Performance of a bioreactor using HCC fillers for sewage treatment

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Abstract: The experiments prepared bio-fillers using corn cobs as raw materials. Heat modification was identified as the optimal method by comparing the physical and chemical properties (roughness, porosity, water immersion stability, and compressive strength) of unmodified, acid modified, alkali modified, and heat modified corn cobs. Subsequently, the heat modification conditions were optimized, and the heat-treated corn cob (HCC) was utilized in a laboratory-scale A/O bio-contact oxidation device to observe the removal efficiency of pollutants while also assessing the lifespan of HCC. The results demonstrated that the roughness, water immersion stability, and porosity of HCC were superior to those of corn cobs treated with the other three methods. The compressive strength of HCC prepared under optimal heat modification conditions (260 ± 5°C for 50 minutes) ranged from 0.92 to 0.99 MPa, with porosity reaching up to 52.03%. Under the conditions of an influent flow rate of 200 L/d, a reflux ratio of 1, an aeration volume of 0.2 m^3/h, and a sludge retention time of 15 days, the average removal rates of COD, TN, NH_4^+-N, and TP from domestic sewage were 90.1%, 72.76%, 89.57%, and 55.50%, respectively. The effluent could be used for agricultural irrigation. The lifespan assessment indicated that HCC fillers could be used for up to 12 months. In summary, corn cobs served as effective fillers for the treatment of rural sewage.

Keywords: Heat-treated corn cob fillers, Heat modification, Sewage treatment, Pollutants removal efficiency

Introduction

As global water scarcity becomes increasingly severe, research and application of sewage treatment and reuse technologies are becoming more critical. The biofilm technology is a common technology used in sewage treatment and reuse, where the filler acts as a carrier for the biofilm, playing a key role[1]. Fillers can be classified into inorganic and organic fillers based on their source and properties [2, 3]. Inorganic fillers primarily include ceramsite and zeolites [4-6]. Ceramsite fillers have good hydrophilicity and large specific surface area, which is conducive to the attachment and growth of microorganisms. However, their production cost is high, and the manufacturing process is complex. Moreover, the regulations of China limit the exploitation and use of clay resources. Similarly, the use of zeolite as a filler is constrained by the limited mineral reserves.

Organic fillers include plastic-based fillers such as Pall rings, polyethylene balls, woodor coal-based activated biochar filler, and biofillers made from agricultural waste (such as straw and fruit shells) [7-9]. However, plastic fillers have poor hydrophilicity, which is not conducive to microbial attachment. The production of activated biochar filler consumes resources, whereas biofillers made from agricultural waste not only have good biodegradability and adsorption properties, but they also effectively remove organic pollutants from sewage. They offer advantages such as resource conservation and the use of solid waste to treat wastewater. Previous studies have shown that corncob has strong mechanical strength and a porous structure[10], making it a potential biofiller. However, most research in water treatment has focused on using corncob as an adsorbent or as a carbon source, with few studies directly using corncob as a biofiller after simple treatment[11-16]. Additionally, in rural areas, most domestic sewage is treated using the biofilm method, but the fillers used are often commercial products like polyurethane sponges or polyethylene balls, which are not economically feasible for rural sewage treatment. At the same time, most corn cobs in rural areas are either burned or directly discarded[17, 18], which not only wastes resources but also pollutes the environment[19]. To address this situation, the experiment considered using corn cobs as a filler in domestic sewage treatment devices, aiming to solve the difficulty of underutilization of corn cobs while providing a method to improve the low treatment rate of rural domestic sewage.

However, corn cobs are not sufficiently biostable and chemically stable due to the presence of soluble organic matter. Therefore, corn cobs were placed in tap water for soaking prior to modification. The corn cobs after drying were treated with modification to further improve these properties. By comparing the physical and chemical properties of four corn cobs treated with heat, acid, alkali, and pure water, it was experimentally found that heat modification is the most effective modification method. Subsequent experiments were conducted to optimize the heat modification conditions. Finally, the pollutants removal effect was observed, and the life of the fillers was evaluated in the application of HCC in the biological contact oxidation reactor, providing reference for promotion and application.

Materials and methods

Sewage and corn cobs

The Sewage was campus sewage from Lanzhou Jiaotong University, with the following water quality characteristics: COD: 176.3-423.1 mg/L, NH_4^+-N: 29.3-89.9 mg/L, TN: 37.2-80.8 mg/L, TP: 2.0-10.9 mg/L, SS: 127-248.9 mg/L. The influent has the characteristics of large fluctuations in water quality similar to that of rural sewage.

The corn cobs, from which the kernels have been removed, were obtained from a farmer's household in Wuwei, Gansu Province.

Setup description

The domestic sewage treatment system utilized an integrated A/O biological contact oxidation device (as shown in Fig 1a). The reactor was constructed from rigid PVC plastic boards, measuring 1.5 m in length, 1.4 m in width, and 1.5 m in height. Sewage passed sequentially through a primary sedimentation zone (0.3 m in length, 0.3 m in width, and an effective height of 0.65 m), an anoxic zone (0.2 m in length, 0.3 m in width, and an effective height of 1 m), an aerobic zone (0.4 m in length, 0.5 m in width, and an effective height of 1 m), and a secondary sedimentation zone (0.52 m in length, 0.52 m in width, and an effective height of 0.55 m). A packing rack (dimensions 0.47 m × 0.38 m × 0.9 m) made of PVC suspended with strings of HCC were placed in the aerobic zone, where the spacing between each string of HCC was 6 cm. Additionally, a string of movable HCC packing was placed to facilitate sampling and observation of the filler and biofilm during the experiment (see Fig 1b).

Fig 1. Apparatus and fillers

Modification methods of corn cobs

Pretreatment methods: corn cobs with a radius of 1.6-1.8 cm were sliced into half-cylinders measuring 2-2.5 cm in length. Subsequently, the corn cobs were perforated, cleaned with tap water, soaked for 24 hours, and finally dried at 80°C.

Modification methods: Acid modification, where they were soaked in a 1.5% H_2SO_4 solution for 24 hours; Alkali modification, where they were soaked in a 1.5% NaOH solution for 24 hours; and Heat modification, where they were heated in a muffle furnace at a set temperature for 50 minutes. All three of the above modification treatments used pretreated corn cobs. The modified corn cobs were rinsed with deionized water to remove residual H_2SO_4, NaOH, or ash, and then dried in an 80°C oven.

Physiochemical analysis

Porosity (p) was measured using the gravimetric method, calculated by dividing the pore volume by the total volume of the corncob[20, 21]. The formula for p was as follows:

$$p = \frac{m_1 - m_0}{\rho \cdot V} \times 100\%$$

where m_1 is the mass of the corn cobs in the fully wetted state, m_0 is the mass of the corn cobs after water had been removed from the pores post-leaching, ρ is the density of water, V is the total volume of the corn cobs in the fully wetted state.

The stability of the corn cobs in water leaching was analyzed by determining the COD_{Cr} concentration in the leachate[22, 23]. The compressive strength tester was utilized to measure the compressive strength of the filler. The surface characterization of corn cobs was observed by scanning electron microscopy (SEM). The darkness depth of modification in heat modified corn cobs was measured using a scale-measurement method.

Sample analyses

Influent and effluent samples were collected every two days for water quality analysis. COD was determined using the potassium dichromate colorimetric method; TN was determined via the persulfate oxidation-UV spectrophotometric method; NH_4^+-N was measured using the Nessler reagent method; TP was analyzed using the molybdenum-antimony method; pH and DO were measured with a direct-reading instrument (HACH HQ30d). COD and TN concentrations and absorbances were measured using the HACH DR5000 water quality analyzer, while NH_4^+-N and TP absorbances were determined using an INESA 721G visible spectrophotometer.

Results and discussion

Comparison of the physical properties

In the actual operation of biological fillers, compressive strength is crucial for assessing the durability of the filler, while microbial attachment is influenced by porosity. Consequently, both compressive strength and porosity serve as indirect indicators of the effectiveness of the modification method. Table 1 illustrates the measurement results of the compressive strength and porosity of corn cobs modified by pure water, acid and alkali modified for 24 h and modified at 260±5 °C for 50 min.

Table 1. Physical properties of four corn cobs

Modification method	Unmodifi-ed	acid modification	alkali modification	heat modification
Compressive strength (MPa)	＞1.88	0.50 ~0.53	0.25~0.35	0.92~0.99
Porosity	45.74%	47.31%	49.38%	52.03%

Table 1 indicates that the compressive strength of unmodified corn cob exceeds 1.88 MPa, with a porosity of 45.74%. The high compressive strength of unmodified corn cob can be attributed to its high content of lignin, cellulose, and hemicellulose [24], which are crosslinked, contributing to the material's impressive compressive capacity. In contrast, the compressive strength of acid modified, alkali modified, and heat modified corn cobs ranges from 0.50 to 0.53 MPa, 0.25 to 0.35 MPa, and 0.92 to 0.99 MPa, respectively, while their respective porosities are 47.31%, 49.38%, and 52.03%.It is evident that the compressive strengths of all three modified corn cobs are lower than that of the unmodified variety, but their porosities are higher. This observation demonstrates that three modification treatments disrupts the structural integrity of the corn cob to some degree, leading to reduced compressive strength simultaneously increased porosity. This phenomenon can be explained by the fact that the various treatments partially decompose cellulose, hemicellulose, and lignin, thereby impairing the cross-linking structure of cellulose-based molecules[25].

Additionally, these changes may be influenced by the dissolution and decomposition of chemical constituents. For instance, Acids and bases hydrolyze some of the hemicellulose and lignin in the corn cob into soluble organic matter. These organics dissolve in solution thereby exposing more cellulose surfaces in the corn cob and increasing porosity. In addition, alkali modification breaks the hydrogen bonds between cellulose molecules and causes the cellulose molecules to rearrange themselves, thus forming a porous material and thus increasing porosity. At temperatures ranging from 200 to 300 °C, cellulose begins to pyrolyze, leading to the production of bio-oil and dehydrated sugars. Simultaneously, the pyrolysis of cellulose generates carbonization intermediates, which further enhance porosity[26, 27]. In conclusion, the order of the compressive strength of corn cob after different modification treatments was as follows: unmodified > heat modified > acid modified > alkali modified. The order of porosity was heat modification > alkali modification > acid modification > unmodified. In terms of compressive strength and porosity, it seems that heat-modified corn cobs are more suitable for use as biological fillers.

Comparison of water immersion stability

The immersion stability of the filler is to judge the chemical stability after it is put into the water. The higher immersion stability, the more stable the performance of chemical stability in water. The immersion stability of biofilters is usually examined by the release of COD under static conditions[22, 23]. The release of COD from corn cobs treated with different modification methods under static conditions is shown in Fig 2.

Fig 2. Water immersion stability of corn cobs under different conditions

The results presented in Fig 2 indicate that all four types of corn cobs released COD into the water at the outset of the experiment. Alkali modified corn cobs exhibited the highest rate of carbon release, which began to slow after 48 hours, ultimately reaching 227.69 mg/L after 120 hours; however, there was no indication of stabilization. The carbon release rates for unmodified and acid modified corn cobs were comparable, with carbon concentrations measured at 74.83 mg/L and 74.90 mg/L, respectively, after 120 hours. In contrast, heat modified corn cobs displayed the slowest carbon release rate, achieving a COD concentration that began to stabilize after 72 hours, with a final carbon release of only 50.12 mg/L at 120 hours.

These observations demonstrate that the soluble organic substances in the four types of corn cobs dissolve in water, leading to an increase in COD levels. As these soluble organic materials gradually dissolve, resulting in a stabilization of COD concentration in the water. The reasons for the different water immersion stability of the three corncobs may be as follows: during the alkali modification process, the OH^- of NaOH break the ether bonds of the lignin in the corncobs, and at the same time dissolve the ester bonds between the lignin and hemicellulose[28, 29]. In addition to this Kathirselvam et al. found that the carboxyl group of hemicellulose disappeared after alkali modification[30]. The above shows that alkali modification hydrolyzes cellulose through various reactions, which in turn produces a large amount of soluble organic matter. These soluble organic matters are partially dissolved in the alkali solution, and the undissolved organic matter could dissolve in water when the corn cob is placed in deionized water. Acid modification mainly destroys the connection between lignin and cellulose, dissolves part of hemicellulose and the hydroxyl part of cellulose[31], and the degree of hydrolysis of biomass is weaker than that of alkali modification, so its water immersion stability is higher than that of alkali modification[32, 33].In the case of thermal modification, some biomass within the corn cob is either carbonized or converted into gaseous products like carbon dioxide, resulting in the lowest carbon release and the highest stability during immersion in water[27, 34].

In summary, among the four types of corn cobs, thermally modified corn cobs demonstrated the slowest carbon release rate and the least carbon release overall. This finding indicates that thermally modified corn cobs possess the highest stability during water immersion among the four variants. Therefore, thermally modified corn cob appears to be the most suitable candidate for use as a biofiller with respect to water immersion stability.

SEM analysis

The roughness of the biofiller is an important factor influencing the attachment of microorganisms. SEM images of corn cobs modified under different conditions are presented in Fig 3.

Fig 3. SEM images of different modified corn cobs

Fig 3 shows that the roughness of the four types of corn cobs ranks as follows: heat-modified > alkali modified > acid modified > unmodified. SEM images at 50x magnification reveal that unmodified corn cobs exhibit numerous whisker-like substances on the surface, characterized by relatively low roughness and the absence of obvious pores. Acid modified corn cobs display fewer whisker-like substances, with a significant increase in roughness, although no noticeable pores are present. Alkali modified corn cobs also contain fewer whisker-like substances compared to unmodified corn cobs, but their roughness is lower and does not feature large pores. In contrast, heat-modified corn cobs lack whisker-like substances on the surface and exhibit significantly increased roughness along with numerous visible pores.

Further examination of SEM images at 5000x magnification reveals that heat-modified corn cobs have a much rougher surface structure and more regular pores than the other types of corn cobs. This enhances the surface area and the number of adsorption sites, providing favorable conditions for microbial attachment, thus making heat-modified corn cobs more suitable as biofilters[35].

Fig 3i and 3j depicts the roughness of HCC fillers after 12 months of use in a biological reactor. It is evident that the surface of the HCC fillers is covered with dried microbial bodies after this duration, indicating that HCC fillers offer an excellent habitat for microbial growth.

Initial selection of heat treatment conditions

Previous studies have demonstrated that corn cobs undergo pyrolysis at temperatures ranging from 130 to 260℃, leading to change in the biomass of it. The pyrolysis process becomes more intense when the temperature rises to between 260 and 400℃[36, 37]. Consequently, the initial range of heat modification temperatures was established between 120 and 300℃, with the modification duration varying from 20 to 60 minutes. The results are presented in Table 2.

Table 2. Apparent properties of HCC fillers under different heat modification condi-tions

Duration （min）	Temperature（℃）									
	120	140	160	180	200	220	240	260	280	300
20	N	N	N	N	N	N	N	N	N	M
25	N	N	N	N	N	N	N	N	B	C
30	N	N	N	N	N	N	N	N	B	C
35	N	N	N	N	N	N	N	B	B	C
40	N	N	N	N	N	N	N	B	M	C
45	N	N	N	N	N	N	B	B	M	C
50	N	N	N	N	N	N	B	M	C	C
55	N	N	N	N	B	B	M	M	C	C

60	N	N	N	B	B	B	M	M	C	C

Note: N in the Table 2 is the abbreviation of none, which represents that there is basically no change in the HCC filler. B is the abbreviation of begin, which represents that the HCC filler starts to carbonize. M is the abbreviation of middle, which represents that the HCC filler has a moderate degree of carbonization. and C is the abbreviation of complete, which represents that the HCC filler is completely carbonized or in the form of ash.

Table 2 demonstrates that the appearance of the corn cobs exhibited minimal changes at temperatures below 160℃, with heating durations of 20 to 60 minutes, indicating a limited effect of the heat treatment. However, the charring rate increased significantly when the temperature exceeded 300℃, and the corn cobs were fully carbonized after being heated for more than 20 minutes. No noticeable charring occurred during heating, within the temperature range of 120 to 220℃ and for a duration of 20 to 60 minutes. Therefore, temperatures of 240 ± 5℃, 260 ± 5℃, 280 ± 5℃, and 300 ± 5℃ were selected for further heat treatment. The degree of carbonization was preliminarily assessed by observing the color change of the corn cobs, as shown in Fig 4.

Fig 4. Comparison of carbonization of HCC fillers under different heat modification conditions

From Fig 4, it is evident that the corn cobs do not exhibit significant carbonization when the temperature is between 240°C and 280°C, and the modification duration ranges from 20 to 30 minutes. However, when the temperature reaches 300°C and the modification duration exceeds 30 minutes, the HCC fillers become fully carbonized, transforming into fragile ash. This can also indicate that the mass (m_0) decreases due to the partial carbonization of the corn cob surface into ash, which is also one of the reasons for the increase of the apparent porosity of HCC. Based on these results, the heat modification temperature was narrowed to between 240°C and 280°C, and the modification duration was set to between 30 and 60 minutes for further optimization.

Optimization of heat treatment conditions

Based on the initial experimental results, the optimized heat treatment conditions were established with a heating temperature between 240°C and 280°C, and a heating duration of 30 to 60 minutes. The carbonization depth, compressive strength, porosity, and water immersion stability of the HCC fillers were carefully examined under these conditions.

Effect of temperature and duration

As shown in Table 3, significant differences were observed in the carbonization depth of corn cobs treated at different temperatures when the heating duration was set to 50 to 60 minutes. The carbonization depth reached 1.7 cm, resulting in nearly complete carbonization when the heating duration reached 60 minutes at a temperature of 280±5°C, which made the corn cobs fragile and reduced their compressive strength to an unsuitable level for biofilter use.Therefore, the physical properties (compressive strength, porosity, carbonization depth) and water immersion stability were further tested in subsequent experiments at temperatures of 240 ± 5°C, 260 ± 5°C, and 280 ± 5°C, with a fixed modification duration of 50 minutes.

Table 3. Variation of carbonization thickness of HCC fillers

Duration （min）	Temperature (℃)	Carbonization Depth (cm)
30	240	0
	260	0.3
	280	0.8
40	240	0.3
	260	0.5
	280	1.1
50	240	0.4
	260	0.7
	280	1.4
60	240	0.6
	260	0.8
	280	1.7

Comparison of compressive strength and porosity of HCC

The compressive strength and porosity of HCC filler modified for 50 minutes at different thermal modification temperatures are shown in Table 4.

Table 4. Compressive strength and porosity of corncob at different modification tem-peratures

Modification temperature	240±5℃	260±5℃	280±5℃
ompressive strength (Mpa)	1.02~1.07	0.92~0.99	0.11~0.13
Porosity	50.34%	52.03%	55.49%

Table 4 demonstrate that the compressive strength of HCC was measured to be 1.02~1.07, 0.92~0.99, and 0.11~0.13 MPa, and the porosity was 50.34%, 52.03%, and 55.49% at the modification duration of 50 min and heat treatment temperatures of 240±5°C, 260±5°C, and 280±5°C, respectively. The results indicate that heating temperature affects both compressive strength and porosity. As the temperature increases, the porosity of the corn cobs rises, while the compressive strength decreases. Specifically, the porosity rises from 50.34% to 52.03%, while the compressive strength declines from 1.02-1.07 MPa to 0.92-0.99 MPa when the temperature increases from 240±5℃ to 260±5℃, which remains acceptable. However, when the temperature is further raised to 280±5℃, the porosity increases to 55.49%, but the compressive strength decreases significantly to 0.11-0.13 MPa, rendering the HCC filler too weak to function as a biological filler. The decrease in compressive strength at higher temperatures is likely attributed to the increased heat decomposition and carbonization of cellulose, hemicellulose, and lignin.

Comparison of water immersion stability of HCC fillers

The water immersion stability of HCC fillers modified at different temperatures is shown in Fig 5.

Fig 5. Rate of COD release from corncob at different modification temperatures

Fig 5 shows that after soaking for 120 hours, the released CODcr concentrations of corn cobs modified at 240±5°C, 260±5°C, and 280±5°C were 91.23 mg/L, 42.35 mg/L, and 43.18 mg/L, respectively. This indicates that higher temperatures lead to stronger water immersion stability. After heating the corn cobs for 50 minutes at 260±5°C and 280±5°C, the water immersion stability of the HCC filler was similar and performed well. This is likely because the increased temperature caused most of the biomass within the corn cobs to be charred or converted into gases such as CO_2, resulting in a reduced soluble organic carbon content. Consequently, this decreased the amount and rate of organic matter released after soaking, thereby enhancing the immersion stability of the corn cobs[38-40]. While the water immersion stability of corn cobs modified at 260±5°C and 280±5°C is similar, the compressive strength of those modified at 260±5°C is significantly greater. Furthermore, the energy consumption for modification at 260±5°C is lower than that at 280±5°C. Based on the comparison of the physical and chemical properties of HCC fillers under different heat modification conditions, the optimal heat modification conditions were determined to be 260±5°C for 50 minutes.

Performance of reactor

COD and BOD_5 removal

Under the conditions of an influent flow rate of 200 L/d, a reflux ratio of 1, an aeration volume of 0.2 m³/h, and a sludge retention time of 15 days, and an aeration rate of q = 0.2 m³/h, the removal efficiencies of COD and BOD_5 in the reactor are presented in Fig 6.

Fig 6. Removal effects of the HCC reactor on (a) COD, (b) BOD

Fig 6a shows that the influent COD ranged from 249.3 to 312.4 mg/L, with an average value of 282.7 mg/L over the course of 20 days of operation. The effluent COD remained stable, varying between 22.7 and 34.3 mg/L, with an average of 27.91 mg/L, corresponding to an average COD removal efficiency of 90.1%. The water quality achieved the outlined in Gansu Province's Discharge Standard of Water Pollutants for Rural Domestic Sewage Treatment Facilities (DB62/T 4014-2019, firstly standard). Thus, the A/O biological contact oxidation reactor utilizing HCC fillers demonstrated good COD removal efficiency.

Fig 6b illustrates the BOD_5 removal efficiency of the reactor. The influent BOD_5 concentration ranged from 150.1 to 172.5 mg/L, with an average value of 168.65 mg/L. Despite fluctuations in influent water quality, the effluent BOD_5 concentration remained stable, ranging between 4.32 and 6.19 mg/L, corresponding to an average BOD_5/COD ratio of 0.20, representing a 66.1% reduction compared to the influent ratio of 0.59. This indicates that the reactor performs well in removing biodegradable organic matter.

Nitrogen and phosphorus removal

Under the conditions of an influent flow rate of 200 L/d, a reflux ratio of 1, an aeration volume of 0.2 m³/h, and a sludge retention time of 15 days, and an aeration rate of q = 0.2 m³/h, the removal efficiencies of NH_4^+-N, TN, and TP in the reactor are presented in Fig 7.

Fig 7. Removal effects of the HCC reactor on (a) NH_4^+-N, (b) TN, and (c) TP

The removal efficiency of NH_4^+-N in the reactor is illustrated in Fig 7a. The influent NH_4^+-N concentration fluctuated between 42.9 and 56.38 mg/L, with an average of 49.93 mg/L, while the effluent NH_4^+-N concentration ranged from 3.37 to 6.55 mg/L, with an average of 5.13 mg/L, which achieved the Level 1 standard of Gansu Province. During stable operation, the NH_4^+-N removal efficiency remained consistent, ranging from 84.73% to 94.02%, with an average of 89.57%. This demonstrates that the A/O biological contact oxidation reactor utilizing HCC fillers effectively removes NH_4^+-N. This means that the roughness and porosity of HCC fillers can provide a good growth environment for nitrifying bacteria and ensure sufficient microbial biomass, which promotes the efficient operation of the reactor.

Fig 7b shows the TN removal efficiency during stable reactor operation. The influent TN concentration fluctuated between 50.28 and 59.25 mg/L, with an average of 55.22 mg/L, while the effluent TN concentration ranged from 13.97 to 17.31 mg/L, with an average of 15.03 mg/L, which achieved the Level 1 standard of Gansu Province. The TN removal efficiency varied from 69.91% to 74.92%, with an average of 72.76%, indicating that the A/O biological contact oxidation reactor utilizing HCC fillers achieves stable and efficient TN removal under the given conditions.

As shown in Fig 7c, the influent TP concentration ranged from 5.72 to 6.66 mg/L, with an average of 6.05 mg/L, while the effluent TP concentration ranged from 2.43 to 2.88 mg/L, with an average of 2.69 mg/L. The TP removal efficiency ranged from 53.05% to 60.96%, with an average of 55.50%, The water quality achieved the Level 2 standard of Gansu Province. If the effluent TP concentration is needed to meet the Level1 standard, additional chemical phosphorus removal will be required.

Service life of HCC fillers

Fig 8 illustrates the changes in compressive strength of the HCC fillers over a 16-month period, from the initial start-up of the biological reactor until the conclusion of the experiment. Data collection was interrupted during months 13 and 14 due to COVID-19.

The compressive strength of the HCC fillers gradually decreased over time. In the first two months, the compressive strength was approximately 0.995 MPa. By the third month, it had significantly decreased, and by the fourth month, it further declined to 0.735 MPa. The decrease in compressive strength was particularly pronounced during the sixth and seventh months, dropping from 0.524 MPa to 0.260 MPa (a nearly 50% reduction). After the seventh month, the rate of decline slowed; by the twelfth month, the compressive strength had decreased to 0.068 MPa. Even at this point, microbial attachment on the filler surface remained intact, and the reactor continued to function normally. However, by the sixteenth month, the compressive strength had further declined to 0.0077 MPa, rendering the filler extremely fragile. Therefore, it is recommended that the HCC filler be replaced every 12 months to ensure the proper operation of the reactor. The decrease in compressive strength of the HCC may be attributed to the gradual decomposition of cellulose and hemicellulose within the modified corn cob by infiltrating bacteria [41].

Fig 8. Variation of compressive strength of HCC filler

Conclusion

Among the various modified corn cobs, heat modified corn cobs exhibited the best physical and chemical properties. The optimal heat modification conditions were determined to be a temperature of 260±5°C for 50 minutes. Under these conditions, the HCC displays good compressive strength, high porosity, and excellent water immersion stability, making it suitable for use as a biofilter. When the biological reactor operated under the conditions of an influent flow rate of 200 L/d, a reflux ratio of 1, an aeration volume of 0.2 m^3/h, and a sludge retention time of 15 days, and an aeration rate of q = 0.2 m^3/h, the effluent quality achieved the Level2 discharge standards outlined in Gansu Province's for COD, TN, NH_4^+-N, and TP. And the effluent was deemed suitable for agricultural irrigation. The HCC filler was able to operate stably for 12 months;

however, to maintain optimal performance in the reactor, it is recommended that the filler be replaced every 12 months. In summary, corn cob filler is suitable for the treatment of rural sewage. The use of corn cob as a biological filler for treating rural sewage offers advantages such as easy availability of materials, simple manufacturing processes, the use of solid waste to treat sewage, and resource utilization of treated sewage.

Acknowledgements

We would like to express our gratitude to all individuals and institutions that provided support and assistance for this research. Special thanks to the team members who contributed valuable insights throughout the study.

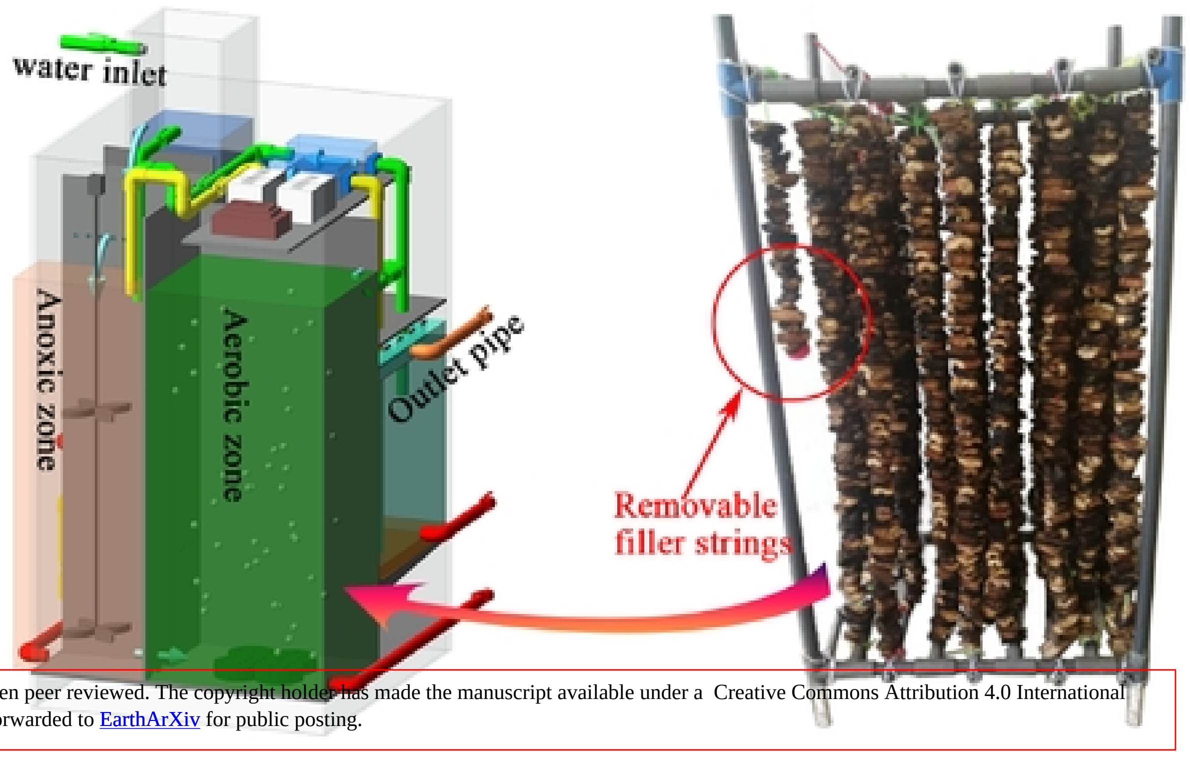
References

1. Lago A, Rocha V, Barros O, Silva B, Tavares T. Bacterial biofilm attachment to sustainable carriers as a clean-up strategy for wastewater treatment: A review. Journal of Water Process Engineering. 2024;63:105368. doi: 10.1016/j.jwpe.2024.105368.
2. Hirai M, Kamamoto M, Yani M, Shoda M. Comparison of the biological NH3 removal characteristics among four inorganic packing materials. Journal of Bioscience and Bioengineering. 2001;91(4):428-30. doi: 10.1016/S1389-1723(01)80165-1.
3. Kim N-J, Hirai M, Shoda M. Comparison of organic and inorganic packing materials in the removal of ammonia gas in biofilters. Journal of Hazardous Materials. 2000;72(1):77-90. doi: 10.1016/S0304-3894(99)00160-0.
4. Chang W-S, Tran H-T, Park D-H, Zhang R-H, Ahn D-H. Ammonium nitrogen removal characteristics of zeolite media in a Biological Aerated Filter (BAF) for the treatment of textile wastewater. Journal of Industrial and Engineering Chemistry. 2009;15(4):524-8. doi: 10.1016/j.jiec.2009.01.009.
5. Cheng Y, Fan W, Guo L. Coking wastewater treatment using a magnetic porous ceramsite carrier. Separation and Purification Technology. 2014;130:167-72. doi: 10.1016/j.seppur.2014.04.030.
6. Ji X, Yang J, Xu L, Li B, Zhao C. A contrast experiment research on rural wastewater treatment efficiency of BAF with zeolite and zeolite-haydite combined packing. IOP Conference Series: Earth and Environmental Science. 2017;64(1):012075. doi: 10.1088/1755-1315/64/1/012075.

7. Singh H, Chauhan G, Jain AK, Sharma SK. Adsorptive potential of agricultural wastes for removal of dyes from aqueous solutions. Journal of Environmental Chemical Engineering. 2017;5(1):122-35. doi: 10.1016/j.jece.2016.11.030.
8. Maslowski M, Miedzianowska-Masłowska J, Strzelec K. The potential application of cereal straw as a bio-filler for elastomer composites. Polymer Bulletin. 2020;77(4):2021-38. doi: 10.1007/s00289-019-02848-2.
9. Li J, Li N, Liu F, Li Y. Development and Optimization of Bioretention Systems with Modified Fillers of Corn Straw Biochar. Water, Air, & Soil Pollution. 2021;232(9):383. doi: 10.1007/s11270-021-05330-w.
10. Zou Y, Fu J, Chen Z, Ren L. The effect of microstructure on mechanical properties of corn cob. Micron. 2021;146:103070. doi: 10.1016/j.micron.2021.103070.
11. Macêdo-Júnior RO, Campos WKS, Buarque FS, Serpa FS, Silva GF, Santos BLP, et al. Utilization of corncob as adsorbent to remove oil and grease from produced water. Petroleum Science and Technology. 2023;41(4):477-92. doi: 10.1080/10916466.2022.2060258.
12. Hien Tran T, Le AH, Pham TH, Duong LD, Nguyen XC, Nadda AK, et al. A sustainable, low-cost carbonaceous hydrochar adsorbent for methylene blue adsorption derived from corncobs. Environmental Research. 2022;212. doi: 10.1016/j.envres.2022.113178.
13. Li J, Feng Y, Qiu Y, Chen D, Liang D, Zhou J, et al. Recovery of electron and carbon source from agricultural waste corncob by microbial electrochemical system to enhance wastewater denitrification. Science of The Total Environment. 2023;878:162926. doi: 10.1016/j.scitotenv.2023.162926.
14. Liu J, Fu X, Yuan R, Chen Z, Zhou B, Chen H. Carbon sources derived from corncobs enhanced nitrogen removal in SBBR treating low C/N domestic sewage. Process Safety and Environmental Protection. 2022;166:628-37. doi: 10.1016/j.psep.2022.08.063.
15. Thamilselvi V, Radha KV. Silver Nanoparticle loaded corncob adsorbent for effluent treatment. Journal of Environmental Chemical Engineering. 2017;5(2):1843-54. doi: 10.1016/j.jece.2017.03.020.
16. Zou L, Xu J, Liu H, Zhou Z, Chen Y, Wang X, et al. The efficiency of enhanced nitrogen and phosphorus removal in a vertical flow constructed wetland using alkaline modified corn cobs as a carbon source. Environmental Technology & Innovation. 2024;35:103690. doi: 10.1016/j.eti.2024.103690.
17. Hao X, Xu F, Zhang J. Effect of pretreatments on production of xylooligosaccharides and monosaccharides from corncob by a two-step hydrolysis. Carbohydrate Polymers. 2022;285:119217. doi: 10.1016/j.carbpol.2022.119217.
18. Wang B, Dong F, Chen M, Zhu J, Tan J, Fu X, et al. Advances in Recycling and Utilization of Agricultural Wastes in China: Based on Environmental Risk, Crucial Pathways, Influencing Factors, Policy Mechanism. Procedia Environmental Sciences. 2016;31:12-7. doi: 10.1016/j.proenv.2016.02.002.
19. Elegbede JA, Ajayi VA, Lateef A. Microbial valorization of corncob: Novel route for biotechnological products for sustainable bioeconomy. Environmental Technology & Innovation. 2021;24:102073. doi: 10.1016/j.eti.2021.102073.

20. Dacewicz E, Grzybowska-Pietras J. Polyurethane Foams for Domestic Sewage Treatment. Materials [Internet]. 2021; 14(4):[933 p.].
21. Yaya Beas RE, Kujawa-Roeleveld K, van Lier JB, Zeeman G. A downflow hanging sponge (DHS) reactor for faecal coliform removal from an upflow anaerobic sludge blanket (UASB) effluent. Water Sci Technol. 2015;72(11):2034-44. doi: 10.2166/wst.2015.427. PubMed PMID: 26606098.
22. Farnane M, Tounsadi H, Machrouhi A, Elhalil A, Mahjoubi FZ, Sadiq M, et al. Dye removal from aqueous solution by raw maize corncob and H3PO4 activated maize corncob. Journal of Water Reuse and Desalination. 2017;8(2):214-24. doi: 10.2166/wrd.2017.179.
23. Xu X, Wang Y, Chen P, Zhao T, Gong Z, Wang B, et al. Removal of NOx from flue gas using different agricultural wastes as carbon sources: Performance and microbial communities. Journal of Environmental Chemical Engineering. 2023;11(3):109804. doi: 10.1016/j.jece.2023.109804.
24. Leyva-Ramos R, Landin-Rodriguez LE, Leyva-Ramos S, Medellin-Castillo NA. Modification of corncob with citric acid to enhance its capacity for adsorbing cadmium(II) from water solution. Chemical Engineering Journal. 2012;180:113-20. doi: 10.1016/j.cej.2011.11.021.
25. Ma W, Zhou D, Zhong D, Li J, Zhang J, Su P, et al. Study of nitrogen removal efficiency of the filled bed reactors using alkali-treated corncobs-sulfur (mixotrophic) for treating the effluent from simulated urban wastewater plants. Bioresource Technology. 2022;349:126630. doi: 10.1016/j.biortech.2021.126630.
26. Jia Y, Zhang H, Gu T, Wu Y, Yang Z, Shao Y, et al. Denitrification in bioretention systems based on corncob biochar produced at low pyrolysis temperature: The efficacy and the mechanisms. Chemical Engineering Journal. 2023;460:141829. doi: 10.1016/j.cej.2023.141829.
27. Zhang C, Chao L, Zhang Z, Zhang L, Li Q, Fan H, et al. Pyrolysis of cellulose: Evolution of functionalities and structure of bio-char versus temperature. Renewable and Sustainable Energy Reviews. 2021;135:110416. doi: 10.1016/j.rser.2020.110416.
28. Fonseca-Correa R, Giraldo L, Moreno-Piraján JC. Trivalent chromium removal from aqueous solution with physically and chemically modified corncob waste. Journal of Analytical and Applied Pyrolysis. 2013;101:132-41. doi: 10.1016/j.jaap.2013.01.019.
29. Liu Y, Xie J, Wu N, Ma Y, Menon C, Tong J. Characterization of natural cellulose fiber from corn stalk waste subjected to different surface treatments. Cellulose. 2019;26(8):4707-19. doi: 10.1007/s10570-019-02429-6.
30. Kathirselvam M, Kumaravel A, Arthanarieswaran VP, Saravanakumar SS. Characterization of cellulose fibers in Thespesia populnea barks: Influence of alkali treatment. Carbohydrate Polymers. 2019;217:178-89. doi: 10.1016/j.carbpol.2019.04.063.
31. Pereira JF, Marim BM, Mali S. Chemical Modification of Cellulose Using a Green Route by Reactive Extrusion with Citric and Succinic Acids. Polysaccharides [Internet]. 2022; 3(1):[292-305 pp.].

32. Jung YH, Kim KH. Chapter 3 - Acidic Pretreatment. In: Pandey A, Negi S, Binod P, Larroche C, editors. Pretreatment of Biomass. Amsterdam: Elsevier; 2015. p. 27-50.
33. Tang J, Lin Z, Li W, Meng Z, Yang J. Effect of Pretreatment on Carbon Release Performance of Corncobs as a Solid Carbon Source. Water, Air, & Soil Pollution. 2023;234(9):570. doi: 10.1007/s11270-023-06564-6.
34. Ceranic M, Kosanic T, Djuranovic D, Kaludjerovic Z, Djuric S, Gojkovic P, et al. Experimental investigation of corn cob pyrolysis. Journal of Renewable and Sustainable Energy. 2016;8(6). doi: 10.1063/1.4966695.
35. Hou Y, Ma F, Fu Z, Li C, An Q, Zhu C, et al. Encapsulation of stearic-palmitic acid in alkali-activated coconut shell and corn cob biochar to optimize energy storage. Journal of Energy Storage. 2023;66:107418. doi: 10.1016/j.est.2023.107418.
36. Arenas Castiblanco E, Montoya JH, Rincón GV, Zapata-Benabithe Z, Gómez-Vásquez R, Camargo-Trillos DA. A new approach to obtain kinetic parameters of corn cob pyrolysis catalyzed with CaO and CaCO3. Heliyon. 2022;8(8):e10195. doi: 10.1016/j.heliyon.2022.e10195.
37. Klaas M, Greenhalf C, Ouadi M, Jahangiri H, Hornung A, Briens C, et al. The effect of torrefaction pre-treatment on the pyrolysis of corn cobs. Results in Engineering. 2020;7:100165. doi: 10.1016/j.rineng.2020.100165.
38. Long Y, Ma Y, Wan J, Wang Y, Tang M, Zheng Q, et al. Hydrolysate from the enzymatic treatment of corn cob as a carbon source for heterotrophic denitrification process. Journal of Water Process Engineering. 2023;51:103473. doi: 10.1016/j.jwpe.2022.103473.
39. Putranto A, Ng Z, Hadibarata T, Aziz M, Yeo J, Ismadji S, et al. Effects of pyrolysis temperature and impregnation ratio on adsorption kinetics and isotherm of methylene blue on corn cobs activated carbons. South African Journal of Chemical Engineering. 2022;42. doi: 10.1016/j.sajce.2022.07.008.
40. Sonu K, Sogani M, Syed Z, Dongre A, Sharma G. Enhanced Decolorization and Treatment of Textile Dye Wastewater Through Adsorption on Acid Modified Corncob Derived Biochar. ChemistrySelect. 2020;5(39):12287-97. doi: 10.1002/slct.202003156.
41. Zhang Y, Chen X, Gu Y, Zhou X. A physicochemical method for increasing methane production from rice straw: Extrusion combined with alkali pretreatment. Applied Energy. 2015;160:39-48. doi: 10.1016/j.apenergy.2015.09.011.



(a) Integrated A/O contact oxidation reactor

(b) Corn Cob Filler Racks

Fig 1. Apparatus and fillers

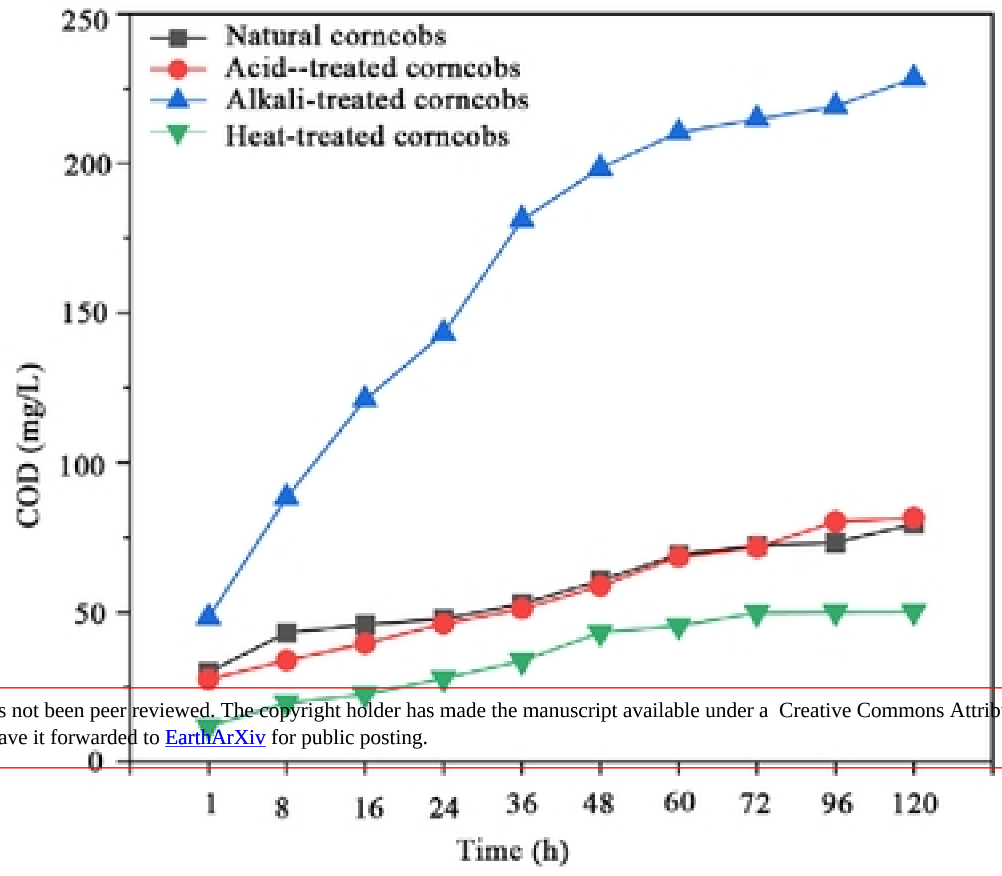


Fig 2. Water immersion stability of corn cobs under different conditions

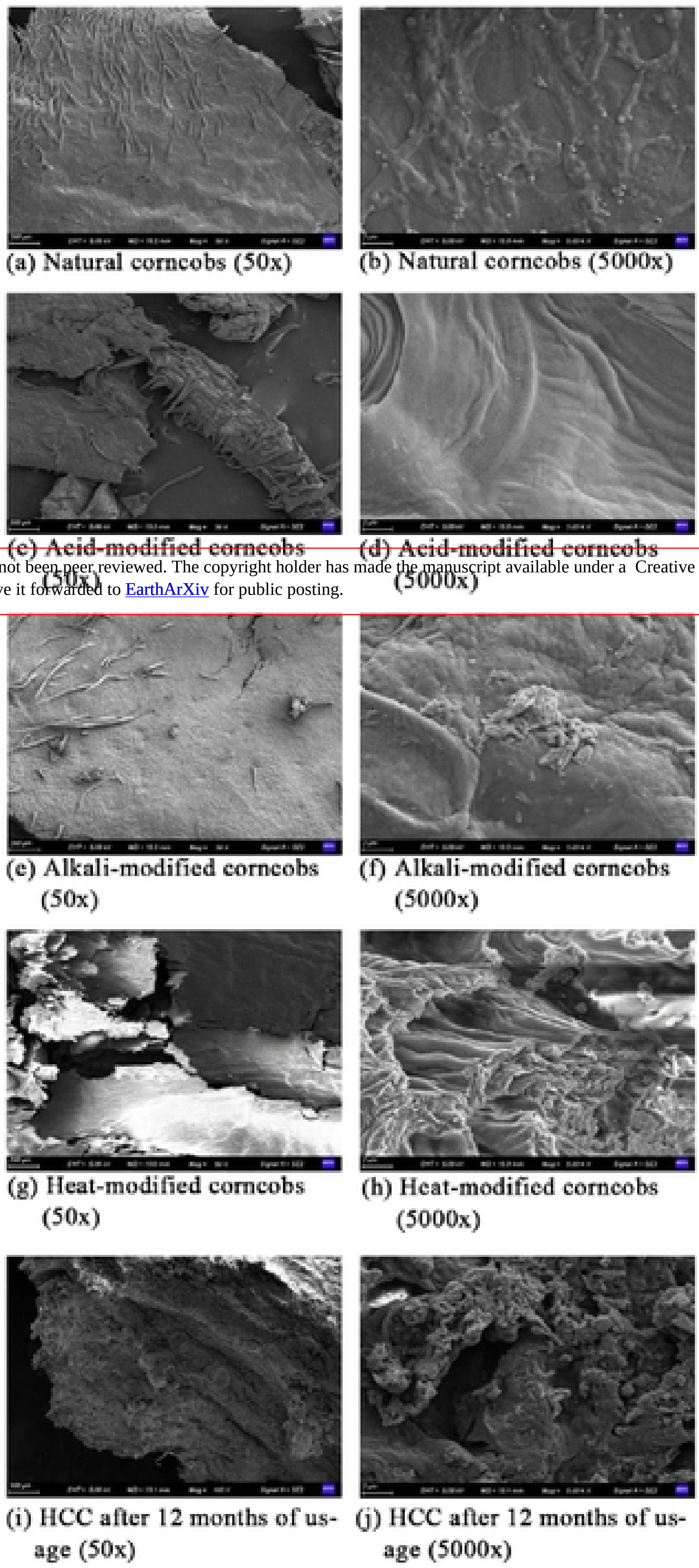


Fig 3. SEM images of different modified corn cobs

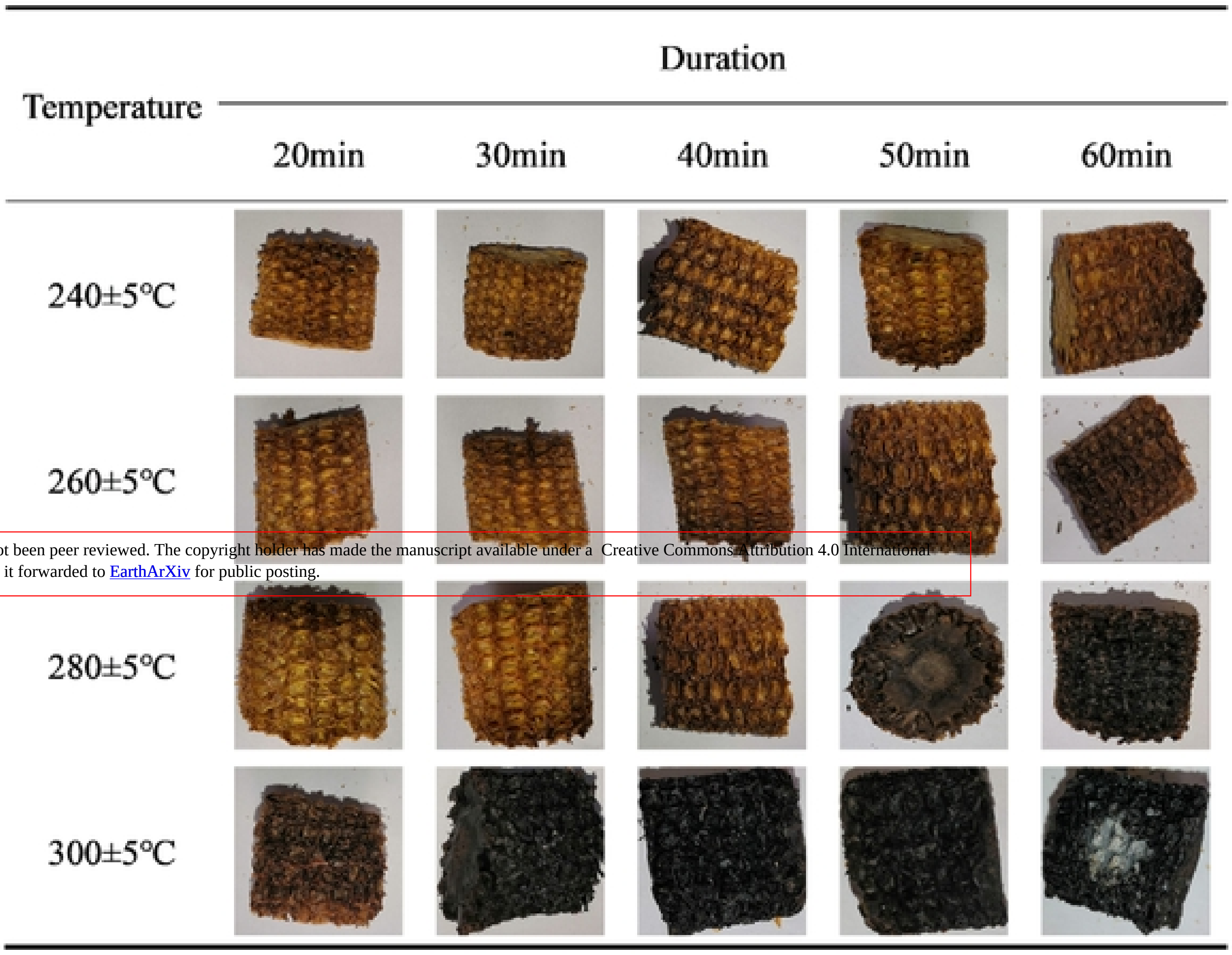


Fig 4. Comparison of carbonization of HCC fillers under different heat modification conditions

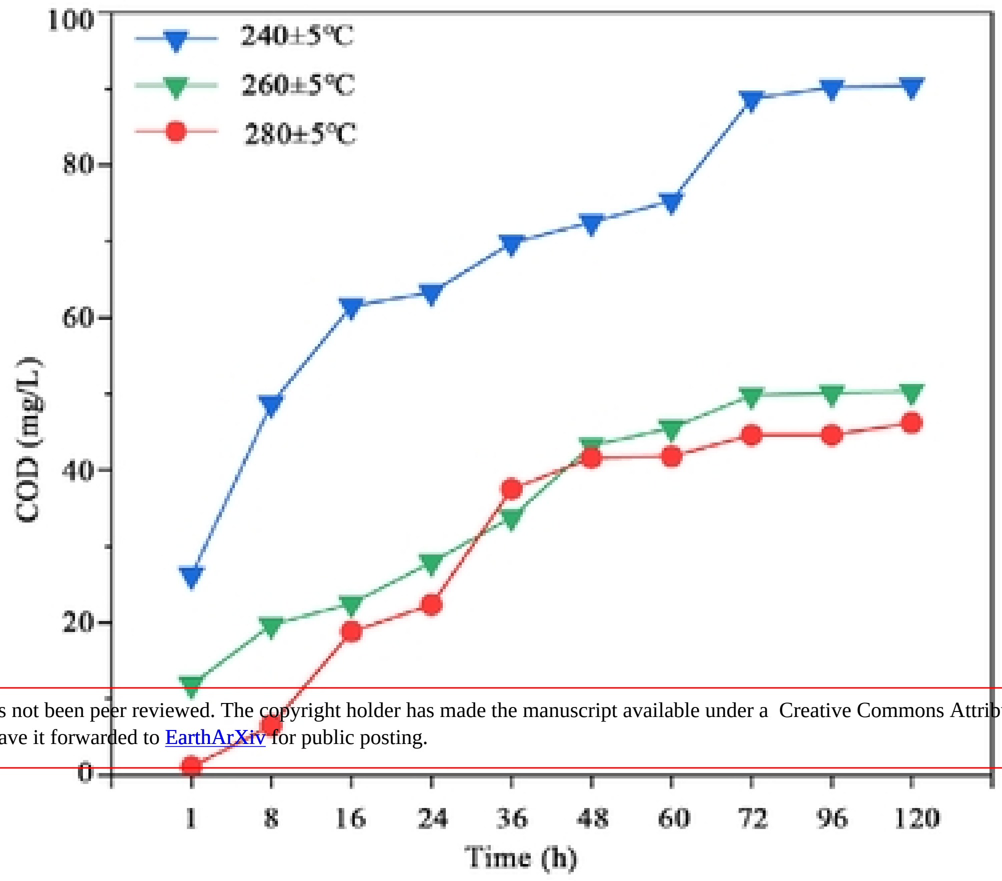


Fig 5. Rate of COD release from corncob at different modification temperatures

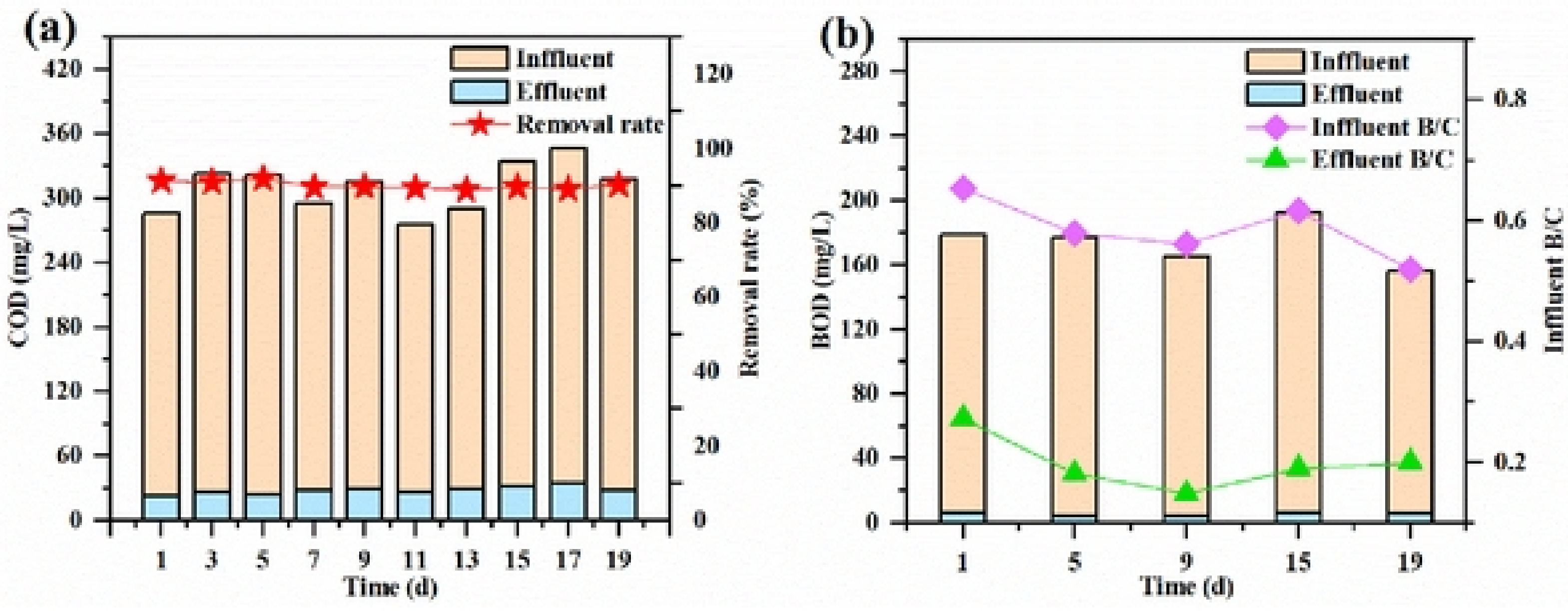


Fig 6. Removal effects of the HCC reactor on (a) COD, (b) BOD

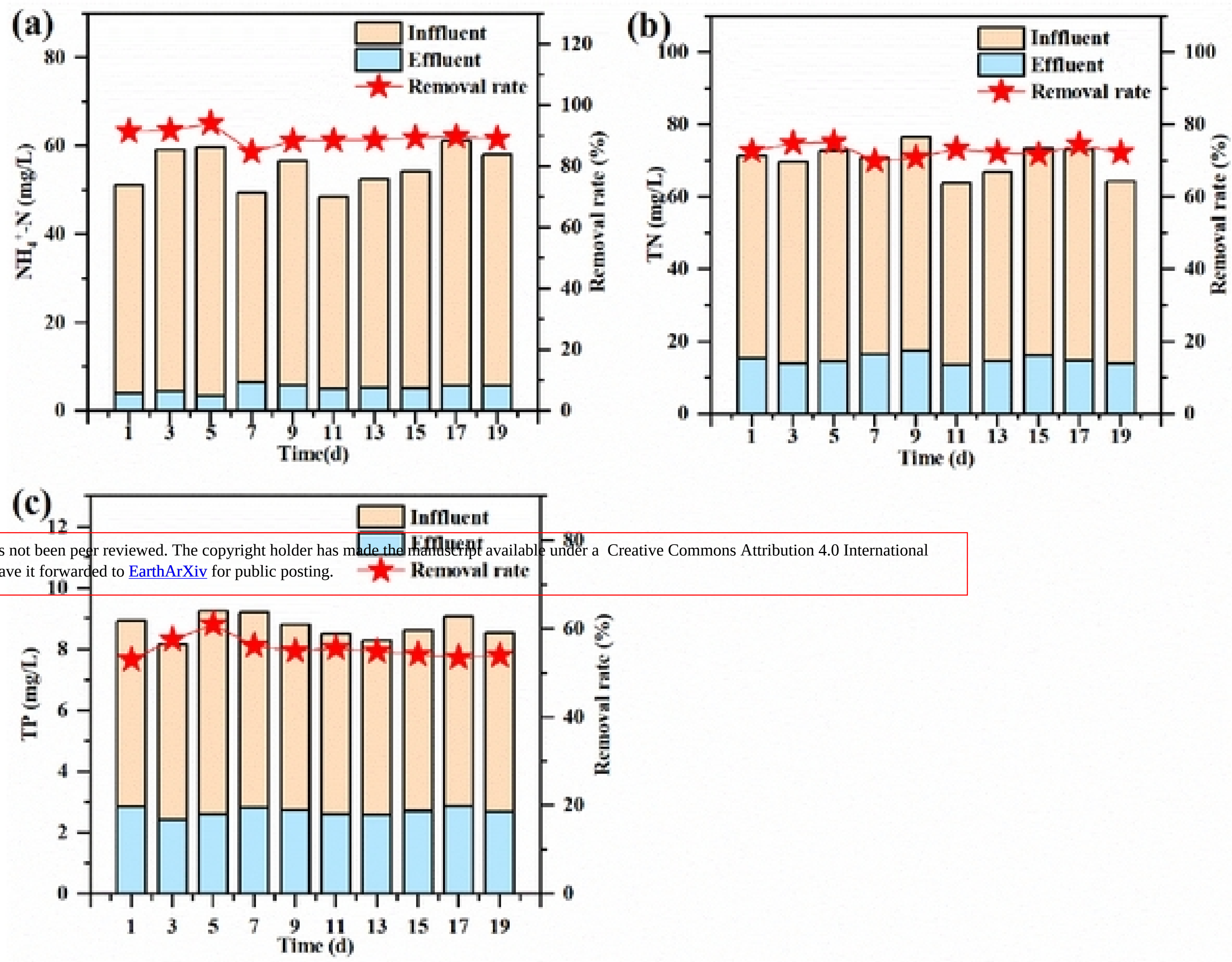


Fig 7. Removal effects of the HCC reactor on (a) NH_4^+-N, (b) TN, and (c) TP

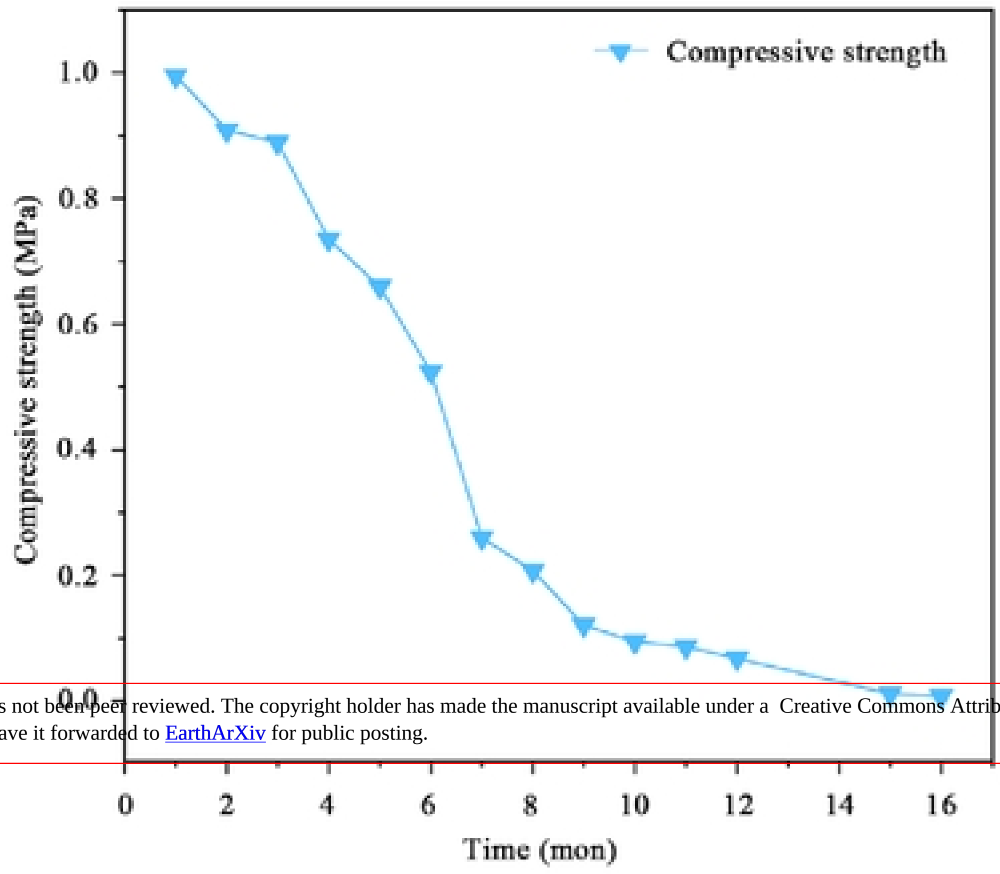


Fig 8. Variation of compressive strength of HCC filler