STUDY on STABILITY of a MODIFIED BANANA PEEL COAGULANT

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Abstract

A new kind of water treatment agents, banana peel (BP) coagulant and its modified oxidation banana peel (OBP) coagulant were prepared, and their storage stability were investigated, such as changes of surface morphology, bond structure and coagulation performance with Scanning Electron Microscopy (SEM), Fourier Infrared (FTIR) and Jar tests, respectively. The results showed that the number and size of the bacterial plaques on BP obviously increased with the increasing of storage time and there were only some obscured signs of plaque formation at 30 d. BP and OBP were mainly composed of carbohydrates, cellulose, lignin, protein, and fatty acids. The removal of turbidity and color by BP and OBP decreased with the increasing of storage time: BP decreased by 33% and 33% at 11 d, and OBP decreased slowly with decreasing by 20.6 and 17% at 30 d, respectively.

Keywords: Banana peel; Coagulant; Modification; Storage; Stability

1. Introduction

For more than fifity years, with the rapid development of agriculture and forestry in China and the great improvement of people's living standard, agricultural and forestry wastes (such as chaff, rice straw, straw, corn stem, peanut shell, bagasse, fruit peel, and so on) increased dramatically in China [1], which gradually become a big problem due to quick development of economy [2]. Like other solid wastes, agricultural and forestry wastes discharged in one point maybe have theirs values in other points. So, more and more experts in the field of water and wastewater treatment are increasingly concerned about this kind of wastes [1,3], in which fruit peel got some people’s attention.

Banana peel comes from banana which is one of the main tropical and subtropical fruits (known as "one of four big fruits" in China). The production of banana increased significantly due to structural adjustment of China's agricultural industrialization. The total yield of banana reached 11.79 million tons in 2014, thus producing a huge amount of banana peel. Generally, the weight of banana peel coming form a banana accounts for about 30–50% of the total weight of a banana [4,5]. In addition, most of banana peel has been discarded into the environment: if not properly disposed, they will cause some negative impact on the environment [2]. Some studies have shown that banana peel was mainly composed of pectin, cellulose, hemicellulose, lignin and other substances containing a large amount of active groups such as hydroxyl and carboxyl [3], in which these active groups could be combined with contaminants in water by chelating, coordinating, complexing, hydrogen bonding and other effects. So, resource utilization of banana peel has gradually become a research hotspot in the field of water and wastewater treatment.

Coagulant including inorganic, organic and microorganic is very important during water and wastewater treating process [7,8]. Natural polymer coagulant is one of organic type. Generally, the preparation method of natural polymer coagulant includes graft copolymerization, oxidation and reduction, etherification reaction and so on [9,10], which have received much more

attention in many countries from the beginning of the 1970s, but it started relatively late in China. Compared with inorganic coagulant [7,8], natural polymer coagulant, as an ecological safe coagulant [3], has advantages (rich source, low price, easy degradability, non-toxicity, and no secondary pollution) and disadvantages (easily attacked by microorganisms, and unstable during storage process).

Presently, the research on the application of banana peel in the field of water and wastewater treatment mainly included adsorption and direct utilization. The studies on the former have been conducted for many years abroad [11,12]. There are also some studies in China [13]. But, the preparation of natural polymer coagulant using banana peel as raw materials was rarely studied.

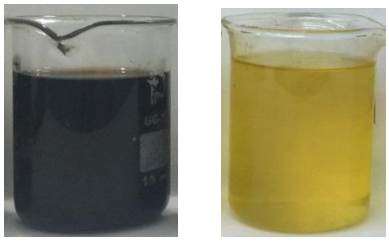
In this work, BP and OBP coagulants were prepared using banana peel as the main raw material. And the influence of storage time on the surface morphology and bond structure of OBP and BP were studied by SEM and FTIR, respectively. Last, the impact of storage time on coagulation performance of OBP and BP in treating a simulated humic acid (HA) water sample was probed using Jar tests, and the coagulation mechanism of OBP was also simply analyzed. The purpose of this work is to provide some basic data for further upgrade preparation of this kind of coagulants and practical application in treating water samples.

2. Material and Methods

2.1. Preparation of BP and OBP coagulants

2.1.1. Preparation of BP

Firstly, some banana peel powder was passed through a sifter (100 meshes) to obtain a sifting substance. 2.5 kg sifting substance was added to 100 L tap water at room temperature under medium stirring for 1–2 min, and was followed by 10 min of standing to obtain an original mixture. Secondly, 1 L NaOH (5 mol/L, industrial grade) was added to the original mixture under rapid stirring at room temperature for 1 min, and was followed by 4 h of standing to obtain a leaching solution. Last, the leaching solution was filtrated with qualitative filter paper to obtain a filtrate which was used as BP coagulant (storage time of 0 d) with pH of 10.95 and density of 1.012 g/mL (Fig.1a), respectively.



(a) BP (b) OBP

Fig.1 Pictures of (a) BP and (b) OBP

2.1.2. Preparation of OBP

0.8 L NaClO (industrial grade) was added to the BP coagulant (prepared in *2.1.1*) at room temperature under medium stirring for 3–5 min, and then was followed by 1 h of standing to obtain OBP coagulant (storage time of 0 d) with pH of 9.46 and density of 1.01 g/mL (Fig.1b), respectively.

BP and OBP were sealed and allowed to store at room temperature, and then was taken out after different storage time for the following tests.

2.2. Influence of storage time on micro-characteristics of BP and OBP

2.2.1. Surface morphology

Liquid BP and OBP samples were withdrawn at storge time of 0, 3 and 11 d (BP at 11 d has been significantly attacked by microorganisms), and 0, 3, 11 and 30 d, respectively, and then were dried at 60 ℃ in oven for more than 12 h to make powder BP and OBP products for SEM analysis with S-2500 Scanning Electron Microscope (Hitachi S-2500, Japan): 5000 times magnification, 5 nm resolution and 10 kV accelerating voltage, respectively.

2.2.2. Structure characteristics

The structure characteristics of solid BP and OBP (prepared in *2.2.1)* were analyzed by KBr pressed disc with VERTEX 70 Fourier Infrared Spectromter (Bruker, German) under 10 MPa.

2.3. Influence of storage time on coagulation performance of BP and OBP

2.3.1. Tested water

HA simulated water was used as the tested water.

Preparation of a HA stock solution: 1 g HA was dissolved in 0.01 mol/L NaOH solution under stirring 2 h and was followed by a filtration through 0.45 μm filters (FuZhou LanLo Filtration Equipment CO., Ltd, China) to obtain a HA stock solution with concentration 1 g/L, which was stored below 4 ℃ before using.

Preparation of a Kaolin stock solution: 15 g Kaolin was added to 1000 mL deionized water under stirring 2 h and was allowed to stand for 3 h, and then the supernatant was withdrawn and used as stock solution and was stirred 5 min again just before using.

Preparation of HA simulated water. 200 mL kaolin stock solution and 400 mL HA stock solution were added to 20 L tap water under medium stirring. After stirring 15 min, a HA simulated water was obtained with the following qualities: turbidity of 37.8–46.7 NTU, color of 0.333–0.421 A, COD_{Cr} of 8.05–8.22 mg/L, pH of 8.25–8.52, and temperature of 15.5–20.5 ℃.

2.3.2. Jar tests

Liquid BP and OBP withdrawn at storage time of 0, 1, 3, 6, 11, 17 and 30 d were used as coagulants for the following Jar tests.

Jar tests were conducted on a Jar test apparatus (ZR4-6 flocculator, China). Dose was 1.5 mg (coagulant)/L (tested water), in which the doe of 1.5 mg/L was slightly lower according to lots of the previous Jar tests. A rapid mix at 200 r/min was performed 1 min after coagulant addition, and was followed by a 10-min and 5-min slow mixing at 60 r/min and 40 r/min, respectively. Then the flocs was allowed to precipitate for 15 min, and the supernatant samples were then withdrawn from a position of 2–3 cm below the surface for the anlysis of turbidity and color by HACH 2100 Turbidity Meter (USA, HACH). Three runs were consucted in this test, the results represented the averages, and the error bars for all the data points represented the standard error of the mean of the three experiments

3. Results and Discussion

3.1. Influence of storage time on micro-characteristics of BP and OBP

3.1.1. Surface morphology

Fig.2 displays the influence of storage time on the surface morphology of BP and OBP under 5000 magnification times. And Table 1 and Table 2 displays the number and distribution (with different size) of bacterial plaques within the area of 10×10 μm marked with the dotted line in Fig.2.

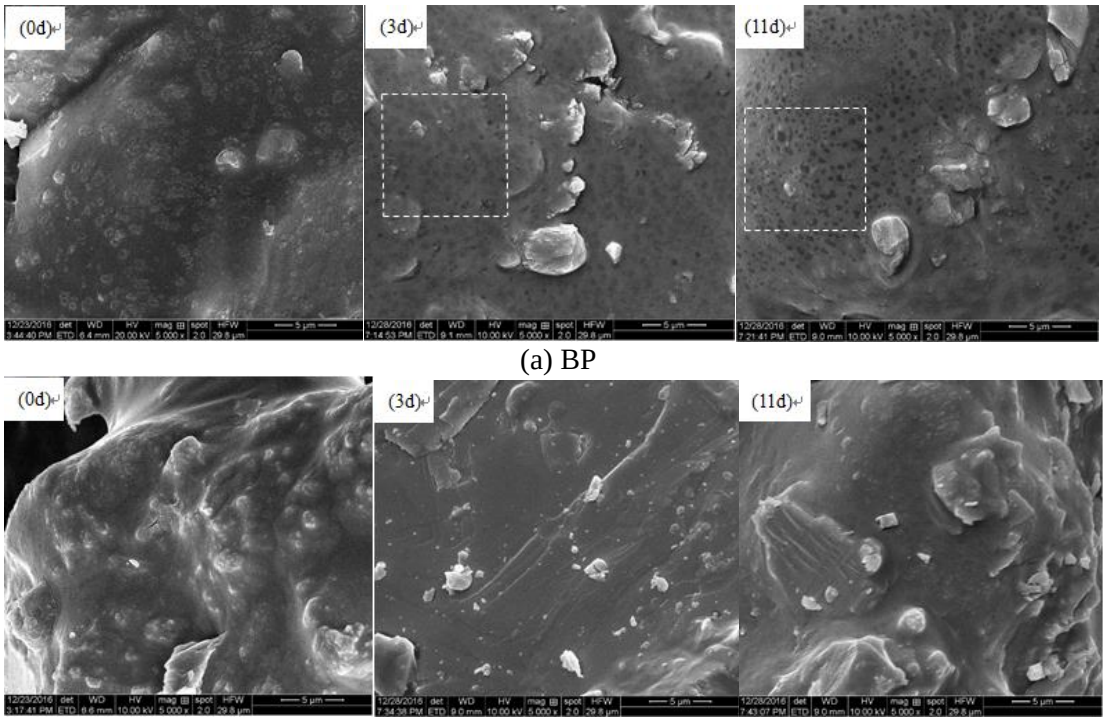
Table 1 The number of bacterial plaques within the area of 10×10 μm in BP and OBP

Coagulant	BP			OBP			
Storage time (d)	0	3	11	0	3	11	30
Total number of plaques	0	>50	>100	0	0	0	0

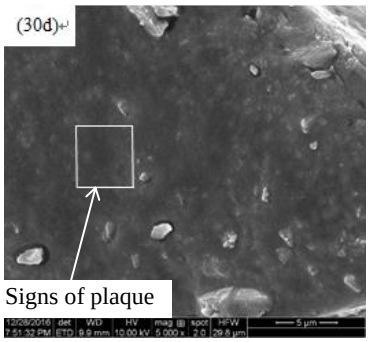
Table 2 Distribution of bacterial plaques with different size within the area of 10×10 μm in BP and OBP

Coagulant		BP			OBP			
Storage time (d)		0	3	11	0	3	11	30
The number of plaques with different size	>0.5 μm	0	7	28	0	0	0	0
	>1 μm	0	0	3	0	0	0	0
	>1.5 μm	0	0	0	0	0	0	0

As shown from Fig.2a, for BP, there were no bacterial plaques on the surface of BP at 0 d, after that, the plaques gradually appeared. More than 50 plaques appeared at 3 d, in which about 21 plaques showed obvious plaque characteristics (referring to the characteristics of more dark) with 7 plaques having size greater than 0.5 μm, and 29 plaques showed a little shallow color. When storage time reached 11 d, the number and size of the plaques obviously increased and more than 100 plaques showed obvious plaque characteristics, in which the plaques larger than 0.5 μm reached 28. This indicated that many homologous microorganisms generated and further reproduced to be some larger colonies having different types of microorganisms, because the edge, color, and shape of the microorganisms were different.



(a) BP



(b) OBP

Fig.2 Surface morphology of (a) BP for storing 0, 3, and 11 d and of (b) OBP for storing 0, 3, 11 and 30 d under 5000 magnification times

For OBP (Fig.2b), there was no obvious plaque formed within 11 d, but there were some obscured signs of plaque formation at 30 d, indicating that the oxidative stabilizer has a great inhibition for microbial activities.

3.1.2. Structure characteristics

Fig.3 displays the influence of storage time on IR spectra of BP and OBP, respectively.

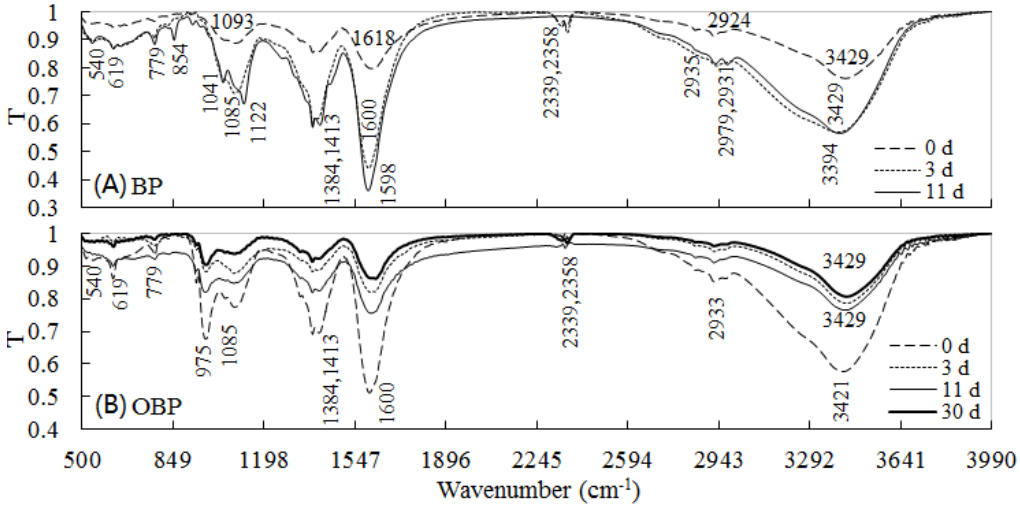


Fig.3 Structure by IR of (a) BP for storing 0, 3, and 11 d and of (b) OBP for storing 0, 3, 11 and 30 d

The comparsion of BP at 0 d (Fig.3a) with OBP at 0 d (Fig.3b) was analyzed firsly.

Compared with BP (Fig.3a), the intensities of different peaks in OBP basically increased, suggesting that the conjugation effect and intensity of the hydrogen bond was strengthened or the amount of hydrogen bond increased. For instance, 3394–3429 cm^{-1} was a broader absorption peak and can be mainly attributed to the stretching vibration of -OH and -NH_2 [14], representing the hydrophilic characteristics [14,15] coming from cellulose. The intensity of the peak of OBP at 3394–3429 cm^{-1} increased largely, suggesting that the association of -OH in cellulose was enhanced, also indicating that the hydrophilicity of OBP may be enhanced. The intensity of the peak of OBP at 1600 cm^{-1} also greatly increased, suggesting that the antisymmetry of C-O-O in carboxylic acids or the hydrogen bond effect in benzene ring skeleton may be enhanced. 2924–2979 cm^{-1} can be assigned to the stretching vibration of saturated C-H in cellulose and hemicellulose [16]. But compared with BP at 2924 cm^{-1}, red shift occurred in OBP (to 2933 cm^{-1}), which may be caused by induction effect, that is, the electronegativity of the atoms attached to C-H in OBP may be greater than that in BP, leading to the enhancing of induction

effect and weakening of double bond in OBP. All of these above changes showed chemical reactions occured between the oxidative stabilizer and BP at the molecular level.

In addition, for BP (Fig.3a) and OBP (Fig.3b) at 0 d, 2339 and 2358 cm^{-1} can be attributed to the anti-symmetric absorption peak of CO_2, maybe mixed with the tested sample during analyzing processes. The strong peaks at 1598–1618 cm^{-1} can be mainly attributed to the stretching vibration of carbonyl and benzene ring skeleton, or variable angle vibration of N-H [17,18], suggesting that there was some carboxylic acids or benzene ring substances. 1384 and 1413 cm^{-1} can be attributed to the symmetric bending vibration of methyl and methylene, scissoring vibration of methyl in both proteins and cellulose, and the symmetric stretching vibration of COO- [19,20]. 975–1122 cm^{-1} can be attributed to the stretching vibration of C-O-C in pyranose ring skeleton [21,22], R-OH in alcohol, C-O or C-N in anhydride, or unsaturated bond of C in polysaccharide and cellulose [23], also indicating there was some more purified cellulose in BP and OBP. 779–854 cm^{-1} can be attributed to the bending vibration of C-H, O-H and C-O [15,24] in glycosides and β-Glycosidic linkages between anhydroglucose units, which were typical fingerprint absorption of cellulose and carbohydrate [25], in which 779 cm^{-1} can be attributed to the vibrations of C-H on the aromatic ring of lignin [26].

The impact of storage time on IR spectra of BP and OBP was analyzed in the following part.

For BP (Fig.3a), the following changes occurred with the increasing of storage time.

(a) The intensities of different peaks in BP basically increased, suggesting the intensity of the hydrogen bond increased and the molecular symmetry may be weakened due to the complex influence of microorganisms on the components and structures of BP. For instance, the intensity of 1598–1618 cm^{-1} increased, probably because the bending deformation occured in adsorbed water in saccharides or complex change of C=O in hemicellulose occured due to the activities of microorganisms [27].

(b) Blue shift or red shift of the peaks at different positions occurred due to some effects: induction effect (blue shift by the electron-withdrawing groups), conjugation effect (red shift), tension effect, hydrogen bonding effect (red shift), especially the effect of complex process caused by the life activities of microorganisms.

(c) Splitting phenomenon of some peaks at 2924–2979 cm^{-1}, 1384–1413 cm^{-1}, and 1041–1122 cm^{-1} appeared, probably due to the changes in the spatial positions of methyl, methylene or other groups connected with carbon chains.

(d) Some new peaks appeared at 540–779 cm^{-1}, suggesting some typical cellulose and saccharides containing aromatics maybe became more purified with the increasing of storage time.

(e) The intensity of each peak within storage time of 3 d changed greatly, but, the rate of changes declined with the further increasing of storage time, suggesting that there may be a great change in the structure or composition of BP at certain time within 3-11 d, which was almost consistent with the results in SEM pictures (Fig.2a). This maybe also caused a sharp drop or a larger inflection point in the coagulation performance of BP after a certain storage time point within 3–11 d, which will be proved in the following Fig.4.

For OBP (Fig.3b), with the increasing of storage time, the intensities of all the peaks were almost weakened, suggesting that the intensity of the hydrogen bond was strengthened, or the symmetry of molecules may be enhanced. Furthermore, there was almost no blue-shift or red-shift and no peak splitting phenomenon or no appearance of new peaks, suggesting that OBP maybe gave a little better stability to some extent, which was consistent with SEM pictures in Fig.1 and will be further proved in the coagulation performance (Fig.4) in the following parts.

The above analysis suggested that the main constituent of banana peel coagulants mainly contains carbohydrates, cellulose, lignin, protein, fatty acids, etc.

3.2 Influence of storage time on coagulation performance of BP and OBP

Fig.4 displays the removal of turbidity and color by BP and OBP in treating a simulated HA test water with dose of 1.5 mg/L and storage time of 0, 1, 3, 6, 11, 17 and 30 d, respectively.

As shown in Fig.4, the turbidity and color removal by BP and OBP decreased with the increasing of storage time, however, after 6 d, BP gave sharp reduction and the coagulation performance by OBP only declined slowly. The coagulation performance of BP and OBP at 0 d was almost the same, with turbidity and color removal of more than 85% and 77%, respectively. After that, the removal of turbidity and color by BP decreased to 52% and 44% at 11 d, and 46% and 39% at 30 d, while OBP still maintained more than 78% and 68% at 11 d, and 64.4% and 60% at 30 d, respectively.

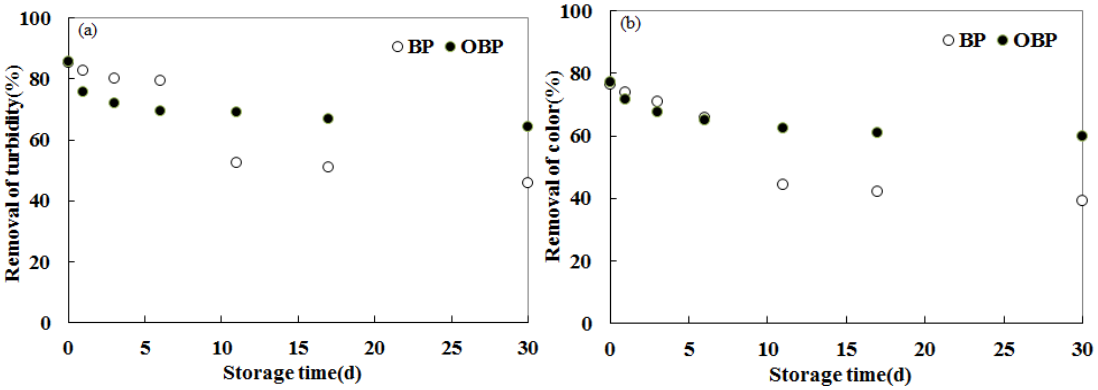


Fig.4 Influence of storage time on removal of (a) turbidity and (b) color by BP (○) and OBP (●) in treating a simulated HA water sample

According to coagulation performance (Fig.4) and structure characteristics (Fig.2: with the increasing of storage time of BP: the weakening of molecular symmetry in the components and more purification of both cellulose and carbohydrate containing aromatic substances; while with the increasing of storage time of OBP: the enhancing of molecular symmetry and weakening of hydrogen bond effect, and the alleviating of double bond properties due to significant induction effect) of the coagulants above-mentioned, the following conclusions can be obtained: better symmetry of molecules and weakened hydrogen bonding effect are good for the stability and coagulation effect, the alleviating of double bond characteristic and weakening of conjugate effect had indefinite influence on coagulation effect, and the purification of both cellulose and carbohydrate containing aromatic substances are not good for the improvement of coagulation performance.

In addition, for BP, excessive corruption of the structure and components of natural organic polymers by microorganisms greatly reduced the effective coagulation function of natural organic polymers of BP. For OBP, due to the inhibitory effect of oxidative stabilizers on plaques, the coagulation action of natural organic polymers always played a major role, but its coagulation effect slowly decreased due to slow corrosion of microorganisms on its organic compounds.

4. Conclusion

The generation of bacterial plaques on the surface of banana peel coagulants was different at different storage time. The number and size of the plaques in BP quickly increased with the

increasing of storage time. While there were only some obscured signs of plaque formation in OBP at 30 d. The main constituent of banana peel coagulants includes carbohydrates, cellulose, lignin, protein, fatty acids, etc.

The turbidity and color removal by BP and OBP decreased with the increasing of storage time, but BP gave sharp declination after 6 d and OBP gave lower declination during storage process. The removal of turbidity and color by BP decreased to 46% and 39% at 30 d, while OBP still maintained more than 64.4% and 60% at 30 d, respectively.

Better symmetry of molecules and weakened hydrogen bonding effect are good for the improvement of coagulation behavior, the alleviating of double bond characteristic and weakening of conjugate effect gave indefinite influence on coagulation effect, and the purification of both cellulose and carbohydrate containing aromatic substances are not good for improving coagulation performance.

Acknowledgements

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