Three kinds of derivative carboxymethyl cellulose (DCMC) materials, CMC-Na, CMC-K, and CMC-NH₄, were prepared from cotton straw fiber. Their chemical structure, film morphology, water retention, biodegradability, and growth promotion were investigated with infrared spectroscopy (IR), scanning electron microscope (SEM), and field experiments. The results showed that the infrared absorption peaks of the three materials were similar. It was observed that the DCMC materials could form films after being sprayed at the amount of 4.00 g/m² and 12.00 g/m², and the film thickness was showed in the order of CMC-K, CMC-NH₄, and CMC-Na. The largest water holding capacity increased significantly after DCMC was sprayed on the soil. The water retention of CMC-Na, CMC-K, and CMC-NH₄ increased by 47.74%, 72.85%, and 61.40% severally while sprayed with 12.00 g/m² compared to the control group (CK), and the water retention rate increased with 6.93, 9.75, and 8.67 times, respectively, on the seventh day. The total number of soil microorganisms increased with the DCMC materials being sprayed; the number in the upper layer increased by 92.31%, 123.08%, and 138.46%, respectively, compared with CK. When the three materials were used to the cornfield at the amount of 100.00 kg/hm², the corn yield increased by 33.11%, 70.93%, and 50.60%, respectively. The DCMC materials, as the sole carbon source, could be degraded by soil microorganisms. The nutrient elements such as NH₄⁺ in the materials could further promote the growth of microorganisms and crops. This study might provide a new way to apply straw-based DCMC in soil water retention, soil amendment, and high value-added transformation of straws in arid areas.

1. Introduction

The Loess Plateau in northwest China is an arid and semi-arid region with about 64,000,000 square kilometers. Loose soil texture and water shortage (only 200–500 mm rainfall yearly) restrict the favorable growth of plants [1, 2]. Water-retaining material plays an important role to deal with the problems above [3]. At present, there are three main types of commonly used water-retaining materials from starch, synthetic resin, and cellulose [4–6]. Polycrylamide (PAM) is widely used for soil water retention [7, 8]. However, the acrylamide (AM) both being epibiotic in PAM and after PAM being degraded is highly toxic and can cause fatal influence to most environmental microorganisms [9, 10]. The biodegradation of AM monomer is slow, which makes it accumulated easily and results in poisoning to the human nervous system [11]. Long-term contact will damage the skin and may also cause mutagenicity and carcinogenicity [12, 13]. Therefore, PAM is harmful to the ecological environment and human health. It is urgent to seek new environmentally friendly water-retaining materials for agricultural development in arid areas.

According to incomplete estimates, the annual output of straw is about 876 million tons in China [14]. The crude fiber content of wheat, corn, cotton, and other straws can reach 30.00%-40.00%, which may be renewable resources with multiple uses [15]. At present, straws are mainly used in manure, feed, fuels, base materials, and building materials [16]. In contrast, many crop straws are still burnt or left unused every year, resulting in a huge waste of resources.
Carboxymethyl cellulose (CMC) is a kind of material obtained after carboxymethylation of cellulose [17]. The chemical structure of straw cellulose contains many hydroxyl groups and possesses certain special functions by introducing certain functional groups which can increase consistency, emulsification, and water retention [18]. CMC is mainly applied in food production, medicine, wastewater treatment, etc. [19–21]. Using cotton pulp as raw material, Hokkanen et al. prepared CMC hydrogel fibers with different degrees of substitution, and the hygroscopicity of distilled water can reach 71.20% [22]. Deng used straw as a raw material to prepare a water retention agent by aqueous solution polymerization, and its water retention rate had reached 71.34% [23]. A water-retaining composite material was prepared by Zhang et al. with carboxymethyl cellulose/chitosan (CMC/CS). Its maximum water retention could reach 60.00% under simulated arid climate conditions for 5 hours [24]. Li et al. found that when hydrophilic polymers of carboxymethyl cellulose were used in sand, its available water content increased up to four times compared to CK [25].

All researches have so far been focused on the preparation technology of cellulose materials and the determination of physical and chemical properties. However, there were few reports on the application of cellulose materials on soil, especially the systematic research on the application effect of cellulose materials sprayed on the soil surface. Therefore, three kinds of DCMC materials, including CMC-Na, CMC-K, and CMC-NH₄, were used in this study. Among them, CMC-Na and CMC-K are carboxymethyl cellulose sodium or potassium obtained after alkalization and etherification of straw cellulose, while CMC-NH₄ is nitrated and ammonia on sodium carboxymethyl cellulose. The three materials were prepared from cotton straw fiber to explore their chemical structure, film morphology, water retention, biodegradability, and growth promotion after being sprayed onto the soil surface, to provide a new way for the application of straw cellulose materials in soil water retention and soil amendment in arid areas such as the Loess Plateau.

2. Materials and Methods

2.1. DCMC Materials and Soil. Three kinds of DCMC materials, carboxymethyl cellulose sodium (CMC-Na), carboxymethyl cellulose potassium (CMC-K), and carboxymethyl cellulose ammonium (CMC-NH₄), were prepared by our group from cotton straw fiber (Figure 1). The material properties are shown in Table 1. CMC-Na was white powder; CMC-K and CMC-NH₄ were white floccules.

The soil used in this study was collected from Nangou Village, Asia District, Yan’an City, Shaanxi Province, China (longitude: 109.300362, latitude: 36.597649). The soil organic carbon, total nitrogen, available phosphorus, and available potassium were 1.07%, 0.05%, 0.37 g/kg, and 12.49 g/kg, respectively. The soil pH value was 8.10.

2.2. Infrared Spectrum Scanning. The chemical structures of the three kinds of DCMC material were characterized by interpreting the infrared spectra (IR). The IR was recorded by a Fourier transform infrared (FTIR) spectrometer of Nicolet Nexus 410 (American Thermo Nicolet Corporation) in wavenumber scanning at 4000-400 cm⁻¹ to identify the functional structure of CMC-Na, CMC-K, and CMC-NH₄.

2.3. Determination of Viscosity of DCMC Materials. A uniform solution of the three materials was prepared into beakers with mass fractions of 0%, 0.50%, 1.00%, 1.50%, and 2.00%, and then, the new DV1 viscometer (Brookfield) was applied to measure the viscosity at 20°C, and then, viscosity curve diagrams at different concentrations were drawn.

2.4. Surface and Profile Morphology of the Films from the Materials. An experiment was set up with flowerpots with an inner diameter of 8.00 cm and a height of 10.00 cm. Each soil sample of 220.00 g collected in Nangou Village was put into a flowerpot. 0.50% solution of 3 kinds of DCMC materials was prepared with tap water separately, and the materials of 4.00 g/m², 8.00 g/m², and 12.00 g/m² were sprayed on the soil surface in the flowerpot. CK was treated with...
the same volume of tap water. These flowerpots were placed indoors with an average temperature of 25-28°C and relative humidity of 37%-42% for 7 days without watering. The experiments were set in three parallels to observe the morphology of the film, comparing the microscopic surface, profile morphology, coverage, and film thickness which were observed with Hitachi S-4800 field emission SEM.

2.5. Measurement of Largest Water-Holding Ratio and Soil Water Retention. 220.00 g of dry soil sample collected from Nangou Village, Yan’an City, was put into each flowerpot, and each flowerpot with soil (marked as $M_0$) was weighted. These pots were sprayed with three kinds of DCMC materials at 4.00 g/m$^2$, 8.00 g/m$^2$, and 12.00 g/m$^2$, respectively, and CK was treated only with tap water. Then, water was added slowly to the soil surface until saturated (marked as $M_n$). These flowerpots were placed indoors under an average temperature of 25-28°C and relative humidity of 37%-42% without watering for 7 days to allow the water to evaporate naturally. The total weight (marked as $M_n$) of these flowerpots was measured every day. The largest soil water-holding rate (WH) was calculated by Equation (1), and the soil water retention ratio (WR) was calculated using Equation (2).

$$\text{WH} = \left(\frac{M_0 - M_1}{M_1}\right) \times 100\%, \quad (1)$$

$$\text{WR} = \left(\frac{(M_n - M_1)}{(M_0 - M_1)}\right) \times 100\%. \quad (2)$$

2.6. DCMC Material Degradation by Soil Microorganisms. 10.00 g collected soil was dissolved in 90 mL of sterile water; then, 1 mL of supernatant was drawn and put into a flask containing 50 mL of inorganic salt liquid medium (ISLM) and shook well. The three DCMC materials and polyacrylamide (PAM) were added separately to the ISLM at 0.50%, 1.00%, 1.50%, and 2.00% mass fractions, respectively. The CK group was treated without DCMC and PAM. The experiment was set up in 3 parallels. The samples were cultivated in a shaking incubator at 160 r/min and 30°C in 0, 5, and 10 days to measure optical density (OD$_{600}$). Then, the degradation effects of both DCMC and PAM were compared, and a feasible utilization of three DCMC materials as the sole carbon source for soil microorganisms would be put forward.

The components of ISLM are as follows: NaCl 0.20 g, NH$_4$NO$_3$ 2.00 g, KH$_2$PO$_4$ 0.50 g, K$_2$HPO$_4$ 0.50 g, MgSO$_4$·7H$_2$O 0.20 g, MnSO$_4$·0.01 g, FeSO$_4$·7H$_2$O 0.01 g, CaCl$_2$·0.10 g, and water 1 L.

2.7. Field Experiment of DCMC Materials on Soil Microbial Growth. A field experiment was set in Nangou Village, Yan’an City. Three DCMC materials were prepared as 0.50% aqueous solutions and sprayed on the surface of slope soil. Each plot of 20.00 m$^2$ was sprayed with DCMC material at a spraying amount of 4.00 g/m$^2$. The CK plot was sprayed with the same volume of water. The soil microbial quantity was recorded in one month.

2.8. Field Experiment of DCMC Materials on Corn Yield. Eight field experimental plots were set up with an area of 25.00 m$^2$ in Nangou Village. Corn was sown on May 2nd, 2019. According to the film feature of the three DCMC materials by the SEM (scanning electron microscope), the
Figure 4: SEM surface film morphology of CMC-Na (a), CMC-K (b), and CMC-NH₄ (c).
spraying rate of 10.00 g/m² was selected in each experimental plot with the same amount of tap water as the control group (CK). On July 3rd, 2019, the three DCMC materials were prepared with a concentration of 0.50% and sprayed on the soil surface at the amount of 100.00 kg/hm². The fresh weight and air-dried weight of corn cobs and kernels were measured on October 10th, 2019.

2.9. Data Processing Method. Microsoft Excel 2010 was used to organize and graph the data. SPSS 20.0 software was used to test the significance of the average number of each treatment at the level of P < 0.05.

3. Results

3.1. Structure Characterization of DCMC Materials. The IR spectra of the three DCMC materials (Figure 2) had the same absorption trend, and the position of the characteristic functional groups was close. The signal at 3420–3442 cm⁻¹ corresponded to the -OH group absorptions, while the signal at 1590–1610 cm⁻¹ corresponded to the symmetric and asymmetric vibration absorption peaks of C=O in the -COO⁻ group, and the signal at 1310–1420 cm⁻¹ corresponded to the C-O stretching vibration and the O-H in-plane deformation vibration and the -CH absorption peak near 2910 cm⁻¹. It had shown that the vibration amplitude of CMC-K and CMC-NH4 at the carboxy absorption peaks was slightly higher than that of CMC-Na.

3.2. Viscosity of DCMC Material. The viscosity of the three DCMC materials with different concentrations is shown in Figure 3. The viscosity ranges were 18-380 mPa·s, 14-950 mPa·s, and 32-840 mPa·s, respectively, when the mass fractions of CMC-Na, CMC-K, and CMC-NH4 were 0.50%-2.00%. The degree of substitution (DS) of CMC-Na, CMC-K, and CMC-NH4 were 0.85-0.95, 0.60-0.80, and 0.78, respectively. Among them, CMC-Na had the highest DS and the lowest viscosity. The viscosity of -OCH2COO-R material was also closely related to the type of R substituent groups. This is consistent with the results reported in the literature [26]. The viscosity increased with the increasing concentration. Under the same concentration, the viscosity strength showed the order as CMC-K>CMC-NH4>CMC-Na.

3.3. Morphological Analysis of Film Forming from DCMC. The film-forming effect was observed by SEM after three DCMC materials were sprayed on the soil surface at 4.00 g/m² and 12.00 g/m², respectively. The SEM was used to observe the film formation after the DCMC materials were sprayed. The film covered the surface soil and partially filled the gaps between soil blocks and increased the cohesion between soil particles and formed larger aggregates, which was consistent with the discovery of Zhou et al. [27]. Figure 4 shows the overlooking SEM image with 110 and 800 magnifications. It was clear that all the three DCMC materials could form films. CMC-K formed film at 4.00 g/m² and 12.00 g/m² evenly, while CMC-NH4 just forms fully covered film at 12.00 g/m². This meant that CMC-K had the best film formation effect, followed by CMC-NH4 under the same spraying concentration.

The SEM images with 1500 magnification (Figure 5) showed that the film thickness of CMC-K, CMC-NH4, and CMC-Na was 2.00-20.00 μm, 1.00-6.00 μm, and 0.50-3.00 μm, respectively, at the amount of 4.00 g/m², 12.00 g/m², and the film thickness raised with the spraying amount increase. Comparing the thickness of three DCMC materials at the spraying amount of 12.00 g/m², there was an order of CMC-K>CMC-NH4>CMC-Na. In addition, it had been found that the film-forming property of the DCMC material was related to the viscosity. Under the same concentration, CMC-K was with the highest viscosity and formed the best film, while CMC-Na had the smallest viscosity and the thinnest film. According to the scanning results above, there were different film-forming properties with different DCMC materials.

3.4. Water Retention Performance of DCMC Materials. The water retention of the three DCMC materials was measured, and the largest water-holding rate (WH) was obtained. The data showed that the addition of 3 kinds of DCMC materials could increase the WH (Figure 6(a)) that was increased with the additional quantity added. At the amount of 12.00 g/m², the WH of CMC-Na, CMC-K, and CMC-NH4 could reach 36.02%, 42.14%, and 39.35%, respectively, and was 47.74%, 72.85%, and 61.40% higher than CK was. There was an order of WH as CMC-K>CMC-NH4>CMC-Na at the same spraying amount. The soil water retention rate (WR) was measured on the 7th day without watering. The results showed that the soil WR with the DCMC material added remained higher than CK did (Figures 6(b)–6(d)). The WR of three kinds of DCMC materials could reach 81.62%, 87.69%, and
84.32%, respectively, under simulated drought and nonwatering conditions. Compared to CK, the WR of three DCMC materials increased by 6.93, 9.75, and 8.67 times, respectively, with 12.00 g/m² of spraying amount on the seventh day. This figure was higher than that in the literature in which the water retention rate of carboxymethyl cellulose-modified materials (CMC/CS) is 60.00% [25]. There was an order of WR capacity as CMC-K>CMC-NH₄>CMC-Na, which was consistent with the viscosity order. This indicated that the WR was positively correlated with the viscosity of the DCMC materials and was consistent with the order of film coverage and thickness. Therefore, the DCMC materials played a role in reducing soil water evaporation and retaining water.

3.5. Biodegradation of DCMC Materials. Both the three DCMC materials and PAM were used as the sole carbon source to test the possibility of them being biodegraded by means of measurement of the OD₆₀₀ value. The result (Figure 7) showed that the three materials could not only be used by soil microorganisms but also promote the growth of microorganisms. On the contrary, the PAM could not be used. The highest OD₆₀₀ value of CMC-K, CMC-Na, and CMC-NH₄ was 1.08, 0.25, and 1.06, respectively, at the concentration of 1.5%. The viscosity of ISLM which contained each of the materials decreased by 95.39%, 79.80%, and 94.47%, respectively, while the OD₆₀₀ value of PAM reduced from 0.10 to 0.06 in ten days, and a reduction of PAM viscosity was observed. The PAM could hardly be used by microorganisms for growth due to its unbiodegradable feature and being harmful to microorganisms. This result was consistent with the finding of Ma et al. who reported that the degradation rate of PAM by soil microorganisms was low [28]. Sojka and Entry also reported that the addition of PAM was harmful to microorganisms and would reduce the total microbial biomass [29]. The data above could be concluded that the three DCMC materials were biodegradable and environmental-friendly than PAM.

3.6. Effect of DCMC Material on Soil Microorganisms. Figure 8 shows the number of microorganisms (NM) in different soil layers after spraying CMC-Na, CMC-K, and
CMC-NH₄ at the content of 4.00 g/m². The NM in the surface layer were 92.31%, 123.08%, and 138.46% higher than the CK sprayed with tap water. Meanwhile, the NM in 5 cm underground soil was 40.91%, 81.82%, and 54.55% higher than the CK. The NM in the soil sprayed with the three DCMC materials were significantly higher than the CK sprayed with tap water. The number of microorganisms in the different soil layers is shown in Figure 8. The yield of cob and kernel is shown in Figure 9.

**Figure 7**: Biodegradation and utilization of DCMC and PAM materials as the sole carbon source by soil microorganisms on growth: (a) CMC-NH₄; (b) CMC-K; (c) CMC-Na₃; (d) PAM.

**Figure 8**: The number of microorganisms in different soil layers.

**Figure 9**: The yield of cob and kernel.
It was disclosed that spraying the DCMC material promoted the growth of soil microorganisms because of its water retention and the supply of nutrients.

3.7. Effect of DCMC Materials on Corn Yield. Figure 9 shows the effect of spraying CMC-Na, CMC-K, and CMC-NH₄ on corn yield. It was found that all the fields sprayed with three DCMC materials could harvest a good yield. The dry corn kernel was 4398.30, 5648.04, and 4976.29 kg/hm², which was 33.11%, 70.93%, and 50.60% higher than CK. This was consistent with the results reported in the literature in which an application of water-retaining materials increased the growth of perennial ryegrass by 44.50% under drought conditions [30].

3.8. Growth-Promoting Mechanisms of DCMC Materials. The three DCMC materials derived from straw cellulose were interlaced and polymerized long-chain molecules. They might form a porous network on the soil surface and cover the soil and then absorb and store a large volume of water until being a gel state, partially fill the gaps between the soil blocks and increase the cohesion between soil particles, and finally form a film after drying. Then, the formed film might close, more or less, the holes on the soil surface and prevent soil moisture from evaporation. Meanwhile, the hydrophilic groups on the multimolecular network, such as -COONa⁺, -COONH₄⁺, -COOK⁺, -OH, K⁺, Na⁺, and NH₄⁺, might lead to a reduction of water evaporation due to water slowly released even immobilized.

Furthermore, the DCMC materials were biodegradable. The degraded membrane materials could provide a carbon source and some nutrients such as K⁺, Na⁺, and NH₄⁺ which would be returned to the soil and help improve the soil microenvironment and promote the number expansion of microorganisms and crop growth. The mechanism of film formation, water retention, and growth promotion is shown in Figure 10. The three DCMC materials might act as a new type of water-retaining materials with the advantage of being biodegradable, environmental-friendly, and pollution-free. Simultaneously, this research might provide a new idea and method for transforming straw resources into a series of spray film materials.

4. Conclusions

Three DCMC materials of CMC-Na, CMC-K, and CMC-NH₄ were developed from cotton straw. All of them could form a film after being sprayed on the soil to prevent soil water from evaporation effectively and increase the soil water holding capacity and water retention rate, leading to
a remarkable effect of improving soil moisture. The water retention property of the three DCMC materials was related to the film thickness and film-forming process which was linked to the viscosity. In general, at a concentration range of 0.05%-2.00%, the higher the spray amount was, the larger the film thickness was, and the better the water retention effect was. Among the three DCMC materials, CMC-K had the highest viscosity, the best film-forming property, and the best water retention effect, followed by CMC-NH 4. All DCMC materials could be degradable to promote growth of soil microorganisms and increase corn yield. Therefore, the CMC material based on crop straw modification might be an environmentally friendly approach for water retention in arid areas and has a broad application prospect in the field of high value-added utilization of crop straws.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare no conflict of interest.

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References


