Original Research Paper

Adsorption and Descaling of Cellucotton and Chitosan-Modified Bentonite for Produced Water

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Abstract: The compatibility of non-identical layers within the water present in the produced oil is poor and ion reactions in the oil mixed with water result in scale formation, thereby having a significant impact on oilfield safety production. In this study, methods for the descaling of produced water from different blocks were studied according to the quality characteristics of the produced water. Results show that scale was produced at a concentration of 94 mg/L when three-phase separated water and formation water were mixed at a volume ratio of 1:0.3. The flocculation performance was optimized when the pH of the mixed water sample was adjusted to 7.5 and addition amount of polyaluminium chloride and polyacrylamide was 80 and 3 mg/L, respectively. In addition, the mixed water sample was adsorbed and descaled using cellucotton and chitosan-modified bentonite. Results show that the method for treating the mixed water sample first with cellucotton followed by the chitosan-modified bentonite shows the optimal adsorption–flocculation performance, thereby reducing the concentration of scale in the treated water to 3 mg/L.

Keywords: Produced Water, Adsorption, Descaling, Chitosan-Modified Bentonite

Introduction

At present, majority of oilfields in China have entered the middle and late exploitation stages, the water content in the produced oil is continuously increasing (and is > 80% in some cases) and the output of oil mixed with water is increasing. Yuan and Wang (2018; Chen et al., 2018) If produced water is discharged directly without reasonable and effective treatment, it will lead deteriorate the surrounding environment and pollute the groundwater resources. Song et al. (2013; Yang et al., 2006) Therefore, the treatment and reinjection of the sewage can meet the production needs of oilfields, conserve considerable water resources and bring certain economic benefits. Yin et al. (2018; Wang et al., 2019a)

There are great differences in the properties of produced water in different areas; however, they all have the characteristics of high oil content, high salinity and complex water quality. Li et al. (2019; Wang et al., 2019b) These characteristics lead to difficulties in the treatment and reinjection of produced water in the later stage. Wu et al. (2010; Liu et al., 2019) At present, the reinjection of produced water from a single block can no longer satisfy the needs of oilfield production. Owing to the development in oilfield production technology, mixed production and injection have become an important technology to enhance oil recovery and fully utilize produced water in oilfields. Tong et al. (2015) However, the properties of produced water from different blocks and ion concentrations in the water differ, which lead to the phenomenon of incompatibility after mixing two water types and producing large amounts of scale which block pipelines and affect water injection in the later stage. (Amiri et al., 2012; Amiri and Moghadasi, 2013). High ion content and incompatibility of mixed water layers in the production wastewater are the internal causes of scaling, whereas water temperature, pH, pressure and salt content are external causes (Helton et al., 2017; Polat et al., 2017). Therefore, scaling control technologies for production wastewater mainly include the following: Reducing the content of scale-forming ions (e.g., the softening method); avoiding incompatibility with water mixing; controlling...

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exogenous conditions (e.g., adjusting pH); and adding scale inhibitor, which is the main method for oilfield scale control (Al-Khaldi et al., 2011; Shukla et al., 2018) that destroys the process of scale crystal formation.

Herein, two kinds of easy-to-scale waters with different properties were premixed to enable the scaling ions in the water to react and scale in advance. The scaling substances in the water were removed through later adsorption-flocculation, which could avoid the meeting and scaling of the later-produced water in the oil layer and impacts on the subsequent exploitation. Using the high-scale mixing proportion of authentic oilfield produced water (wastewater), this study explored changes in the flocculation reagent system, i.e., pH, Polyaluminium Chloride (PAC) and Polyacrylamide (PAM) and adsorption agent system, i.e., chitosan-modified clay and cellucotton, to determine the effects on the properties of mixed water scaling. By comparing different combinations of descaling effects on the control of fouling within the mixed water, it was found that “cellucotton plus chitosan-modified clay” secondary adsorption and flocculation precipitation could be combined to form a hybrid high-scale adsorption descaling technology for produced water.

Materials and Methods

Reagents and Instruments

The experimental reagents were ammonium chloride, liquid ammonia, eriochrome black T, hydroxylamine hydrochloride, anhydrous ethanol, sodium hydroxide, zinc oxide, barium chloride, sodium hexametaphosphate and anhydrous sodium carbonate, which are all analytically pure; Polyaluminium Chloride (PAC), Polyacrylamide (PAM), chitosan-modified bentonite (homemade, Yu et al., 2018) and cellucotton.

Experimental instruments were a constant temperature oscillating incubator (TS-200B), vacuum pump (SHB-III), electronic analytical balance (CP114) and an electrothermal constant temperature drying oven (101 Type).

Experimental Methods

Water Quality Analysis

Water samples were analyzed according to Oilfield Water Analysis Method (SY/T5523-2006) and Recommended Indexes and Analysis methods of Water Injection Quality in Clastic Reservoirs (SY/T5329-2012).

Adsorption and Descaling

(1) The three-phase separated water and formation water were mixed according to the volume ratio of 1:0.3 and then the cellucotton was added followed by adsorption in the oscillating incubator at 40°C for 2 days. After removing the cellucotton, the flocculation sedimentation experiment on the mixed water sample was conducted and adsorption effect was investigated based on the ion concentration in the treated water.

(2) After mixing the three-phase separated water and formation water at a volume ratio of 1:0.3, a certain amount of chitosan-modified bentonite was added followed by adsorption at 40°C for a certain time. The flocculation sedimentation experiment of the mixed water sample was conducted and adsorption effect was investigated based on the ion concentrations in the treated water.

Determination of Scale Amount

Treated water was filtered through a 0.45-μm filter membrane by suction and maintained at 40°C for 3 days. The weight change before and after the treatment was measured to determine the amount of scale in the treated water.

Determination of Light Transmittance

Ultraviolet spectrophotometer (UV-2350) was used to determine the light transmittance of produced water before and after flocculation at 420 nm.

Results and Discussion

Water Quality Analysis and Compatibility Analysis of Formation Water and Three-Phase Separated Water

To ensure accurate treatment and reinjection of the produced water from oilfields, it is necessary to analyze the quality of the reinjected water. The results of water quality analyses of formation water and three-phase separated water are shown in Table 1.

The formation water belonged to the typical Na₂SO₄ type and the SO₄²⁻ anion concentration was 2313.02 mg/L; the three-phase separated water was CaCl₂-type water and the Ca²⁺ concentration was 2462.92 mg/L. If the two water types are mixed, the scaling phenomenon is very likely to appear and if they are reinjected directly without treatment, serious blockage of the pipeline and even blockage of the stratum will be caused, resulting in an impact on the effect of water injection in the later stage. Forming precipitation will be easy to scale in the form of the following reaction:

\[ \text{Ca}^{2+} + \text{SO}_4^{2-} \rightarrow \text{CaSO}_4 \]

As shown in Fig. 1, the concentrations of calcium ions (Ca²⁺) and sulfate ions (SO₄²⁻) and total hardness in the mixed water samples exhibited obvious downward trends after 8 h mixing, indicating that the ions in the water reacted with each other to form CaSO₄ scale.
Optimization of Coagulation Experiment Conditions

Optimization of pH

The pH value of the mixed water was adjusted after mixing the three-phase separated water and formation water according to the volume ratio of 1:0.3. Then, 100 and 1 mg/L of PAC and PAM, respectively, were added to flocculate the mixed water sample. The optimized pH value was selected by taking the light transmittance as the index. The results are shown in Fig. 2.

With the increased pH value, the light transmittance of the supernatant initially decreased and then increased. The light transmittance was approximately 82% and 90% at pH 7.5 and 9, respectively. However, white precipitates were produced after a certain time period (Fig. 2) as the pH value increased; these may have been formed because the Ca and Mg ions in water were under alkaline conditions. Furthermore, a large amount of sludge was produced in the flocculation treatment (Fig. 3), which resulted in difficulties for the follow-up treatment. Therefore, a pH value of 7.5 was adopted for the flocculation experiment after comprehensive consideration.

Optimization of the Addition Amount of PAC

The three-phase separated water and formation water were mixed according to the volume ratio of 1:0.3 and then the pH was adjusted to 7.5. Different amounts of PAC and 1 mg/L of PAM were added in the mixed water solution for flocculation treatment and the optimal addition amount of PAC was selected by taking the light transmittance as the evaluation index. The results are shown in Fig. 3.

![Fig. 1: Concentration of ions in the mixed water sample at different time points](image)

![Fig. 2: Light transmittance of mixed water supernatant after treatments at different pH values](image)
Fig. 3: Effect of different addition amounts of PAC on light transmittance of mixed water supernatant after flocculation treatment

Table 1: Water quality of formation water and three-phase separated water

| Sample                  | Salinity /mg·L⁻¹ | Ca²⁺  | Mg²⁺  | Cl⁻   | CO₃²⁻ | HCO₃⁻ | SO₄²⁻ | pH  | Water type   |
|-------------------------|------------------|-------|-------|-------|-------|-------|-------|-----|--------------|
| Formation water         | 5210.83          | 540.08| 199.95| 1146.64| 0     | 119.29| 2313.02| 6.5 | Na₂SO₄      |
| Three-phase separated   | 25388.24         | 2462.92| 102.10| 14870.39| 0     | 198.01| 726.01 | 6.5 | CaCl₂       |

As shown in Fig. 3, the light transmittance of supernatant first increased and then decreased with increasing PAC. The treatment effect was optimal when the addition amount of PAC is 80 mg/L, with the light transmittance of the supernatant reaching 96.8%. Therefore, the optimal amount of flocculant of 80 mg/L was used in the later flocculation experiment.

Optimization of the Addition Amount of PAM

The three-phase separated water and formation water were mixed according to the volume ratio of 1:0.3 and then the pH was adjusted to 7.5, followed by the addition of 80 mg/L of PAC and different amounts of PAM. The optimal addition amount of PAM was selected by considering the light transmittance as the evaluation index. The results are shown in Fig. 4.

Figure 4 shows that with the increase of the addition amount of PAM, the light transmittance of the supernatant first increased and then decreased. When the addition amount of PAM was 3-5 mg/L, the light transmittances of the supernatants were > 98%. Therefore, the addition amount of PAM herein was optimized to be 3 mg/L by considering economic benefits. In conclusion, the optimized experimental conditions for flocculation experiments are as follows: pH Value of 7.5, addition amount of PAC and PAM of 80 and 3 mg/L, respectively.

Experiment on Adsorption and Descaling of Chitosan-Modified Bentonite

Effect of Adsorption Time on Scale Removal

After the two water types were mixed according to a volume ratio of 1:0.3, 400 mg/L of modified clay was added to the mixture; this was followed by the adsorption experiment at 40°C for a certain time period. Then, the flocculation sedimentation experiment of the mixed water was conducted and the adsorption performance was evaluated by the ion concentration in the treated water.

The surface of chitosan-modified clay particles features both hydroxyl and carboxyl groups, which can absorb the scale crystals and induce accumulation on the surface. Then, the scale crystals can be precipitated by flocculation to remove scale crystals from water (Yu et al., 2018).

As shown in Fig. 5, after treating the mixed water samples with adsorption-flocculation using chitosan-modified bentonite, the concentrations of the scaling ions in the water changed with the increase of adsorption time and the SO₄²⁻ concentration first decreased and then increased. The changing trends in the calcium and magnesium ion concentrations in water were not significant, while the scale of water samples treated by adsorption materials decreased obviously. After 20 min of adsorption, the SO₄²⁻ ion concentration decreased to its lowest value, indicating that the chitosan-modified bentonite has the largest adsorption capacity of scaling ions. 
ions in water. Therefore, 20 min was determined as the optimal adsorption time herein.

**Descaling Performance of Chitosan-Modified Bentonite**

After mixing the two water types according to the volume ratio of 1:0.3, different amounts of chitosan-modified bentonite were added followed by adsorption for 20 min at 40°C. The flocculation sedimentation experiment on the mixed water sample was then carried out and the adsorption performance was evaluated based on the concentrations of ions in the treated water. The experiment results are shown in Fig. 6.

The scaling ions in the mixed water samples decreased significantly after the addition of different amounts of modified bentonite for the adsorption-flocculation treatment. When the addition amount of modified bentonite was 500 mg/L, the SO$_4^{2-}$ concentration decreased from 1052.80 to 810.79 mg/L. Besides, with an increase in the amount of added modified bentonite, the scale amount in the water treated by adsorption-flocculation also decreased (to 24 mg/L), while the scale amount in water treated by direct flocculation was 94 mg/L, showing that the scale amount was significantly lower after the adsorption-flocculation treatment. Therefore, the addition of modified clay was optimized to be 500 mg/L herein.

**Fig. 4:** Effect of different addition amounts of PAM on light transmittance of mixed water supernatant after flocculation treatment

**Fig. 5:** Changes in ion concentrations in water samples treated with adsorption-flocculation using chitosan-modified bentonite at different adsorption times
Fig. 6: Changes in ion concentrations in water samples after adsorption and flocculation using different amounts of chitosan-modified bentonite

Table 2: Changes in ion concentrations in water samples after cellulocotton adsorption

| Treatment            | Ca\(^{2+}\) (mg/L) | Total hardness (mg/L) | SO\(_4^{2-}\) (mg/L) | Scale amount (mg/L) |
|----------------------|--------------------|-----------------------|-----------------------|---------------------|
| Flocculation         | 1843.68            | 1940.92               | 1021.52               | 94                  |
| Adsorption-flocculation | 1823.64           | 1911.15               | 983.65                | 17                  |

Table 3: Changes in ion concentrations in water samples after adsorption and flocculation of cellulocotton and chitosan-modified bentonite

| Methods of adding chitosan-modified bentonite | Ca\(^{2+}\) (mg/L) | Total hardness (mg/L) | SO\(_4^{2-}\) (mg(L) | Scale concentration (mg/L) |
|-----------------------------------------------|--------------------|-----------------------|-----------------------|---------------------------|
| - Directly adding chitosan-modified bentonite | 1887.77            | 1997.16               | 1086.54               | 17                        |
| Adding suspension                             | 1973.94            | 2043.22               | 1043.74               | 7                         |
|                                               | 1777.55            | 1848.04               | 940.85                | 3                         |

Adsorption and Descaling Performance of Cellulocotton

After the two water types were mixed according to the volume ratio of 1:0.3, the scaling ions in water were treated by cellulocotton for adsorption. The results are shown in Table 2.

As shown in Table 2, the concentration of scaling ions in the water decreased after adsorption-flocculation treatment, indicating that the addition of cellulocotton had a certain effect on the adsorption of scaling ions in the mixed water. The amount of scale in the treated water was also determined; after adsorption-flocculation treatment it decreased to 17 mg/L, thereby indicating that the descaling performance of cellulocotton was superior to that of chitosan-modified bentonite.

Coadsorption Descaling Performance of Cellulocotton and Chitosan-Modified Bentonite

Through the above experiments it was found that the amount of scale in the water sample treated with cellulocotton for adsorption was obviously smaller. The mixed water sample was treated with these two adsorption materials for adsorption-flocculation to achieve coadsorption descaling and achieve an overall improved descaling performance. The results are shown in Table 3.

Table 3 shows that after initially descaling by treating the mixed water sample with cellulocotton, 500 mg/L of chitosan-modified bentonite was then added to further reduce the amount of scale in the mixed water sample. After coadsorption and descaling by the two materials, the amount of scale in the mixed water sample was obviously reduced. In addition, when the chitosan-modified bentonite suspension was added in the mixed water, the descaling performance was further enhanced, achieving a scale concentration of only 3 mg/L in the treated water. After coadsorption-flocculation treatment, the scaling ion concentrations were also decreased, indicating that cellulocotton and chitosan-modified bentonite can effectively absorb scaling ions and achieve the effect of scale removal. (Nan et al., 2015)
Conclusion

Based on the above research, the mixed high-scaling produced water adsorption and descaling technology of the combination of fiber cotton and chitosan modified clay with secondary adsorption and flocculation was proposed for the first time. The main conclusions include the following:

1. Analysis of water quality shows that the three-phase separated water belonged to CaCl₂-type water and the formation water belonged to Na₂SO₄-type water. When these were mixed at a volume ratio of 1:0.3, CaSO₄ scale was produced at the highest concentration of 94 mg/L.

2. Optimal conditions of coagulation treatment are as follows: pH Value of 7.5 and addition of 80 and 3 mg/L of PAC and PAM, respectively.

3. The mixed water sample was adsorbed and descaled by cellucotton and chitosan-modified bentonite, showing that cellucotton has a better descaling performance with a scale concentration of 17 mg/L in the water sample following the adsorption-flocculation treatment.

4. Scale was removed by coadsorption-flocculation with cellucotton and chitosan-modified bentonite. The optimal performance was achieved when scale was first treated with cellucotton, followed by a 500 mg/L suspension of chitosan-modified bentonite for adsorption; the result was a scale concentration of 3 mg/L in the treated water.

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Author’s Contributions

Tao Yu: Writing the article, research concept and design.
Ying Wang: Research concept and design.
Chengtun Qu: Collect and/or assembly of data.
Jinling Li: Critical revision of the article.
Bo Yang: Final approval of article.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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