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APPLICATION OF A CS/ATP COMPOSITE FLOCCULANT FOR RECYCLING THE MAIN COMPONENTS FROM A BEZAFIBRATE SYNTHESIS WASTE SOLUTION

UPORABA CS/ATP KOMPOZITNEGA FLOKULANTA ZA RECIKLIRANJE GLAVNIH KOMPONENT V BEZAFIBRATNI SINTEZI ODPADNE RAZTOPINE

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A chitosan/attapulgite (CS/ATP) composite flocculant with excellent adsorption was prepared from chitosan (CS) and attapulgite clay (ATP). The micro morphology and structure of the composite flocculant were characterized with SEM and IR. The effect of the CS/ATP composite flocculant on the recovery of the main components from the bezafibrate (BZ) wastewater of a pharmaceutical plant was investigated. The influences of the flocculation temperature, mixing time and standing time on the flocculation effect were investigated by determining the BZ content of the recovered crude products as the evaluation index so as to obtain the best recovery process. The experimental results show that the best flocculation condition is created when we add 20 mg/mL of CS/ATP to the waste liquid, stir it at 30 °C for 10 min and allow it to stand for 30 min. Compared with the traditional recovery process, the BZ content of the recovered crude products can be increased from 47 % to 74 % when using the CS/ATP composite flocculant. This flocculant can effectively overcome the defects of single material residues and difficult separation, accelerate the settlement of impurities in a waste liquid effectively, and can be used in the field of solution clearing and waste liquid separation.

Keywords: chitosan, attapulgite, flocculant, bezafibrate waste solution, recycling

Avtorji so iz mešanice hitosana (CS) in atapulgitne gline (ATP) pripravili novo vrsto hitozan/atapulgitnega (CS/ATP) kompozitnega flokulanta z odlično adsorpcijsko flokulacijo oz. sposobnostjo kosmičenja. Mikromorfologijo in strukturo kompozitnega flokulanta so določili z vrstičnim elektronskim mikroskopom (SEM) in infrardečim spektrometrom (IR). Nato so ugotavljali vpliv CS/ATP kompozitnega flokulanta na popravek glavnih komponent bezafibratnih (BZ) odplak iz farmacevtske tovarne. Ugotavljali so vpliv flokulacijske temperature, časa mešanja in stojnega časa na vpliv flokulacije. Indeks ovrednotenja, s katerim so dobili najboljši proces očiščenja odplak, je predstavljal vsebnost oz. količino odstranjenih snovi v BZ odplakah. Eksperimentalni rezultati raziskave so pokazali, da so najboljše pogoje flokulacije dosegli pri dodatku 20 mg/mL CS/ATP, mešanju raztopine 10 min pri temperaturi 30 °C in njeni odstavitvi za 30 min. Primerjava s standardnim procesom poprave oz. čiščenja je pri uporabi CS/ATP kompozitnega flokulanta vsebnost BZ v ostanku narasla s 47 % na 74 %. Kompozitni flokulant dejansko učinkovito premaga napake ostankov posameznega materiala in izboljša težavno ločevanje ter pospeši posedanje nečistoč v odpadni tekočini oz. odplakah. Zato se lahko uporablja na področju razbistrenja raztopin in ločevanja nečistoč v odplakah.

Ključne besede: hitosan, atapulgit, flokulant, bezafibratna odpadna raztopina, recikliranje

1 INTRODUCTION

Bezafibrate (BZ), belonging to fibrates, is a first-line drug in the treatment of various types of lipid metabolic disorders.[1,2] The synthesis of BZ includes two steps of acylation and condensation, in which the condensation reaction leads to an increase in the coproducts as the reaction temperature rises rapidly in a short time due to spontaneous exothermic heat. However, there is still about 7 % of BZ in the remaining waste liquid (the high-performance liquid method)[3] after the crystallization and solvent recovery of the mother liquor in this reaction. The crude BZ obtained with the traditional recovery is directly discarded by enterprises due to a large amount of impurities, high viscosity and high purification cost. Therefore, developing a green method with a simple operation and low cost to recover BZ from waste liquids is an effective way to improve the product yield and reduce the production cost. Previous studies have found that the major impurities in a waste liquid can be removed by using the carbon dioxide precipitation method,[4] but simple filtration and general centrifugation methods cannot separate BZ because the precipitation is often difficult to settle due to small impurity particles, large viscosity of the waste liquid, and is even suspended in the form of colloid in the waste liquid.

Attapulgite (ATP), a non-metallic clay mineral, formed from the layered chain structures of hydrated magnesium aluminum silicates, has a large specific surface area and an internal porous characterization due to

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large channels resembling zeolite. In recent years, ATP has been developed considerably in the wastewater treatment industry. Due to its excellent adsorption and decolorization performance, non-toxic, pollution-free and in-depth research on the treatment of pharmaceutical and chemical waste liquids has been carried out.[5–7] Especially after organic modification, ATP improves its hydrophobicity and enhances its adsorption capacity for organic matter as some of the crystal water and adsorbed water inside and outside the lattice is replaced by organic matter.[8,9] However, it is difficult to form only ATP as a powder adsorbent, and perform a solid-liquid separation of liquid with high viscosity. Chitosan (CS), a biodegradable natural amino polysaccharide polymer compound, is an excellent natural cation clarifier, and it is commonly used for the flocculation and clearing of Chinese drug extracts and fruit juices as it is non-toxic and tasteless.[10,11] This study intends to realize the recovery of BZ from a waste solution, using CS to modify ATP and prepare a chitosan/attapulgite (CS/ATP) composite flocculant to enhance the adsorption performance of ATP on organic impurities, improving the separation effect of the impurities in the waste solution of BZ synthesis.

2 EXPERIMENTAL PART

2.1 Materials

BZ control products were purchased from the National Institutes for Food and Drug Control (batch No.100732-200501), BZ waste liquid was from Jiangsu Tasly Diyi Pharmaceutical Co., Ltd. (lot No.20170509), CS from Zhejiang Golden-Shell Pharmaceutical Co., Ltd. (95 % deacetyl), ATP was from Jiangsu Jiuchuan Nano Material Technology Co., Ltd. (100 screen), chromatographically pure methanol was from Tianjin Oubokai Chemical Co., Ltd., water was deionized water and other, analytically pure reagents were purchased from Sinopharm Group Chemical Reagent Co., Ltd.

2.2 Instruments

We used a 1100LC HPLC, G1315B UV detector (Agilent), Nicolet 5700 infrared spectrometer (Thermo Electron), S-3000N scanning electron microscope (Hitachi, Japan), IKA-Werke thermostatic magnetic stirrer (Guangzhou Yike Laboratory Technology Co., Ltd.) and Allegra X-30 centrifuge (Beckman, USA).

2.3 Preparation of CS/ATP

1 g of CS was added to 100 mL of 1 % (w/w) acetic acid solution, which was stirred slowly and heated to 40 °C so that CS dissolved completely and a CS solution was obtained. ATP was added to the CS solution (w_{CS} : w_{ATP} = 6 : 100) slowly and stirred in (400 min^{-1}) continuously at room temperature for 24 h. After being allowed to stand for 8 h, the upper acetic acid solution was dumped, the solid product was washed with water to become neutral and dried at 60 °C for 12 h. The CS/ATP complex obtained was ground, screened through a 100 mesh sieve and sealed in a dryer for storage.

2.4 BZ recovery from the waste liquid

2.4.1 Traditional post-processing method (method A)

The BZ waste solution was diluted with water at a ratio of 1 : 25 (*v*/*v*), acidified and the pH was adjusted to 3–4 with 15 % of HCl. The solution was allowed to stand until the precipitation was complete, then it was filtered and dried to obtain the BZ crude product.

2.4.2 CO_2 precipitation method (method B)

The BZ waste solution was diluted with water at a ratio of 1 : 25 (*v*/*v*) and CO_2 was passed into the solution under airtight conditions. Then the solution was centrifuged (5000 min^{-1}) after 40 min to get the supernatant, which was acidified and allowed to stand until the precipitation was complete, then filtered and dried to get the BZ crude product, as with method A.

2.4.3 CS flocculation method (method C)

After passing CO_2 into the solution according to method B, a 1.2 % (*w*/*w*) CS solution was added to the solution, which was filtered after 30 min of flocculation. The filtrate was acidified, allowed to stand until the precipitation was complete, then filtered and dried to get the BZ crude product as with method A.

2.4.4 ATP adsorption method (method D)

After passing CO_2 into the solution according to method B, a certain amount of ATP was added to the solution, which was stirred for 10 min and filtered after being allowed to stand for 30 min. The filtrate was acidified, allowed to stand until the precipitation was complete, filtered and dried to get the BZ crude product as with method A.

2.4.5 CS/ATP flocculation adsorption method (method E)

After passing CO_2 into the solution according to method B, a 1.2 % (*w*/*w*) CS solution was added to the solution, which was filtered after 30 min of flocculation. A certain amount of CS/ATP was added to the filtrate, which was stirred for 10 min and filtered after standing for 30 min. The secondary filtrate was acidified, allowed to stand until the precipitation was complete, filtered and dried to get the BZ crude product as with method A.

2.5 Measurement of the BZ content

HPLC analyses were performed in a Hypersil ODS2 column (4.6 mm × 250 mm and 5 μm), at a column temperature of 30 °C with a mobile phase of 0.01 mol/L potassium dihydrogen phosphate solution (the pH was adjusted to 3.8 with phosphoric acid) – methanol (40 : 60, *v*/*v*), at a flow rate of 1 mL/min, an injection volume of 10 μL and a detection wavelength of 228 nm. The samples were the BZ crude products recovered with different

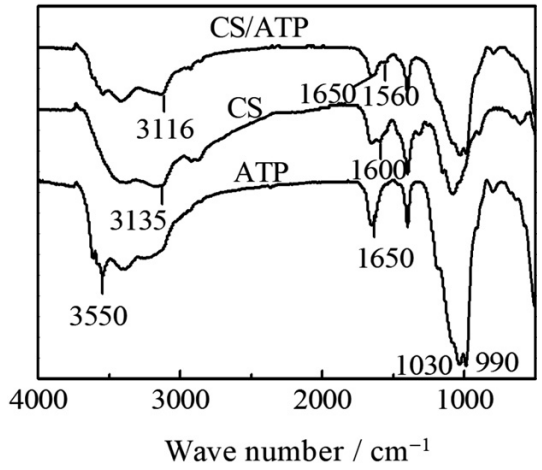

Figure 1: FTIR spectra of ATP, CS and CS/ATP

methods. 100 mg of a sample was dissolved with the mobile phase to prepare the solution with a certain concentration. The solution was filtered with a 0.25 μm microporous membrane and injected into a liquid chromatographic analysis system. The chromatogram was recorded and the content was determined with the area normalization method.

3 RESULTS AND DISCUSSION

3.1 Characterization of the CS/ATP composite flocculant

3.1.1 FTIR of the materials

ATP, chitosan and their complex of CS/ATP were characterized by the FTIR spectra, and the results are shown in **Figure 1**. When a degree of CS deacetylation of 95 % was used, the peak of CS at 1600 cm^{-1} belonged to the bent vibration peak of the amino group, which was blue shifted to 1560 cm^{-1} in the CS/ATP complex. Moreover, the stretching vibration peak at 3550 cm^{-1} which was attributed to Si-OH in ATP became weak in the complex, indicating that the amino group in CS formed hydrogen bonds with the hydroxyl group in ATP.[12] The OH bending vibration peaks of 1650 cm^{-1} attributed to the ATP coordination water and the adsorbed water become weak in the complex. The characteristic absorption double peaks of ATP at 1030 cm^{-1} and 990 cm^{-1} caused by the stretching vibration of the Si-O-Si bond also appeared in the complex, indicating that ATP had successfully recombined with CS.[13]

3.1.2 Microstructure of the material

Electron micrographs of ATP and its complex CS/ATP are shown in **Figure 2**. This figure shows that ATP is a kind of fibrous rod-like crystal, easy to agglomerate in bundles due to a large specific surface area. In the composite with chitosan, the rod crystals of ATP are covered with a layer of polymer, forming a composite material with organic-phase chitosan as the matrix and inorganic-phase ATP as the core, having a denser structure compared with ATP. However, when compared with the single polymerization system, the presence of the inorganic phase provides the dispersion medium for chitosan and gives it a rough microstructure, providing a structural basis for its adsorption and flocculation properties. At the same time, the presence of chitosan also provides the material basis for the processing and moulding of ATP.

3.1.3 Flocculation morphology

According to the experimental optimum process conditions for the flocculation of the BZ waste solution by ATP/CS, ATP and CS, the flocculated waste solution was diluted with deionized water at a certain concentration, and the structures of the flocs were photographed and observed, as shown in **Figure 3**.

Figure 3 shows the flocs produced after the addition of ATP, CS and ATP/CS to the waste solution, respectively. It can be seen that after adding ATP to the waste solution, ATP flocculates with the adsorption of impurities through the van der Waals force, and the floc particles are small and loose, with a slow settling speed and difficult filtration. After adding CS to the waste solution, although CS can form larger flocs by bridging through the electrostatic gravitational force, there are still a large number of fine flocs, affecting the settling speed. On the

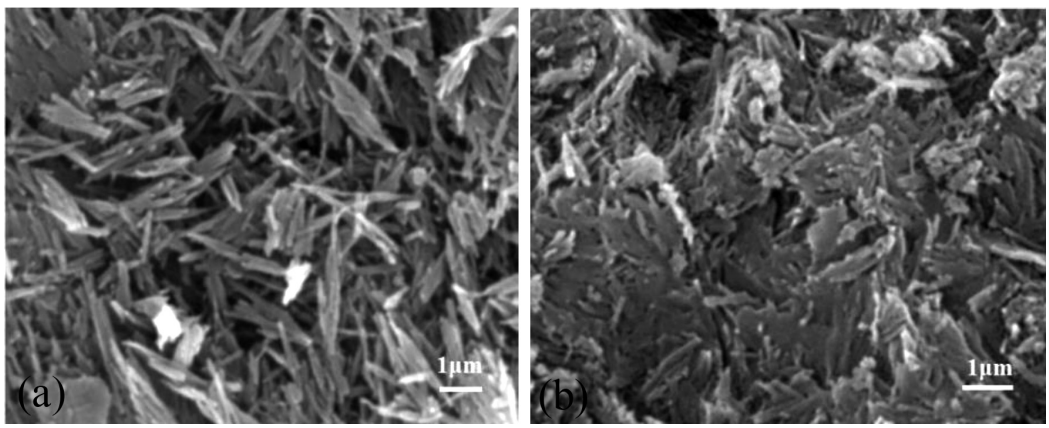

Figure 2: SEM micrographs of: a) ATP, b) CS/ATP

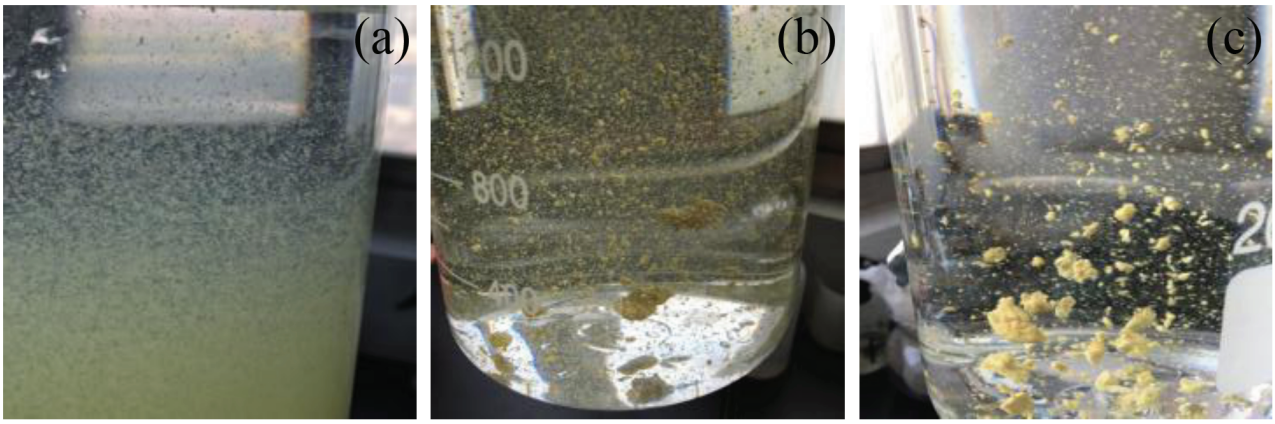

Figure 3: Observation of flocculation morphology: a) ATP, b) CS, c) ATP/CS

contrary, after adding ATP/CS, large and dense flocs are generated, easy to separate. It can be seen that ATP with good adsorption performance quickly adsorbs impurities, while the CS polymer compound with the bridging effect makes the flocs larger, accelerating the settling of the flocs, and has a netting effect, which can clarify the waste solution and separate impurities in a short time. Here, the effect is obviously better than in the case of the adsorption and flocculation effect of only CS or ATP.

3.2 Recovery of BZ from the waste solution

3.2.1 Comparison of different recovery processes

The effects of different recovery processes on the content of BZ in the waste solution are shown in **Figure 4**. Compared with the conventional recovery method (A), the CO_2 precipitation method (B) makes it difficult to filter the fine precipitation formed as larger particles in the viscous liquid because the treatment target is a viscous waste solution with lots impurities, thus causing the content of BZ in the resulting crude product to be lower than that of the conventional recovery method. However, using the C method that adds CS to the flocculate in the waste solution after the CO_2 precipitation, the content of BZ in the resulting crude product is significantly higher than that of the B method, increasing from 44 % to 57 %; the solution is clear after the flocculation and the flocs at the bottom can be removed by filtration, showing that chitosan has an obvious charge neutralization and adsorption bridging effect on the precipitation formed by CO_2 and other tiny impurities in the waste solution.[14] The effect of the ATP treatment (the D method) is similar to that of the C method, indicating that the large specific surface area of ATP allows it to have a significant adsorption effect on impurities and also enables fine precipitates to form larger precipitates by depositing them on the surface of ATP for easy filtration.

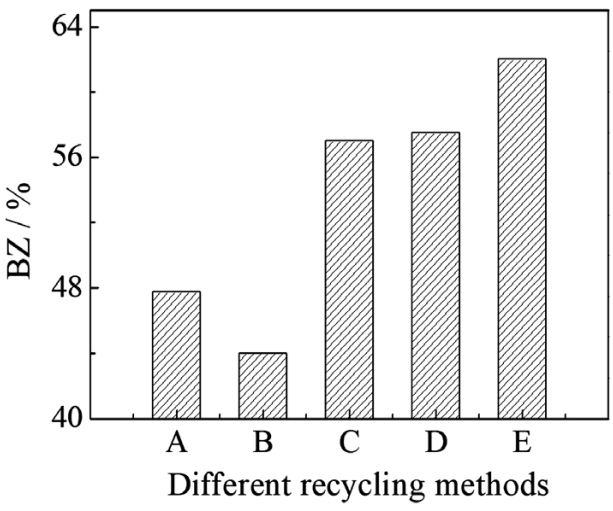

Figure 4: Effects of different recovery processes on the BZ content in the waste solution

The CS/ATP complex (the E method) formed by compounding chitosan and ATP has the best effect on the impurity removal in the waste solution, and the recovered crude product contains up to 62 % of BZ, which is due to the fact that on the one hand, the floc formed by chitosan only was lighter and less likely to settle, while the presence of ATP effectively increased the floc weight, making the aggregated floc more compact. In addition, the rough microstructure of the complex is conducive to the adhesion of fine precipitation and flocs, speeding up the settling speed and making it easier to remove them.[15,16] On the other hand, based on the FTIR spectra from **Figure 1**, it can be suggested that the three-dimensional network structure formed by the hydroxyl group on ATP and the amino group on CS through hydrogen bonding in the complex also has a netting effect on the precipitated particles.

3.2.2 Effect of the flocculation temperature

The variation in the BZ content in the waste solution with the flocculation temperature is shown in **Figure 5**. With the increase in the temperature, the content of BZ gradually increases and reaches the highest value at 30 °C. Due to the fact that with the temperature increase, the Brownian motion of particles in the waste solution is strengthened, the collision frequency between the particles increases and the electrical neutralization and ad-

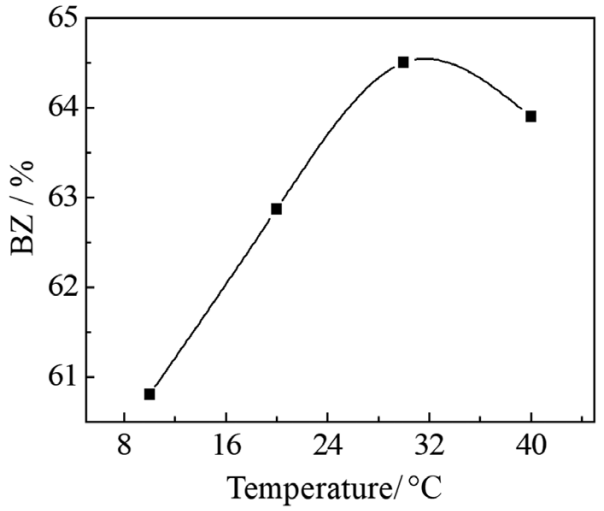

Figure 5: Effect of the flocculation temperature on the BZ content in the waste solution

sorption bridging effects are gradually enhanced, while the temperature continues to increase and the effective number of collisions per unit time increases, leading to the self-polymerization reaction of the flocculant itself, which affects the flocculation effect.[17] At the same time, the acceleration of the reaction rate also makes the fine particles unfavourable for settling.

3.2.3 Effect of the flocculant dosage

The effect of the flocculant dosage on the BZ content in the waste solution is shown in **Figure 6**. The BZ content tends to increase and then decrease with the flocculant dosage, reaching the maximum value at 20 mg/mL. This is due to the fact that when the amount of flocculant is low, the electrical neutralization and adsorption bridging effects between the flocculant and impurity molecules are extremely weak, resulting in insufficient flocculation.[14] On the other hand, when the amount of flocculant is too high, an excessive amount of positively charged particles is adsorbed on the surface of colloidal particles, and bridging cannot be formed between the particles under the effect of their electrostatic repulsion because the premise for flocculation is that the surfaces of the particles in a solution should be left blank to produce bridging adsorption. So a continued increase in the amount of flocculant produces a colloid protecting effect, which enhances the stability of the particle system and makes it less likely to settle. On the other hand, CS is positively charged and an excessive amount of flocculant can also reduce the BZ content with the adsorption on the dissociated negative ions of BZ.

3.2.4 Stirring and standing time

After adding the flocculant, the effect of the solution stirring and standing time on the BZ content in the waste solution is shown in **Figure 7**. The stirring time is one of the important factors affecting the flocculation effect. The whole flocculation process consists of two stages: mixing and reaction. In the mixing stage, stirring can promote the full contact of the objects, while in the reaction stage, a stirring time that is too long leads to the fragmentation of the formed flocs. In addition, the standing stage of flocculation is the process of floc gathering and settling. If the time is too short, the flocs do not settle completely, causing difficulties during separation; if the time is too long, the flocs may adsorb the main components in the solution, resulting in a reduction in the main-component content. As shown in **Figure 7**, the best flocculation effect was achieved after 10 min of stirring and standing.

3.2.5 Orthogonal test

An L_9 (3^4) orthogonal test was designed based on the above experimental results to further optimize the flocculation process, and the lever factors are shown in **Ta-**

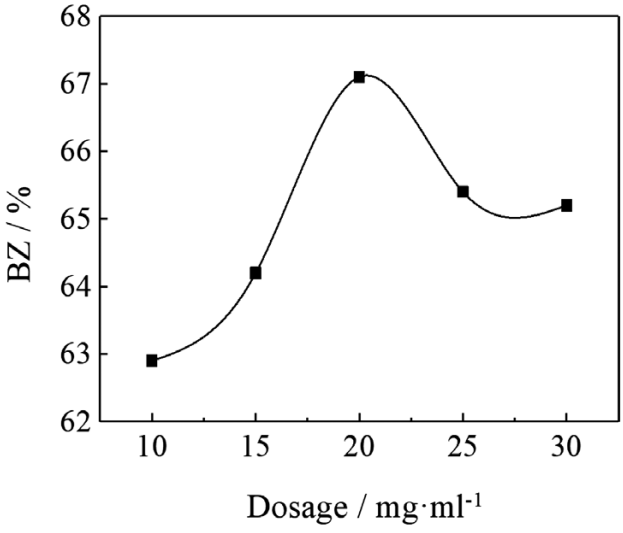

Figure 6: Effect of the flocculant dosage on the BZ content in the waste solution

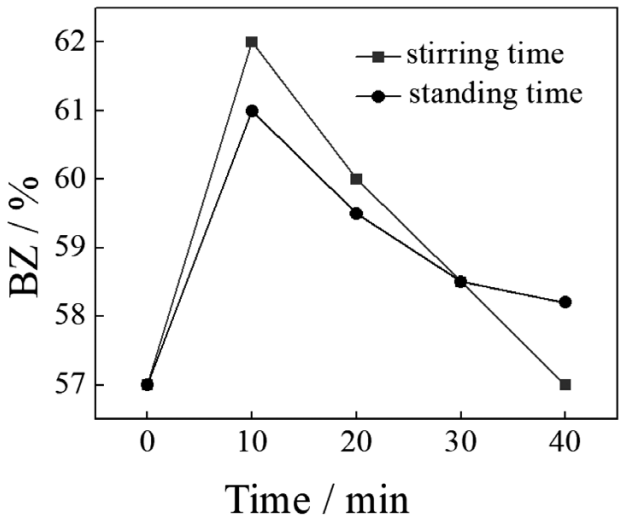

Figure 7: Effect of the stirring and standing time on the BZ content in the waste solution

ble 1. The optimum flocculation process was determined with an extreme difference analysis based on the experimental results, with a flocculation temperature of 30 °C, CS/ATP dosage of 20 mg/mL, stirring time of 10 min, and standing time of 30 min. The order of the influencing factors was standing time > flocculant dosage > flocculation temperature > stirring time. A validation experiment for this optimal flocculation condition was performed, and its result showed that the BZ content of the crude product recovered from the waste solution was 74 %.

Table 1: Orthogonal-factor table for the recovery technology using CS/ATP

Level	Factor			
	Temperature (°C)	Dosage (mg/mL)	Stirring time (min)	Standing time (min)
1	20	15	10	10
2	30	20	20	20
3	40	25	30	30

3.3 Comparison of recovery processes

A comparison of the best process obtained with the orthogonal test and the conventional recovery process is shown in **Figure 8**; the results show that the crude product obtained with the ATP/CS flocculation treatment had a BZ content of 74 %. The crude product was then recrystallized once with ethanol (95 %), and the BZ content reached 98 % with a yield of 20 %. The crude product obtained with the conventional recovery was very sticky due to the BZ content of only 47 %, and the content reached 81 % after one recrystallization. The synergistic adsorption and flocculation of ATP and CS in the compound flocculant promoted the sedimentation of fine impurities suspended in the waste solution, which was conducive to the separation of impurities and the increase in the BZ content in the waste solution, thus more favourable to the recovery of BZ from the waste solution.

4 CONCLUSIONS

The preparation of the CS/ATP composite flocculant with the synergistic effect of adsorption and flocculation using CS and ATP as raw materials is simple and easy, suitable for industrial mass production, and can effectively recover a high-purity BZ crude product from a BZ synthesis waste solution, thus reducing the production cost.

Through a single-factor experiment and orthogonal test, the best flocculation conditions for using CS/ATP in a BZ waste solution were created when 20 mg/mL of CS/ATP were added to the solution at 30 °C, stirred for 10 min and allowed to rest for 30 min. Under these conditions, the flocculant not only facilitated the recovery of BZ from the waste solution, but also increased the BZ content in the crude product from 47 % to 74 %, and the content of crude product from 81 % to 98 % after one recrystallization.

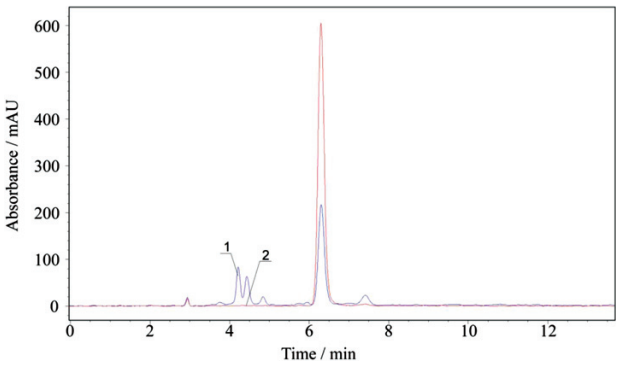

Figure 8: HPLC of the conventional recovery process (1) and ATP/CS recovery process (2)

The CS/ATP composite flocculant is a natural green composite material, which avoids the disadvantages of the residuals of a single CS flocculant and difficult separation after a single ATP adsorption. It effectively accelerates the settling of impurities in a waste solution, and can be used in the fields of solution clearing and waste solution separation and purification.

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