reactants), and reaction temperature—on decolorization performance were rigorously investigated. Optimal flocculation performance was achieved at a St:AM:AANa molar ratio of 1:1:1, with MBA and initiator dosages of 0.2 wt% and 0.6 wt%, respectively (both calculated relative to total reactant mass), and a synthesis temperature of 70 °C. Under these conditions, CSPA–PAC achieved removal efficiencies of 98.97% for Disperse Red(FB) and 99.56% for Disperse Yellow(RGFL). Moreover, the system demonstrated robust operational flexibility, maintaining >90% decolorization across a broad CSPA dosage range (40–70 mg/L) and acidic-to-neutral pH range (pH 1–7).

Keywords: cassava starch,acrylamide, sodium acrylate,MBA,dye removal

Introduction

Textile dyeing and printing effluent is one of the major sources of discharge in the textile industry.

Its main characteristics include a massive volume of water, complex water quality, significant dynamic changes in water quality, and prominent economic cost constraints [6].Although the pollution caused by dyeing and printing effluent has attracted widespread international attention, and some relatively mature treatment technologies have now been implemented on a large industrial scale, problems such as high treatment costs, low treatment efficiency and the difficulty in degrading treatment chemicals still persist. Therefore, the development of more efficient, economical and environmentally friendly water treatment chemicals plays a crucial role in the sustainable development of the textile dyeing and printing industry[1] .

Currently, commonly used treatment methods include filtration, activated carbon adsorption, coagulation and chemical flocculation; among these, coagulation is widely applied due to its simple process flow, ease of operation and effective decolourisation.Existing organic flocculants are primarily based on polyacrylamide (PAM); although they offer stable and effective treatment, they suffer from drawbacks such as high treatment costs, toxic residual monomers and poor biodegradability[2] .Therefore, this paper utilises cassava starch as the raw material. On the one hand, the molecular chains of cassava starch contain a large number of active hydroxyl groups and a highly branched structure, which facilitates chemical modification[4] ; on the other hand, the raw material is inexpensive, environmentally friendly, biodegradable, non-toxic and harmless, and the modified products contain no neurotoxic monomers, making subsequent sludge treatment safer, which aligns with the concept of environmentally friendly development[5] .Nair B S[3] used cassava starch as the raw material and prepared a PMAM flocculant using a free-radical-initiated polymerisation process, which significantly improved the flocculation performance.

In this study, the aqueous solution polymerisation method was employed[9]. Under a system using ammonium persulphate and sodium bisulphite as initiators, acrylamide (AM),sodium acrylate (AANa) monomers into the starch molecular chains via graft copolymerisation[7]. Simultaneously, the ‘bridging’ effect of MBA linked the grafted starch chains together, forming a three-dimensional cross-linked network, ultimately yielding a cross-linked graft-modified anionic starch flocculant (CAPA)[8] .The effects of synthesis conditions—such as the monomer ratio, the ratio between monomers, and the amount of cross-linking agent—on flocculation performance were investigated using Fourier-transform infrared spectroscopy (FT-IR),scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance carbon spectroscopy (^{13}C-NMR) to characterise the structure of the flocculant under optimal synthesis conditions[11]. The study also investigated the decolourisation rates of the modified starch flocculant,polyacrylamide (APAM) and carboxymethyl cellulose (CMC) at different dosages, as well as the effect of different pH values on the modified starch flocculant. Finally, the optimal synthesis conditions and the optimal flocculation conditions were determined[12].

1 Experimental Section

1.1 Materials and Apparatus

Materials: Tapioca starch, Guangxi Nongken Mingyang Starch Development Co., Ltd.; Acrylamide (AM, chemical pure), Shanghai Rown Chemical Reagents Co., Ltd.; Acrylic acid (AA, analytical pure), Ammonium persulfate ($(NH_4)_2S_2O_8$, analytical pure), Tianjin Damao Chemical Reagents Factory; N,N'-methylenebisacrylamide; Sodium bisulfite ($NaHSO_3$, analytical pure), Tianjin Xinbote Chemical Co., Ltd.; Sodium hydroxide (NaOH, analytical pure), Tianjin Jiangtian Chemical Technology Co., Ltd.; Polyaluminum chloride (PAC, industrial grade), Henan Aierfuke Chemical Co., Ltd.; Disperse Red (FB, analytical pure), Disperse Yellow (RGFL, analytical pure), Tianjin Guangfu

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InstituteInstruments: Nicolet iS50 Fourier Transform Infrared (FTIR) Spectrometer, Thermo Fisher Scientific, USA; Flex SEM1000 Desktop Scanning Electron Microscope–Energy Dispersive X-ray Spectroscopy (SEM–EDS) System, Hitachi High-Technologies Corporation, Japan; Octane SUPER Energy-Dispersive X-ray Spectrometer (EDS), Thermo Fisher Scientific, USA; UV–Vis Spectrophotometers (Models: Evolution 201, 220, and 260 Bio), Thermo Fisher Scientific, USA; METTLER TOLEDO pH Meter, Shanghai Zhongchen Digital Technology Co., Ltd., China.

1.2 Synthesis of CSPA

Weigh out 10 g of cassava starch and dissolve it in 60 ml of deionised water. Gelatinise in a water bath at 90 °C for 30 minutes, then cool to 70 °C (cooling rate).Add a specified amount of AM, AANa and MBA solutions; stir for 10 minutes, then slowly add a dropwise stream of the initiator system comprising ammonium persulphate and sodium bisulphite. After 3 hours of reaction, add 1 g of sodium benzoate and 1 g of potassium sorbate, and continue stirring for 5 minutes to obtain a viscous product. Wash with anhydrous ethanol,dried in an oven at 70 °C, then ground and sieved to yield the product CSPA. The reaction mechanism and product structure are shown in Fig.1:

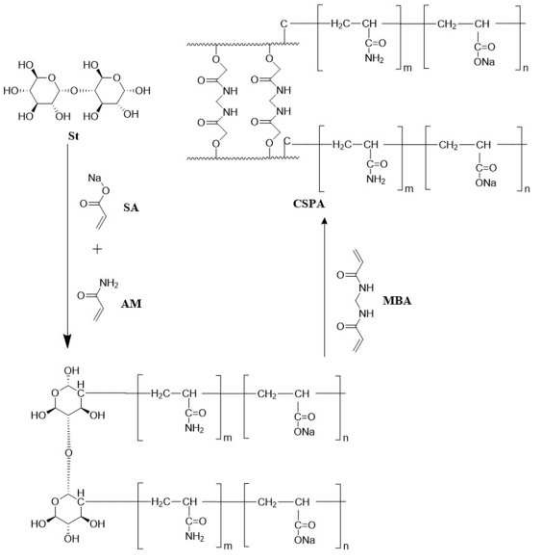


Fig. 1 Synthesis mechanism of GSPA

1.3 Structural Characterisation and Performance Testing

1.3.1 Structural Characterisation

Nuclear Magnetic Resonance（13C-NMR) analysis: Take 100–200 mg of dried sample, grind it into a fine powder and sieve through a 200-mesh sieve; pack the uniform powder tightly into a 4 mm ZrO_2 rotor, setting the rotor speed to 5–10 kHz.

X-ray photoelectron spectroscopy (XPS) analysis: emission energy set at 50 eV, with an energy step of 0.1 eV; binding energies were corrected using C1s (284.8 eV) as an internal standard.

X-ray diffraction (XRD) analysis: Analysis of the crystallinity of starch before and after modification using an X-ray diffractometer. Dried and sieved samples were scanned at a rate of 5° per minute over an angular range of $2\theta = 10°\sim80°$ to investigate changes in the crystallinity and molecular chain morphology of the starch flocculant before and after modification.

Fourier transform infrared spectroscopy (FTIR) analysis: Using the potassium bromide (KBr) pellet method, 10 mg of sample was thoroughly mixed with 100 mg of KBr powder and pressed into a

pellet; the sample was then scanned over the wavenumber range 4000 cm^{-1} to 500 cm^{-1} ;

Scanning electron microscopy (SEM) analysis: Following vacuum gold sputtering of the samples, the surface morphology was observed at an accelerating voltage of 10 kV and magnifications of 2000 and 5000, and the roughness and pore structure of the samples before and after modification were compared;

1.3.2 Flocculation Performance Testing

Testing of the decolourisation efficiency of the synthesised flocculants. The maximum absorption wavelength of FB was measured at 580 nm and that of RGFL at 436 nm using a visible spectrophotometer. Dye wastewater containing FB and RGFL at different concentration gradients was prepared; the absorbance was measured at each dye's respective maximum absorption wavelength, and concentration–absorbance calibration curves were plotted.A good linear relationship indicates that the system conforms to the Lambert–Beer law; on this basis, the wastewater decolourisation rate can be calculated[10] .

Aqueous solutions of the synthesised CSPA flocculant and PAC were prepared with mass fractions of 1‰ and 4%, respectively. First, a specific volume of PAC aqueous solution was added to 100 ml of a 600 mg/L dye solution (FB or RGFL), stirred at 200 r/min for 1 minute; then, a specific volume of CSPA aqueous solution was added, and the mixture was stirred at 100 r/min for 1 minute.After allowing the mixture to settle for 30 minutes, the supernatant was collected using a pipette, and the absorbance $A_t$of the decolourised simulated wastewater was measured. The experiment was repeated three times, and the average value was taken as [11] . The decolourisation rate was calculated using Equation (1).

$$\eta = \frac{A0 - At}{A0} \times 100\% \quad (1)$$

Where: η is the decolourisation rate; A_0 is the absorbance of the simulated effluent before decolourisation; At is the absorbance of the simulated effluent after decolourisation.

2 Results and Analysis

2.1 Experimental Investigation into Flocculant Synthesis

2.1.1 Investigation of the Effect of Raw Materials and the Molar Ratio of AM to AANa

Under conditions where the molar ratio of the graft monomers AM and AANa was fixed at 1:1, the cross-linking agent concentration was 0.2 per cent, the initiator concentration was 0.6 per cent (expressed as a percentage of the total mass of raw materials), and the reaction temperature was 70 °C, the effect of the molar ratio of starch to the graft monomers AM and AANa on flocculation performance was investigated. The results are shown in Fig.2.

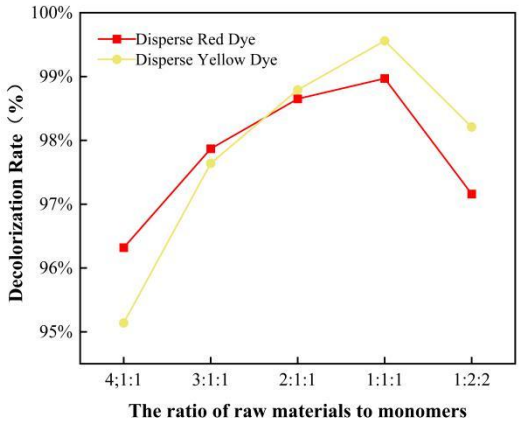


Fig. 2 Effect of the Molar Ratio of Raw Material to AM and AANa on Decolourisation Rate

As can be seen from the figure, as the proportion of monomers increases, the decolourisation rates of FB and Disperse Yellow improve significantly. The optimum is reached when the molar ratio of raw material to monomers is 1:1:1, at which point the decolourisation rates of both FB and RGFL are at their highest. However, when the proportion of monomers is even higher, the decolourisation rates actually decrease.

This is because, as the proportion of grafted monomers increases, the grafting rates of amide and carboxyl groups on the flocculant's molecular chains rise significantly, leading to an increase in anionic charge density and a stronger electrostatic neutralisation effect on the positively charged disperse dye particles; simultaneously, the water solubility and extensibility of the molecular chains improve, whilst the adsorption and cross-linking capacity of the polymer chains is also enhanced. The synergistic effect of these two factors promotes the efficient removal of dyes.However, when the monomer ratio is too high, excessive grafting leads to an excessively high anionic charge density. This results in overly strong electrostatic repulsion between molecular chains and excessive chain stretching, thereby weakening the polymer's bridging and entrapment-sweeping capabilities. At the same time, an excess of hydrophilic groups reduces the hydrophobicity of the flocs, which is detrimental to the aggregation and sedimentation of dye particles, leading to a decline in decolourisation performance[12] .

2.1.2 Effect of the molar ratio between monomers AM and AANa

Under conditions where the molar ratio between the fixed raw material (tapioca starch) and the monomers AM and AANa was 1:2, the cross-linking agent was used at 0.2 per cent (by mass of the total raw material), the initiator at 0.6 per cent (by mass of the total raw material), and the reaction temperature was 70 °C, the effect of the molar ratio between monomers AM and AANa was investigated; the results are shown in Fig.3.

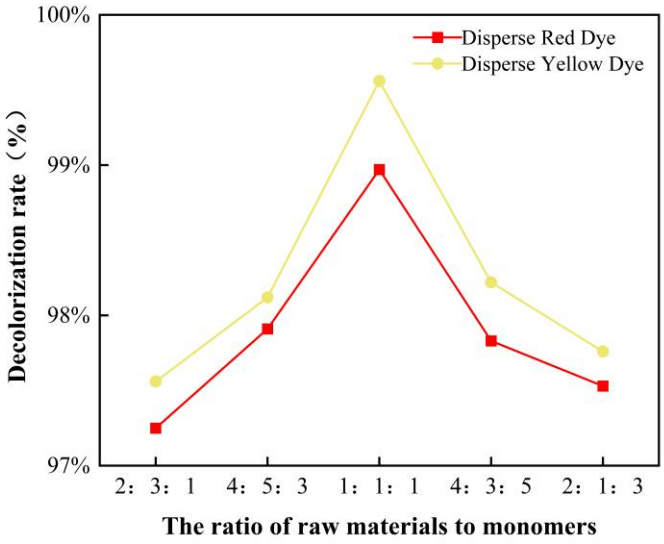


Fig. 3 The Effect of the Molar Ratio Between Single AM and AANa

It can be seen that as the amount of AANa increases, the flocculant's decolourisation effect on the dyes gradually improves, with the optimal result achieved when the molar ratio of AM to AANa is 1:1. This is because when the proportion of AM is high, there are too many hydrophobic amide groups, resulting in reduced molecular chain flexibility, a smaller cross-linking span, and insufficient sites for dye adsorption;conversely, when the AANa proportion is too high, there are excessive hydrophilic carboxyl groups, resulting in products with excessive water solubility; the flocculant struggles to settle and separate from the aqueous solution, and the dye is redispersed into the water along with the dissolved polymer, leading to a decrease in the decolourisation rate .

2.1.3 Effect of MBA

Under conditions where the molar ratio of the feedstock cassava starch to the grafting monomers AM and AANa was 1:1:1, the initiator dosage was 0.6 per cent (by mass of the total feedstock), and the reaction temperature was 70 °C, the effect of the MBA crosslinker dosage was investigated; the results are shown in Fig.4.

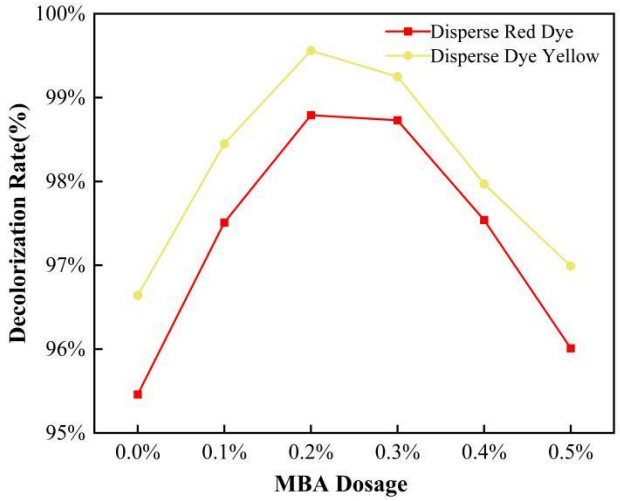


Fig. 4 The Effect of MBA Dosage

As can be seen from the figure, the decolourisation rates for both dyes initially increased and then decreased with increasing MBA dosage, reaching a maximum when the MBA dosage reached 0.2 per cent (by mass of the total raw material). This is because the double carbon-carbon double bonds in the crosslinker MBA can simultaneously link multiple grafted molecular chains, forming a three-dimensional crosslinked flocculant.When the MBA dosage is low, cross-linking is insufficient, the network structure is incomplete, and the flocculation and adsorption capacity is limited; when the MBA dosage is too high, excessive cross-linking causes molecular shrinkage and the blocking of active sites, leading to a decline in flocculation performance.

2.1.4 Effect of Initiator Dosage

Under conditions where the molar ratio of the feedstock cassava starch to the grafting monomers AM and AANa was 1:1:1, the cross-linking agent dosage was 0.2 per cent (by mass of the total feedstock), and the reaction temperature was 70 °C, the effect of initiator dosage was investigated; the results are shown in Fig.5.

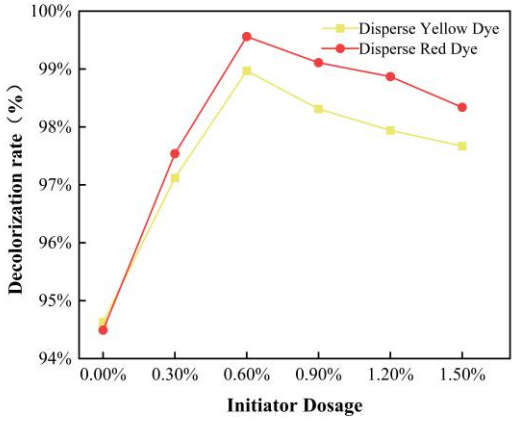


Fig. 5 The Effect of Initiator Dosage

As can be seen from the figure, as the initiator dosage increased, the decolourisation rates of FB and RGFL rose rapidly and continuously; when the initiator dosage reached 0.6 per cent, the

decolourisation rates of both dyes peaked; however, once the critical dosage was exceeded, the decolourisation rates of both dyes declined gradually in unison.This is because, at low initiator dosages, the number of free radicals in the system is low, there are insufficient starch activation sites, the grafting reaction efficiency is low and the molecular weight is relatively small; consequently, the flocculant exhibits weak bridging and electrostatic neutralisation capabilities, resulting in poor adsorption and flocculation effects on FB and RGFL, and a low decolourisation rate.When the initiator concentration exceeds 0.6% and continues to increase to 1.5%, the excessively high free radical concentration facilitates bimolecular termination, resulting in a decrease in the molecular weight of the flocculants; simultaneously, the side reaction of monomer homopolymerisation increases, grafting efficiency decreases, and ultimately the decolourisation rate declines.

2.1.5 Effect of Synthesis Temperature

The effect of synthesis temperature was investigated under conditions where the molar ratio of the base material (tapioca starch) to the graft monomers AM and AANa was 1:1:1, the cross-linking agent was used at 0.2 per cent (by mass of the total raw materials), and the initiator was used at 0.6 per cent (by mass of the total raw materials). The results are shown in Fig.6.

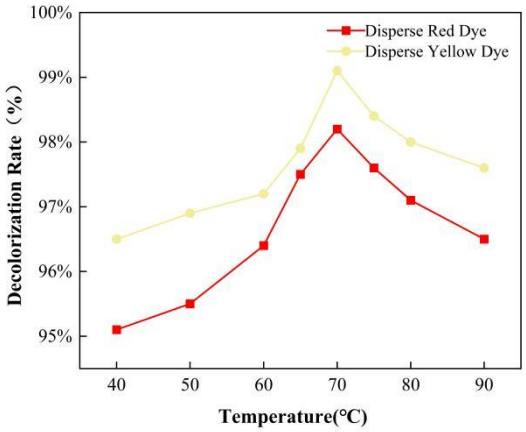


Fig. 6 The Effect of Synthesis Temperature

The synthesis temperature influences the molecular structure and flocculation performance of the flocculant by regulating the rate of free radical generation, whilst simultaneously controlling the degree of copolymerisation and the MBA cross-linking process. As shown in the figure, low temperatures result in insufficient initiation, leading to low grafting and cross-linking rates;as the temperature rises, grafting gradually becomes more complete and cross-linking more uniform, forming a loose, porous, highly charged three-dimensional network, with optimal results achieved at 70 °C; conversely, excessively high temperatures trigger side reactions such as monomer homopolymerisation, starch chain breakage and uneven cross-linking, which significantly damage the flocculant's skeletal structure and adsorption functional groups, leading to a decrease in the decolourisation rates of FB and RGFL

2.2 Structural Characterisation of the Flocculant

2.2.1 Analysis of ^{13}C-NMR

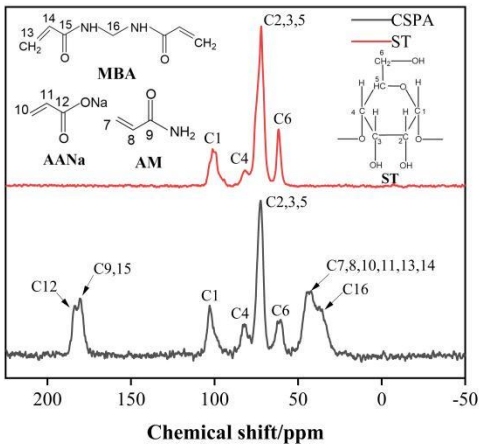


Fig. 7 ^{13}C-NMR spectra of St and CSPA

Fig.7 shows the^{13}C nuclear magnetic resonance spectra of native starch and modified starch. The C1–C6 labels in St correspond to the six carbon atoms in the starch glucose ring;the chemical shift at approximately 102 ppm corresponds to C1, the isomeric carbon of the glucose ring, which is largely shielded by two adjacent highly electronegative oxygen atoms; approximately 84 ppm corresponds to C4, whilst the absorption peak near 72 ppm represents the overlapping signals of C2, C3 and C5; approximately 62 ppm is attributed to the hydroxymethyl group at C6, consistent with the characteristic carbon spectrum of natural cassava starch.

The modified starch retains all the characteristic peaks of starch C1–C6; carbonyl carbons (C9, C12, C15) appear between 150 and 200 nm, corresponding to the amide carbonyl (C9) of AM, the sodium carboxylate carbonyl of AANa, and the amide carbonyl(C15);Since native starch lacks carbonyl structures, this peak is a characteristic signal of the grafted side chains; simultaneously, in the chemical shift range of 30–45 ppm, saturated alkyl carbon signals appear, attributable to the copolymerised alkyl carbon chains (C7, C8, C10, C11, C13, C14) and the methylene cross-linking bridge carbon (C16) in MBA.The olefinic carbon peaks corresponding to the carbon–carbon double bonds of the original monomers have completely disappeared from the carbon spectrum, confirming that the carbon–carbon double bonds of the AM and AANa monomers were fully opened and graft polymerisation was completed under a radical-initiated system. The MBA bifunctional monomer successfully participated in intermolecular covalent cross-linking reactions, ultimately leading to the successful construction of a three-dimensional cross-linked grafted starch polymer flocculant that combines a starch polysaccharide backbone withamide groups and anionic sodium carboxylate groups .

2.2.2 Analysis of XPS

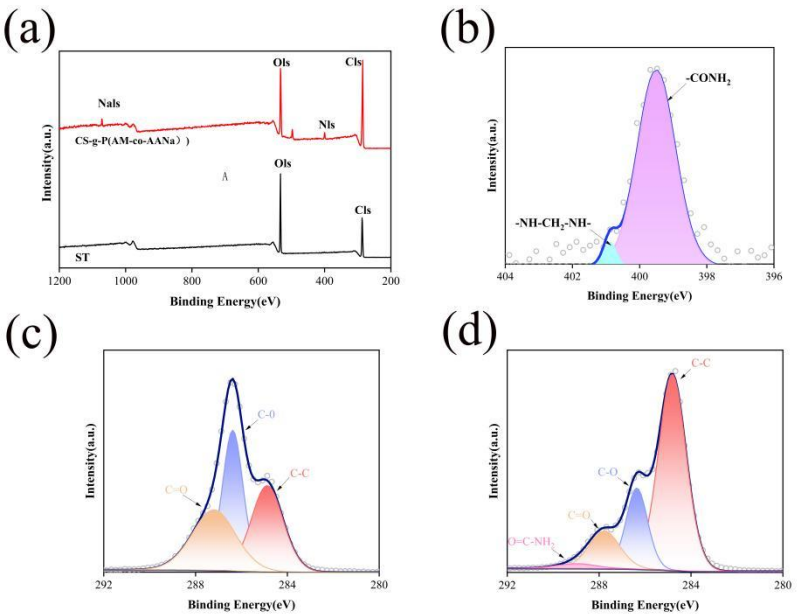


Fig. 8 XPS analysis of St and CSPA(a);N 1 s peak of CSPA(b);C 1 s peak of St(c) and CSPA(d)

As shown in Fig.8a, the full spectra of the native cassava starch and the modified starch flocculant are presented. The full spectrum of the native cassava starch contains only the C1s and O1s peaks, whereas the full spectrum of the modified starch flocculant exhibits additional Na1s and N1s peaks.This clearly indicates the successful implementation of the graft copolymerisation reaction; the N element originates directly from the amide group of the AM, whilst the Na element clearly indicates the presence of sodium carboxylate on the AANa side chains.

As shown in Fig.8b, this is the fitted spectrum of the N1s peak for the modified starch. Raw cassava starch is a simple polysaccharide containing no nitrogen whatsoever, whereas the modified starch exhibits an amide group at 399.5 eV; the presence of this peak indicates that the surface is covered by a large number of grafted side chains and a cross-linked network;simultaneously, a secondary amine group appears at 409.6 eV, which is a structural feature unique to the MBA, directly demonstrating that the MBA cross-linking agent has been successfully incorporated into the polymer network.

As shown in Fig.8c and 8d, the C 1s XPS deconvolution spectra of native starch and modified starch flocculant, respectively, reveal distinct chemical state distributions. In native starch, the C–O peak at 286.0 eV dominates overwhelmingly, attributable to the abundant hydroxyl (–OH) groups present on the glucose units along the natural starch polymer chain. The C–C peak at 284.8 eV arises from the carbon backbone of the glucopyranose rings. The minor C=O peak observed at higher binding energy likely originates from trace impurities—such as co-extracted lipids or proteins—associated with the native starch sample.

In contrast, the modified starch exhibits a significantly enhanced C–C peak intensity and a markedly reduced C–O peak intensity. This shift reflects the successful incorporation of acrylamide and sodium acrylate monomers, as well as crosslinking by MBA to form a three-dimensional polymeric network.Notably,the emergence of the O=C–NH_2 peak absent in the native starch spectrum-provides direct spectroscopic evidence for both graft copolymerization and crosslinking reactions.

2.2.3 Analysis of XRD

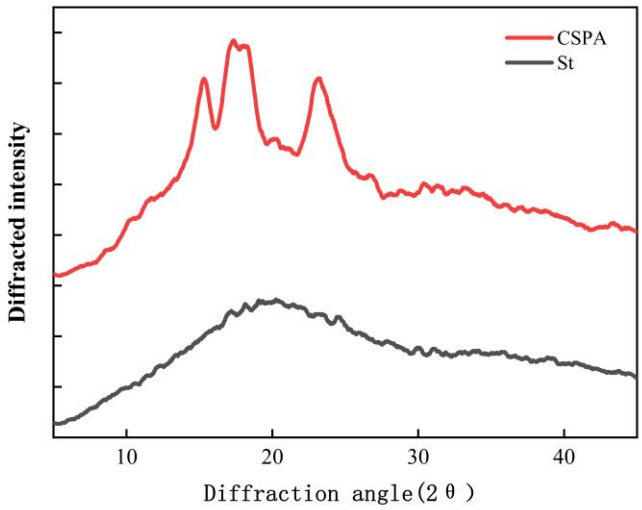


Fig. 9 XRD analysis of St and CSPA

The fig.9 shows the X-ray diffraction patterns of native starch and CSPA. The XRD pattern of native cassava starch (St) exhibits a broad diffuse diffraction peak at 2θ = 17–20°, which is characteristic of the semi-crystalline structure typical of natural starch.Following the preparation of CSPA via MBA cross-linking and graft copolymerisation with acrylamide and sodium acrylate, the diffraction pattern underwent marked changes: a series of sharp diffraction peaks appeared at 2θ ≈ 14.7°, 17.2°, 19.6° and 22.5°, whilst the broad native diffraction peak of the original cassava starch disappeared. This indicates that the grafting and cross-linking chemical reactions disrupted the original crystalline structure of the starch granules; simultaneously, the grafted side chains and the cross-linking network induced macromolecular chain reorganisation, forming new ordered crystalline regions, thereby significantly increasing the product's degree of crystallinity.CSPA still exhibits an amorphous diffuse background in the high-diffraction-angle region, suggesting that the product has a semi-crystalline structure. The presence of extensive amorphous regions facilitates the swelling and unfolding of the flocculant in water, providing an abundance of active groups that promote the flocculation and removal of dyes from wastewater.

2.2.4 Analysis of FTIR

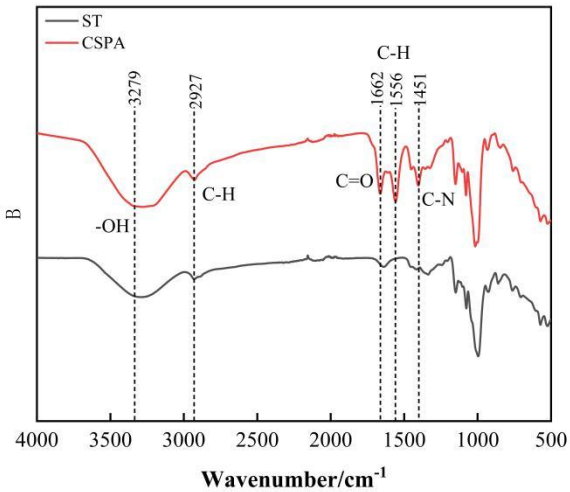


Fig. 10 Infrared spectroscopy analysis diagram

The fig.10 shows the infrared spectra of native starch and modified starch. Native starch exhibits a broad stretch peak of hydroxyl groups-OH at 3279 cm^{-1}, whilst in the modified starch this peak is broadened; this is due to the superposition and coupling of the stretching vibrations of the amide groups (N–H) introduced by the grafted side chains with those of the hydroxyl groups. The peak corresponding to 2927 cm^{-1}, which is stronger than that of the native starch; this is attributable to the stretching of saturated C–H bonds, confirming that alkyl groups have been grafted onto the side chains·In the range of 1500–1700 cm^{-1}, the absorption peaks of the modified starch are significantly enhanced, with characteristic peaks appearing at 1662 cm^{-1} (C=O stretching vibration) and 1556 cm^{-1}(coupled with the C–N stretching vibration) are present; these are all typical absorption features of acrylamide groups, confirming that AM has been successfully grafted onto the starch molecular chains. Furthermore, the N–H bending vibration indirectly confirms the formation of the imidamide structure (-NH-CH_2 -NH-); the peak at 1453 cm^{-1} is likely associated with the bending vibration of the carboxyl group (-COO^-) in sodium acrylate, indicating that AANa has also been grafted. Both samples retain the characteristic absorption of the starch glycosidic bonds in the 1000–2000 cm^{-1} range, suggesting that the starch backbone remains intact.In summary, acrylamide and sodium acrylate were covalently grafted onto the starch chains, and the cross-linking agent successfully participated in the polymerisation.

2.2.2 Analysis of SEM

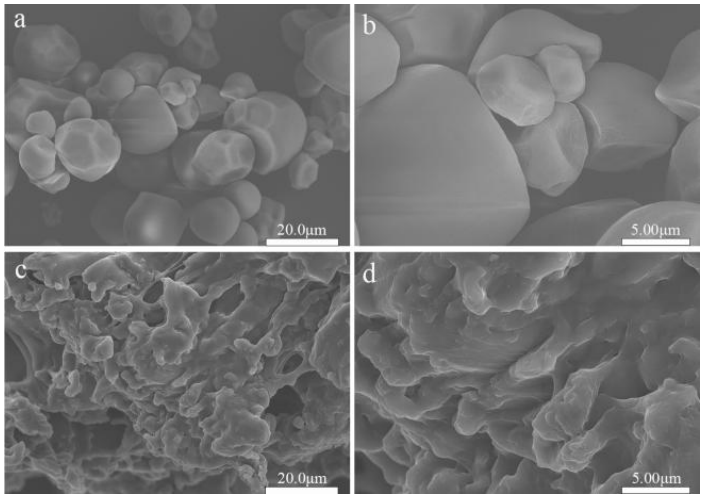


Fig.11 Scanning Electron Microscope Image

The surface microstructure of native cassava starch and CSPA was characterised using SEM. As shown in Fig.11a and 11b, native cassava starch exhibits a relatively regular elliptical or hemispherical morphology, with smooth, dense particle surfaces and an intact structure. This structure indicates strong hydrogen bonding between the native starch molecular chains, which also results in a limited number of active sites and restricted flocculation properties.In contrast, following cross-linking and graft copolymerisation modification, the originally intact spherical particles shown in Fig.11c and 11d have completely disappeared; the starch particles have become extremely rough, loose and porous, exhibiting a continuous and coherent three-dimensional network structure, with distinct wrinkled lamellae and a rough, porous surface. This structure significantly increases the material's specific surface area, exposing more anionic carboxyl and amide groups, thereby providing abundant sites for the electrostatic adsorption and hydrogen bonding of dye molecules; meanwhile, the three-dimensional cross-linked network enhances floc aggregation and sedimentation performance through the synergistic

action of adsorption bridging and entrapment-sweeping mechanisms, providing a microstructural basis for the excellent decolourisation and flocculation performance of the modified product.

2.3 Effects on Dye Removal Performance

2.3.1 Effect of Flocculant Dosage

The dosage of flocculants plays a decisive role in dye removal efficiency. In this study, anionic polyacrylamide (APAM) and carboxymethyl starch (CMC) were compared with CSPA to investigate the decolourisation rates of FB and RGFL achieved by these three different flocculants at various dosages; the results are shown in Fig.12.

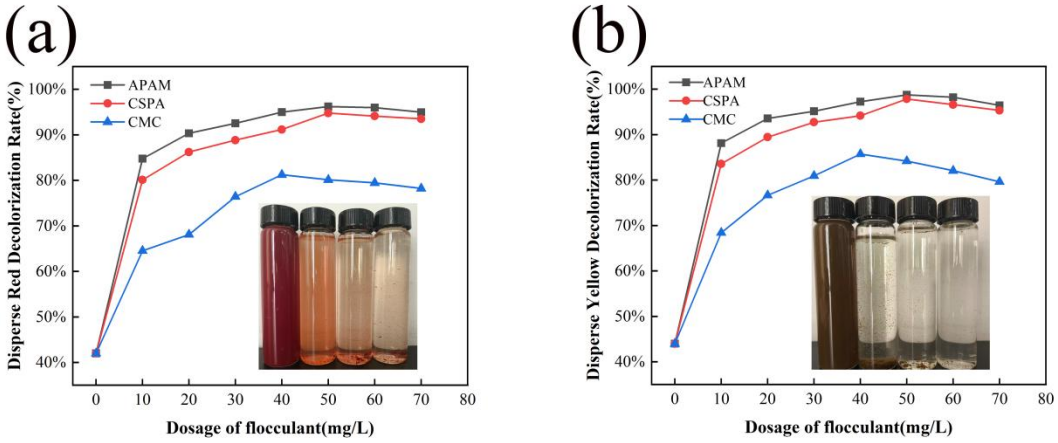


Fig.12 Effect of Flocculant Dosage

As can be seen from Fig.12, as the flocculant dosage increases, the decolourisation rates for both dyes exhibit a pattern of 'initial increase followed by stabilisation'.This is because, at low dosages, the flocculant molecules are able to effectively neutralise the surface charge of the colloids and adsorb the dye molecules, resulting in a rapid rise in the decolourisation rate; when the flocculant dosage reaches 50 mg/L, the decolourisation rates for both dyes reach their optimum, at which point the adsorption sites are saturated and the bridging effect is maximised;When the flocculant dosage is increased further—that is, once the critical dosage threshold is exceeded—the majority of adsorbable dye molecules in the water have already been bound. The remaining active sites of the flocculant are unable to capture any more dye, the surfaces of the colloidal particles become covered, and the bridging effect diminishes; consequently, as the dye removal rate ceases to increase, it tends to stabilise.

A comparison of flocculant types shows that modified starch flocculant achieves a far superior decolourisation rate to carboxymethyl starch, and is only slightly less effective than anionic amide.Compared with anionic amide (APAM), although it is slightly inferior in peak height due to its lower molecular weight, it still demonstrates good competitive potential, and its advantages in terms of biodegradability and environmental friendliness are very significant.Compared with carboxymethyl starch (CMC), modified starch flocculants possess a higher molecular weight and better cross-linking ability, overcoming the limitations of natural starch to achieve a higher decolourisation rate for dyes, whilst significantly broadening the optimal dosage window. In summary, when considering both environmental friendliness and the effectiveness of treating dyeing and printing effluent, modified starch flocculants demonstrate broad prospects and potential for development.

2.3.2 Effect of pH

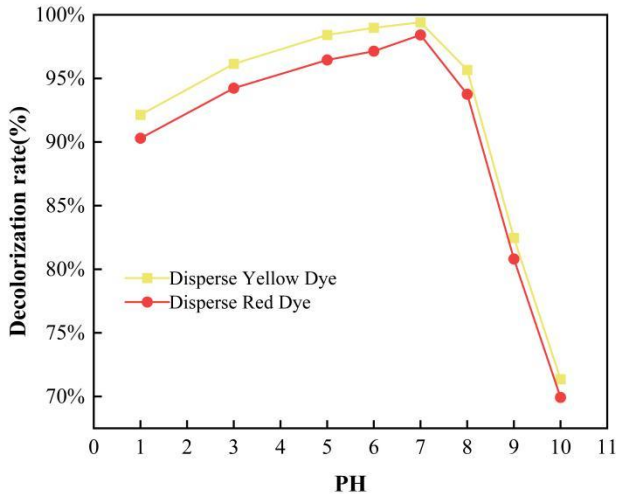


Fig.13 The Effect of Temperature

PH plays a crucial role in dye removal performance. The decolourisation rates of FB and RGFL when PAC and the modified flocculant are used in combination are shown in the figure. It is evident from Figure 11 that, within the pH range of 1–7, the removal rates for both dyes are high; furthermore, as the pH increases, the decolourisation rate shows an upward trend, reaching a maximum at pH 7;on the one hand, this is because under acidic conditions (pH < 7), PAC exists in the form of simple hydrated ions with a high positive charge, maximising its electrostatic neutralisation and adsorption bridging capabilities; on the other hand, under these conditions, the grafted groups of the modified starch also promote floc formation through bridging and adsorption.When the pH is alkaline (pH > 7), the decolourisation rate of disperse dyes drops sharply. This is because PAC degrades from an efficient electrostatic neutraliser to an inefficient precipitant, and the adsorption and bridging effects of the modified starch flocculant are severely impeded by electrostatic repulsion and molecular curling.In summary, when the pH is within the neutral or weakly acidic range (pH 5–7), both PAC and the modified starch flocculant demonstrate higher treatment efficiency and synergistic effects.

3 Conclusions

The following conclusions can be made:

Using St, AM, AANa, MBA as raw materials via aqueous copolymerisation to produce a cross-linked grafted anionic starch flocculant (CSPA). CSPA was used in synergy with PAC to simulate the treatment of FB and RGFL textile dyeing effluents. The study analysed and explored the synergistic mechanism of action with PAC, as well as optimised the synthesis conditions for CSPA. It was found that the best results for the synergistic treatment of textile dyeing effluents with CSPA and PAC were achieved under the following conditions: a ratio of St to AM to AANa of 1:1:1, an MBA content of 0.2 per cent, an initiator content of 0.6 per cent and a synthesis temperature of 30 °C.

Structural characterisation results indicate that the appearance of characteristic peaks for amide and carboxyl groups in the FTIR spectrum confirms the successful grafting of AM and AANa; the presence of a secondary amide structure confirms that MBA has successfully participated in the polymerisation; SEM analysis revealed that the surface of the modified starch had transformed from smooth particles to a rough, porous structure; the appearance of N1s and Na1s peaks in the XPS spectrum indicated the successful incorporation of AM and AANa; the fitting of the C1s and N1s peaks confirmed the presence of imidamide groups, which also indicated successful cross-linking.

Flocculation experiments indicate that the dosage of flocculant and the pH level have a significant impact on flocculation efficiency. The results show that when the dosage is 50 mg/L and the pH reaches 7, the decolourisation rate for both dyes exceeds 98 per cent. The flocculation window for the combined use of PAC and CSPA is relatively wide; good flocculation performance is maintained within a pH range of 3 to 7, with removal rates for both dyes exceeding 94 per cent.

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