REMOVING AMMONIUM FROM WATER USING MODIFIED CORNCOB-BIOCHAR

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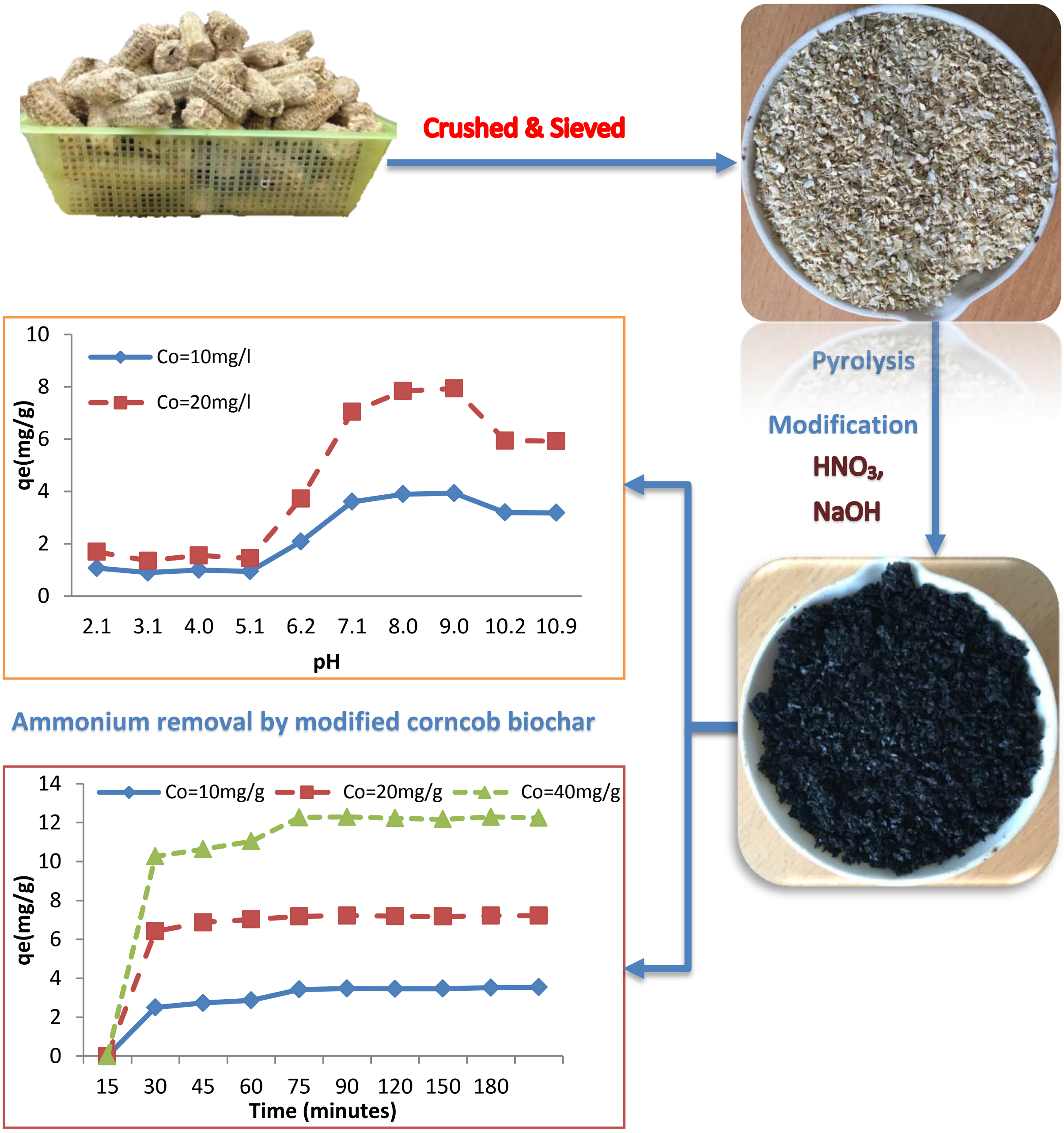
GRAPHICAL ABSTRACT



ABSTRACT

Ammonium pollution in groundwater and surface water is of major concern in many parts of the world due to the danger it poses to the environment and people's health. This study focuses on the development of a low cost adsorbent, specifically a modified biochar prepared from corncob. Evaluated here is the efficiency of this new material for removing ammonium from synthetic water (ammonium concentration from 10-100mg/L). The characteristics of the modified biochar were determined by Brunauer-Emmett-Teller (BET) test, Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). It was found that ammonium adsorption on modified biochar strongly depended on pH. Adsorption kinetics of NH_4^+-N using modified biochar followed the pseudo-second order kinetic model. Both Langmuir and Sips adsorption isotherm models could simulate well the adsorption behavior of ammonium on modificated biochar. The highest adsorption capacity of 22.6 mg NH_4^+-N/g modified biochar was obtained when the biochar was modified by soaking it in HNO_3 6M and NaOH 0.3M for 8h and 24h, respectively. The high adsorption capacity of the modified biochar suggested that it is a promising adsorbent for NH_4^+-N remediation from water.

Keywords: Adsorption, Ammonium, Biochar, Corncob

1. INTRODUCTION

Ammonium is one of the major pollutants affecting both groundwater and surface water. Although the natural level of ammonium in surface water and groundwater is low (below 3mg/L), the high ammonium concentrations are found in some areas. In Vietnam, high ammonium concentrations of 70 mg/L and more than 55mg/L were found in groundwater in Nam Du and Phu Lam villages, Hanoi (Lindenbaum, 2012 and Vietnam Environment Agency, 2016). The high level of human activities such as intensive development of livestock farms or the severe usage of nitrogen fertilizers are the causes of the high levels of ammonium in these areas (Vietnam Environment Agency, 2016; WHO, 2016). High ammonium concentrations are also found in the surface water in Vietnam. Recent reports by the Hanoi Centre for Environmental and Natural Resources Monitoring and Analysis (2016) show that the ammonium concentration in Van Chuong lake in Hanoi was 15.5mg/L, 31 times higher than surface water quality standards of Vietnam.

Current water treatment methods such as coagulation and filtration are not able to remove ammonium effectively, especially in decentralized water treatment systems. Adsorption is considered to be an economic and effective method for removing ammonium (Moradi, 2011; Yahaya et al., 2011). A number of adsorbents such as, biochar, activated carbon (AC), zeolite with and without modification have been trialed for removing ammonium via the water treatment process (Balci and Dinçel, 2002; Vassileva et al., 2008; Lin et al., 2009; Huang et al.,2010; Huo et al.,2012; Otal et al., 2013; Cui et al., 2016).

A previous study by Moreno-Castilla et al. (2000) confirmed that the surface chemistry plays a more important role than the BET surface area of adsorbents and the pore structure in adsorbing inorganic compounds from groundwater. The modification strategy is a popular method to change the surface chemistry and improve the adsorption efficiency of adsorbents. The oxidation process with H_3PO_4, HNO_3, H_2O_2 or $KMnO_4$ has been applied for modifying the AC's surface characteristics (Moreno-Castilla et al., 2000; Soto-Garrido et al., 2003; Vassileva et al., 2008; El-Wakil et al., 2014). Soto-Garrido et al., (2003) investigated the chemical modification of activated carbon made from peach stones in adsorbing ammonium. Their results indicated that modified activated carbon with HNO_3 6M was more efficient in ammonium adsorption than when applying H_2O_2 6M. More recently, El-Wakil et al. (2014) analyzed the removal of Pb^{2+} from groundwater by modified activated carbon generated from hyacinth. In their study, hyacinth was sequentially impregnated with H_3PO_4 and HNO_3 solutions (impregnation ratios of 1:3 and 1:1 w/v, respectively). Halim et al. (2013) also found that the activated carbon modified by HNO_3 (37%) and NaOH 1M had better ammonium adsorption capacity than the original activated carbon. Each gram of this material could adsorb 19.34 mg ammonium, four time higher than the original one (4.5 mg/g) when treating groundwater of 685-735mg NH_4^+/L.

Biomass recently has been used to produce AC for removing different pollutants from water due to its low cost and wide availability. Corncob waste is generally used as a food source for livestock and the excess can be burnt. In Vietnam, million tons of agricultural by-products like corn cob, rice straw, etc., are burnt every year in the field which causes air, soil and water pollution. The reuse of these low cost agricultural by-products as new adsorbents for wastewater treatment will contribute to the reduction of green-house emissions. To improve their value, corncob should be used to produce AC which can then be applied to removing pollutants such as ammonium from water. Because the adsorption capacity of AC prepared from corncob is still limited, this AC needs to be modified to improve its adsorption capacity. Thus, in this study corncob was firstly carbonized at 400^0C to produce corncob biochar (BCC). The BCC was then modified by HNO_3 and NaOH to produce a modified corncob-biochar which could very efficiently adsorb ammonium to a high degree. The objective of this paper is to: (i) determine the best conditions for preparing a modified corncob biochar; and (ii) evaluate the performance of this material in removing ammonium from water through the equilibrium and kinetics studies.

2. MATERIALS AND METHODS

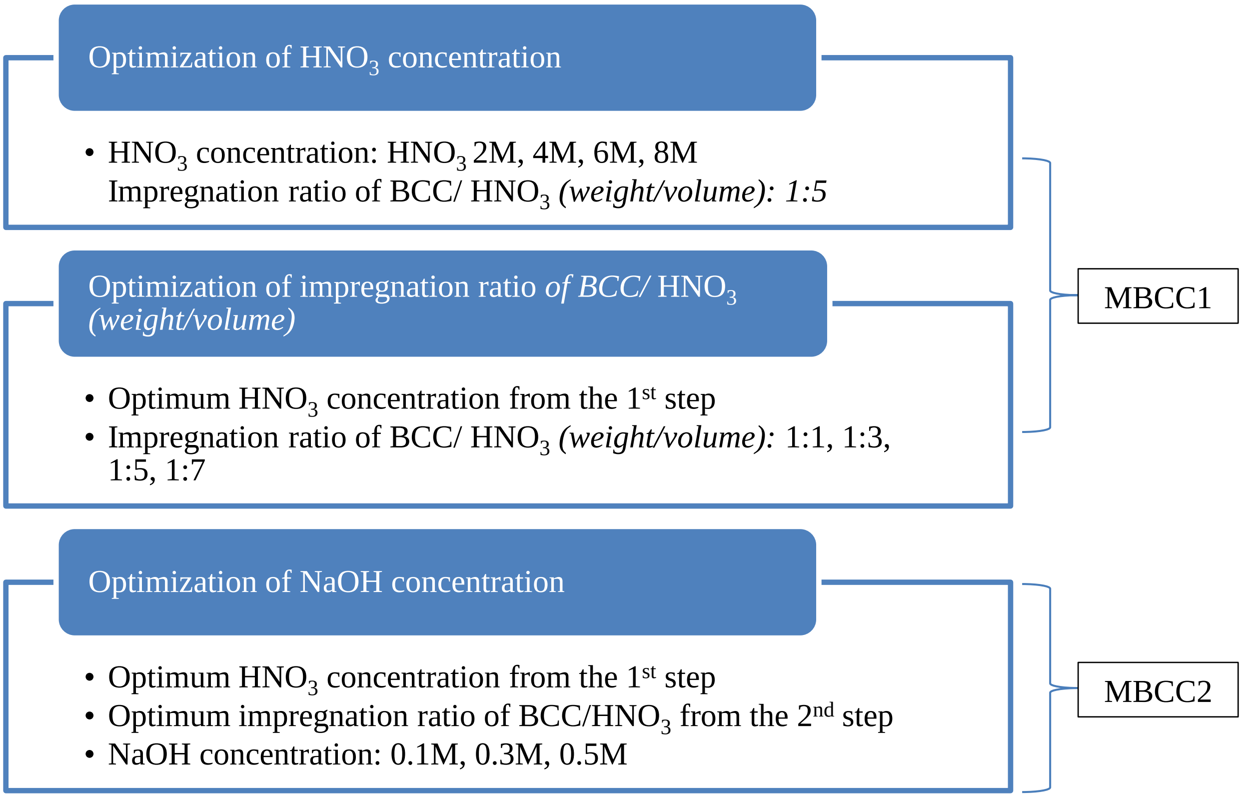
2.1. Materials

A stock solution of NH_4^+-N with a concentration of 1.0 g/L was obtained by dissolving accurately weighed 3.82 g NH_4Cl (analytical grade) in 1000 mL of deionized, distilled water in a volumetric flask. The corncob sample used in this study was collected from Da Bac district, Hoa Binh province, Vietnam. Its average moisture and ash contents were 15.71% and 8.81%, respectively.

2.2. Optimization of biochar modification

The corncob was firstly washed three times with tap water, three times with distilled water and dried in an oven at 100^0C for 2 hours. The dried corncob was then crushed and sieved to a size of 0.5-2mm. The corncob biochar BCC was prepared by heating it under slow pyrolysis at 400^0C for 1h in a furnace (Nabertherm, model L3/11/B170, Germany). BCC was then modified by soaking it in a solution of HNO_3 for 8 hours. Following that, the biochar was washed three times with distilled water. This is the first modified corncob biochar –the MBCC1. For optimizing the modified conditions for MBCC1, the HNO_3 concentration and impregnation ratio (weight/volume) of BCC/ HNO_3 were varied from 2M to 8M and 1:1 to 1:7, respectively. The MBCC1 was then soaked in NaOH solution for 24 hours, and then was washed several times with distilled water until a pH of 7-8 was reached. The dried product was referred to as the second modified corncob-biochar - MBCC2. Here the NaOH concentration was varied from 0.1M to 0.5M and the impregnation ratio (weight/volume) of MBCC1/NaOH of 1:20 was used. The impregnation ratio of 1:20 was selected following the findings of Trinh (2009). The HNO_3, NaOH concentrations and impregnation ratio of BCC/HNO_3 that led to the highest NH_4^+-N adsorption amount were chosen as the optimum scenario for preparing modified corncob biochar.

The experimental conditions for optimization are summarized in the following flowchart.



2.3. Characteristics of Modified Corncob Biochar

The MBCC1 and MBCC2 samples produced at the optimizated conditions and BCC were used for characterization. The textural characteristics of samples were determined by N_2 adsorption at 77K with an accelerated surface area and porosimeter (ASAP-200, Micromeritics). Specific surface area was calculated from the isotherms using the Brunauer–Emmett–Teller (BET) equation. SEM images were recorded using an electron microscope S-4800 (FE-SEM, Hitachi).

The surface chemical group of BCC, MBCC1, MBCC2 in terms of both quantity and quality was assessed by Boehm titration. Titration was conducted to determine the surface functional groups of the produced char. Solutions of NaOH (0.05 mol/L), $NaHCO_3$ (0.05 mol/L) and Na_2CO_3 (0.05 mol/L), and 50 mL of each solution were added to 0.5 g of each product in bottles and placed in a shaker for 24 hours; after shaking, the sample was filtered. The 10 mL filtrate was titrated using standard HCl 0.05 mol/L for basic solutions (NaOH, $NaHCO_3$ and

Na_2CO_3). For the titration of NaOH solutions, phenolphthalein was used as an indicator while for Na_2CO_3 and $NaHCO_3$, methyl orange indicator was employed. The acidic groups were calculated on the basis that: NaOH neutralizes carboxylic, lactonic and other acidic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ neutralizes only the carboxylic group.

Surface functional groups on the sample were studied utilizing a Fourier Transform Infrared Spectrometer (FTIR, NEXUS 670, Nicolet, USA). The spectra were recorded from 4000 to 400 cm^{-1}. By comparing them to the standard frequency patterns, various characteristic chemical bonds (or stretchings) were determined, from which certain surface functional groups could be derived.

2.4. ***The study of ammonium adsorption by adsorbents***

Experiments were conducted using Jar test equipment (model: JLT6 Jar test/Flocclulator, Italy) with a rotational speed of 100 rev/min. In the study, 0.5 g adsorbent (BCC, MBCC1, and MBCC2) was placed into 250 mL ammonium solution.

The effect of pH on the adsorption of ammonium by modified biochar was studied by varying the pH of NH_4Cl solution from 2 to 11 using diluted HCl 0.1M or NaOH 0.1M

For the kinetics study, samples were collected after 5, 10, 15, 30, 60, 90, 120, 150 and 180 min mixing between adsorbent with ammonium solution of predetermined concentrations (10, 20, and 40 mg/L of ammonium). The adsorption equilibrium analysis was conducted with ammonium solutions of 10, 20, 40, 60, 80, and 100mg/L. The samples were then collected after the mixing time of 120 min. For the ammonium analysis, samples were filtered and the ammonium concentration in the solution was determined via a colorimetric method (Rozic et al., 2000), using UV-VIS spectrophotometer (model: UV-752, USA) at $\lambda = 640nm$. Finally, the amount of ammonium in the adsorbent (qe (mg/g)) was calculated by the mass transfer balance relationship, $q_e = (C_o - C_e)V / W$. Here C_0 and Ce (mg/L) represent the influent and equilibrium concentrations, respectively.

3. RESULTS AND DISCUSSION

3.1. Optimization of biochar modification

3.1.1. Ammonium adsorption capacities of BCC, MBCC1 and MBCC2

An initial test was carried out to compare the performance of original corncob biochar BCC with modified corncob biochar MBCC1 and MBCC2. Here, MBCC1 was prepared by soaking BCC with HNO_3 4M and the impregnation ratio BCC/HNO_3 of 1:5. MBCC2 was prepared by modifying MBCC1 with NaOH 0.3M and impregnation ratio MBCC1/NaOH of 1:20. The amount of ammonium adsorbed by corncob biochars (qe (mg/g)) with and without modification is presented in Table 1.

Table 1

Comparison of NH_4^+adsorption of BCC, MBCC1 and MBCC2

C_O (mg/l)	Adsorption amount q_e (mg/g)		
	BCC	**MBCC1**	**MBCC2**
20	2.45	2.60	3.52
40	2.95	4.00	5.58
60	3.5	8.60	11.67

The above results show that corncob biochar is able to adsorb ammonium. However, the amount adsorbed by BCC is small (less than 3.5mg/g) and its value could be improved when it was modified by HNO_3 and NaOH, especially for water with high concentration of NH_4^+-N. The amount of NH_4^+-N adsorbed on modified biochar is found to be higher than that adsorbed by original biochar. This improvement can be explained by the increase in active functional groups. These include, for example, carboxylic, lactonic and acidic groups for adsorpting NH_4^+-N. The detailed analysis is presented in the next section (section 3.2). The results also showed that the adsorption capacity of MBCC2 for NH_4^+-N was higher than that of MBCC1. This can be explained by the fact that when MBCC1 was soaked with NaOH, acid functional groups on the surface of MBCC1 reacted with NaOH to form RCOONa. The RCOONa in MBCC2 helped to increase the segregation of modified biochar MBCC2 in water and thus increased the ammonium exchange capacity of MBCC2 (Halim et al., 2013).

Based on the above findings, the adsorption capacity of MBCC2 was found to be the better than the MBCC1. Therefore the following experiments focused on evaluating the performance of MBCC2.

3.1.2. Effect of HNO_3 concentration on modification

The effect of HNO_3 concentration on the performance of MBCC2 was evaluated at the impregnation ratio of BCC/HNO_3 solution of 1:5 (weight/volume). The primary experiment shows that BCC was damaged when it was soaked with HNO_3 at a high temperature of over 80^0C. Therefore the modification with HNO_3 was only conducted at room temperature (25^0C). The amounts of ammonium adsorbed by MBCC2 produced from different HNO_3 concentrations of 2M, 4M, 6M, and 8M are presented in Table 2.

Table 2

Effect of HNO_3 concentration on amount adsorbed by MBCC2

C_0 (mg/l)	**Adsorption amount q_e (mg/g)**			
	MBCC2 (2M)	**MBCC2 (4M)**	**MBCC2 (6M)**	**MBCC2 (8M)**
20	2.28	3.52	7.67	7.07
40	3.48	5.58	12.05	11.90
60	8.70	11.67	13.64	11.94

The experimental results indicate that adsorption capacity of modified corncob biochar could be improved by modifying it with HNO_3 and the concentration of HNO_3 had a strong effect on the modified product. The HNO_3 concentrations of 2M and 4M were not enough to create the highly active surface functional groups. At 60 mg NH_4^+/L, the highest NH_4^+ amount adsorbed by MBCC2 only reached 11.67mg/L when the modified corncob biochar was produced from the modification process with a HNO_3 concentration of less than 4M. The NH_4^+ amount adsorbed by MBCC2 reached the highest value of 13.64 mg/g in the case of corncob activated carbon was impregnated with HNO_3 6M. The lower adsorption capacities when the 2M and 4M solutions of HNO_3 were utilized can be explained by the limited number of acidic groups created on the corncob activated carbon surface.

The further increase in HNO_3 concentration from 6M to 8M, in contrast, did not improve the adsorption capacity of MBCC2. This increase even led to a decline in adsorption capacity at all initial ammonium concentrations. This phenomenon can be explained as follows. When the HNO_3 concentration was too high, the oxidation process was strong enough to break down part of the structure of corncob activated carbon and reduce its efficiency. Consequently, the HNO_3 concentration of 6M was chosen in the subsequent experiments.

3.1.3. Effect of impregnation ratio on modification

The effect of impregnation ratio between corncob biochar and HNO_3 on the adsorption capacity of modified corncob biochar is presented in Table 3.

Table 3

Effect of impregnation ratio of corncob biochar and HNO_3 on the NH_4^+ amount adsorbed by MBCC2

Co (mg/l)	Adsorption amount q_e (mg/g)			
	MBCC2 (1:1)	MBCC2 (1:3)	MBCC2 (1:5)	MBCC2 (1:7)
10	2.33	2.41	3.04	2.98
20	4.92	5.01	7.67	6.00
40	7.61	7.74	12.05	12.02

When increasing the impregnation ratio from 1:1 to 1:5 (weight/volume), the adsorption capacity for ammonium was increased accordingly. However, this value was marginally decreased when this ratio rose to 1:7 in all the studied ammonium concentrations. Thus, the HNO_3 6M and impregnation ratio of 1:5 were chosen as the optimum acid modification state and used in the subsequent experiments.

3.1.4. Effect of NaOH concentration on modification

The experiments to assess the effect of NaOH concentration (0.1M, 0.3M and 0.5M) on preparing MBCC2 were conducted at HNO_3 concentration of 6M and BCC/HNO_3 impregnation ratio of 1:5 (Table 4).

Table 4

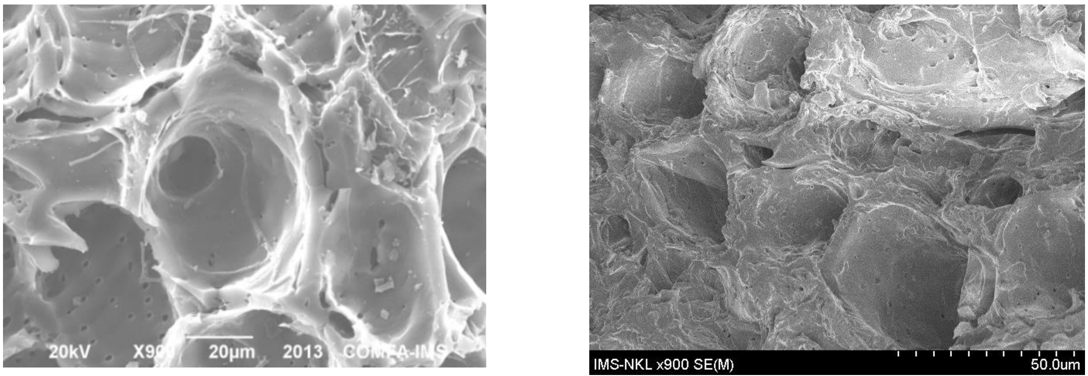
Effect of NaOH concentration on the NH_4^+ amount adsorbed by MBCC2

Co (mg/l)	Adsorption amount q_e (mg/g)		
	MBCC2 (NaOH 0.1M)	MBCC2 (NaOH 0.3M)	MBCC2 (NaOH 0.5M)
10	2.47	3.04	3.42
20	4.93	7.67	7.45
40	8.26	12.05	11.86

The results show that when NaOH concentration was altered from 0.1M to 0.3M, the capacity of MBCC2 to adsorb the ammonium increased. However, this adsorption capacity decreased slightly when the NaOH concentration exceeded 0.3M. The reason for this is similar to what happened when HNO_3 concentration rose from 6M to 8M. Therefore, NaOH of 0.3M was chosen as the optimal concentration for modification of corncob biochar.

3.2. Characteristics of biochar and modified biochar

The SEM micrograghs of BCC and MBCC2 (Fig. 1) indicate that their structures were homogeneous. The structure of MBCC2 was not much different from that of BCC. The BET results reveal that the modification led to an increase in average pore volume, from $0.39m^3/g$ for the BCC to $0.61m^3/g$ for the MBCC2. However, the surface area was found to reduce significantly after modification, from $0.959\ m^2/g$ to $0.051\ m^2/g$ for the BCC and MBCC2, respectively. It was also observed that the pores of BCC were in microporous form whereas those of MBCC2 were not. The combination of micropores with the larger pores due to the chemical modification can explain the increase in pore volume and decrease in surface area.



BCC MBCC2

Fig. 1. SEM images of BCC and MBCC2

The chemical characteristics analyzed by Boehm titration of BCC, MBCC1 and MBCC2 are presented in Table 5.

Table 5

Chemical characteristics of corncon biochar, and modified corncob biochar

Biochar	Carboxylic (mmol/g)	Lactonic (mmol/g)	Acidic (mmol/g)
BCC	0.6194	1.479	2.584
MBCC1	1.3682	2.745	4.298
MBCC2	0.8715	1.864	3.466

The data in Table 5 illustrate that the amount of carboxylic and lactonic functional groups in MBCC1 were approximately double that of BCC. The other acidic functional group in the MBCC1 was also increased significantly. These results indicate that more active functional groups for adsorpting NH_4^+-N was presented in the modified material which consequently led to an improvement in the NH_4^+-N adsorption capacity of the modified biochar. The MBCC2 contains more carboxylic, lactonic and acidic groups than the original corncob biochar. However, there were less of these functional groups in MBCC2 compared to the MBCC1. The transfer from acidic forms into salt forms on the surface of modified corncob biochar when MBCC1 was soaked into NaOH could explain this phenomenon.

The FTIR results of BCC, MBCC1 and MBCC2 are presented in Fig. 2. It shows that the spectrum of BCC did clearly change after modification. Here the adsorption spectrum wavelength was varied from 400 to 4000 cm^{-1}.

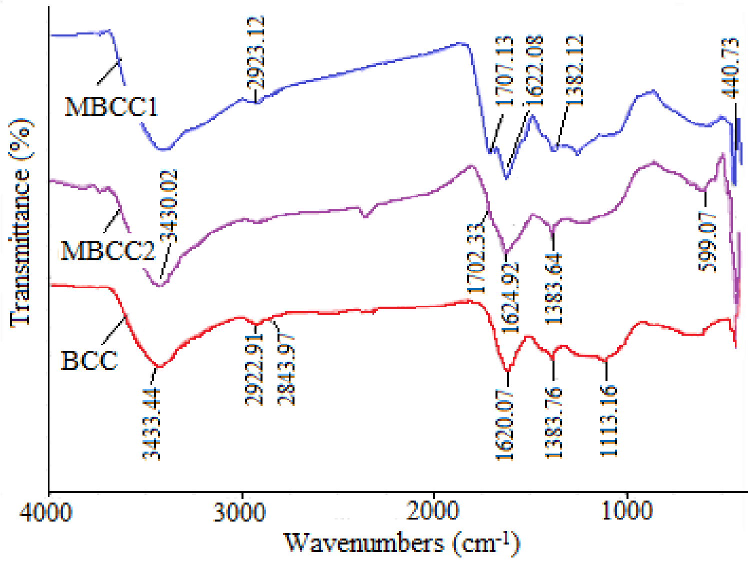


Fig. 2. The FTIR spectum of BCC, MBCC1 and MBCC2

Fig. 2 shows that the adsorption groups of O-H (at peak at wavelength of 3433 cm^{-1}) and C=C (at peak at wavelength of 1620 cm^{-1}) appeared in BCC. The O-H and C=C groups also appeared in the MBCC1 and MBCC2 (at peak at wavelength of 3430 cm^{-1} and 1622 - 1624 cm^{-1}, respectively). However, the absorption intensity of the O=H group of MBCC1 and MBCC2 was higher than that of BCC. Furthermore the modification led to the appearance of C=O group (at 1702-1707 cm^{-1}) in the MBCC1 and MBCC2. This indicates that the functional group of carboxylic acid did develop in both MBCC1 and MBCC2. Also the adsorption intensities of O-H and C=O groups of MBCC2 were lower than that of MBCC1 (Fig. 2). The reaction between the O-H group in the carboxylic acid with NaOH during the second modification step could be the reason for this decrease.

3.3. Ammonium removal by MBCC2

3.3.1. Effect of pH

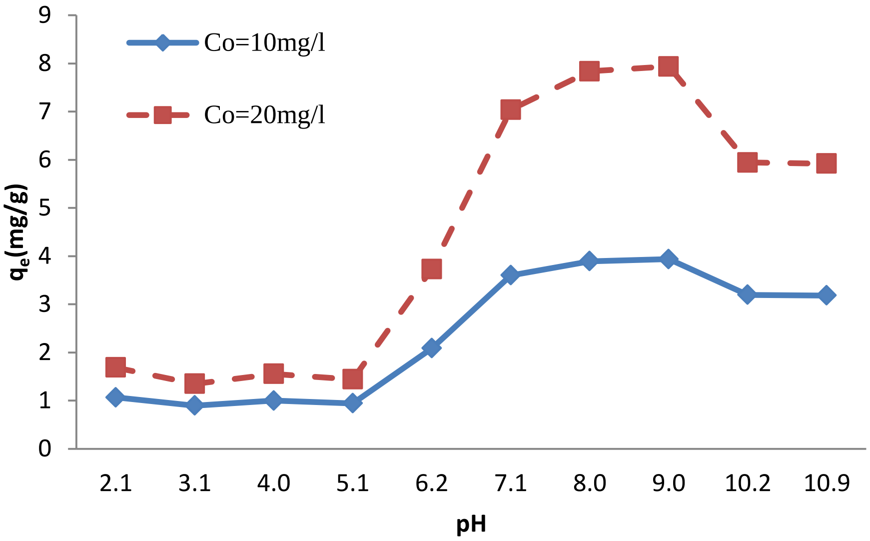


Fig. 3. Effect of pH on ammonium removal of MBCC2

Experimental results show that the amount of ammonium adsorbed by MBCC2 (Qe) was low when the pH ranged from 2 to 5. However, it increased significantly when pH was increased from 5 to 8 and reached its highest value between 8 and 9 mg/L (Fig. 3). In fact, at pH between 8 and 9, ammonium adsorption reached 3.9 mg/g and 7.9 mg/g at intial ammonium concentration of 10 and 20 mg/L, respectively. The continued increase of pH to more than 10 led to a margical decline in the adsorption amount of ammonium in the MBCC2.

The above results can be explained by the effects of pH on the existing state of NH_4^+ ions in water and the ion state of surface functional groups of MBCC2. In solution, depending on the level of pH, ammonium is mostly present as NH_4^+ or $NH_{3(aq)}$ forms. In the acidic environment, most ammonium exists in NH_4^+ form in water (Marañón et al., 2006). The adsorption capacity was low at pH less than 5 because of the strong competition between H^+ and NH_4^+ ions in the solution. The decrease of ion H^+ in the solution when increasing the pH of solution from 5 to 7 could help increase the adsorption capacity of MBCC2. Here, the adsorption of ammonium in water followed the ion exchange mechanism. Similar results have been documented by other researchers (Halim et al., 2013; Zeng et al., 2013). The adsorption capacity of MBCC2 for ammonium increased when the pH was increasd to more than 7. The reason for this phenomenon was the electrostatic attraction mechanism in which NH_4^+ interacted with the negatively charged surface of MBCC2.

Experimental study on the effect of pH on the ammonium removal was carried out with ten pH values from 2.1 to 10.9. The pKa of ammonium is 9.3 so there was no ammonium stripping in most pH conditions studied (8 out of 10 conditions used). Experimental results show that the adsorption capacity of material decreased with the increasing of pH from 9 to 10.2 and 10.9. It indicated that at these high pH experimental conditions, ammonium stripping was not a main mechanism. In these conditions, most of the ammonium could be transformed into the NH_3(aq) form. Here the electrostatic attraction mechanism was no longer effective. This led to a reduction in the amount of ammonium removed. This finding is similar to the findings of Guo et al., (2005) and Vassileva et al., (2008). In the experiments, 250mL of samples were added into 250 mL conical flasks which were then covered by flasks' lids. The air volume in each flask was small (less than 10mL). Therefore, the ammonium removal by air stripping and evaporation during the experiments was minimized and could be ignored.

3.3.2. Effect of contact time on adsorption capacity of ammonium

The effect of contact time on ammonium adsorption is shown in Fig. 4. Adsorption capacity of ammonium increased significantly for the first 30 min and reached its maximum after 60 min. The NH_4^+ amount adsorbed by MBCC2 was 3.47 mg/g; 7.24 mg/g and 12.31mg/g after 60 min for an intial ammonium concentration of 10, 20 and 40 mg/L, respectively. After 60 min, adsorption capacity of ammonium did not increase when contact time was further increased. This indicated that the adsorption of ammonium by MBCC2 reached the point of saturation after 60 minutes of contact time.

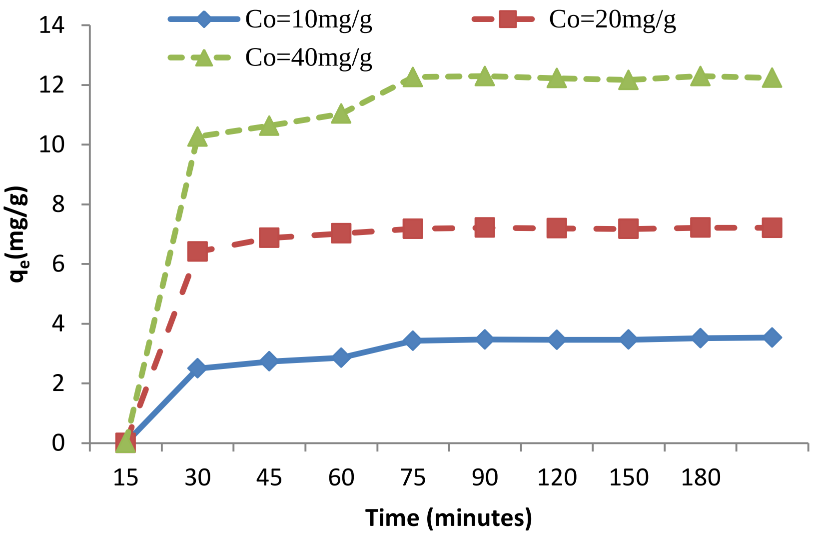


Fig. 4. Effect of contact time on ammonium adsorption by MBCC2

3.4. Adsorption isotherm

Adsorption isothermal equilibrium of MBCC2 for ammonium can be described using the Langmuir, Freundlich and Sips isotherms (Fig. 5). The Langmuir isotherm (Langmuir, 1918) is given by:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{1}$$

Where: q_m: saturated maximum monolayer adsorption capacity (mg/g); Ce: equilibrium concentration (mg/L), and b: Langmuir constant related to the binding energy of adsorption (L/mg).

The Freundlich isotherm (Freundlich, 1906) is an empirical equation. The equation of this model is written in equation 2:

$$q_e = K_F C^{1/n} \tag{2}$$

Where: K_F and n are Freundlich constant and an experimental constant, respectively. They indicate the adsorption capacity and adsorption intensity of the adsorbent.

The Sips model is the combination of both the Langmuir and Freundlich isotherm models. The Sips isotherm model can be written as follows:

$$q_e = \frac{q_m (bC_e)^{1/n}}{1 + (bC_e)^{1/n}} \tag{3}$$

From the experimental data, the parameters of the Langmuir, Freundlich, and Sips were determined and the values are presented in Table 6.

Table 6

Paramaters of Langmuir, Freundlich, and Sips for ammonium adsorption of MBCC2

	Freundlich model			Langmuir model			Sips model			
	R^2	K_F	1/n	R^2	q_m	b	R^2	1/n	q_m	b
MBCC2	0.921	3.195	0.427	0.981	22.63	0.062	0.999	0.852	18.92	0.029

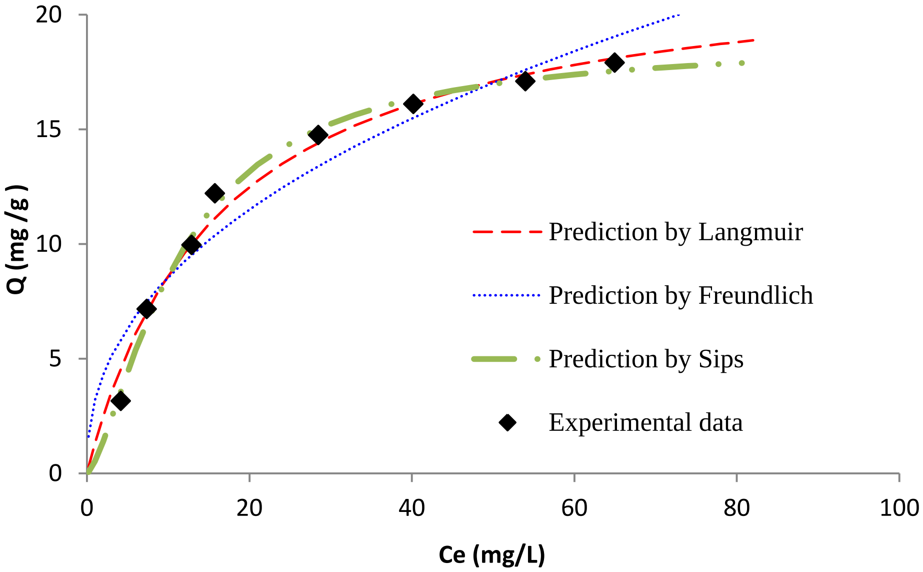


Fig. 5. Equilibrium adsorption prediction of ammonium on MBCC2 by Langmuir, Freundlich, and Sips models (contact time = 120min, Co =20 mg/L)

The regression efficient (R^2) obtained from the Langmuir and Sips models were closer to 1 and was much higher than that of the Freundlich model. In other words, Langmuir and Sips isotherms fitted well the NH_4^+ adsorption on MBCC2. Thus, it can be concluded that the monolayer Langmuir adsorption isotherm explained better the adsorption of NH_4^+ on MBCC2**.**

The favorable nature of adsorption can be expressed as R_L and calculated by the following equation (Hall et al., 1966):

$$R_{L}= \frac{1}{1+bC_0} \qquad (4)$$

Where b is the Langmuir constant, Co is the initial ammonium concentration and R_L is the dimensionless separation factor. The value of R_L for MBCC2 was calculated as 0.06 and this indicates that the adsorption was a favorable process.

The maximum adsorption capacity, calculated from Langmuir isotherm, of BCC for ammonium was only 3.93 mg/g while that of MBCC2 was nearly 6 times higher, reaching 22.6 mg/g. This proved that modification of BCC with HNO_3 and NaOH helped to increase significantly the maximum adsorption capacity.

The MBCC2, although having a low specific surface, was able to adsorb large amounts of ammonium. Adsorption capacity for ammonium of by MBCC2 was also higher than that of several modified activated carbons (see Table 7). This shows that the specific surface of biochar is not a major factor for ammonium adsorption from water. This conclusion agrees with several previous studies (EL-Wakil et al., 2014; Takashi et al., 2006). According to Takashi et al., (2006), bamboo activated carbon carbonized at 400^0C only had a specific surface of 2.17 m^2/g, however, its adsorption capacity of ammonium was higher than that of activated carbon with a specific surface of 1,670 m^2/g.

Table 7

Comparison of ammonium adsorption capacity of different adsorbents

Adsorbents	NH_4^+ concentration range (mg/L)	Maximum adsorption capacity (mg NH_4^+/g)	References
Slag Honeycomb cinder Coal gangue	10-300	3.1 5.0 6	Zhang et al., (2013)
Biochar 400 modification with H_2SO_4	1-50	10	Takashi et al., (2006)
Biochar 700 modification with H_2SO_4		3	
Activated carbon modification with H_2SO_4		6	
Activated carbon modification with Fe	100	19	Le Leuch and Bandoz (2007)
Activated carbon modification with Cr	100	14.5	
Modified activated carbon with HNO_3, NaOH	685-735	19.34	Halim et al., (2013)
Modified activated carbon with HNO_3	500	18	Soto-Garrido et al., (2003)
Peach stones-granular activated carbons	500	10	
BCC	100	3.93	This research
MBCC2	100	22.6	

3.5. Adsorption kinetics of MBCC2

The dynamic behavior of adsorption of ammonium onto MBCC2 is determined from the kinetics experimental data. In this study, the experimental data were fitted with different adsorption kinetics models including pseudo-first order (Tseng et al., 2009), pseudo-second order (Kumar and Sivanesan, 2006), Elovich (Li et al., 2009) and Avrami (Lopes et al., 2003). Equations of these models are presented as follows:

$$\text{Pseudo-first order} \quad : \; q_t = q_e - q_e e^{-k_1 t} \qquad (5)$$

$$\text{Pseudo-second order} \; : \; q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad (6)$$

Elovich : $qt = \beta.\ln(\alpha\beta t)$ (7)

Avrami : $q_t = q_e\{1 - \exp[k_{AV.t}]nav\}$ (8)

Where, q_e: adsorption capacity in balance; K_1, $K_{2,}$ and K_{av} are constant rates of pseudo-first order, pseudo-second order, and Avrami models, respectively; α is the initial adsorption rate (mg/g.min); β is the adsorption constant (g/mg) in the Elovich model; and $N_{AV\,1}$ is the Avrami exponent of time in the Avrami model.

In the kinetics studies, the average relative error (ARE) was also calculated (equation 9):

$$ARE = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{q_{te} - q_m}{q_{te}}\right|_i \qquad (9)$$

Where q_{te} (mg/g): amount of ammonium adsorbed on MBCC2, determined from the experimental study, q_{tm} (mg/g): amount of ammonium adsorbed on MBCC2 predicted from the kinetics model, N: number of measurements. In contrast to R^2 value, the kinetics model is better fitted if their ARE is lower. The kinetics parameters were calculated by non-linear regression using excel spreadsheet and optimized with the 'solver' add-in. Apart from R^2, average relative error (ARE) was calculated for validation of kinetics models to experimental data to have a understanding of the adsorption process.

The model prediction data and experimental data are shown in Fig. 6. The models' parameters are summarized in Table 8. The simulation shows that the pseudo-second order model possessed the best fit with experimental data with the highest R^2 (0.965) and the lowest ARE (1.432). Furthermore, the calculated q_e value by the pseudo-second order model was close to the experimental value. This finding demonstrates that: firstly, the ammonium sorption onto MBCC2 follows the pseudo-second order; and secondly, the rate of sorption was controlled by the chemical sorption process (Zhu et al., 2012).

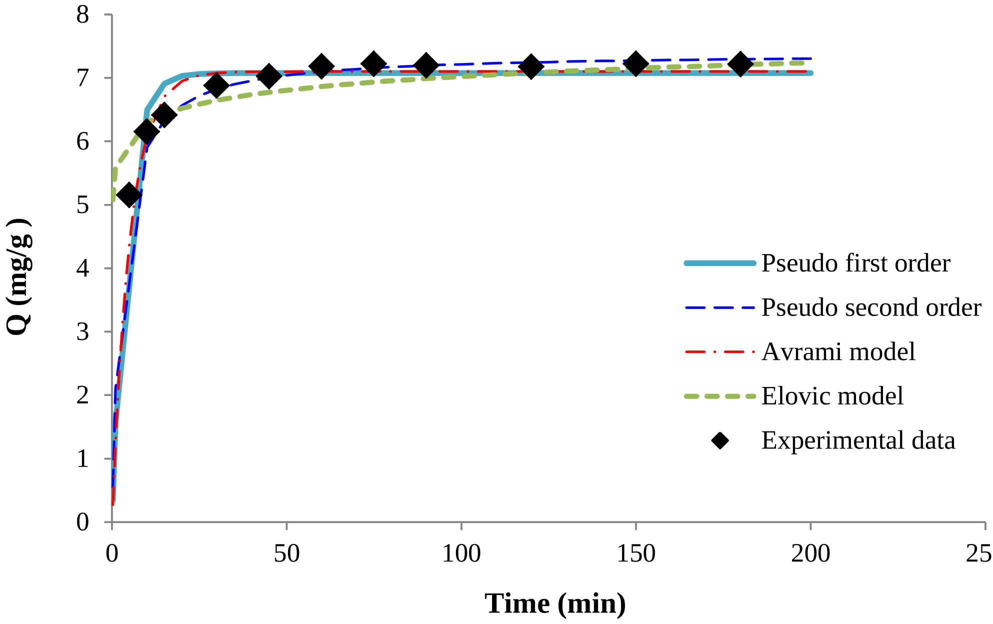


Fig. 6. Kinetics modelling of ammonium sorption onto MBCC2 (Co: 20 mg/L; adsorbent amount: 2g/L; initial pH: 7)

Table 8

Kinetics modelling parameters of ammonium sorption on MBCC2

Model	Parameter	Value	Model	Parameter	Value
Pseudo-first order	q_e	7.077	Pseudo-second order	q_e	7.397
	K_1	0.25		K_2	0.054
	R^2	0.882		R^2	0.965
	ARE	2.661		ARE	1.432
Avrami	q_e	7.10	Elovich	α	1.8×10^8
	K_{av}	0.693		β	0.313
	N_{av}	0.28		R^2	0.710
	R^2	0.824		ARE	3.766
	ARE	2.978			

CONLUSIONS

This study shows that modification of surface of carbonized biochar made from corncob could significantly enhance ammonium adsorption efficiency. Here the biochar was modified effectively by treating it with HNO_3 and NaOH. The acid concentration of 6M, impregnation ratios (weight/volume) of BCC/ HNO_3 1:5 (w/v) and then soaking in NaOH 0.3M constituted the best conditions for treating ammonium. The equilibrium data fitted well to the Langmuir and Sips models, and maximun adsorption capacity as determined by the Langmuir model was 22.6mg/g. The optimum pH for adsorping ammonium by MBCC2 was between 8 and 9. The reaction reached equilibrium within 60 min and the kinetics of adsorption followed the pseudo-second order model. This study shows that MBCC2 has the potential to work as an adsorbent with very high adsorptive capacity for the removal of ammonium from water (groundwater and surface water). Its application can be extended to wastewater treatment. The exhausted adsorbents containing high ammonium could directly be used as soil conditioners. This approach reduces the need to regenerate the adsorbent and the maintenance requirements for the treatment system. Further studies on desorption, adsorption interference (such as calcium, magnesium, iron, organic) with the MBCC2 are planned to be carried out before considering the application of this material in water and wastewater treatment systems.

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