**Reuse of concentrated cellulose wastewater: microwave-assisted synthesis of
organic fertilizer with water-retaining property**

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Abstract

In this study, concentrated cellulose wastewater was re-utilized to synthesis water-retaining organic fertilizer by microwave-assisted polymerization which expanded the field of reapplication of cellulose wastewater. The content of the monomer, the microwave reaction power, the diatomite and the cross-linker were considered to investigate the influence of organic fertilizer absorbency on distilled water and sea water. The results showed that the water absorbency of the synthesized organic fertilizer was 117.67 and 82.32 g/g in distilled water and sea water, respectively. In addition, the contents of organic matter, nitrogen, phosphorus, potassium and heavy metals (Cr(III), Cd(II) and Hg(II)) in the obtained fertilizer samples were detected and the results revealed that all the contents complied with the standard for organic fertilizer in China.

Keywords: Cellulose wastewater; Waste reusing; Microwave-assisted polymerization;

Organic fertilizer

1. Introduction

Bioethanol fuels can be obtained in industrial scales by fermentation of pretreated cellulose containing crops, such as rice straw, wheat straw, corn straw and bagasse which are common agricultural products worldwide [1-3]. During the fermentation process, large amount of cellulose industry wastewater produces with high level of chemical oxygen demand (COD), biochemical oxygen demand (BOD) and lower pH discharge into environment [4]. The organic wastewater without purification or intelligent recycle will pollute the quality of the water environment.

Several techniques have been supposed to deal with the cellulose wastewater, such as precipitation, coagulation, adsorption, biological methods, chemical oxidization and membrane filtration etc [5, 6]. It is reported that the advantages of the biological treatment are capital investment and operating costs [7]. Chemical oxidization is considered as another efficient method to degrade organics in wastewater. However, most of these technologies have limited development due to the drawback of the appearance of solid waste after cellulose wastewater treatment [8, 9]. The traditional disposal of solid waste by burning releases a large amount of pollutants and greenhouse gases mainly carbon dioxide into the atmosphere which would cause environmental pollution and global warming.

Cellulose wastewater mainly contains cellulose fibers, soluble lignin and suspended solid concentrations [10]. Considerable attention has been directed toward the recovery of materials and decreasing costs [11, 12]. Singh [13] group has reported the using of treated effluent water in ethanol production from cellulose. However, it has not been found any reports on the resource reutilization of cellulose containing wastewater. Thus, our work was focused on the reuse of the concentrated cellulose wastewater rather than incineration or landfill. The carbon in the waste from the wastewater could be converted into products but not carbon dioxide during this research.

Microwave irradiation technology has been explored in chemical synthesis because it can increase reaction rate by offering rapid and efficient heating. The unique aspect of microwaves is internal heating and the microwave energy interacts

with the starting materials directly. Compared with conventional heating, microwave can reduce reaction time from hours to minutes even to seconds [14, 15]. Hence, microwave-assisted method has received considerable attention as a promising method for synthesis. There are few reports on the preparation of organic fertilizer by microwave. For example, organic-inorganic fertilizers with controlled release were synthesized by using microwave irradiation and the organic fertilizers can also be obtained from aromatic plants processed by microwave-assisted hydrodistillation [16, 17].

The main purpose of this study is to microwave-assisted synthesis a kind of water-retaining organic fertilizer by reusing the concentrated cellulose wastewater. Then we investigate the factors that affect the water absorbency, such as the concentration of monomer, the diatomite amount, the cross-linker concentration and the irradiation power. Finally, we analyze the contents of composition in the synthesized organic fertilizer according to standard for organic fertilizer in China (NY 525-2012).

2. Experiment

2.1 Materials and equipment

Cellulose wastewater (COD: 55000 mg/L, solid content: 4.5 mg/L) was supplied by Lv Yuan Company. The diatomite was obtained from Qingdao, Shandong province, China. Xanthan gum (XG) and acrylic acid (AA) were provided by Tianjin Guangfu Institute of Fine Chemicals, China. N,N-methylenebisacrylamide (MBA) and potassium peroxodisulfate were obtained from Sinopharm Chemical Reagent Co.,

China. All chemicals were analytical reagent grade and were used as received without further purification.

The microcomputer microwave chemical reactor (WBFY-205) used in this study was purchased from Shanghai Yue-Zhong instrument equipment Co., Ltd. The microcomputer microwave chemical reactor is equipped with a magnetic stirring system and the reactor is an open reaction system (Fig. S1).

2.2 Pretreatment of the cellulose wastewater

The concentrated cellulose wastewater (CC) was obtained through reduced pressure distillation at 70°C and 0.08 MPa vacuum degrees.

2.3 Microwave-assisted synthesis of water-retaining fertilizer

The water-retaining fertilizer was synthesized as follows: XG (0.6 g), CC (0.3 g) and diatomite (0.5 g) were dispersed in 20 mL KOH in a one-necked flask with strongly magnetic stirring at minimum power for 1 min in the microcomputer microwave chemical reactor. Then 5 g AA (neutralization degree of 70%), 0.2512 g $K_2S_2O_8$ and 0.1880 g MBA were added in the flask. The mixture was irradiated in the microwave oven at 300 W for 30 sec. The resulting gel product was dried at 50°C and sifted through a 50-mesh sieve.

2.4 Organic fertilizer characterization and analysis

Fourier transform infrared spectroscopy (FTIR) spectra of the fertilizer were obtained using Bruker TENSOR 27 FTIR and the spectra were recorded in 400-4000 cm^{-1} range. The morphologies of the organic fertilizer were observed by scanning electron microscopy (SEM, JEOL JSM-5600LV). The contents of organic matter,

nitrogen, phosphorus, potassium and heavy metals (Cr(III), Cd(II) and Hg(II)) of the synthesized organic fertilizer were analyzed based on the standard for organic fertilizer in China (NY 525-2012).

2.5 Water absorbency analysis

Half a gram of the sample was immersed into distilled water and sea water at room temperature for 2 h, respectively. Then the swollen sample was separated from the unabsorbed solution by 100-mesh gauze. The water absorbency Q_{eq} (g/g) was calculated by the following equation:

$$Q_{eq} = (M_2 - M_1) / M_1 \quad (1)$$

where M_1 is the weight of the swollen sample and M_2 is the weight of the dry sample (g), Q_{eq} is the equilibrium water absorbency.

3. Results and Discussion

3.1 Effect of AA concentration

In order to investigate the effect of monomer concentration on water absorbency, the water absorbency of the samples with variable content of AA was evaluated in distilled water and sea water. As shown in Fig. 1, the water absorbency of the fertilizer was firstly increased as AA contents increasing, and then decreased with further increase of AA in distilled water and sea water. The maximum water absorbency was 73.01 g/g in distilled water and 62.83 g/g in sea water when AA concentration was 13%. The initial increase of AA contributing to the water absorbency is due to the diffusion of AA molecules into the polysaccharide backbones and higher AA content could enhance the hydrophilic ability. The decrease of water absorbency with the

further increase in AA concentration may be due to the amount of AA which is more helpful to homopolymerization than graft copolymerization. In addition, excess AA may increase the viscosity of the reaction medium which hinders the movement of the macroradicals and AA molecules [18].

3.2 Effect of the microwave irradiation power

Microcomputer microwave chemical reactor was initially employed to improve the reuse efficiency of cellulose wastewater concentration. A number of microwave irradiation reactions with different power were carried out and the results were shown in Fig. 2. It was found that 250 W is the optimal microwave reaction power. The initiator decomposition rate was accelerated when the power increased from 150 W to 250 W. It was proved that higher power would provide more energy and opportunity for the reaction. However, the water absorbency decreased remarkably when the microwave irradiation power exceeded 250 W. The explanation was the excess irradiation would cause more homopolymerization and water molecules would not enter into the organic fertilizer freely. These similar observations have been reported by Ge et al [19].

3.3 Effect of diatomite concentration

The effect of the diatomite concentration (0-3.7 wt%) on water absorbency of the fertilizer was shown in Fig. 3. The results showed that the maximum Q_{eq} reached 95.50 and 50.05 g/g in distilled water and sea water, respectively. The diatomite content could improve the water absorbency in distilled water and sea water when the diatomite concentration increased from 0 to 2.0 wt%, while the absorbency decreased

when the diatomite content was higher than the optimum value. This phenomenon could be explained by the fact that diatomite interfered with polymerization by increasing the viscosity of the reaction medium [20], which could weaken the strong hydrogen-bonding and polymeric chains physical intertwining [21].

3.4 Effect of the cross-linker concentration

The effect of different concentrations of MBA was investigated and the result was shown in Fig. 4. The water absorbency of the organic fertilizer increased with the increase of cross-linker content when the content of MBA was lower than 0.075% in distilled water and in sea water. The maximum Q_{eq} reaches 117.67 and 82.32 g/g in distilled water and sea water, respectively. The result was in conformity with Flory's network theory [22]. Increasing the cross-linker below the optimum value (0.075%) could enhance the nodes of network and cross-linker density, which was contributed to the absorbing of water. However, when the content of MBA exceeded 0.075%, the elasticity of polymer chains of the organic fertilizer decreased. Similar results have been reported by Chen and Zhang [20, 23].

3.5 Characterization and analysis

According to the FTIR characterization of the CC, diatomite and organic fertilizer, the characteristic adsorption peak of CC at 1113 cm^{-1} is ascribed to the stretching vibrations of C-OH and the peak at 1644 cm^{-1} is due to the bending vibrations of -OH. However, these adsorption peaks of CC almost disappeared and the new peaks at 1543 , 1454 and 1413 cm^{-1} appeared in the spectra of organic fertilizer. These new peaks are attributed to asymmetric stretching and symmetric stretching of

-COO- groups. It was indicated that potassium acrylate has been grafted onto CC framework. Moreover, the strong absorption peak at 1099 cm^{-1} ascribed to $=\text{Si-O}$ stretching vibration of diatomite became weak and the Si-O-Si bending vibration at 468 cm^{-1} appeared in the organic fertilizer FTIR spectrum.

Figure 5(a) and (b) revealed that the morphology image of the organic fertilizer containing 0 wt% and 2 wt% diatomite, respectively. Obviously, it could be seen that the organic fertilizer containing 0 wt% diatomite showed a smooth surface without any pores. While the organic fertilizer containing 2 wt% diatomite showed a coarse and porous surface. It was indicated that the diatomite particles could disperse in the organic fertilizer.

In order to evaluate the organic fertilizer, three samples were synthesized through the optimum formula (AA: 13%, MBA: 0.75%, diatomite: 2%, Power: 250 W) and different indexes were detected, such as the organic matter and total nutrient. The results showed that these organic fertilizers might be suitable for farmland use in the coastal area. In addition, the contents of heavy metals (Cr(III), Cd(II) and Hg(II)) were lower than the standard. Table 1 shows that some concentrations determined based on the NY 525-2012 standard, and the results conformed with the certified values.

4. Conclusion

The organic fertilizer with water-retaining property was successfully prepared from concentrated cellulose wastewater via microwave. This novel method of reusing cellulose wastewater concentration could be regarded as a good illustration for waste

cellulose reutilization. The water absorbency of the fertilizer in distilled water and sea water was studied under different contents of monomer, cross-linker, diatomite and reaction power. The maximum water absorbency of the organic fertilizer was 117.67 and 82.32 g/g in distilled water and sea water, respectively. In addition, the content of organic matter, nutrient and heavy metals were also analyzed and the results conformed with the certified values.

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Figure Captions

Fig. 1 Effect of acrylic acid concentration on distilled/sea water absorbency of the fertilizer.

Fig. 2 Effect of the power on distilled/sea water absorbency of the fertilizer.

Fig. 3 Effect of diatomite concentration on distilled/sea water absorbency of the fertilizer.

Fig. 4 Effect of MBA concentration on distilled/sea water absorbency of the fertilizer.

Fig. 5 SEM images of (a) organic fertilizer without diatomite and (b) organic fertilizer with diatomite (2 wt%).

Figures

Fig. 1 Effect of acrylic acid concentration on distilled/sea water absorbency of the fertilizer.

Fig. 2 Effect of the power on distilled/sea water absorbency of the fertilizer.

Fig. 3 Effect of diatomite concentration on distilled/sea water absorbency of the fertilizer.

Fig. 4 Effect of MBA concentration on distilled/sea water absorbency of the fertilizer.

Fig. 5 SEM images of (a) organic fertilizer without diatomite and (b) organic fertilizer with diatomite (2 wt%).

Table

Table 1 Some indexes about the obtained organic fertilizer.

Sample	Q _d	Q _s	OM	N	P	K	TN	Cr(III)	Cd(II)	Hg(II)
	(g/g)	(g/g)	(%)	(%)	(%)	(%)	(%)	(mg/kg)	(mg/kg)	(mg/kg)
1	106.23	83.27	83.4	0.56	0.42	3.92	4.90	3.92	-	0.73
2	115.57	88.56	87.6	0.58	0.45	4.14	5.17	3.66	-	0.69
3	110.39	84.14	85.9	0.55	0.44	4.23	5.22	3.85	-	0.67

Q_d: the water absorbency in distilled water; Q_s: the water absorbency in sea water;

OM: the organic matter; TN: the total nutrient

Graph abstract

cellulose wastewater

concentrated wastewater

organic fertilizer

effluent water

diatomite

MBA

AA

cellulose unit