

# Ammonium Sorption onto Polymeric Adsorbing Material from Corn Stalks Oxidized and Loaded with Magnesium

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Corn stalks were modified by magnesium loading and an oxidation process and then characterized by a series of methods. The ammonium in wastewater showed high sorption efficiency onto the polymeric adsorbing material during the process, with a biochars dosage of 20 g/L for 8h.  $Mg^{2+}$  was the dominant cation exchanger on the modified corn stalk, and it played an important role in ammonium sorption. Large amounts of  $NH_4^+$  were exchanged onto the corn stalk, and they formed strong complexes with oxygen-containing groups on the corn stalk surface through polar bonds, resulting in the removal of  $NH_4^+$  from the solution.  $Na^+$  present in wastewater was the major influence on ammonium sorption onto the corn stalk.

*Keywords:* Ammonium sorption; Polymeric adsorbing material; Modified corn stalk

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## INTRODUCTION

Ammonium ( $NH_4^+$ ) is the inorganic ion form of N contained in domestic and industrial wastewater or decomposed from organic N compounds in those wastewaters. However, high concentrations of N in wastewater increase oxygen demand and eutrophication (Wu *et al.* 2004). Ammonium may have harmful effects on animal and human health, and it attacks the rubber components of water plumbing systems.

Some methods of  $NH_4^+$  removal are biological nitrification-denitrification, air-stripping, and ion exchange. The ion exchange method usually utilizes organic resins, but they are very expensive (Li *et al.* 2010). The use of polymeric adsorbing material as an ion exchanger has become one of the more efficient methods for removing  $NH_4^+$ .  $NH_4^+$  ions are removed from aqueous solutions by biochar *via* cation exchange or by adsorption into the pores of the aluminosilicate structures. Biochar is a carbonaceous organic matter generated by heating under oxygen-limited conditions, comparable to charcoal (Sun *et al.* 2010). Ammonium retention by biochar may be readily explained by electrostatic adsorption onto the negatively charged oxygen-containing surface functional groups (Ebiura *et al.* 2005). Freshly produced biochars typically have very low ability to adsorb ammonium (Zhang *et al.* 2011). Over time, the biochar surfaces are oxidized, and cation retention increases to greater levels (Cantrell *et al.* 2005; Xie *et al.* 2006). Oxidation may also be achieved intentionally as part of an effort to improve nutrient retention by biochars. Wastewater may contain various cations (calcium, magnesium, sodium, and potassium), anions (chloride, phosphate, and sulfate), and organic acids (oxalic, citric, and malic), which may affect  $NH_4^+$  sorption by the adsorbing material. In the present study, polymeric adsorbing material was produced from corn stalks and characterized by a series of methods to determine  $NH_4^+$  removal from wastewater. The influence of various parameters in the process on ammonium sorption was also studied. This study provides the necessary

theoretical basis for the application of modified corn stalks for ammonium sorption from wastewater.

## EXPERIMENTAL

### Materials

Samples of corn stalks were collected from agricultural fields in Tianjin in northern China. After drying at 60 °C in an oven for 16 h, the samples were ground into particles and passed through a 0.7-mm screen. The powdered biomass was tightly placed in a ceramic pot and then pyrolyzed in a muffle furnace under a N<sub>2</sub> atmosphere. The pyrolysis was programmed to drive the internal biomass chamber temperature to 500 °C at a rate of 5 °C/min and then to hold at the peak temperature for 2 h before cooling to room temperature. This produced the polymeric adsorbing material denoted as B<sub>0</sub>. MgO powder and the powdered biomass were mixed in deionized water and wet ball-milled to decrease the particle size. The mass ratio of MgO powder and the powdered biomass was set at 1:10 (Liu *et al.* 2013). The mixture was heated for 5 h at 105 °C to remove water and pyrolyzed in a muffle furnace under the same conditions. This produced the polymeric adsorbing material denoted as B<sub>1</sub>. The polymeric adsorbing material B<sub>1</sub> was then oxidized using 30% H<sub>2</sub>O<sub>2</sub> at 30 °C for 6 h, using a solid-to-liquid ratio of 1:10 (w/v), and was denoted as B<sub>2</sub>.

### Characterization

Elemental (C, H, and N) analyses were conducted using a CHN Elemental Analyzer (Vario El cube, Germany). The oxygen content was determined by a mass balance. The O/C atomic ratio was calculated to evaluate the aromaticity and polarity of the polymeric adsorbing materials. Surface element analysis was conducted using energy dispersive X-ray spectroscopy (EDS 1791-N-016-000, HYDAC, Germany). Fourier transform infrared (FTIR) analysis (Tensor 27, Bruker, Germany) was performed in the 400 cm<sup>-1</sup> and 4000 cm<sup>-1</sup> region with 50 scans being taken at 2 cm<sup>-1</sup> resolution to identify the surface functional groups. The specific surface area and porosity properties of the polymeric adsorbing materials were measured by N<sub>2</sub> adsorption isotherms with the Brunauer-Emmett-Teller (BET) method using a surface area analyzer (Tristar 3000, Micromeritics, USA).

### Adsorption Experiments

Batch adsorption experiments were conducted in centrifuge tubes at room temperature. All adsorption experiments were performed in triplicate. For these experiments, 0.1 g to 2.0 g of the dried adsorbing material were added into 200-mL centrifuge tubes containing 100 mL of solution with 50 mg of ammonium-nitrogen (NH<sub>4</sub>-N) per liter. As a comparison, the dried adsorbing material was added into 200-mL centrifuge tubes containing 100 mL of wastewater with 50 mg of NH<sub>4</sub>-N, 9.3 mg of Ca<sup>2+</sup>, 2.3 mg of Mg<sup>2+</sup>, 13.3 mg of Na<sup>+</sup>, and 1.3 mg of K<sup>+</sup> per liter. The tubes were shaken at 400 rpm in a mechanical shaker for 1 to 11 h. The supernatant was carefully aspirated using a Pasteur pipette. The initial NH<sub>4</sub>-N concentration (C<sub>0</sub>) and residual NH<sub>4</sub>-N concentration (C<sub>e</sub>) in the supernatant were determined using an inductively-coupled plasma spectrometer (ICP) (VISTA-MPX, Varian, USA), which was also used for concentration determination of the other cations. Ammonium sorption efficiency ( $\eta$ ) onto the adsorbing material, was obtained according to Eq. 1,

$$\eta = (C_o - C_e) / C_o \quad (1)$$

where  $C_o$  and  $C_e$  (mg/L) are the initial and residual aqueous sorbate ( $\text{NH}_4^+$ ) concentrations, respectively.

## RESULTS AND DISCUSSION

### Characteristics of the Polymeric Adsorbing Materials

The basic physicochemical properties of the polymeric adsorbing materials derived from corn stalks are presented in Table 1. The C and O contents of the different materials were in the range of 55.32% to 63.21% and 19.15% to 29.35%, respectively. The molar O/C ratio of  $B_2$  was higher than in the other materials, suggesting that more oxygen-containing functional groups were preserved, and that the surface remained hydrophilic. Polarity and hydrophilic properties are beneficial to the sorption of polar water-soluble contaminants, such as  $\text{NH}_4^+$  (Liu *et al.* 2013). The surface area (SA) of the materials ranged from 10.38  $\text{m}^2/\text{g}$  to 11.22  $\text{m}^2/\text{g}$ , but the pore diameter (PD) of most of the samples was around 2 nm. Total pore volume (TPV) of the materials ranged from 0.036  $\text{cm}^3/\text{g}$  to 0.052  $\text{cm}^3/\text{g}$ .  $B_o$  had a larger surface area than the other materials, indicating that abundant MgO may have been located onto the surface of  $B_1$  and  $B_2$ .

**Table 1.** Physicochemical Properties of Polymeric Adsorbing Materials Derived from Corn Stalks

Sample	Component (%)				Ratio O/C	SA ( $\text{m}^2/\text{g}$ )	TPV ( $\text{cm}^3/\text{g}$ )	PD (nm)
	C	H	N	O				
$B_o$	63.21	3.53	1.02	19.15	0.30	11.22	0.052	1.82
$B_1$	61.56	3.32	0.93	21.23	0.34	10.38	0.036	1.79
$B_2$	55.32	3.03	0.96	29.35	0.53	10.85	0.039	1.80

**Table 2.** Major Functional Groups in Polymeric Adsorbing Materials Detected by FTIR

Wavenumber ( $\text{cm}^{-1}$ )	Functional Groups	Relative Peak Values in FTIR Spectra of Materials <sup>a</sup>					
		$B_o$	$B_o\text{-N}^b$	$B_1$	$B_1\text{-N}^b$	$B_2$	$B_2\text{-N}^b$
3397	-OH	1.00	1.10	1.03	1.21	1.10	1.00
3056	Olefinic C-H	1.00	1.05	1.01	0.87	0.91	1.02
2908	-CH <sub>2</sub>	1.00	1.01	1.07	1.01	1.06	0.99
1590	Anti-Symmetric C=O	1.00	0.68	0.98	0.71	1.56	0.88
1387	Symmetric C=O	1.00	0.63	1.02	0.66	1.53	0.76
1135	C-O-C	1.00	0.57	1.10	0.67	1.31	0.69
900-750	Aromatic C-H	1.00	1.13	0.98	0.92	0.97	1.11

<sup>a</sup> Peak values in the FTIR spectra of  $B_o$  were set as the reference value 1.00.

<sup>b</sup> Biochars  $B_o$ ,  $B_1$ , and  $B_2$  used after  $\text{NH}_4^+$  sorption in wastewater were denoted as  $B_o\text{-N}$ ,  $B_1\text{-N}$ , and  $B_2\text{-N}$ , respectively.

A large number of functional groups were shown on the surfaces of the materials (Table 2), which may be beneficial for sorption. All materials had similar peaks on the FTIR spectra, which may be attributed to the uniform pyrolysis temperature used. The band at 3397  $\text{cm}^{-1}$  represents the stretching vibration of hydroxyl groups. The peaks at 3056  $\text{cm}^{-1}$  can be assigned to the C-H stretching vibrations of olefin. The bands at 2908  $\text{cm}^{-1}$  were assigned to -CH<sub>2</sub> groups. The two bands at 1590  $\text{cm}^{-1}$  and 1387  $\text{cm}^{-1}$  represent the

anti-symmetric and symmetric C=O stretching vibrations of carboxyl groups. The band at  $1135\text{ cm}^{-1}$  is assigned to C-O-C stretching vibrations in the aliphatic ethers, which represent the oxygenated functional groups of lignin. The peaks from  $900\text{ cm}^{-1}$  to  $750\text{ cm}^{-1}$  are assigned to the aromatic C-H out-of-plane bending vibrations (Fu and Mazza 2011; Liu *et al.* 2012).

### Effects of Polymeric Adsorbing Material Dosage on Ammonium Sorption

As shown in Fig. 1A, the ammonium in the solutions showed high sorption efficiency onto the polymeric adsorbing materials during the sorption process. An increase in materials dosage (from 2 g/L to 16 g/L) increased the sorption efficiency rapidly. When the dosage reached 20 g/L, the sorption efficiency maintained a steady level. Different materials can also affect the ammonium sorption, which was the main cause of different degrees of ammonium sorption in this process (Zhang *et al.* 2005). Because  $\text{Mg}^{2+}$  is the dominant cation exchanger (Wang *et al.* 2011), material B<sub>2</sub> played a more important role in ammonium sorption than the other materials in this study. This indicated that different types of materials have different characteristics, and thus may exhibit different  $\text{NH}_4^+$  cation selectivity (Tang *et al.* 2005; Pinkert *et al.* 2009). Because of the complete cation exchange, the sorption efficiency of ammonium on B<sub>2</sub> was high during the process (Wang *et al.* 2011).

### Effects of Sorption Time on Ammonium Sorption

Figure 1B shows the effects of sorption time on ammonium sorption onto the polymeric adsorbing materials. With increased sorption time, the ammonium sorption efficiency onto all 3 kinds of materials increased. When the sorption time reached 8 h, the sorption efficiency maintained a steady level. Comparing the sorption efficiency curves, the ammonium sorption efficiency onto B<sub>0</sub> and B<sub>1</sub> was lower than the sorption efficiency onto the oxidized material, B<sub>2</sub>. The role of the oxygen-containing functional groups on the materials must also be taken into consideration. The oxidized material, B<sub>2</sub>, had larger sorption capacity for  $\text{NH}_4^+$ , which corresponded to its high molar O/C ratio. According to the FTIR spectra analysis, B<sub>2</sub> had more oxygen-containing functional groups compared to the other materials. These results indicated that the oxygen-containing functional groups were involved in the sorption of ammonium. Apparently, the polarity and hydrophilic properties of the material surfaces were beneficial to ammonium sorption by forming surface complexes with carboxyl and carbonyl functional groups.

### Effects of Adsorption System on Ammonium Sorption

As shown in Fig. 1C, the ammonium sorption efficiency in wastewater was lower than the other systems with an adsorbing materials dosage of 20 g/L for 8 h. This result was due to the impact of various cations in the wastewater, which affected  $\text{NH}_4^+$  removal by the adsorbing materials (Lee *et al.* 2009; Fu and Mazza 2011). In wastewater, the concentration of major competing cations ranged from 13.18 mg/L to 133.09 mg/L (Table 3). The amounts of Na and Ca were abundant. The presence of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  cations in the solution decreased  $\text{NH}_4^+$  adsorption efficiency. Previous studies have reported that  $\text{NH}_4^+$  adsorption was mainly influenced by the presence of competing cations in the concomitant system (Zhang *et al.* 2005; Li *et al.* 2010). As shown in Fig. 1C, the ammonium sorption efficiency in the ammonium-Na solution containing an equal amount of  $\text{Na}^+$  was approximately the same as that of the wastewater system. However, the ammonium sorption efficiency in the ammonium-Ca solution containing an equal amount of  $\text{Ca}^{2+}$  was higher than that of the wastewater system. This result indicated that  $\text{Na}^+$  in

wastewater might have been the major influence on ammonium sorption onto the adsorbing materials.

**Table 3.** ICP-Detectable Major Cations in Various Solutions

Compounds	Concentration (mg/L)				
	NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>
Wastewater	500.00	93.12	22.93	133.09	13.18
Ammonium Solution	500.00	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>
Ammonium-Na Solution	500.00	— <sup>a</sup>	— <sup>a</sup>	133.09	— <sup>a</sup>
Ammonium-Ca Solution	500.00	93.12	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>

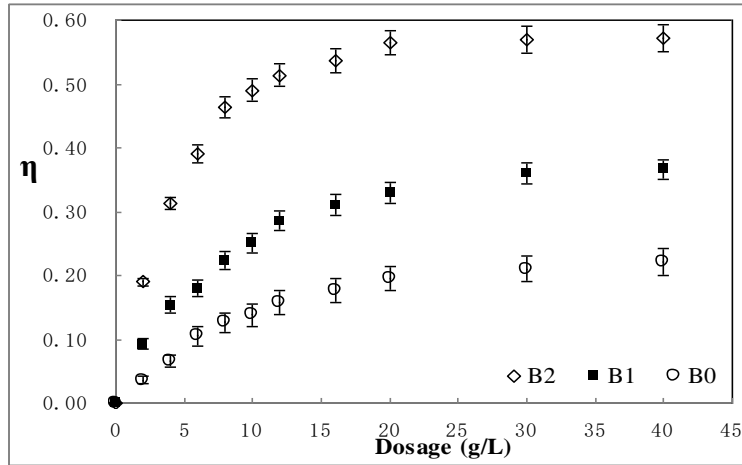
<sup>a</sup> Not detectable

Figure 1C compares the ammonium sorption efficiency onto the adsorbing materials in various adsorption systems. In these systems, the ammonium sorption efficiency onto B<sub>0</sub> was the lowest, while the sorption efficiency onto B<sub>2</sub> was highest. Because of the strong adsorbability, material B<sub>2</sub> kept a higher level of ammonium sorption efficiency than the other adsorbing materials in wastewater containing interfering ions. Cation exchange was considered to contribute to ammonium sorption onto the adsorbing materials. The amount of NH<sub>4</sub><sup>+</sup> sorbed was highly correlated with the amount of Mg<sup>2+</sup> on the biochars that was released into the equilibrium solution. Generally speaking, polymeric adsorbing materials derived from corn stalks are electronegative because they are saturated with cations (Wu *et al.* 2004; Oh *et al.* 2005). The exchange ability between cations depends on the ion valence and the radius of the hydration ion. Mg<sup>2+</sup> was the dominant cation exchanger on the modified corn stalks, and thus played a more important role in ammonium sorption.

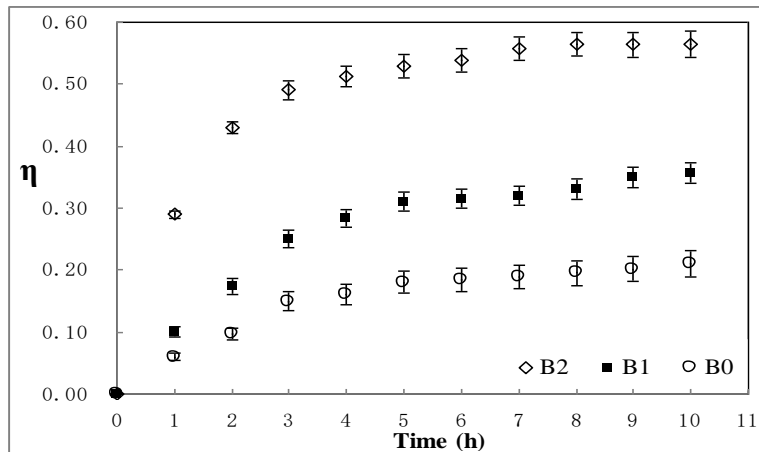
### Mechanisms of Ammonium Sorption onto Polymeric Adsorbing Materials

Cation exchange is a possible mechanism involved in NH<sub>4</sub><sup>+</sup> sorption onto polymeric adsorbing materials (Zhang *et al.* 2011). To evaluate the contribution of cation exchange to NH<sub>4</sub><sup>+</sup> sorption, the amounts of cations released from the adsorbing materials after NH<sub>4</sub><sup>+</sup> sorption were determined (Table 4). The amount of NH<sub>4</sub><sup>+</sup> sorbed had a correlation with the amount of Mg<sup>2+</sup> released from the adsorbing materials. The B<sub>2</sub> material released more Mg<sup>2+</sup>, approximately 10 times that of B<sub>0</sub>, and consistently exhibited greater sorption capacity. These results implied that Mg<sup>2+</sup> contributed to NH<sub>4</sub><sup>+</sup> sorption through cation exchange. Furthermore, the content of Na<sup>+</sup> on the surface of the materials increased. Thus, Na<sup>+</sup> in the solution was adsorbed onto the adsorbing materials, which showed strong ability for cation exchange. Compared to B<sub>2</sub>, B<sub>1</sub> had a different sorption capacity with a similar amount of Mg<sup>2+</sup> released, indicating that cation exchange was not the sole mechanism responsible for NH<sub>4</sub><sup>+</sup> sorption onto the biochars.

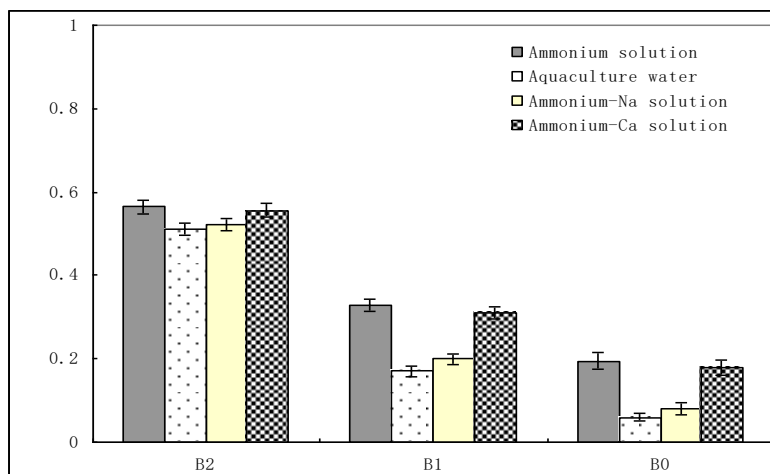
The role of functional groups was also considerable in NH<sub>4</sub><sup>+</sup> sorption onto the polymeric adsorbing materials. The modified corn stalks were rich in oxygen-containing groups, which could form strong surface complexes with the NH<sub>4</sub><sup>+</sup> (Xu *et al.* 2013). The FTIR spectra of B<sub>2</sub> before and after NH<sub>4</sub><sup>+</sup> sorption showed an obvious reduction in the peaks of carboxyl C=O and C-O-C stretching vibrations at 1590, 1387, and 1135 cm<sup>-1</sup>, as shown in Table 2, indicating that the surface complexation of NH<sub>4</sub><sup>+</sup> with oxygen-containing groups may have contributed to NH<sub>4</sub><sup>+</sup> sorption. A similar change occurred in the other adsorbing materials after the NH<sub>4</sub><sup>+</sup> sorption process, indicating that the same functional groups were involved in NH<sub>4</sub><sup>+</sup> sorption onto the adsorbing materials.



A



B



C

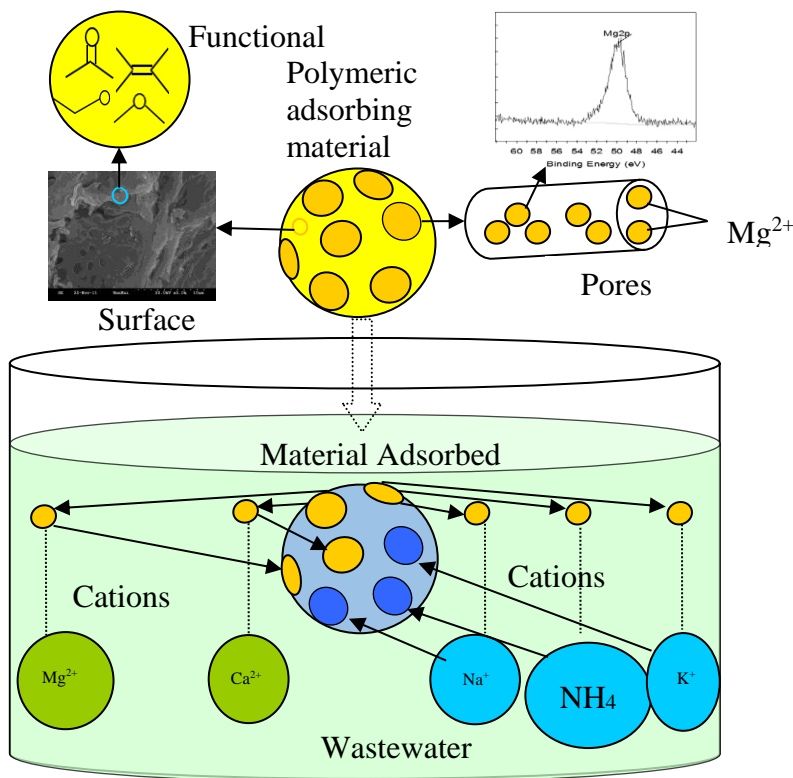
Fig. 1. Effects of polymeric adsorbing material dosage (A), sorption time (B), and adsorption system (C) on ammonium sorption efficiency ( $\eta$ )

**Table 4.** EDS-Detectable Major Cations on the Polymeric Adsorbing Materials

Samples	Concentration (mg/g)		
	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>
B <sub>0</sub>	5.62	5.21	3.11
B <sub>0</sub> -N <sup>a</sup>	3.76	3.13	6.56
B <sub>1</sub>	5.12	52.35	3.08
B <sub>1</sub> -N <sup>a</sup>	3.63	31.15	8.28
B <sub>2</sub>	5.09	51.21	3.00
B <sub>2</sub> -N <sup>a</sup>	3.70	33.32	10.76

<sup>a</sup> B<sub>0</sub>, B<sub>1</sub>, and B<sub>2</sub> used after NH<sub>4</sub><sup>+</sup> sorption in wastewater were denoted as B<sub>0</sub>-N, B<sub>1</sub>-N, and B<sub>2</sub>-N, respectively.

One possible mechanism for ammonium sorption onto modified corn stalks in wastewater is proposed in Fig. 2. Large amounts of Mg<sup>2+</sup> on the polymeric adsorbing materials were released into the wastewater, and they produced more sorption sites for cation exchange onto the materials. The cation exchange ability from wastewater onto the adsorbing materials depended on the ion valence and radius of the hydration ion, and it increased in the order of Ca<sup>2+</sup> < Mg<sup>2+</sup> < NH<sub>4</sub><sup>+</sup> < Na<sup>+</sup>. First, a small amount of the cations Na<sup>+</sup> and K<sup>+</sup> in the equilibrium solution could have been exchanged onto the adsorbing materials. Afterwards, as a major cation, large amounts of NH<sub>4</sub><sup>+</sup> were exchanged onto the adsorbing materials in the same manner, forming strong surface complexes with oxygen-containing groups through polar bonds, resulting in the removal of NH<sub>4</sub><sup>+</sup> from the solution.

**Fig. 2.** Mechanism for ammonium sorption onto polymeric adsorbing material in wastewater

## CONCLUSIONS

1. Ammonium in wastewater showed high sorption efficiency onto the modified polymeric adsorbing materials during the process, with a material dosage of 20 g/L for 8 h.
2.  $Mg^{2+}$  and  $Na^+$  was the dominant cations exchanger on the modified corn stalks, and it played an important role in ammonium sorption.
3. Large amounts of  $NH_4^+$  were exchanged onto the adsorbing materials and formed strong complexes with oxygen-containing groups on the material surface through polar bonds, resulting in the removal of  $NH_4^+$  from the solution.

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## REFERENCES CITED

- Cantrell, D. G., Gillie, L. J., Lee, A. F., and Wilson, K. (2005). "Structure-reactivity correlations in Mg Al hydrotalcite catalysts for biodiesel synthesis," *Appl. Catal. A-Gen.* 287(2),183-190. DOI:10.1016/j.apcata.2005.03.027
- Ebiura, T., Echizen, T., Ishikawa, A., Murai, K., and Baba, T. (2005). "Selective transesterification of triolein with methanol to methyl oleate and glycerol using alumina loaded with alkali metal salt as a solid-base catalyst," *Appl. Catal. A-Gen.* 283 (1-2), 111-116. DOI:10.1016/j.apcata.2004.12.041
- Fu, D. B., and Mazza, G. (2011). "Aqueous ionic liquid pretreatment of straw," *Bioresource Technol.* 102, 7008-7011. DOI:10.1016/j.biortech.2011.04.049
- Lee, S. H., Doherty, T. V., Linhardt, R. J., and Dordick, J. S. (2009). "Ionic liquid mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis," *Biotechnol. Bioeng.* 102(5),1368-1376. DOI:10.1002/bit.22179
- Li, C., Knierim, B., Manisseri, C., Arora, R., Scheller, H. V., Auer, M., and Singh, S. (2010). "Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification," *Bioresource Technol.* 101, 4900-4906. DOI:10.1016/j.biortech.2009.10.066
- Liu, D. T., Xia, K. F., Cai, W. H., Yang, R. D., Wang, L. Q., and Wang, B. (2012). "Investigations about dissolution of cellulose in the 1-allyl-3-alkylimidazolium chloride ionic liquids," *Carbohydr. Polym.* 87, 1058-1064. DOI:10.1016/j.carbpol.2011.08.026
- Liu, L., Ju, M. T., Li, W. Z., and Hou, Q. D. (2013). "Dissolution of cellulose from AFEX-pretreated *Zoysia japonica* in AMIMCl with ultrasonic vibration," *Carbohydr. Polym.* 98, 412-420. DOI: 10.1016/j.carbpol.2013.06.030



- Oh, S. Y., Yoo, D. I., Shin, Y., Kim, H. C., Kim, H. Y., and Chung, Y. S. (2005). "Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy," *Carbohydr. Res.* 340(15), 2376-2391. DOI:10.1016/j.carres.2005.08.007
- Pinkert, A., Kenneth, N., Marsh, S. P., and Mark, P. S. (2009). "Ionic liquids and their interaction with cellulose," *Chem. Rev.* 109(12), 6712-6728. DOI: 10.1021/cr9001947
- Sun, H., Ding, Y. Q., Duan, J. Z., Chen, P., Lou, H., and Zheng, X. M. (2010). "Transesterification of sunflower oil to biodiesel on ZrO<sub>2</sub> supported La<sub>2</sub>O<sub>3</sub> catalyst," *Bioresource Technol.* 101, 953-958. DOI:10.1016/j.biortech.2009.08.089
- Tang, A., Zhang, H., and Chen, G. (2005). "Influence of ultrasound treatment on accessibility and regioselective oxidation reactivity of cellulose," *Ultrason. Sonochem.* 12, 467-472. DOI:10.1016/j.ultsonch.2004.07.003
- Wang, X. J., Li, H. Q., Cao, Y., and Tang, Q. (2011). "Cellulose extraction from wood chip in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl)," *Bioresource Technol.* 102, 7959-7965. DOI:10.1016/j.biortech.2011.05.064
- Wu, J., Zhang, J., Zhang, H., He, J. S., Ren, Q., and Guo, M. L. (2004). "Homogeneous acetylation of cellulose in a new ionic liquid," *Biomacromolecules* 5(2), 266-268. DOI:10.1021/bm034398d
- Xie, W. L., Peng, H., and Chen, L. G. (2006). "Calcined Mg-Al hydrotalcites as solid base catalysts for methanolysis of soybean oil," *J. Mol. Catal. A-Chem.* 246(1-2), 24-32. DOI:10.1016/j.molcata.2005.10.008
- Zhang, H., Wu, J., Zhang, J., and He, J. S. (2005). "1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: A new and powerful nonderivatizing solvent for cellulose," *Macromolecules* 38(20), 8272-8277. DOI:10.1021/ma0505676
- Zhang, J. M., Lv, Y. X., and Luo, N. (2011). "Application research progress of ionic liquids in cellulose chemistry," *Polym. Bull.* 10, 138-153. DOI:10.14028/j.cnki.1003-3726.2011.10.007

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