

## Adsorption of Zn(II) by Corncob Microwave Pretreated and Modified with Succinic Anhydride

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A new adsorbent was prepared by modifying microwave pretreated corncob with succinic anhydride. The microwave pretreated corncob and un-pretreated corncob were both modified with succinic anhydride to get the products **C 1** and **C 2** from original corncob (**C 0**). Mass per cent gains (MPG) of both products were tested. The adsorptions of **C 1**, **C 2** and **C 0** with  $Zn^{2+}$  were studied. SEM, XPS and FTIR were utilized to investigate the structure and morphology of **C 1**. The results showed that **C 1** had a fold phase covered with carboxyl groups which resulted in a high adsorption of metal ion. In the range of experiments, mass per cent gains of **C 1** achieved 41.4 % in optimal microwave conditions, which exhibited an increase of 12.9 % from **C 2** (28.5 %). After being treated with  $Zn^{2+}$  at room temperature, **C 1** could reach a saturated adsorption capacity of 2.028 mmol/g, increased 1.747, 0.457 mmol/g in relation to **C 0** (0.281 mmol/g) and **C 1** (1.773 mmol/g), respectively. Its adsorption followed isotherm of Langmuir. The results indicated that the adsorption properties of **C 1** were improved obviously. It can be used as a potential metal ion adsorbent.

**Key Words:** Corncob, Succinic anhydride, Microwave, Adsorption.

### INTRODUCTION

There are abundant corncobs with good stability and mechanical strength in China. Some researchers immersed corncob in different acid or alkaline solution for activation to adsorb different metal waste which could produce porous structure and improve adsorption properties<sup>1-3</sup>. The products have low adsorption while these methods are simple pre-processes of corncob. Further studies were reported by chemical modification of biomaterials. Bagasse reacted with succinic anhydride acts as a metal adsorbent<sup>4</sup>. Cellulose was treated with concentrated alkaline solution and reacted with cyclic anhydride to prepare a metal adsorbent<sup>5</sup>. However, these methods existed defect of long pretreatment time, complex operation and low removal rate.

Microwave pretreatment takes only short time but can increase the porosity of matrix material and contact area of reaction efficiently<sup>6</sup>. Microwave pretreated **C 0** was reacted with succinic anhydride to prepare an efficient adsorbent in this study. The adsorptions of **C 1**, **C 2** and **C 0** treated with  $Zn^{2+}$  were studied.

## EXPERIMENTAL

Corncob was purchased from Yunnan market of China. Succinic anhydride, pyridine,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and sodium bicarbonate were purchased from Shanghai Chemical Reagent Company, China.

**Preparation of C 0, C 1 and C 2:** Corncob was smashed and sifted through 100 mesh sifter, washed with distilled water and dried to obtain C 0. 1 g C 0 was treated with 800 W microwave irradiation for 6 min, then transferred to a 100 mL round flask. 1.5 g succinic anhydride was added to react with C 0 under 20 mL of pyridine reflux for 1 h. Product was filtered in sintered filter after cooling down, washed with distilled water and ethanol alternately, dried at 60 °C in an oven. After drying it was stirred constantly in a saturated sodium bicarbonate solution for 0.5 h, filtered by using sintered filter, washed with distilled water and ethanol alternately. Finally, it was dried to obtain C 1. C 2 was prepared as C 1 not treated with microwave. Synthesis route of C 1 was shown in Fig 1.

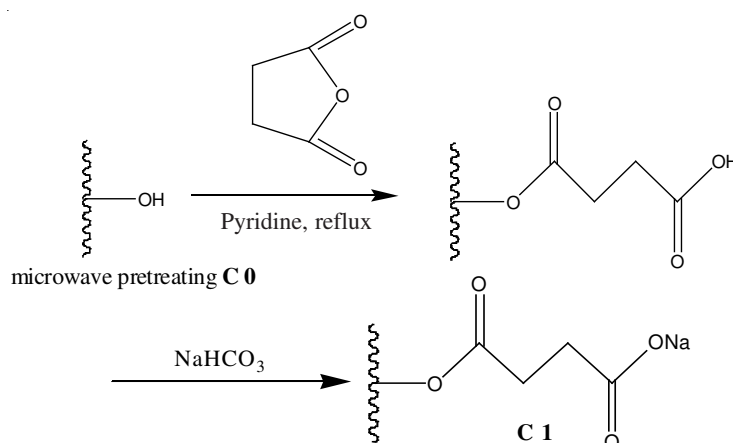


Fig. 1. Synthesis route used to obtain C 1

**Adsorption:** C 1, C 2 and C 0 were utilized to remove  $\text{Zn}^{2+}$  in the water. Experiment with each sample and  $\text{Zn}^{2+}$  were performed to determine the adsorption equilibrium time. The interval times used were from 5 to 60 min, 5 to 70 min and 10 to 130 min for C 1, C 2 and C 0, respectively. An amount of 0.04 g from C 1 and C 2, 0.3 g from C 0 were placed in a 100 mL conical flask with 25 mL of 1 g/L  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  under constant oscillating. After filtered, the filtrate was analyzed with the atomic absorption spectrometer (Duracell, AA-6501). For describing the adsorption isotherm of C 1, C 2 and C 0. C 1 was added in a 100 mL conical flask with 25 mL of 5 different concentrations (700, 800, 900 and 1000 mg/L) of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  at different temperatures (25, 35 and 45 °C). C 2 and C 0 were both treated in accordance with C 1 at 25 °C. After oscillating for the adsorption equilibrium time, the product was filtered and the filtrate was determined.

**Characterization:** Scanning electron microscopy (XL30SEM), X-ray photoelectron spectroscopy (PHI5600) and FT-IR (4000-400  $\text{cm}^{-1}$ , WQF-200) were used to characterize the properties of **C 1**.

## RESULTS AND DISCUSSION

**Effect of microwave on mass per cent gains (MPG):** Power and pretreatment time of microwave are the most important factors for the modification of corncob. Mass per cent gains of **C 1** and **C 2** were listed in Table-1. On one hand, MPG of **C 1** was always higher than **C 2**. It was due to the damage of crystalline region inside corncob by microwave radiation, which was favourable for the spread of succinic anhydride to have a reaction with function groups of corncob<sup>7</sup>. Thus MPG of **C 1** increased obviously. On the other hand, MPG of **C 1** increased with the increasing of microwave power and pretreatment time. And it can achieve 41.4 % after being treated with 800 W of microwave for 6 min. At that power, expanding time again could not increase MPG of **C 1**. Finally, the power of 800 W and pretreatment time of 6 min were chosen. Synthesis of **C 1** was at optimal condition and the mass per cent gain (MPG) was calculated according to:

$$\text{MPG (100 \%)} = \frac{m_1 - m_0}{m_0} \times 100 \quad (1)$$

where  $m_1$  is the mass (g) of the modified corncob and  $m_0$  is the mass (g) of the unmodified corncob.

TABLE-1  
MASS PER CENT GRAINS (MPG) OF **C 2** AND **C 1** AT DIFFERENT  
MICROWAVE POWER AND PRETREATMENT TIME

| Materials  | Microwave powder (W) | Time (min) | MPG (%) |
|------------|----------------------|------------|---------|
| <b>C 1</b> | 600                  | 10         | 30.3    |
|            | 600                  | 20         | 40.1    |
|            | 600                  | 30         | 40.6    |
|            | 700                  | 8          | 33.2    |
|            | 700                  | 12         | 40.7    |
|            | 700                  | 16         | 41.2    |
|            | 800                  | 3          | 34.7    |
|            | 800                  | 6          | 41.4    |
|            | 800                  | 9          | 41.7    |
| <b>C 2</b> | –                    | –          | 28.5    |

**Characterization:** SEM micrographs of corncob substances were displayed in Fig. 2. The image of **C 0** (Fig. 2a) showed that its surface structure was close and ordered while the surface structure of **C 1** (Fig. 2b) was loose and disorder. The **C 1** appeared with porous and uneven, which was beneficial to adsorb  $\text{Zn}^{2+}$ .

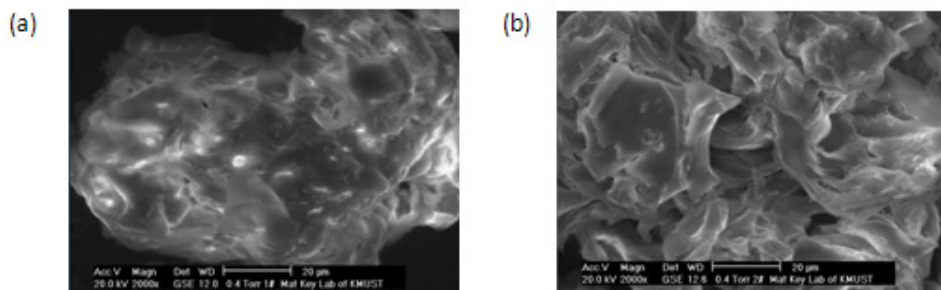


Fig. 2. SEM images (20 kV) of **C 0** (a) and **C 1** (b)

FTIR spectra of **C 0** and **C 1** showed in Fig. 3. Compared to **C 0** (Fig. 3a), **C 1** (Fig. 3b) had a weak peak at  $1745\text{ cm}^{-1}$  which was corresponding to carbonyl stretching vibration of **C 1**. There was the overlapping of ester carbonyl absorption peak at  $1750\text{ cm}^{-1}$  and carboxylic acid carbonyl absorption peak<sup>8</sup> at  $1712\text{ cm}^{-1}$ . These difference proved that corncob was esterificated by succinic anhydride and carboxyl was introduced to corncob successfully.

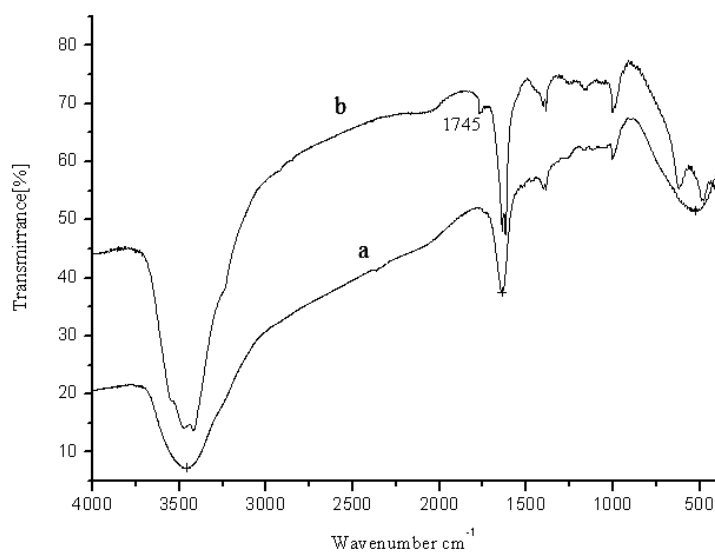


Fig. 3. FTIR spectra of **C 0** (a) and **C 1** (b)

XPS C 1s spectra of **C 0** and **C 1** showed in Fig. 4. There was no signal at 289 eV in C 1s spectrum of **C 0** (Fig. 4a), but there was an obvious signal with **C 1** (Fig. 4b) at 289 eV, which was attributed to carboxyl or ester carbon<sup>9</sup>. Comparative contents of four forms of C in **C 0** and **C 1** were listed in Table-2. C/O of samples dropped from 3.35 to 3.26 with modified corncob. This was due to introduction of succinic anhydride, which made increasing of oxygen content. It confirmed that succinic anhydride had been coupled to corncob.

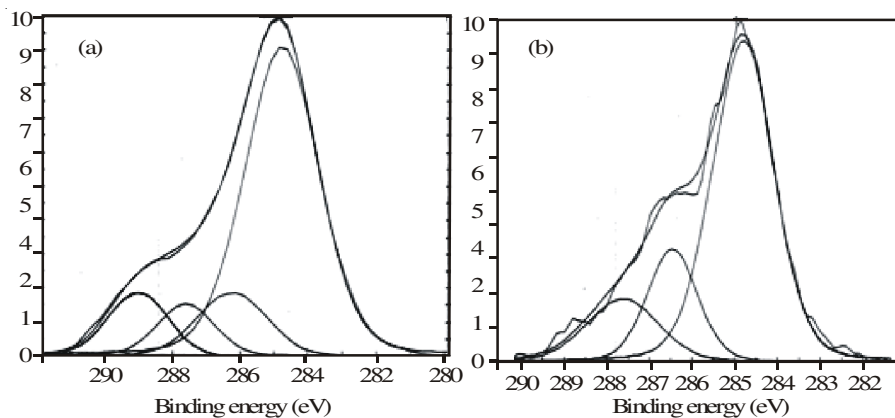


Fig. 4. XPS C 1s spectra of C 0 (a) and C 1 (b)

TABLE-2  
COMPARATIVE CONTENTS OF FOUR FORMS OF CORNCOB IN C 0 AND C 1

|     | Peak                    | C-C    | C-O    | C=O    | COO-   | C/O  |
|-----|-------------------------|--------|--------|--------|--------|------|
| C 0 | EB/eV                   | 284.82 | 286.47 | 287.63 | -      |      |
|     | Area (%)                | 1840   | 524    | 421    | -      | 3.35 |
|     | Comparative content (%) | 65.7   | 19.02  | 15.28  | -      |      |
| C 1 | EB/eV                   | 284.8  | 286.24 | 287.61 | 289.04 |      |
|     | Area (%)                | 12124  | 2165   | 1508   | 1816   | 3.26 |
|     | Comparative content (%) | 68.84  | 12.29  | 8.56   | 10.31  |      |

**Adsorption:** The adsorption kinetic of  $Zn^{2+}$  by C 1, C 2 and C 0 were studied. The results showed in Fig. 5. The adsorption rate of C 1, C 2 and C 0 increased with the contact time extending. The equilibrium time of C 1, C 2 and C 0 was 40, 50 and 110 min, respectively. Adsorption rate ( $\eta$  %) was calculated according to the following formula:

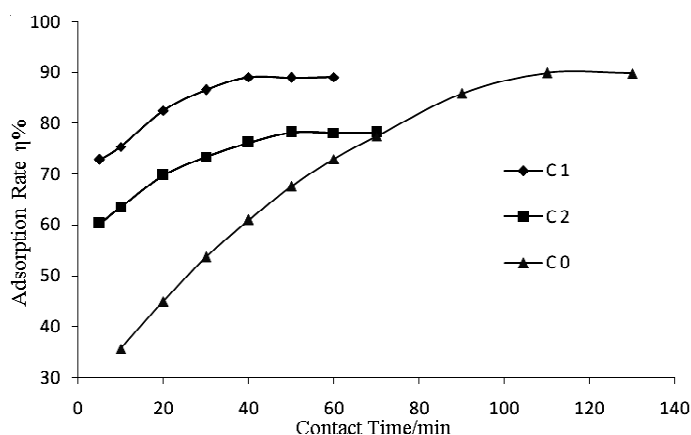


Fig. 5. Effect of the contact time on adsorption rate

$$\eta(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C$  are the concentration (mmol/L) of  $Zn^{2+}$  pre and post adsorption, respectively. Adsorption isotherm of **C 1**, **C 2** and **C 0** was determined on the basis of the equilibrium time. Langmuir isotherm showed better agreement with the real adsorption processes for **C 1**, **C 2** and **C 0**. And it is expressed as:

$$\frac{1}{Q_e} = \frac{1}{(bQ_{\max}C_e)} + \frac{1}{Q_{\max}} \quad (3)$$

where  $C_e$  (mmol/L) is the equilibrium concentration of solutions,  $Q_e$  (mmol/g) and  $Q_{\max}$  (mmol/g) are the equilibrium loading capacity and the saturated adsorption capacity, respectively.  $b$  (L/mmol) is Langmuir constant. Adsorption isotherms of **C 1**, **C 2** and **C 0** were shown in Table-3. The results indicated that adsorption properties of modified corncob (**C 1** and **C 2**) were better than **C 0**. And the saturated adsorption capacity of **C 1** was larger than **C 2**, which indicated that microwave pretreatment can be considered as an effective method for improving the modification of corncob. Higher temperature was in favour of adsorption of **C 1** and the saturated adsorption capacity increased with temperature increasing. **C 1** achieved the saturated adsorption capacity of 2.053 mmol/g at 45 °C. It can be utilized as a high-performance adsorbent for metal ions.

TABLE-3  
ADSORPTION ISOTHERMS OF **C 1**, **C 2** AND **C 0**

| Material   | Temp. (°C) | Fitting curves of the Langmuir isotherm         | R <sup>2</sup> | Q <sub>max</sub> (mmol/g) |
|------------|------------|---|----------------|---------------------------|
| <b>C 1</b> | 25         | 1/Q <sub>e</sub> = 0.009/C <sub>e</sub> + 0.493 | 0.998          | 2.028                     |
|            | 35         | 1/Q <sub>e</sub> = 0.007/C <sub>e</sub> + 0.491 | 0.995          | 2.037                     |
|            | 45         | 1/Q <sub>e</sub> = 0.006/C <sub>e</sub> + 0.487 | 0.996          | 2.053                     |
| <b>C 2</b> | 25         | 1/Q <sub>e</sub> = 0.010/C <sub>e</sub> + 0.564 | 0.999          | 1.773                     |
| <b>C 0</b> | 25         | 1/Q <sub>e</sub> = 0.855/C <sub>e</sub> + 3.561 | 0.998          | 0.281                     |

## Conclusion

After esterification modified corncob, containing carboxy group, could be a new adsorbent of metal ions. Mass per cent gains (MPG) of **C 1** and **C 2** from **C 0** were 41.4 and 28.5 %, respectively. And the adsorption properties were both enhanced compared with **C 0**. **C 1** made a best adsorption. It exhibited an increase in  $Q_{\max}$  for 1.747 and 0.475 mmol/g in relation to **C 0** and **C 2** at 25 °C, respectively. That suggested microwave pretreatment was an efficient method of pretreatment. Adsorption behaviour of **C 1** was in accordance with adsorption isotherm of Langmuir. And higher temperature was in favour for adsorption. It can be utilized as an efficient adsorbent for metal ions.

### REFERENCES

1. Q.L. Zhang, W.P. Zhang, G.Y. Dang and X.Q. Tang, *Pollut. Control Technol.*, **21**, 21 (2008).
2. W.H. Wang, Y.M. Feng, X.L. Chang and Y. Sun, *Technol. Water Treatment*, **30**, 95 (2004).
3. B.Q. Zhen, *Technol. Develop. Chem. Ind.*, **35**, 22 (2006).
4. C.F. Liu, R.C. Sun, J. Ye and J.L. Ren, *Chem. Ind. Forest Prod.*, **26**, 105 (2006).
5. L.V.A. Gurgel, O. Karnitz Jr. and R.P.D. Freitas Gil, *Bioresour. Technol.*, **99**, 3077 (2008).
6. P.S. Guo, H.L. Liu, J.X. Ning and X.J. Tang, *Can. Internat. Educ. J.*, **60**, 394 (2009).
7. J. Gao and L.G. Tang, Bei Jing: Science Press, edn. 1, pp. 66-67 (1999).
8. R. Jayakumar, J. Bala and S. Nanjundan, *Eur. Polym. J.*, **36**, 1659 (2000).
9. G.M. Dorris and D.G. Gray, *Cellul. Chem. Technol.*, **12**, 721 (1978).

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