Application of Nanocellulose in Oilfield Chemistry

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ABSTRACT: The preparation and classification of nanocellulose are briefly introduced, and the modification of nanocellulose and the application of modified nanocellulose in oilfield chemistry are reviewed. The principles and methods of surface modification, including surface adsorption, oxidation, acetylation, silanization, etherification, and polymer grafting, are summarized. Meanwhile, this paper focuses on the application of nanocellulose research progress in drilling fluid, enhanced oil recovery, and oilfield sewage treatment. In addition, the application issues and natural advantages of nanocellulose are analyzed, and suggestions and ideas on how to expand its application are put forward. Finally, the development and potential application of nanocellulose in oilfield chemistry are proposed.

1. INTRODUCTION

With the increasing demand for oil and natural gas energy in recent years, the conventional oil and gas fields have been in their late stages of development, and the cost of exploitation is increasing every year. The unconventional development of oil and gas is limited by technology, resulting in difficult exploitation and low development efficiency.1,2 How to alter the development method and realize low-cost, green, and sustainable development are the primary challenges faced by the current oilfield development. Oilfield chemistry solves various problems in oilfield development by adding chemical agents to the fluid to change the performance of the fluid. Traditional oilfield chemicals have shortcomings in the formation of high temperature and high pressure, such as inactivation, large amount, pollution, and damage to the formation. Therefore, there is an urgent need for new materials with stable performance and environmental friendliness.

Cellulose is one of the most abundant natural biopolymer materials on earth.3–5 It is estimated that about 7.5 × 10^10 tons of cellulose are produced in the world every year.6,7 The physical properties of nanocellulose, including high strength and flexibility, are determined by its rigid rodlike crystal structure.8–9

With nanocellulose as a carrier, new functions are incorporated into nanocellulose through physical and chemical methods of modification. These functional nanomaterials have been widely used in energy, medical, food, and other fields.10,11

At present, the nanocellulose industry is developing rapidly, which has been gradually realizing industrialized production. Since 2015, the number of patent applications for nanocellulose has been increasing year by year. In the past 6 years, the application research of nanocellulose in drilling fluids, enhanced oil recovery, oilfield sewage treatment, etc. has developed rapidly (shown Table 1).

Table 1. Patent Distribution of Nanocellulose in Oilfield Chemistry

| Application Field       | Types of Nanocellulose | Types of Function                                      | Number of Patents |
|-------------------------|------------------------|--------------------------------------------------------|-------------------|
| Drilling Fluid          | CNF, CNC               | rheology modifier, fluid loss agent, plugging agent    | 24                |
| Enhanced Oil Recovery   | CNF, CNC               | stable foaming agent, stable emulsion agent,          | 34                |
| Oilfield Sewage         | CNF, CNC               | nano-oil-displacing agent, adsorbent                   | 56                |

Since there are issues of energy shortage and environmental pollution, nanocellulose, as a renewable, green, and environmentally friendly nanomaterial, has inherent advantages such as low density, degradability, less damage to the formation, and controllable structure. Therefore, it has very broad potential application in oilfield chemistry.

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Table 2. Classification of Nanocellulose

| sort                          | method of preparation   | sources                                  | diameter (nm) | length (nm) |
|-------------------------------|-------------------------|------------------------------------------|---------------|-------------|
| cellulose nanocrystalline (CNC) | chemical preparation    | microcrystalline cellulose, cotton, wood, etc. | 5−70          | 100−250     |
| cellulose nanofiber (CNF)      | physical preparation    | wood, sugar beet, cotton, etc.           | 5−60          | 1000−10 000 |
| bacterial nanocellulose (BNC)  | biological preparation  | Acetobacter xylinum, Acetobacter pasteurii, Azotobacter, etc. | 20−100        |             |

2. RESULTS AND DISCUSSION

Traditional oilfield chemical development technology restricts the sustainable development of petroleum. In the past, a large number of difficult-to-degrade, harmful, and formation-damaging chemical reagents were injected into the formation every year. These conventional chemicals have many issues, including poor adaptability, instability at high temperatures, difficulty to degrade, and polluting the formation. Therefore, high-performance, environmentally friendly, and nontoxic new materials, which meet the sustainable development requirements of future oilfield development, are urgently needed in the oilfields to replace traditional chemical reagents. As a new type of green and environmentally friendly degradable material with a wide range of sources, nanocellulose materials are favored by petroleum researchers since they meet the technical needs of the industry.

Nanocellulose can be applied to many areas in oilfield chemistry through modification, such as drilling fluid chemistry, oil production chemistry, gathering chemistry, etc. Currently, there are still many problems that need to be resolved. For example, production costs need to be further reduced; unmodified nanocellulose materials have poor stability under conditions with high mineralization ions and are easy to agglomerate; how to achieve redispersion of the nanocellulose in water after modification since some hydrophobic modification processes require organic solvents. However, the unique properties of nanocellulose and the environmentally friendly development methods of future oilfield transformation make nanocellulose a promising material for wide applications. Most oilfield developments are performed by water flooding. Because nanocellulose itself contains a large number of hydrophilic groups, it disperses well in water. In the future, nanocellulose materials need to be redispersed in water after modification and the usage of organic solvents should be reduced. By changing the means of modification, the integration of multiple functions, such as amphiphilicity, salt tolerance, etc., on the same nanocellulose material can be realized, which can let the nanocellulose be solely used as a nano-oil-displacing agent to enhance oil recovery (EOR). In addition, the rheological and mechanical properties of nanocellulose endow it with good application potentials in synergizing surfactants or polymers to increase oil recovery. With the advancement of the industrial preparation of nanocellulose, oilfield chemical products based on nanocellulose will appear on a large scale in the future.

3. PREPARATION AND CLASSIFICATION OF NANOCELLULOSE

Nanocellulose is rod-shaped cellulose with a diameter below 100 nm and length ranging from tens of nanometers to tens of microns. Two steps are required to obtain nanocellulose from biomass. First, the lignocellulosic material needs to be deconstructed and pretreated to obtain a cellulose product; second, the cellulose is further decomposed to obtain nanostructured cellulose. Because strong covalent bonds and hydrogen bonds exist in the lignin, hemicellulose, and cellulose layers in lignocellulose, it is difficult to obtain cellulose. Therefore, in the pretreatment process, it is necessary to degrade the noncellulose content of lignocellulose while retaining cellulose. In the actual operation process, chemical methods and mechanical methods are usually combined to treat cellulose fibers to destroy the structure in the biomass to obtain nanocellulose.

Klemm et al. sorted nanocellulose into three types according to the preparation method and the size of cellulose (as shown in Table 2): The cellulose prepared by the chemical method is called cellulose nanocrystalline (CNC) by the physical−mechanical treatment is called cellulose nanofiber (CNF) and by the biological method is called bacterial nanocellulose (BNC).

In recent years, nanocellulose preparation technology has gradually entered the industrialized era from the laboratory. At present, the maximum processing capacity of CNC prepared by the mechanic method can reach 2000 kg/day. The development of chemical pretreatment and fibrillation technology prompts to reduce the overall cost of the first-generation CNF (down to $20−70/kg). By 2030, more advanced manufacturing processes will increase the production efficiency of CNF, and the cost of second-generation CNF is expected to be further reduced to about $5/kg.

The commercialization process of CNC has been carried out all over the world. Compared with CNF, the complexity of CNC production process leads to fewer manufacturers. Sulfuric acid hydrolysis and oxidation are the two main production processes, and the most commonly used raw material is bleached wood pulp. The maximum processing capacity of CNC prepared by the sulfuric acid hydrolysis method can reach 1000 kg/day, but it is expensive. BNC has not been industrially produced due to the long preparation time. With the improvement of the industrialized preparation of nanocellulose and the reduction of cost, the advantages of nanocellulose in oilfield chemical products will become more prominent.

4. MODIFICATION OF NANOCELLULOSE

Although nanocellulose itself has excellent properties, further modification is needed to broaden its applications. There are active sites on the surface of nanocellulose, which can be chemically modified under certain conditions. Three hydroxyl groups exist in each cellobiose molecular ring, among which the secondary (C2, C3) and primary (C6) alcohol groups can be substituted by other functional groups and long chains or be oxidized. At present, the surface modification of nanocellulose mainly includes noncovalent bond modification, 2,2,6,6-tetramethylpiperidine oxide (TEMPO) oxidation, acetylation, dialysis, etherification, polymer grafting, etc. Nanocellulose could currently be applied to oilfield chemistry through noncovalent bond modification synergy and chemical modification.

4.1. Noncovalent Bond Modification. The noncovalent bonds are formed on the surface of nanocellulose through...
electrostatic and van der Waals force or hydrogen bonds, imparting many properties to the nanoparticles. Substances such as surfactants, oligomers, or copolymers can be adsorbed onto the surface to cover or wrap nanocellulose, realizing the noncovalent bond modification.\(^21\) Adding nanocellulose to the chemical agent in the oilfield can not only enhance the performance of the chemical agent through synergy but also reduce the amount of chemical agent used.

Heux et al. reported using surfactants to stabilize the dispersion of CNC particles in nonpolar solvents for the first time.\(^23\) The results showed that the surfactant was adsorbed on the surface of nanocellulose via noncovalent bonds to change the charge of CNC, resulting in the improvement of its stability and dispersibility. Recently, many studies have reported that nanocellulose has good dispersibility in the aqueous phase,\(^23\) organic solvents,\(^24\) and polymer solutions\(^25\) by adsorbing anionic surfactants. However, in practical applications, cationic surfactants are often used to modify the surface of nanocellulose via noncovalent bonds,\(^26\) and the positively charged cationic surfactants can be attracted to the surface of CNC or the chemical agent in the oilfield chemistry, excellent salt resistance and dispersion are important factors for the successful application of new materials. Functional hydrophilic groups are introduced on the surface of nanocellulose by TEMPO oxidation, which improves the dispersibility and salt resistance of nanocellulose in water. In addition, the reaction is carried out in the aqueous phase, which is environmentally friendly, and the resulting carboxyl group can be further modified via a substitution reaction.

4.3. Acetylation. The main purpose of acetylation is to increase the hydrophobicity of nanocellulose. The acetylation of nanocellulose is usually catalyzed by acetic anhydride, dry acetic acid, and sulfuric acid or perchloric acid.\(^34\) Sassi et al.\(^35\) first reported two main mechanisms of acetylation, including the fibrosis process and the homogeneous process. Two modifiers, acetic anhydride and acetic acid, were used to modify nanocellulose. During the fibrosis process, diluents, such as toluene and other organic solvents, were added to the reaction medium, so that the resulting acetylated cellulose was insoluble in the solvent, which had a high degree of acetylation and retained the original form. While in the homogeneous process without the addition of diluent, the acetylated nanocellulose was soluble in the catalytic reaction medium composed of acetic acid and sulfuric acid, the morphology of nanocellulose would undergo substantial changes after acetylation.

Çetin et al.\(^36\) used carbonate to catalyze the transesterification of vinyl acetate and then modified the CNC surface with acetyl groups. Studies showed that only the surface of nanocellulose was functionalized, but the original size and crystallinity were retained. Bulota et al.\(^37\) used acetic anhydride to perform acetylation on the mechanically separated CNC. The results of this study indicated that the performance of the prepared polyacrylic acid–acetylated CNC composite could be significantly affected by the higher degree of substitution (DS) of CNC.

Hydrophobic modification of nanocellulose can be carried out by acetylation modification, and the original shape and crystal structure of the nanocellulose are retained after modification, which renders nanocellulose with the potential to be used as adsorption materials and stable emulsions in oilfield chemistry. However, the reaction process is carried out in an organic solvent so that the modification method needs to be further improved to increase the utilization rate of the organic solvent to meet the requirement of “green chemistry”.

4.4. Silanization. Silanization is also a simple method for increasing the hydrophobicity of nanocellulose, in which alkyl dimethyl chlorosilane is usually used for silylation.\(^38\) Andresen et al.\(^39\) successfully used chlorodimethylisopropyl silane to silylate the surface of CNC. CNF remained intact under the condition of a moderate substitution degree (between 0.6 and 1) and could be used to stabilize water-in-oil lotion. Gousse et al.\(^40\) prepared modified nanocellulose via partial silanization by utilizing a type of alkyl(dimethyl)chlorosilane. The results of this study showed that when the degree of substitution (DS) was
between 0.6 and 1, the silanized CNC was homogeneously dispersed in organic solvents; when DS was less than 0.6, the crystal form of CNC was preserved intact; when DS was greater than 1, the crystal form of CNC was destroyed. Zhang et al.41 studied a kind of methylsilanized flexible nanocellulose sponge to remove the slick oil in water. The methyltrimethoxysilane sol-containing CNF aqueous suspension was freeze-dried to produce functional sexual sponge material with a porosity of up to 99%. The silylated nanocellulose sponge was more flexible than traditional inorganic porous materials. In addition, the silanized sponge also had great hydrophobic and lipophilic properties, which could be used to effectively remove dodecane from the water surface. This type of material has excellent selectivity and recyclability, suggesting that silanization is a modification method that endows multifunctionality to nanocellulose.

The silanization preparation is a simple process without environmental pollution. In addition, there are many kinds of silane agents that are available for use in this process, and the hydrophobicity of the modified nanocellulose is great. It has the potential to be used as adsorption materials and to reduce the viscosity of heavy oil in oilfield sewage treatment. However, the silanization process relies heavily on organic solvents and thus requires more complicated solvent exchange after modification. It is necessary to further improve the modification methods and increase the recycling rate of organic solvents.

4.5. Etherification. In the etherification process, new ester bonds \((R-O-R')\) are generated on the surface of nanocellulose materials with hydroxyl groups. This reaction is of vital industrial significance in the process of preparing carboxymethyl cellulose.42 This method can promote the defibrillation reaction of cellulose to obtain nanoscale CNF. First, the fiber is pretreated with alkali metal hydroxide (such as NaOH), and then, monochloroacetic acid or sodium salt is used to convert the hydroxyl group into the carboxymethyl group.42 The disadvantage of this method is that toxic halogenated hydrocarbons are used in the reaction process, which will increase the hydrophilicity of the obtained CNF. The grafting of certain cationic groups onto the surface of nanocellulose is also called etherification reaction, such as the nucleophilic reaction between the activated hydroxyl group on the CNC backbone and the epoxy group of epoxypropyltrimethylammonium chloride (EPTMAC). This reaction obtains a stable aqueous suspension with gel properties.43 The etherification reaction of cellulose has been extensively studied in the past 30 years, and the regioselectivity mechanism of cellulose has been continuously improved by suitable solvents.44 The etherification reaction only occurs on the surface of the particles without selectivity to specific hydroxyl groups. The carboxymethyl cellulose prepared by this reaction has been widely used in drilling fluids. However, toxic substances are produced in the etherification reaction process, which is not in line with the concept of environmental protection.

4.6. Polymer Grafting. Grafting polymers onto the surface of nanocellulose is one of the methods for changing the chemical properties of cellulose.45 In polymer–nanocellulose composites, the abrasion resistance and salt resistance properties of nanocellulose can be improved and the shape of the nanocellulose can be maintained, while its hydrophilicity/hydrophobicity can be changed.46 Based on the different methods used, polymer grafting can be divided into three categories (Figure 1):47 grafting-to, grafting-from, and grafting-through. In the grafting-to method, the reactive polymer end is usually coupled with the hydroxyl group on the cellulose backbone, and a purified and well-characterized polymer or peptide chain is grafted onto the cellulose surface;
in the grafting-from method, the first step is to use the initiator to functionalize the cellulose and then the monomers are directly polymerized from the surface. Compared with the grafting-to method, a higher content of polymer–nanocellulose composites can be obtained by this method. As for the grafting-through method, the nanocellulose is first functionalized with a polymerizable substance, such as the molecule with one vinyl group, and then the functionalized nanocellulose is mixed with comonomers to initiate the polymerization reaction.

Wei et al. designed a nanocellulose-reinforced particle gel called NC-st-PG in response to the large difference in permeability between fractures and matrix in oil reservoirs. It was prepared by sparsely interpenetrating cellulose CNF and CNC, respectively, into a polyacrylamide (PAAm) matrix. By introducing rigid NC segments without compromising the elasticity of the gel, the PAAm network has been significantly strengthened. The swelling and thermal decomposition of NC-st-PG are inhibited by NCC and NCF. These characteristics make NC-st-PG possess excellent stability in continuous shear fracture.

The polymer grafting modification method has a higher grafting rate, which can ensure the stability of nanocellulose under harsh conditions. Due to the excellent rheological and mechanical properties of nanocellulose itself, the polymer–nanocellulose composites have great potential in enhancing oil recovery.

5. APPLICATION OF NANOCELLULOSE IN OILFIELD CHEMISTRY

As the demand for oil continues to grow and the development intensity increases year by year, traditional oilfield chemical reagents are encountering huge challenges. In harsh oil reservoir conditions, traditional chemicals have limitations, including poor adaptability, instability at high temperatures, damage to the reservoir, and pollution to the formation, that need to be solved urgently. It is necessary to develop high-performance, environmentally friendly, and nondamaging novel oilfield chemical reagents to satisfy the rapid development of future oilfield technology and fast-growing market needs. Nanocellulose is a kind of biopolymer with large reserves, wide source, and excellent performance. It has been industrialized in fields including food, chemicals, pharmaceuticals, and so on. In recent years, the excellent properties of nanocellulose, such as mechanical properties, degradability, low density, and compatibility of environmentally friendly, have attracted many researchers to explore its application in oilfield chemistry, especially in drilling research on liquid chemistry, enhanced oil recovery, and oilfield wastewater treatment.

5.1. Application of Nanocellulose in Drilling Fluid. Drilling fluid plays an important role in the drilling process, among which rheology and fluid loss are two critical performance indicators for the drilling fluid. Adding traditional materials such as starch and xanthan gum (XG) to the drilling fluid can adjust its viscosity, suspend solid particles, and reduce fluid loss. However, as the formation depth continues to deepen, the reservoir conditions are gradually becoming worse and worse, resulting in difficulty of the aforementioned material properties to be maintained with a further decline in the performance of the drilling fluid. Nanocellulose, with excellent mechanical properties and thermal stability, can be used to resist harsh environments. By adding the nanocellulose into the drilling fluid, the rheology and the fluid loss of the drilling fluid, as well as its thermal stability, can be greatly improved. Nanocellulose forms a spatial network structure in the drilling fluid, which could be destroyed under shearing, and the rate of reformation is also very fast. Therefore, the drilling fluid has a certain dynamic shear and excellent shear thinning. Nanocellulose could also effectively block the micro-nanopores in the filter cake and the formation, thereby achieving the effect of reducing fluid loss.

In recent years, many studies have been carried out on the application of nanocellulose in drilling fluids to achieve low fluid loss and improve rheology. Hall et al. studied the water-based mud formulation of CNF with high performance and its derivatives. Different nanocellulose and derivatives, such as CNF, carboxymethyl cellulose nanofibers (C-CNF), TEMPO-oxidized cellulose nanofibers (TO-CNF), and cationic cellulose nanofibers with quaternary amine groups (Cat-CNFs), were used to formulate cement slurry, and the performance of the slurry was studied. To prevent shale from swelling and collapsing in water, the high-resistance water-based mud was typically used in the shale section of the formation. Cationic nanofibers and quaternary ammonium salt compounds could stabilize shale by reducing the amount of water invading the shale layer to prevent shale expansion. The rheological properties of the mud are shown in Figure 2.

Figure 2. Viscosity distribution of CNF and XG suspension at 150 °C and 0.86 MPa. Reprinted (adapted or reprinted in part) with permission from Hall, L. J.; Deville, J. P.; Araujo, C. S.; Li, S.; Rojas, O. J. In Nanocellulose and Its Derivatives for High-Performance Water-Based Fluids; SPE, 2017. Copyright 2017 Society of Petroleum Engineers.

Compared with xanthan gum, CNF has higher thermal stability and could maintain the overall integrity even at higher temperatures, while xanthan gum degraded after heat treatment. Therefore, viscosity was lost.

Li et al. studied the application of CNC as the rheology modifier in drilling fluids. The results showed that the water-based bentonite slurry had better rheological properties, higher thermal stability, smaller water loss, and thinner mud cake deposition with the addition of CNC. Moreover, polyanionic cellulose was added to the CNC-containing bentonite mud to work synergistically with CNC, leading to further improvement of the rheological properties and filtration control performance of the mud. The American Petroleum Institute (API) fluid loss performance of bentonite mud was further improved with the increase of CNC concentration.
The application of nanocellulose in drilling fluids has been studied for many years. Nanocellulose has outstanding properties in mechanics and thermodynamics, but its temperature and salt resistance are still not ideal, which is also the direction of future research for this application.

5.2. Application of Nanocellulose in Enhancing Oil Recovery. The application of nanocellulose in enhancing oil recovery is mainly explored in the aspects of foam stabilization, emulsion stabilization, oil-displacing agents, etc.53

5.2.1. Nanocellulose-Stabilized Foam. Foam flooding is one of the most important oil recovery techniques in the development of oil and gas fields.56 Nanocellulose particles can be adsorbed at the gas–liquid interface, which significantly improves the stability of the foam system.60,61

Wei et al.62 studied the stability of surface-grafted nanocellulose (sg-NC) in the surfactant foam system, as shown in Figure 3. By directly measuring the oil/water/solid interface behavior, foam morphology, foam attenuation, interfacial expansion rheology, and other properties, the synergy between sg-NC and surfactants was studied. The results showed that the incorporation of sg-NC nanoparticles in the surfactant solution could further reduce the oil/water interfacial tension, as well as enhance the emulsification and wettability of the surfactant. Because of the presence of sg-NC, the thickness of the surfactant foam was significantly increased and the discharging of liquid was hindered. In the microscopic visualization model, it was observed that the sg-NC-containing foam membrane had good stability when migrating in the porous medium. Moreover, the remaining oil from the water flooding could be used, thereby improving the oil recovery.

In addition, Wei et al.63 also designed a series of lignin-containing cellulose nanofibers (L-CNFs) that are green and environmentally friendly and used them to stabilize the interface of the liquid foam to realize oil production. The foam scanner was used to study the ability and stability of foam formation, as well as the influence of lignin content on the liquid discharge rate, bubble burst rate, interface expansion and viscoelasticity, and bubble migration in a porous medium. Through observation, it was found that the addition of L-CNF significantly improved the foam drainage rate.

Foam flooding has been widely used in oilfields as a technique to enhance oil recovery. The stability of the foam system directly determines the effect of foam flooding to increase oil recovery. Nanocellulose interacts with surfactants on the liquid film through a synergistic effect to increase the liquid-carrying capacity of the liquid film and improve the stability of the foam.

5.2.2. Nanocellulose-Stabilized Emulsion. Nanocellulose with excellent stability has attracted widespread attention in terms of stabilizing emulsions.54 Nanocellulose can be irreversibly adsorbed at the oil-water interface, making the emulsion formed by nanoparticles very stable.65 There are two main theories for this phenomenon: (1) nanocellulose is adsorbed on the interface between the oil and water phases, forming a dense particle film. The nanoparticle film formed at the interface can prevent droplets from coalescing to stabilize the droplets.66 (2) These nanocellulose particles form a network of stable droplets.67 Nanocellulose materials have high aspect ratios and amphiphilic properties. Therefore, a more hydrophobic crystal plane or a more hydrophilic crystal plane of nanocellulose could be turned toward the surrounding medium, which depends on the hydrophobicity/hydrophilicity of the cellulose surface medium. This amphiphilic nature opens up the potential application of nanocellulose as an emulsion stabilizer.

In recent years, there have been many studies on nanocellulose materials as emulsion stabilizers. Studies have shown that nanocellulose with different grades, including cellulose microfibril (CMF), nanocellulose fiber (CNF), nanocrystalline cellulose (CNC), and bacterial nanocellulose (BNC), can stabilize the oil-in-water emulsion in its original state.65,70

Gestranius et al.71 studied the phase behavior and droplet size of oil-in-water emulsions stabilized by three kinds of nanocellulose materials. Without the use of additives, the three nanocellulose materials (20−35% oil, 0.1−1.5% nanocellulose) all formed oil-in-water emulsions. In addition, all of the emulsion layers quickly became creamy, and the emulsion layers remained stable for at least 1 month. The emulsion containing 0.1% CNF and TEMPO-oxidized cellulose nanofibril (T-CNF) was unstable during shearing. After centrifugation, only a small amount of the emulsion layer was retained, and there was a clear oil layer on the surface. Figure 4 shows the micrographs of 0.1% CNF and 1.0% T-CNF emulsions before and after centrifugation. Also, the results indicated that the droplet size in the CNF emulsion was increased significantly.

![Figure 3. Schematic diagram of nanocellulose-stabilized foam.](image)

![Figure 4. Micrographs of CNF and T-CNF at 0.1 and 1.0% concentrations.](image)
Parajuli et al.\textsuperscript{72} utilized CNC without surfactants added to increase the oil-water interface area of crude oil and improve the biodegradability of crude oil through emulsification. The results showed that with salinity and divalent ions, the concentration and physicochemical properties of CNC also had certain effects on the stability and biodegradability of the emulsion. In addition, when the CNC concentration was higher than 0.8 wt %, the degree of droplet coalescence in the emulsion prepared by API was greater, with coalescence being significant in mineralized water (ionic strength, $I = 1.9$ M). Because of the ionic strength, the degree of droplet coalescence in the emulsion prepared by SSW was smaller. In NaCl solutions with ionic strengths of 0.32, 0.65, 0.95, and 1.9 M, no coalescence was observed, as shown in Figure 5.

After adding the emulsion, the nanocellulose could be adsorbed at the oil-water interface, and the coverage rate can reach 63.1%. The negative charge on the surface produces strong electrostatic repulsion between adjacent droplets, inhibiting the coalescence of the droplets and improving the stability of the emulsion.

5.2.3. Cellulose-Based Nano-Oil-Displacing Agent. In recent years, many studies have investigated the use of nanocellulose as a separate oil-displacing agent to enhance oil recovery (EOR).\textsuperscript{73,74} A key factor in applying nanocellulose to EOR is its high thermal stability. Li et al.\textsuperscript{75} proposed the potential application of nanocellulose in EOR and believed that the regenerated nanocellulose dispersion had high salt resistance and heat resistance, making it an ideal material for improving oil recovery.

Molnes et al.\textsuperscript{76,77} studied the injectability of cellulose nanocrystals (CNC) with different concentrations into high-permeability sandstone cores in mineralized water with low salinity and investigated the effects of different ion concentrations on the dispersibility and rheology of CNC. The results showed that the CNC dispersions with concentrations ranging from 0.5 to 2.0 wt % had good injectability into sandstone, and the viscosity measurement of the produced fluid proved that CNC particles could migrate within the cores without being adsorbed (as shown in Table 3). In addition, CNC dispersions had good stability at low salinity. Kusanagi et al.\textsuperscript{78} studied the core displacement of nanofibers. By controlling the fluid flow rate, 0.4 wt % nanofibers was injected into different cores with AlCl$_3$ as the cross-linking agent. The cross-linked nanocellulose could improve the fluidity of nanofluids, and the recovery rate could be increased from 13.3 to 24.3%.

Liu et al.\textsuperscript{79} simultaneously grafted the hydrophilic N,N-dimethylacrylamide (DMA) and the hydrophobic butyl acrylate (BA) onto the surface of CNF through ammonium nitrate initiated radical polymerization, as shown in Figure 6. The CNF samples were characterized by Fourier transform infrared (FT-IR) spectroscopy, focused beam reflectance measurement (FBRM), and rheological measurement before and after modification. The results of FBRM characterization showed that the salt (NaCl) tolerance of CNF dispersions was increased from 1 to 8 wt % after grafting DMA (2 g/L) and BA (3 g/L) at the same time. In addition, the rheological analysis results showed that the thermal stability and “thickening” effect of the modified CNF dispersions were greatly improved.

Raza et al.\textsuperscript{80} studied the oil displacement mechanism of nanocellulose crystal (CNC) fluids, and the results showed that CNC nanofluids could increase the viscosity of the aqueous phase and reduce the interfacial tension of oil-water. At a concentration of 1 wt %, the nanofluid fingers formed and flowed in their corresponding channels, which then merged with each other and drove the oil out of the channels by expanding the width of the fingers in the direction perpendicular to the fluid. At a concentration of 2 wt %, the viscosity of the nanofluid was higher and the interfacial tension of oil-water was lower, causing the oil to drain out of the pores like a piston. As shown in Figure 7, the micron-sized nanofluid could penetrate the oil phase and form micro-

![Figure 5](https://doi.org/10.1021/acsomega.1c02095)

**Figure 5.** Resistance to emulsion creaming: (a) effect of CNC concentration in API brine, (b) effect of divalent cations at 0.8 wt % CNC, and (c) effect of ionic strength at 0.8 wt % CNC. Pictures in the bottom panels (d) and (e) are representative samples of emulsions immediately after emulsification and after 24 h.\textsuperscript{72} Reprinted (adapted or reprinted in part) with permission from Parajuli, S.; Alazzam, O.; Wang, M.; Mota, L. C.; et al. Colloids Surf. A 2020, 596, 124705. Photograph courtesy of Parajuli, Sanjiv.” Copyright 2020 Elsevier B.V.

| Concentration | Core Permeability (mD) |
|---------------|------------------------|
| Initial       | 210                    |
| 0.5 wt % CNC  | 161                    |
| 1 wt % CNC    | 106                    |
| 2 wt % CNC    | 73                     |

Table 3. Permeability Measurements before, between, and after Core Flooding Experiments with Increasing CNC Concentrations.
emulsion along the interface in the oil phase. The formation of the emulsion reduced the effective interfacial tension between the oil and water phases, resulting in a further increase of the fluidity of the fluid.

To improve the salt tolerance/sensitivity of CNF, Wang et al. introduced cationic charges into the anionic charged TEMPO-mediated oxidized cellulose nanofibers (TOCNFs) to prepare zwitterionic cellulose nanofibers (ZCNFs). This product has excellent salt sensitivity and tolerance, which could expand the application of nanocellulose in oil recovery or wastewater treatment.

As a nano-oil-displacing agent, nanocellulose can spread to most pores in the formation due to its small size, but further modification is needed to achieve great salt tolerance and redispersion in water. The excellent performance of nanocellulose in increasing the oil recovery leads to its wide application potential.

5.3. Application of Nanocellulose in Oilfield Sewage Treatment. In the process of oilfield development, billions of gallons of produced water and treated water are generated as waste every year. Water may be contaminated at all stages of oil production, such as oil spills during offshore oil exploration and oil transportation. Pollutants in produced water are a mixture of formation water, injected water, and treatment chemicals used in drilling or oil extraction. Produced water contains a variety of organic and inorganic components so that direct discharge of this water will pollute soil and surface/groundwater. The use of renewable materials and biomass raw materials for sewage treatment can not only reduce carbon emissions but also decrease the cost of sewage treatment. For example, the use of natural or modified cellulose nanomaterials as adsorbent materials in removing crude oil, heavy metals, suspended particles, and other pollutants in oilfield wastewater has great potential in real-world applications.

Li et al. modified the cellulose fibers prepared from corn stover by acetylation to enhance the lipophilicity of the cellulose materials and conducted experimental studies on using the modified cellulose fibers as oil-absorbing materials. The results showed that the adsorption capacities of these materials for different oils were 42.53 g crude oil/g, 52.65 g engine oil/g, and 57.64 g vacuum pump oil/g. Figure 8 shows the adsorption process of acetylated cellulose fibers. Cornstalk
is a cheap raw material that could be easily obtained. Therefore, the effectiveness, low cost, and excellent biodegradability of this material enabled it to replace chemical absorbents, which had the potential for large-scale applications in the petroleum industry. Zheng et al.84 prepared a green and environmentally friendly method for mixing aerogel of poly(vinyl alcohol) (PVA) and cellulose nanofiber (CNF), which had excellent performance in oil absorption and heavy metal ion removal. The adsorption capacity of the aerogel on crude oil was 63.5 g/g. Compared with pure PVA aerogel, it could filter out heavy metal ions, including Hg²⁺, Pb²⁺, Cu²⁺, and Ag⁺, more effectively. The adsorption capacity of PVA/
CNF aerogel was 157.5 mg Hg²⁺/g, 110.6 mg Pb²⁺/g, 151.3 mg Cu²⁺/g, and 114.3 mg Ag⁺/g, while the adsorption capacity of pure PVA aerogel was 22.0 mg Hg²⁺/g, 24.5 mg Pb²⁺/g, 28.9 mg Cu²⁺/g, and 39.5 mg Ag⁺/g.

Yu et al. modified nanocellulose crystals (CNC) with succinic anhydride to obtain SCNC. The SCNC was further treated with saturated NaHCO₃ to get NaSCNC. Using SCNC and NaSCNC as adsorption materials, the adsorption capacities on Pb²⁺ and Cd²⁺ were tested. The maximum adsorption capacities of SCNC for Pb²⁺ and Cd²⁺ were 367.6 and 259.7 mg/g, respectively, and the maximum adsorption capacities of NaSCNC for Pb²⁺ and Cd²⁺ were 465.1 and 344.8 mg/g, respectively. The results showed that NaSCNC had higher adsorption capacity and higher selectivity for both Pb²⁺ and Cd²⁺, further proving that the adsorption mechanism of NaSCNCs was mainly ion exchange, which was the reason why the adsorption capacity of NaSCNCs was better than that of SCNCs. Therefore, for nanocellulose materials containing carboxyl groups, the conversion of carboxyl groups into carboxylates will greatly increase their adsorption capacity.

Suopajärvi et al. studied the flocculation performance of five nanocellulose crystals (CNCs) with different carboxyl group contents. Using bleached birch chemical pulp as raw material, different CNC samples with carboxyl group contents of 0.38, 0.69, 0.75, 120, and 1.75 mmol/g, respectively, were synthesized through the reaction of sodium periodate and sodium chlorite. The results showed that CNC with a carboxyl content of 1.75 mmol/g could remove 80% of turbidity and 60% of chemical oxygen demand (COD) in the water. Increasing the concentration of CNC could further enhance the amount of flocculation to a maximum of 5 mg/L. In addition, the pH value had little effect on the flocculation performance of nanocellulose.

Nanocellulose can be used as adsorption material for oilfield sewage treatment, replacing traditional chemical reagents used in the past and greatly reducing costs and carbon emissions, which can be reused as well.

![Figure 8. Adsorption process of acetylated cellulose fiber.](https://doi.org/10.1021/acsomega.1c02095) Reproduced from Li, D.; Zhu, F. Z.; Li, J. Y.; Na, P.; Wang, P. Ind. Eng. Chem. Res. 2013, 52, 516–524. Photograph courtesy of "Dan Li." Copyright 2013 American Chemical Society.
Notes
The authors declare no competing financial interest.

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