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# A Study of Adsorption of Modified Corn Stalk on PCP

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**Abstract** The comprehensive utilization of corn stalks is an urgent agricultural and environmental problem to be solved in China. In this test, we use corn stalk as adsorbent for adsorption of PCP in water, and compare the impact of three modification methods (alkali treatment, pyrolysis, graft copolymerization) on corn stalk adsorption properties. Results show that the modified corn stalk's adsorption of PCP is increased from 5.4 mg/g to 13.9 mg/g, 17.8 mg/g and 22.5 mg/g, respectively; the corn stalk after graft copolymerization and modification has the greatest adsorption capacity; after modification, both the adsorption capacity and adsorption rate constant of corn stalk on PCP are increased significantly.

**Key words** Corn stalk, PCP, Adsorption, Modification

## 1 Introduction

PCP (Pentachlorophenol) is often widely used as herbicides and pesticides, but it is toxic and carcinogenic<sup>[1]</sup>. PCP enters the water through a variety of ways, causing a serious threat to the ecological environment and human health. The adsorption method is an effective method to rapidly remove PCP from the water. Corn stalks have a huge annual yield, but most of them are not effectively used, causing environmental pollution and waste of resources, so it is necessary to explore resource-oriented utilization of corn stalks<sup>[2]</sup>. The corn stalks are porous and often used as adsorbent, but the adsorption capacity is small<sup>[3]</sup>. Therefore, this paper compares the impact of three modification methods (alkali treatment, pyrolysis, graft copolymerization) on corn stalk's adsorption of PCP in order to achieve resource-based utilization of waste.

## 2 Materials and methods

**2.1 Modification treatment** The corn stalk is taken from the suburbs of Binzhou, and after being dried, pulverized and sifted, it is used for modifying treatment. (i) Corn stalk alkali modification. The corn stalk is mixed with 1 mol/L NaOH solution, stirred with a magnetic stirrer for 24 h and dried after leaching and washing. (ii) Corn stalk pyrolysis modification. A certain number of corn stalks are weighed and placed in a crucible and pyrolyzed in a muffle furnace at 450 °C for 4 h (sparged with nitrogen to maintain a reducing atmosphere), and dried after natural cooling. (iii) Corn stalk graft copolymerization. A certain number of corn stalks are weighed and placed in 250 mL round bottom flask with

three necks, and heated at 100 °C for 60 min after adding 10 mL of epichlorohydrin and 20 mL of dimethylformamide; then 10 mL of diethylenetriamine is added to react at 100 °C for 60 min; finally 30 mL of triethylamine is added to react at 100 °C for 120 min, and it is washed and dried.

**2.2 Adsorption test** 0.1 g of unmodified corn stalk powder or 0.1 g of corn stalk powder under three modification treatments (alkali treatment, pyrolysis, graft copolymerization) is put in 250 mL Erlenmeyer flask, respectively, and 100 mL of 25 mg/L PCP solution is added for adsorption test in air bath constant temperature shaker at 25 °C and 100 rpm. The sampling is conducted at regular time intervals, and the supernatant is centrifuged in a high speed centrifuge. After adding color-developing agent, the spectrophotometry is used to determine the concentration of PCP. Corn stalk adsorption amount  $q_e$  (mg/g) is calculated as follows<sup>[4]</sup>:

$$q_e = (c_e - c_0) \times V/m \quad (1)$$

where  $c_e$  and  $c_0$  are the PCP concentration (mg/L) after adsorption equilibrium and before adsorption, respectively;  $V$  is the solution volume (L);  $m$  is the mass of corn stalk (g).

**2.3 Adsorption kinetics analysis** The pseudo kinetic equation is used for fitting of adsorption data and studying the adsorption kinetic characteristics of corn stalk under different modification treatments on PCP<sup>[5]</sup>. Pseudo-first-order kinetics equation is as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where  $t$  is time (min);  $q_e$  is the equilibrium adsorption amount (mg/g);  $q_t$  is the adsorption amount at time  $t$  (mg/g);  $k_1$  is the pseudo-first-order adsorption rate constant ( $\text{min}^{-1}$ ).

## 3 Results and discussions

**3.1 The adsorption properties of unmodified corn stalks on PCP** The unmodified corn stalks are taken for PCP adsorption test and compared with the modified corn stalks. The adsorption test results of unmodified corn stalk on PCP are shown in Table 1. In 0–60 min, the adsorption amount of unmodified corn stalk on PCP increases rapidly with time and then tends to stabilize, and

Received: June 15, 2017 Accepted: August 15, 2017

Supported by Shandong Higher Education Institution Science and Technology Plan Project (J16LD03); Natural Science Foundation of Shandong Province (ZR2014EEP009); Doctoral Scientific Research Foundation of Binzhou University (2014Y17); Shandong Key Research and Development Plan (2015GNC111018, 2016GSF117021).

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reaches adsorption equilibrium after 120 min. The adsorption amount of unmodified corn stalk on PCP is 5.4 mg/g, and the PCP removal rate is 21.6%.

**3.2 The adsorption properties of modified corn stalks on PCP** The corn stalks after alkali treatment, pyrolysis, graft copolymerization are selected for PCP adsorption test, and the test results are shown in Table 2. After the modification, the adsorption of corn stalk on PCP also first increases rapid and then tends to stabilize. After reaching the adsorption equilibrium, the adsorption amount of the corn stalk under alkali treatment on PCP is

13.9 mg/g, and the PCP removal rate is 55.7%; the adsorption amount of the corn stalk under pyrolysis on PCP is 17.8 mg/g, and the PCP removal rate is 71.2%; the adsorption amount of the corn stalk under graft copolymerization on PCP is 22.5 mg/g, and the PCP removal rate is 89.8%. Experimental results show that after modification, the adsorption capacity of corn stalk on PCP is significantly improved, and in the three modification methods, the corn stalk under graft copolymerization has the maximum adsorption of PCP and the modification effect is good.

**Table 1** The adsorption properties of unmodified corn stalk on PCP

Time//min	PCP concentration//mg/L	PCP removal rate//%	Adsorption amount//mg/g
0	25.0	0.0	0.0
30	21.4	14.4	3.6
60	20.0	20.0	5.0
120	19.8	20.8	5.2
180	19.6	21.6	5.4

**Table 2** The adsorption properties of modified corn stalk on PCP

Methods	Alkali treatment			Pyrolysis			Graft copolymerization		
	Concentration mg/L	Adsorption amount// mg/g	Removal rate %	Concentration mg/L	Adsorption amount// mg/g	Removal rate %	Concentration mg/L	Adsorption amount // mg/g	Removal rate %
0	25.0	0.0	0.0	25.0	0.0	0.0	25.0	0.0	0.0
30	18.7	6.3	25.1	10.7	14.3	57.1	7.4	17.6	70.5
60	11.9	13.1	52.4	8.4	16.6	66.3	5.0	20.0	80.0
120	11.7	13.3	53.3	7.9	17.0	68.0	3.1	21.9	87.6
180	11.1	13.9	55.7	7.2	17.8	71.2	2.6	22.5	89.8

**3.3 The kinetics characteristics of adsorption of corn stalks on PCP** The pseudo-first-order kinetics equation is used for data fitting of adsorption of corn stalk on PCP under different modification conditions, and calculation of equilibrium adsorption capacity and adsorption rate constant (Table 3). From Table 3, it is found that the correlation coefficient  $R^2$  of experimental data and model is high, indicating that the pseudo-first-order kinetics equation is suitable for describing the kinetics process of adsorption of corn

stalk on PCP. Under three modification treatments (alkali treatment, pyrolysis, graft copolymerization) and non-modification of corn stalk, the change trend of equilibrium adsorption theoretical value ( $q_e$ ) calculated by the equation is close to that of experimental value, and the adsorption rate constant ( $k_1$ ) also gradually increases, which indicates that both the adsorption amount and adsorption rate of modified corn stalk on PCP increase<sup>[6]</sup>. It is consistent with the actual adsorption test results of corn stalk on PCP.

**Table 3** Kinetics equation fitting parameters of adsorption of corn stalk on PCP

Parameters	Modification methods			
	Non-modification	Alkali treatment	Pyrolysis	Graft copolymerization
$q_e$ (mg/g)	5.6000	14.7000	18.5000	24.2000
$k_1$ (min <sup>-1</sup> )	0.0209	0.0276	0.0291	0.0312
$R^2$	0.9262	0.9294	0.9483	0.9720

## 4 Conclusions

In this paper, we study the impact of modification on the PCP adsorption of corn stalk. When the corn stalk is unmodified, the PCP adsorption amount is 5.4 mg/g but the PCP removal rate is only 21.6%. After alkali treatment, pyrolysis and graft copolymerization on corn stalk, the equilibrium adsorption amount of PCP is increased to 13.9 mg/g, 17.8 mg/g and 22.5 mg/g, respectively, while the PCP removal rate is increased to 55.7%, 71.2% and 89.8%, respectively. The PCP adsorption amount and adsorption rate constant of modified corn stalk are significantly higher than those of unmodified

corn stalk, and the modification effect is in the order of graft copolymerization > pyrolysis > alkali treatment.

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(From page 46)

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