

Article

Assessment of the Rheological Behavior of Polymer–Oxidant Mixtures and the Influence of the Groundwater Environment on Their Properties

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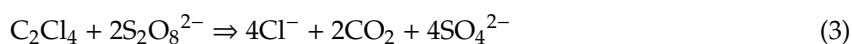
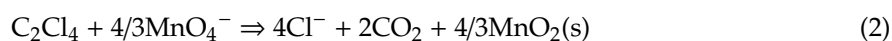
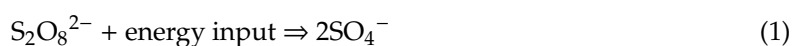
Abstract: Shear-thinning polymers have been introduced to contaminant remediation in the subsurface as a mobility control method applied to mitigate the inefficient delivery of remedial agents caused by geological heterogeneity. Laboratory experiments have been conducted to assess the compatibility of polymers (xanthan and hydrolyzed polyacrylamide (HPAM)) and oxidants (KMnO_4 and $\text{Na}_2\text{S}_2\text{O}_8$) through quantitative evaluation of the viscosity maintenance, shear-thinning performance, and oxidant consumption. The mechanism that causes viscosity loss and the influence of the groundwater environment on the mixture viscosity were also explored. The xanthan– KMnO_4 mixture exhibited the best performance in both viscosity retention and shear-thinning behavior with retention rates higher than 75% and 73.5%, respectively. Furthermore, the results indicated that xanthan gum has a high resistance to MnO_4^- and that K^+ plays a leading role in its viscosity reduction, while HPAM is much more sensitive to MnO_4^- . The viscosity responses of the two polymers to $\text{Na}_2\text{S}_2\text{O}_8$ and NaCl were almost consistent with that of KMnO_4 ; salt ions displayed an instantaneous effect on the solution's viscosity, while the oxide ions could cause the solution's viscosity to decrease continuously with time. Since xanthan exhibited acceptable oxidant consumption as well, xanthan– KMnO_4 is considered to be the optimal combination. In addition, the results implied that the effects of salt ions and the water pH on the mixture solution could be acceptable. In the 2D tank test, it was found that when xanthan gum was introduced, the sweeping efficiency of the oxidant in the low-permeability zone was increased from 28.2% to 100%. These findings demonstrated the feasibility of using a xanthan– KMnO_4 mixture for actual site remediation.

Keywords: polymer; solution viscosity; shear-thinning behavior; compatibility; groundwater environment; aquifer; contaminant hydrogeology

1. Introduction

In situ chemical oxidation (ISCO) is a chemical approach applied to treat organic contaminants in the subsurface, which can be traced back to the early 1990s [1–6], when groundwater contaminated by chlorinated solvents was widespread [7]. Among these compounds, chloroethenes such as perchloroethene (PCE) most commonly exist in the subsurface [8,9] due to their wide use as degreasing solvents and dry cleaners in industry and to poor emission management afterward. Once existing in groundwater, these substances do not readily degrade or dissolve naturally, and as a dense nonaqueous phase liquid (DNAPLs), PCE is not stationary in aquifers, usually sinking and leaving a trail of contamination, which makes it more difficult to locate the source zone in the strata and leads to much lower treatment efficacy [10]. The use of potassium permanganate (KMnO_4) in the treatment of drinking water and wastewater has lasted for many years [11,12], and this approach is receiving

increased attention as an effective technology in addressing chloroethenes such as PCE in ISCO. When dissolved in water, permanganate dissociates to form the permanganate anion, which has a relatively high oxidation potential ($E^0 = 1.7$ V), and according to the research of Wiberg and Saegebarth [13], metal-oxo reagents can powerfully attack the carbon–carbon double bonds, which all make KMnO_4 an attractive chemical reagent in the treatment of PCE. Furthermore, the oxidizing process of MnO_4^- is achieved by electron transfer, which is relatively slow and appears to be more suitable for subsurface treatment [8]. Another test oxidant is sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), which has received growing attention in the field of ISCO in recent years, and its oxidation reaction is completed by free radical production, a mechanism quite different from that of KMnO_4 . Numerous studies have revealed that persulfate anions can be activated to enhance the production of sulfate free radicals ($\text{SO}_4^{\cdot-}$), a more powerful oxidizing agent than persulfate anions, with a standard redox potential of $E^0 = 2.6$ V, which is capable of disrupting chlorinated solvents [14,15]. Recently, thermal activation treatment of sodium persulfate has been increasingly applied in ISCO. The energy supplied by heating causes the cleavage of the peroxide bond of the persulfate anion, thereby forming two sulfate radicals (Equation (1)) [16–18] that can attack organic contaminants rapidly. The reactions of oxidative degradation of PCE (C_2Cl_4) by MnO_4^- and $\text{S}_2\text{O}_8^{2-}$ are depicted in Equations (2) and (3):



Since the efficiency of ISCO is highly dependent on the extent to which the remedial reagents contact the target contaminants, effective delivery of the remediation amendments is essential for successful treatment [19,20]. However, geological heterogeneity usually induces fluid bypassing by creating preferential flow paths within high-permeability zone (hpz) while leaving the low-permeability zone (lpz) bypassed; thus, the intended target area that the remedial reagent can ultimately sweep is limited [21]. Moreover, as part of the contaminants in the lpzs remain untreated, it increases the potential that they will eventually diffuse back into adjacent hpzs via matrix diffusion during or after initial treatment, which is known as rebound [19,22,23]; all these effects lead to the poor performance of ISCO observed both in the laboratory and field scales.

In recent work, shear-thinning polymers have been introduced to the remediation of groundwater contamination [23–36], which is a mobility control method used in the petroleum industry. By the addition of polymer, the viscosity of the displacing fluid increases, and the mobility of the fluid within the hpzs decreases, which promotes enhanced transverse fluid movement of fluids into adjacent lpzs and minimizes the effects of the aquifer heterogeneities [28,32,37]. However, most of the research has focused on the coupling of polymer–water or polymer–surfactant-based remediation approaches [26,27,29,30,35,36], and the coupling of chemical oxidants and polymers remains less extensively considered. The first evidence of this coupling was proposed by Smith et al. [32], who demonstrated its feasibility by conducting compatibility experiments with commonly used polymers (xanthan and hydrolyzed polyacrylamide (HPAM)) and chemical oxidants (KMnO_4 and $\text{Na}_2\text{S}_2\text{O}_8$). McCray et al. [28] further assessed this compatibility and demonstrated the potential of this approach applied in ISCO for PCE oxidized by laboratory experiments. To the best of our knowledge, the analysis of viscosity compatibility in existing studies is limited to investigating the retention rate, while no research associated with the quantitative analysis of solution rheological behavior changes has been reported. In addition, the effect of groundwater environmental factors on polymer–oxidant mixtures is rarely mentioned, not to mention the analysis of the relative influence intensity of common anions and cations existing in groundwater on the solution.

This paper focuses on assessing the compatibility of polymer–oxidant mixtures through quantitative evaluation of viscosity maintenance, shear-thinning performance, and oxidant consumption, as well as exploring the mechanism that causes viscosity loss. Considering the

actual site conditions, the influences of the groundwater environment, including the groundwater pH, the main salt ions, and their relative effect strength on the viscosity and the rheological behavior of the polymer–oxidant mixture were also evaluated to assess the feasibility of this method.

2. Materials and Methods

2.1. Materials

Xanthan powder for this work was obtained from Aladdin (G104873, Shanghai, China). HPAM (anionic), produced by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized (DI) water was obtained through a NANO pure UV ultrapure water system (Millipore, Darmstadt, Germany), which had a resistance of 18.2 MΩ cm. Potassium permanganate (KMnO₄) was obtained from Beijing Chemical Works (Beijing, China), and sodium persulfate (Na₂S₂O₈, analytical purity) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride (MgCl₂), calcium chloride (CaCl₂), sodium nitrate (NaNO₃), sodium bicarbonate (NaHCO₃), and sodium sulfate (Na₂SO₄) were of analytical purity and obtained from Xilong Chemical Co., Ltd. (Beijing, China). These materials were used to investigate the effects of common groundwater ions on polymers. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the pH of the mixed solutions to the desired values.

2.2. Methods

Solid polymer powder was slowly added into deionized water, and a glass stir bar was used to ensure even distribution. Then, the solution was continuously stirred for 3–4 h on a magnetic stirrer at room temperature (25.0 ± 2 °C). The polymer concentration was prepared at 3.2 g/L for stocking, and at least 12 h of rest was necessary prior to the experiment. Once diluted to the desired concentration, the polymer solutions were used quickly to avoid undesirable reactions or viscosity loss. Both oxidant solutions were prepared prior to each experiment and used quickly to prevent possible degradation by light or heat. Salt solutions were prepared in deionized water, and the cation concentration was the same as that in the oxidant solution.

The viscosities of the polymer solutions and polymer–oxidant mixtures were measured by a Brookfield DV3TLV Viscometer (Brookfield Engineering Laboratories, Lorch, Germany). The viscosity profiles (shear rate versus viscosity as well as viscosity versus time) of the pure polymer solutions were determined before the batch tests. In the batch tests, the mixing ratio of each polymer formulation with the oxidant solution was 1:1 by volume, and the experiments were conducted in 250 mL amber conical flasks covered with tin foil to maintain darkness. The mixtures were continuously stirred on a magnetic stirrer at room temperature (25.0 ± 2 °C). Each of these tests was carried out in duplicate. A range of 800, 1600, and 3200 mg/L polymer concentrations was adopted in the batch tests, enabling comparison between viscosities at different times of polymer concentrations. This approach also provides three orders of magnitude of initial viscosity values of xanthan, which is approximately 6–1100 centipoise (cP). The slightly higher viscosity than the “reasonable” viscosity applied for subsurface injection [19] is determined in expectation of a possible viscosity loss after mixing with the oxidant. Considering that the KMnO₄ concentrations used in field applications vary from 250 mg/L to 60 g/L [10], the oxidant amount applied here was 500 mg/L. The concentrations of Na₂S₂O₈ were set to oxidize equal molar amounts of PCE as KMnO₄ according to Equations (2) and (3). As activated sodium persulfate technology is increasingly used in practical site remediation, in this study, sodium persulfate oxidants were added to the polymer solution in their activated forms.

The details of the batch tests are presented in Table 1. The batch tests were all conducted in the dark and stirred over the test period. The permanganate tests were performed at room temperature (25.0 ± 2 °C), while heated persulfate tests were performed in a water bath at 40.0 ± 2 °C for thermal activation [14]. The mixture solution viscosities were monitored at 4, 8, 24, 48, and 72 h time intervals, and the monitoring period was determined based on the research carried out by Krembs [38], who

analyzed hundreds of field-scale application cases and found that the median duration of delivery events of permanganate and persulfate was approximately 3 days. The shear rates tested varied from 50 to 200 s⁻¹, which is an extension of the existing research range of 1–100 s⁻¹. This range was set to cover a variety of aquifer matrices and conditions [19]. In the batch tests, polymer–water controls were used to measure and quantify the influence of the oxidant on the polymer viscosities under the same polymer concentrations. The second set of controls, consisting of polymer and salt, were used to differentiate pure electrostatic effects produced by the potassium ions from oxidative effects by the permanganate, both of which may have an impact on the polymer viscosity.

Table 1. Experimental conditions for the batch tests.

Sample	Polymer (mg/L)	Oxidant (mg/L)		Salt (mg/L)	
		[KMnO ₄]	[Na ₂ S ₂ O ₈] ^b	[KCl] ^a	[NaCl] ^a
Polymer–oxidant	800, 1600, 3200	500	1130	0	0
Polymer–salt	800, 1600, 3200	0	0	236	555
Polymer–water	800, 1600, 3200	0	0	0	0
Pure oxidant	0	500	1130	0	0

^a The K⁺/Na⁺ ion concentrations by adding KCl/NaCl in the polymer–salt control were equal to the K⁺/Na⁺ ion concentrations maintained by KMnO₄/Na₂S₂O₈ in the polymer–oxidant test. ^b According to Equations (2) and (3), the oxidation of one mole of PCE requires 4/3 moles of KMnO₄ or 2 moles of Na₂S₂O₈, with a molar ratio of 2:3.

The concentrations of oxidants were monitored at 4, 24, 48, and 72 h time intervals by a Hach DR-6000 spectrophotometer. The absorbance for permanganate is at 525 nm, and the absorbance for persulfate is at 450 nm [39]. Two individual samples were taken from each test, and the acceptable range of data deviation was within 3%. Considering that the use of oxidizer permanganate generates a certain amount of manganese dioxide precipitation, the solutions were filtered through a 0.22 µm membrane before analysis to avoid possible interference.

NaCl, KCl, MgCl₂, and CaCl₂ were added to the polymer–oxidant solution with consistent chloride ion concentrations. The same operation was performed for NaCl, NaNO₃, NaHCO₃, and Na₂SO₄ with consistent sodium ion concentrations in order to assess the relative magnitude of the effect of cations and anions on the rheological behavior of the mixed solutions. The salt solution was mixed with the polymer–oxidant solution at a volume ratio of 1:1, and the concentration of salt ions added ranged over five orders of magnitude, from 10⁻⁵ to 10⁻¹ mol/L. The solution's rheological behavior was tested immediately after mixing to assess the effects of the salt concentration. Additions of 0.5 M NaOH or HCl were used to adjust the pH of the polymer–oxidant solution to the desired values. All experiments were performed in a 250 mL Erlenmeyer flask at room temperature (25.0 ± 2 °C) with a glass stir bar to ensure that the solution was completely mixed. All the polymer–oxidant solutions used in the ion and pH tests were obtained by a 1:1 mix of 1600 mg/L polymer and oxidant solution. The polymer and oxidant applied here was the combination assessed to be of the best compatibility in batch tests.

Transport Experiments. An 2D glass tank with 50 cm in length, 35 cm in width, and 3.3 cm in depth was used, which allowed the visual observation of the movement of flooding solutions into the tank. On the glass plate at the inlet and outlet ends of the tank, small holes with a diameter of 1.5 mm were evenly arranged to ensure uniform distribution of fluid. Commercial silica sand (Aladdin, Shanghai, China) of 20–40 and 40–60 mesh were chosen to create hpz and lpz, respectively. Consistent filling steps, soil weights, and template tools were conducted to ensure uniformity between experiments. The lpz was arranged in the middle of the tank, with 1/2 of the length and width of the 2D system, and the volume accounted for 1/4 of the total system volume (Figure 1). The 2D filling system had an average porosity of about 0.373 and a total pore volume (PV) of ~2288 mL. The sweeping efficiency applied here was defined as the percentage of the swept area divided by the total area. Photos of the 2D-Tank captured by digital camera during experiment were processed using ImageJ software (National Institutes of Health, Bethesda, MD, USA).

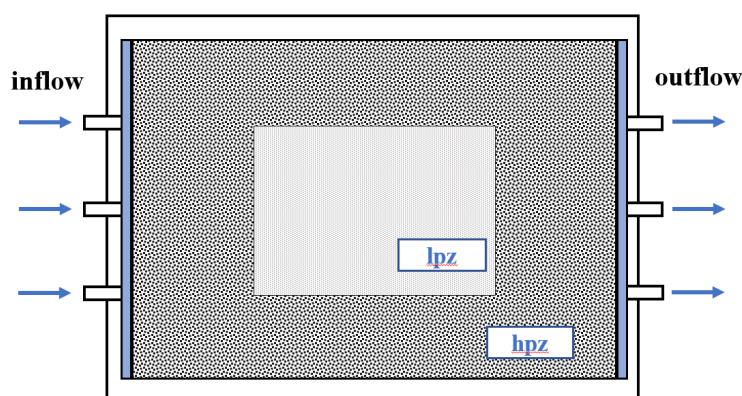


Figure 1. Schematic of the 2D heterogeneous system.

Prior to the flooding test, deionized water and actual groundwater were injected into the packed 2D system to simulate a saturated aquifer system. The groundwater was extracted from a well 128 m below ground surface located in Pinggu District (Beijing, China), its parameters were listed in Table 2. During the flooding test, the injection flow was controlled by a peristaltic pump at a consistent flow rate of 24.5 mL/min. Three sets of experiments were set up for comparative analysis, the inflow was composed of (i) 250 mg/L KMnO_4 (Exps. A1 and A2); (ii) 250 mg/L KMnO_4 mixed with 200 mg/L xanthan (Exps. B1 and B2, the initial system was saturated with deionized water); and (iii) 250 mg/L KMnO_4 mixed with 200 mg/L xanthan (Exps. C1 and C2, the initial system was saturated with groundwater).

Table 2. The values of the groundwater parameters.

Parameters	Value
Na^+ (mg/L)	4.98
K^+ (mg/L)	0.49
Mg^{2+} (mg/L)	32.70
Ca^{2+} (mg/L)	88.23
Cl^- (mg/L)	5.38
NO_3^- (mg/L)	10.91
HCO_3^- (mg/L)	305
SO_4^{2-} (mg/L)	6.47
pH	8.21

3. Results and Discussion

3.1. Chemical Properties of the Polymer Solutions

3.1.1. Viscosity Profiles for the Polymer Solutions

The initial viscosities of six different concentrations of polymers were tested (Figure A1). Both polymer solutions exhibited shear-thinning behavior; that is, the viscosity decreased with increasing shear rate for both polymers. The viscosity changed more markedly with the shear rate at lower shear rates. In addition, the rheological property of the polymer solution was also more pronounced with increasing concentration, and at low concentrations, the polymers almost lost their shear-thinning behaviors, such as xanthan gum at a concentration of 0.2 g/L and HPAM at a concentration of 0.2 g/L or 0.5 g/L. Compared with HPAM, xanthan gum showed higher viscosities under the same conditions within all the test ranges. For example, the viscosity differences ranged from 0.65 cP (at a concentration of 0.2 g/L and a shear rate of 200 s^{-1} , where the viscosities of xanthan gum and HPAM were 2.53 and 1.88 cP, respectively) to as large as 67 cP (at a concentration of 3 g/L and a shear rate of 40 s^{-1} , where the viscosities of xanthan gum and HPAM were 79.2 and 11.88 cP, respectively). As clearly seen from

the viscosity profile, the results implied that xanthan gum may have the better thickening effect of the two substances on the solution when the same concentration is added.

3.1.2. Viscosity Retention over Time

As shown in Figure 2, the xanthan gum solution displayed a relatively high viscosity retention at both concentrations, and the viscosity of the xanthan gum solution showed a steadily declining trend during the test period of 5 days. After 5 days, the viscosity retention rates were within 79–88% and 89–93% for 0.8 g/L and 1.6 g/L, respectively. For HPAM, the solution viscosity change seemed to be segmented. The results showed that HPAM at a concentration of 0.8 g/L maintained a stable retention level (>97%) within 3 days, and a drastic decrease was observed with a viscosity retention rate of 59–87%. A similar trend also occurred at a concentration of 1.6 g/L, and the viscosity retention rate was greater than 97% in the first two days. From day 3, the retention rate was maintained between 70–93%. For both polymer solutions, higher concentrations usually resulted in lower viscosity loss rates. Furthermore, over time, the shear rate had an increasingly pronounced effect on the viscosity retention rate of both polymers. For example, at the initial time, the difference in the viscosity retention rate of all solutions at 50 s^{-1} and 200 s^{-1} was less than 2%, and the differences increased after 5 days, especially for HPAM, for which the difference exceeded 23% at both concentrations. Considering that the median duration of delivery events of permanganate and persulfate in ISCO was approximately 3 days [10], both polymers exhibited high viscosity maintenance over 3 days, which suggests that it is feasible to use these two polymers to increase the viscosity of remedial reagents.

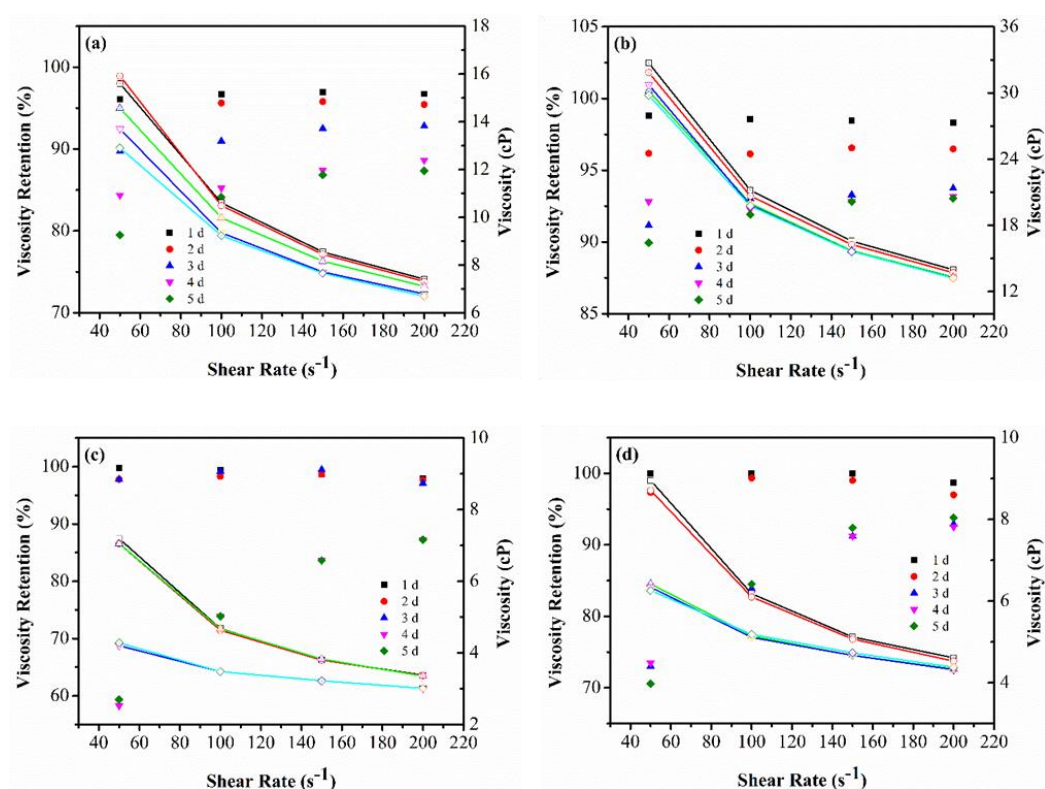


Figure 2. Viscosity change of the polymer solutions with time: (a) 0.8 g/L xanthan solution; (b) 1.6 g/L xanthan solution; (c) 0.8 g/L HPAM solution; (d) 1.6 g/L HPAM solution. The filled symbols indicate “Viscosity Retention” and the white symbols indicate “Viscosity”.

3.2. Polymer–Oxidant Mixture Compatibility

3.2.1. Viscosity and Rheological Behavior of the Polymer–Oxidant Mixture

(1) Viscosity retention

First, 500 mg/L KMnO_4 and 1130 mg/L $\text{Na}_2\text{S}_2\text{O}_8$ were introduced to three concentrations of polymer solutions (800, 1600, 3200 mg/L) to assess the compatibility; since the results presented similar trends for these three cases, only the 1600 mg/L polymer concentration is discussed as a representative example (Figures A2 and A3 for 800 and 3200 mg/L, respectively). Within the test period, the viscosity of the xanthan- KMnO_4 mixture exhibited a high retention rate (by comparing the viscosity of the mixture solution with that of the pure xanthan solution), and under all tested shear rates, this rate did not change much with time. After 72 h more than 76% of the viscosity was still maintained (Figure 3a). Different from the viscosity of the xanthan- KMnO_4 mixture, the viscosity of the HPAM- KMnO_4 solution was apparently affected by the contact time (Figure 3b). After exposure to oxidants for 4 h, the viscosity retention rate was approximately 87%, and after 8, 24, 48, and 72 h, the viscosity retention rates were approximately 76%, 68%, 63%, and 61%, respectively, displaying an obvious declining trend. For both polymer- KMnO_4 mixtures, the effect of the shear rate on the viscosity was negligible, with a variation range of less than 6%.

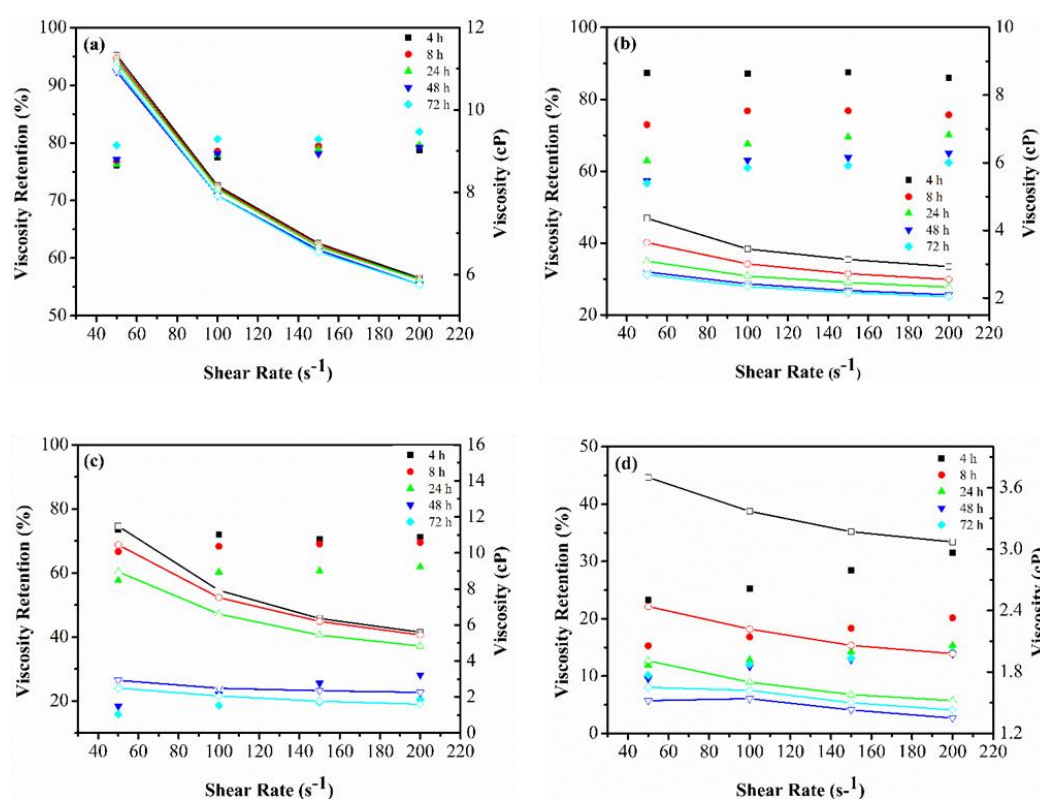


Figure 3. Viscosity retention and shear-thinning behavior of the polymer-oxidant mixtures with time: (a) xanthan- KMnO_4 ; (b) HPAM- KMnO_4 ; (c) xanthan- $\text{Na}_2\text{S}_2\text{O}_8$; (d) HPAM- $\text{Na}_2\text{S}_2\text{O}_8$. The filled symbols indicate "Viscosity Retention" and the white symbols indicate "Viscosity".

Figure 3c,d display the solution viscosity changes of xanthan and HPAM within 72 h after adding activated $\text{Na}_2\text{S}_2\text{O}_8$. HPAM experienced a dramatic decline in viscosity after 4 h of exposure, with less than 32% of the initial viscosity remaining, and this trend persisted over time, leading to almost complete viscosity loss after 72 h (Figure 3d). For the xanthan gum solution, in the first 24 h, the solution exhibited an acceptable viscosity retention rate, which was approximately 70%, 68%, and 60% at 4 h, 8 h, and 24 h, respectively; however, less than 30% remained 48 h later, showing minor evidence for its shear-thinning behavior.

(2) Shear-thinning performance

If the variation of the apparent viscosity of the solution in a certain fixed shear rate interval is used as an indicator to assess the strength of the shear-thinning performance (STP) in this interval, then it can be expressed as follows:

$$STP = \frac{\eta_{r_1} - \eta_{r_2}}{r_2 - r_1} \times 100\% \quad (4)$$

where r_1 and r_2 are shear rates, and $r_1 < r_2$; η is the apparent viscosity at a certain shear rate. A larger STP value indicates that the solution exhibits a higher degree of shear thinning and better rheological behavior.

As shown in Table 3, comparing the pure polymer solution and the polymer–oxidant mixture, the addition of both oxidants had an obvious negative effect on the solution rheological behavior, especially on the HPAM–Na₂S₂O₈, with the STP value decreasing from 1.06% to 0.42% after mixing for 4 h, and the variation was as high as 60%. Moreover, the rheological property of HPAM was significantly changed with time by the effect of the oxidant and showed a gradual downward trend within 72 h (from 0.95% to 0.43% and 0.42% to 0.15% for HPAM–KMnO₄ and HPAM–Na₂S₂O₈, respectively). In contrast, the rheological properties of the pure HPAM solution in the control group remained stable during the test period (the STP values changed within 6%). According to these results, it is considered that the weakening of the rheological properties may be attributed to the fact that HPAM was continuously degraded by the oxidizing agent, causing a loss in HPAM concentration, which led to a decrease in the solution shear-thinning degree. For xanthan, the addition of KMnO₄ reduced its shear-thinning degree to approximately 73.5% of that of the pure xanthan conditions; however, its rheological properties were less affected by the exposure time, with an STP reduction ratio of less than 2%, which was similar to that of the pure xanthan; therefore, it can be assumed that xanthan gum is highly resistant to KMnO₄. Conversely, xanthan's resistance to Na₂S₂O₈ was most apparent over time. This result reflected that the rheological behavior of the mixture performed well during the initial 24 h, and then, the rheological behavior experienced a sharp loss 48 h later. The STP value presented a rapid decline from 2.75% at 24 h to 0.45% at 48 h. Hence, it is suspected that the degradation of xanthan by Na₂S₂O₈ tends to be cumulative. That is, when the action accumulates to a certain extent, it may cause instantaneous breaking of the molecular bond, and as a result, the concentration of xanthan is lowered after a period of time, making it impossible to maintain the original degree of shear thinning. Thus, it is apparent that within 3 days, the xanthan–KMnO₄ combination exhibited the best shear-thinning performance in these tests.

Table 3. STP value of the pure polymer/polymer–oxidant mixture solution ($r_1 = 50 \text{ s}^{-1}$, $r_2 = 200 \text{ s}^{-1}$).

	Duration	Pure Polymer		Polymer–Oxidant Mixture			
	(h)	xanthan	HPAM	xanthan–KMnO ₄	HPAM–KMnO ₄	xanthan–Na ₂ S ₂ O ₈	HPAM–Na ₂ S ₂ O ₈
STP (%)	4	4.91	1.06	3.61	0.95	3.92	0.42
	8	4.83	1.08	3.58	0.73	3.33	0.31
	24	4.84	1.07	3.53	0.51	2.75	0.26
	48	4.61	1.07	3.49	0.45	0.45	0.11
	72	4.61	0.99	3.50	0.43	0.6	0.15

3.2.2. Effect of Oxidant Ions on the Solution Viscosity

Figure 4 illustrates the viscosity effects of both oxidant ions and the corresponding salt ions on the polymer solutions. It can be seen in Figure 4a,b that, when introducing KCl and KMnO₄ to the xanthan solution, a considerable amount of viscosity decrease occurs within 4 h compared with the results for the pure xanthan solution (10.53 cP for pure xanthan, 8.32 cP for xanthan–salt, and 8.16 cP for xanthan–KMnO₄ under the shear rate of 100 s^{-1}), and subsequently, the viscosity remained stable with a slight decline after 72 h (8.2 cP for xanthan–salt, 7.92 cP for xanthan–KMnO₄). The effect of KMnO₄ on the viscosity of xanthan gum solution was slightly greater than that of KCl, and the trends of the overall viscosity changes among these two solutions and the pure xanthan were consistent,

which suggested that the effect of the KMnO_4 and KCl on the xanthan solution was achieved in a short time. If KMnO_4 has an effective degradation effect on xanthan, the solution should exhibit a change that continues to decrease over time. Therefore, it can be inferred that xanthan gum has a high resistance to MnO_4^- and that K^+ plays a leading role in the viscosity reduction of xanthan gum solution. For the HPAM solution, the results presented by adding KCl and KMnO_4 were fairly different. KCl showed little effect on the solution viscosity. In the 72 h test period, the viscosity changed slightly with time, and the retention rate was always approximately 95%. The effect of KMnO_4 on HPAM was significantly influenced by time, and the difference in viscosity between these two increased with time, from 0.35 cP to 1.34 cP. Thus, it may be reasonable to assume that HPAM is much more sensitive to MnO_4^- than xanthan, and, compared to K^+ , MnO_4^- played a more vital role in the viscosity reduction of the HPAM solution.

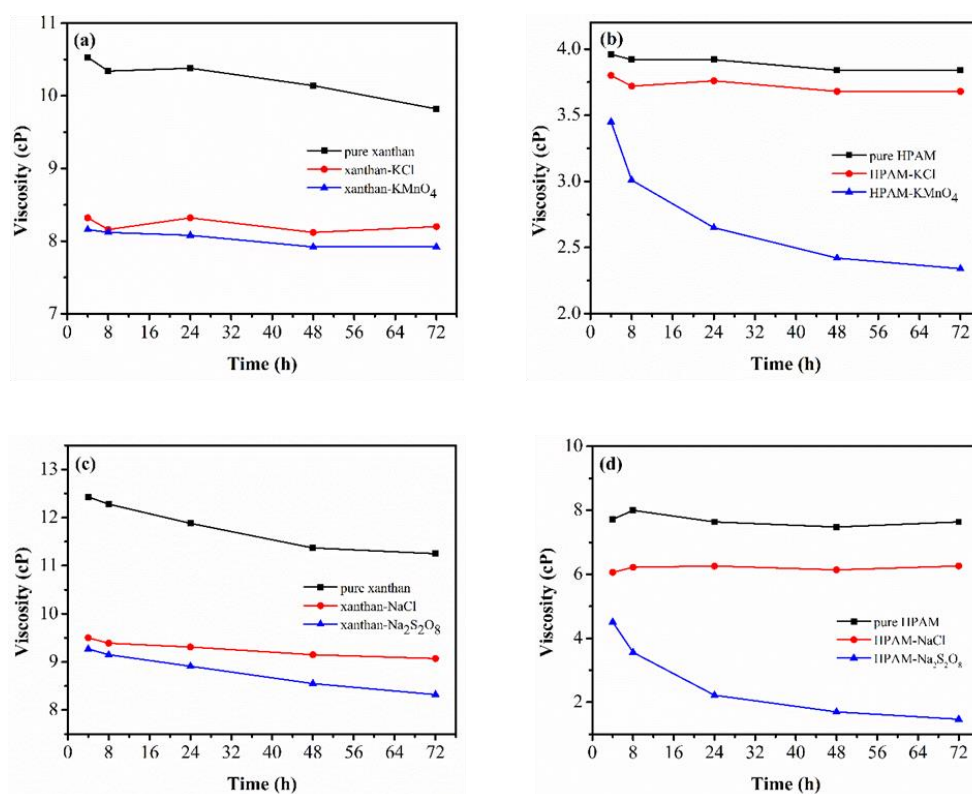


Figure 4. Effects of oxidant ions and salt ions on the solution viscosity. (a) xanthan- KMnO_4 ; (b) HPAM- KMnO_4 ; (c) xanthan- $\text{Na}_2\text{S}_2\text{O}_8$; (d) HPAM- $\text{Na}_2\text{S}_2\text{O}_8$.

The viscosity responses of the two polymers to $\text{Na}_2\text{S}_2\text{O}_8$ and NaCl were essentially consistent with that of KMnO_4 . As presented in Figure 4c,d, the difference between the retained viscosity of xanthan- $\text{Na}_2\text{S}_2\text{O}_8$ mixture and xanthan- NaCl was much less than that between the HPAM- $\text{Na}_2\text{S}_2\text{O}_8$ and HPAM- NaCl tests, which indicated that $\text{S}_2\text{O}_8^{2-}$ may play a stronger role in the decreasing viscosity of the HPAM solution than of the xanthan solution. Salt ions displayed an instantaneous action on the solution viscosity, while the oxide ions could cause the solution viscosity to decrease continuously with time.

Although $\text{Na}_2\text{S}_2\text{O}_8$ can effectively degrade chlorinated contaminants and does not produce solid byproducts (in contrast to KMnO_4), which makes it an attractive candidate oxidant, when exposed to this oxidizing agent, neither the xanthan nor the HPAM polymer exhibited satisfactory viscosity retention but rather lost most of the initial solution viscosity. Therefore, in the subsequent evaluation of oxidant consumption, only the combination of xanthan and HPAM polymer with KMnO_4 was considered due to their relatively strong viscosity retention and shear-thinning performance.

3.2.3. Oxidant Consumption

Although the HPAM solution viscosity was significantly affected by the permanganate oxidant, the overall consumption of oxidant was less than 15% after the 72 h experiment time in all three HPAM concentration cases, as shown in Figure 5. The maximum oxidant consumption occurred at the highest concentration of HPAM. Similar to the case of HPAM, when the concentration of the xanthan solution increased, its consumption of permanganate increased as well. In addition, xanthan exhibited a higher consumption of permanganate than HPAM; after 72 h, the total oxidant consumption of xanthan ranged from 10% to 30% and varied with the solution concentration.

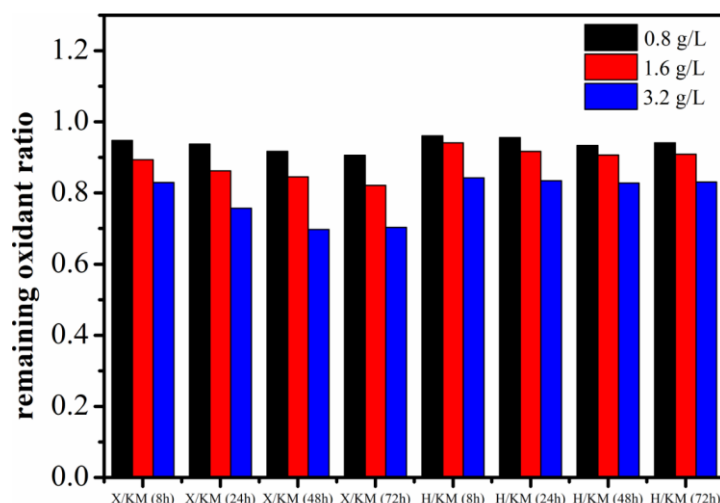


Figure 5. Oxidant consumption of the xanthan-KMnO₄ mixture.

Thus, by comprehensive evaluation of the mixture viscosity maintenance, shear-thinning performance and oxidant consumption, the combination of xanthan gum and KMnO₄ was considered to be the optimal combination.

3.3. Effects of the Groundwater Environment on the Polymer–Oxidant Mixture

3.3.1. Effect of Common Salt Ions

As the best compatible combination assessed in batch tests, the xanthan-KMnO₄ mixture was used in this part of the test.

(1) Effect of salt ions on solution viscosity

Although the solution viscosity varies with the shear rate, its fluctuation trend at each shear rate showed consistency. The detailed analysis of the viscosity change here assumes a shear rate of 100 s^{-1} (medium level within the test range). For MgCl₂, NaNO₃, and Na₂SO₄, the solution viscosity showed a steadily decreasing trend with increasing addition amount. Relative to the initial viscosity of the xanthan-KMnO₄ mixture (5.54 cP), when a salt concentration of $100 \times 10^{-3} \text{ mol/L}$ was added, the viscosity retention rates for MgCl₂, NaNO₃, and Na₂SO₄ were approximately 70%, 75.8%, and 80.7%, respectively (Table 4). In contrast, an obvious rise in the solution viscosity was observed during the addition of KCl, NaCl, NaHCO₃, and CaCl₂. A low concentration ($0.01 \times 10^{-3} \text{ mol/L}$) of KCl displayed a slight viscosity thickening effect; however, as the KCl concentration increased, the solution viscosity began to decrease. A similar phenomenon occurred with NaCl and NaHCO₃: when the amount added reached $0.1 \times 10^{-3} \text{ mol/L}$, the viscosity rebound was approximately 11.7% and 8.0%, respectively. The addition of $100 \times 10^{-3} \text{ mol/L}$ CaCl₂ also resulted in a significant increase in the solution viscosity, which was approximately 15.2% higher than the initial viscosity. Except for CaCl₂, the maximum viscosity loss occurred at the highest concentration ($100 \times 10^{-3} \text{ mol/L}$) of the salts, but all losses were below 30%.

Table 4. Viscosity of the xanthan–KMnO₄ mixture after the addition of salt ions at 100 s^{−1}.

		Salt Concentration (10 ^{−3} mol/L)				
		0.01	0.1	1	10	100
Apparent viscosity (cP)	NaCl	5.03	5.62	5.11	4.36	4.35
	KCl	5.66	4.83	4.63	4.2	4.08
	CaCl ₂	5.32	4.87	4.71	4.2	6.38
	MgCl ₂	5.19	5.03	4.59	4.2	3.84
	NaNO ₃	5.5	5.11	5.11	4.24	4.2
	NaHCO ₃	5.35	5.78	5.31	4.36	4.16
	Na ₂ SO ₄	5.11	4.95	4.83	4.67	4.47

The relative effects of the cations Na⁺, K⁺, Mg²⁺, and Ca²⁺ on the solution viscosity were greatly affected by the concentration. When a small amount was added, the effect of Na⁺ was the largest. With increasing concentration, K⁺ and Mg²⁺ showed a more pronounced effect, while Ca²⁺ maintained a moderate effect on the viscosity under all concentrations. In addition, the effect of SO₄^{2−} on the solution viscosity was apparently higher than that of the other anions at lower concentrations (10^{−5}, 10^{−4}, 10^{−3} mol/L); as the concentration increased, its impact gradually decreased. In contrast, for HCO₃[−] and NO₃[−], the intensity of the ionic effect was positively correlated with the concentration.

(2) Effect of salt ions on the rheological behavior of the xanthan–KMnO₄ mixture

Compared with the other cations, Ca²⁺ could significantly affect the solution rheological behavior. A low concentration of CaCl₂ caused a decline in the STP value, and when its concentration reached 10^{−1} mol/L, the rheological behavior of the solution was greatly enhanced with an STP value of 5.44% (Table 5). Similar trends were also observed when MgCl₂ was added, and a low concentration could slightly weaken the rheological behavior of the solution. When the concentration increased to 10 × 10^{−3} mol/L, a small upward trend occurred (STP = 2.67%, which was larger than 2.10% for 1 × 10^{−3} mol/L). The effects of Na⁺ and K⁺ on the rheological behavior of the mixture solution were relatively stable; in general, an increase in the concentration caused the rheological behavior to be weaker, and among these cations, Na⁺ had the least effect on the STP, which was reflected in the fact that the STP value did not change much at each concentration. Moreover, lower concentrations of NaNO₃, NaHCO₃, and Na₂SO₄ could slightly improve the solution STP (when the concentration was between 0.01 and 0.1 × 10^{−3} mol/L, the STP values of NaNO₃, NaHCO₃, Na₂SO₄ were all above the initial value of 3.2%), and as the concentration increased, this effect was stably diminished; for example, when the addition amount increased to 1 × 10^{−3} mol/L, the rheological behavior of the mixed solutions was close to that of the initial state (3.2%) and showed a gradual weakening trend with increasing concentration. In contrast, the addition of NaCl resulted in a continued weakening of the solution's rheological behavior. Among the species added, HCO₃[−] exhibited the most obvious effect on that solution STP, while the effects of NO₃[−] and SO₄^{2−} were similar. For Cl[−], at higher concentrations, its effect on solution was more pronounced than that of other ions.

Table 5. STP value of the xanthan–KMnO₄ mixture after the addition of salt ions (the initial STP value was 3.2%).

		Salt Concentration (10 ^{−3} mol/L)				
		0.01	0.1	1	10	100
STP (%)	NaCl	3.13	3.07	2.68	2.74	2.52
	KCl	2.70	2.91	2.91	2.31	2.35
	CaCl ₂	2.17	2.33	1.90	2.00	5.44
	MgCl ₂	2.84	2.80	2.10	2.67	2.58
	NaNO ₃	3.53	3.42	3.26	2.82	2.35
	NaHCO ₃	3.63	4.13	3.00	2.89	1.33
	Na ₂ SO ₄	3.46	3.48	3.12	2.74	2.21

Although the salt ions showed a certain degree of influence on the viscosity and rheological behavior of the xanthan–KMnO₄ mixture in the range of test concentrations, considering that the concentration range set in the test was relatively large, combined with the actual groundwater conditions, this impact could be acceptable.

3.3.2. Effect of pH

The initial pH of the xanthan–KMnO₄ mixture was measured to be 6.43, or weakly acidic. The solution pH was adjusted to increase/decrease at a rate of 1 each step, and six pH values were obtained, which were 4.51, 5.46, 6.43, 7.53, 8.49, and 9.46. These values fell within the pH range of all five categories of groundwater quality standards. Figure 6 illustrates the rheological behavior of the mixture solution and its apparent viscosity changes with changing pH values. Under all pH conditions, the mixture solution exhibited good shear-thinning characteristics, and the degree of shear thinning varied slightly with the pH value (from pH 4.51 to 9.46, the STP values were 10.38, 11.09, 11.35, 11.36, 11.09, and 10.79) (Figure 6a). The shear-thinning performance was better when the solution approached neutral conditions, which was consistent with the results for the solution viscosity under a variety of shear rate conditions (Figure 6b). As the degree of acidity or alkalinity increased, the viscosity presented a downward trend, especially under alkaline conditions. The trend was steeper, and the lowest solution viscosity occurred when the pH was 9.46, with a viscosity retention range of 91–95% (compared with the viscosity under initial conditions, where pH = 6.43) that varied with the shear rate. Even so, the viscosity loss was still within the range of 10%. The results implied that the impacts of the groundwater pH on the rheological behavior of the xanthan–KMnO₄ mixture and its viscosity were minor.

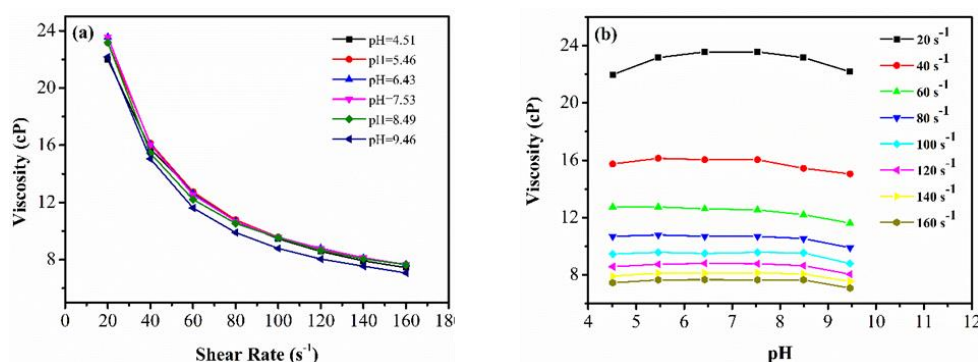


Figure 6. (a) Rheological behavior of the mixture solution under several pH conditions and (b) the viscosity as a function of pH values for several shear rates.

3.4. Sweeping Efficiency

As presented in Figure 7, under all three conditions, the movement of the injected flow in the lpz was apparently slower than that in the hpz, and Figure 7A1 showed a more obvious fingering phenomenon. However, after the addition of xanthan, this phenomenon was greatly weakened (as shown in Figure 7B1,C1). Comparing Figure 7B1 with Figure 7C1, it can be found that when the heterogeneous system was saturated with groundwater, the improvement of fingering phenomenon was not so remarkable as that when introducing the deionized water. This could be mainly due to the fact that when contacting with groundwater, the viscosity of xanthan–KMnO₄ mixture was reduced by ions effects; however, the overall viscosity retention was still considerable; therefore, the improvement was still obvious when compared with pure KMnO₄ injection.

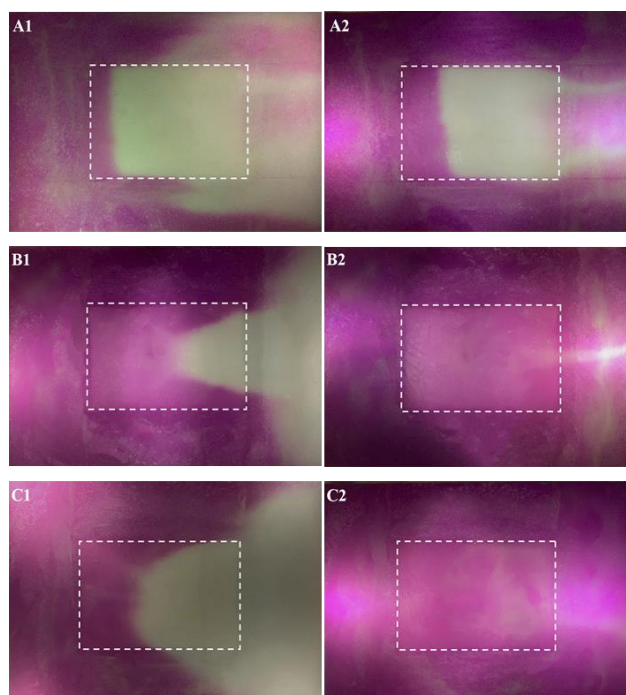


Figure 7. Photographs of solution movement in the 2D tank (photographs **A1,A2** for Exps. A1 and A2; **B1,B2** for Exps. B1 and B2; **C1,C2** for Exps. C1 and C2. **A1,B1,C1** show the movement of the injected solution during the flooding process, while **A2,B2,C2** present the coverage of the solution in the 2D tank when flooding finished).

When injection finished (the area covered by KMnO_4 was no longer expanded), significant differences between treatments were observed (Figure 7A2,B2,C2). In the case of pure KMnO_4 injection, the sweeping efficiency of solution in the lpz was only 28.2% (Figure 7A2). However, when xanthan was introduced to KMnO_4 solution, the sweeping efficiency of the mixture was dramatically raised, and at the end of injection, it eventually reached 100% for both cases of simulated aquifer environments (Figure 7B2,C2). The experimental results demonstrated that the use of xanthan can evidently improve the sweeping efficiency of oxidant KMnO_4 in the low-permeability zone in a saturated aquifer.

4. Conclusions

In summary, by analyzing the viscosity changes of polymer–oxidant solutions, we found that within the test period, the viscosity of the xanthan– KMnO_4 mixture exhibited the highest retention ratio, which exceeded 75%, and its rheological behavior was less affected by the exposure time with an STP reduction ratio of less than 2%. Forty-eight hours after its exposure to $\text{Na}_2\text{S}_2\text{O}_8$, the mixture presented a retention ratio of less than 30%, and less evidence was collected regarding its shear-thinning behavior. Conversely, the addition of both oxidants presented significant negative impacts on the viscosity and rheological behavior of the HPAM solutions. The results indicated that xanthan gum has a high resistance to MnO_4^- and that K^+ plays a leading role in the viscosity reduction of xanthan gum solution. For the HPAM solution, KCl showed little influence on the solution viscosity, while the effect of KMnO_4 on HPAM was significantly influenced by time. It may be reasonable to assume that HPAM is much more sensitive to MnO_4^- than xanthan and that compared to K^+ , MnO_4^- plays a more vital role in the viscosity reduction of the HPAM solution. The viscosity responses of the two polymers to $\text{Na}_2\text{S}_2\text{O}_8$ and NaCl were approximately consistent with that of KMnO_4 . Although xanthan gum demonstrated a greater oxygen consumption than HPAM, by comprehensive evaluation of the mixture viscosity maintenance, the shear-thinning performance, and the oxidant consumption, xanthan– KMnO_4 is considered to be the optimal combination.

It was found that the xanthan–KMnO₄ mixture viscosity showed a steadily decreasing trend with increasing amounts of MgCl₂, NaNO₃, and Na₂SO₄, while KCl, NaCl, NaHCO₃, and CaCl₂ presented a thickening effect in a certain concentration range. However, in most cases, the viscosity decreased with increasing salt concentration, and the maximum viscosity losses were all less than 30%. The relative effects of ions on the solution viscosity were greatly affected by their concentration. At lower concentrations, Na⁺ and SO₄^{2−} showed a stronger effect on the viscosity than the effect of other anions and cations, while K⁺, Mg²⁺, HCO₃[−], and NO₃[−] played a more dominant role as the concentration increased. Compared with the other cations, Ca²⁺ could more significantly affect the solution rheological behavior, and Na⁺ showed the least effect. Among the anions, HCO₃[−] exhibited the most obvious effect on the solution STP. Although the salt ions showed a certain degree of influence on the viscosity and rheological behavior of the xanthan–KMnO₄ mixture, combined with the actual groundwater conditions, these impacts could be acceptable. Furthermore, the results implied that the impacts of the groundwater pH on the rheological behavior of the xanthan–KMnO₄ mixture and its viscosity were minor. The experimental results in the two-dimensional simulated saturated aquifer system further demonstrated the feasibility of using the shear-thinning polymer xanthan in combination with KMnO₄ for field-scale applications.

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Appendix A. Viscosity Profile of Polymers

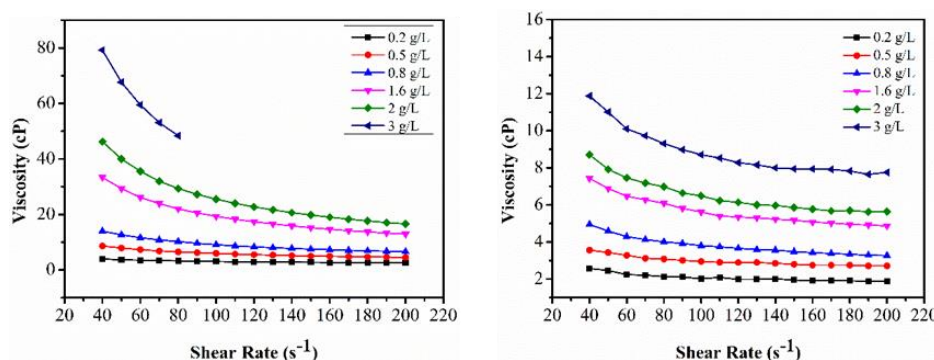


Figure A1. Viscosity profile of xanthan gum and HPAM.

Appendix B. Viscosity Retention and Shear Thinning Behavior of the Polymer–Oxidant Mixtures

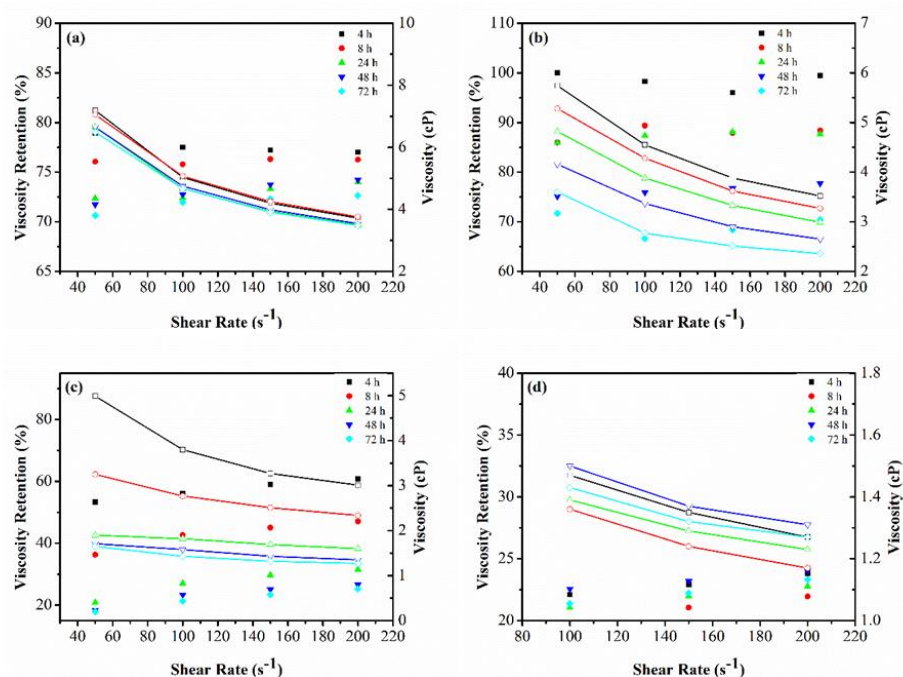


Figure A2. Viscosity retention and shear thinning behavior of the polymer–oxidant mixtures with time: (a) xanthanKMnO₄; (b) HPAMKMnO₄; (c) xanthanNa₂S₂O₈; (d) HPAMNa₂S₂O₈. The concentration of polymer is 0.8 g/L. The filled symbols indicate “Viscosity Retention” and the white symbols indicate “Viscosity”.

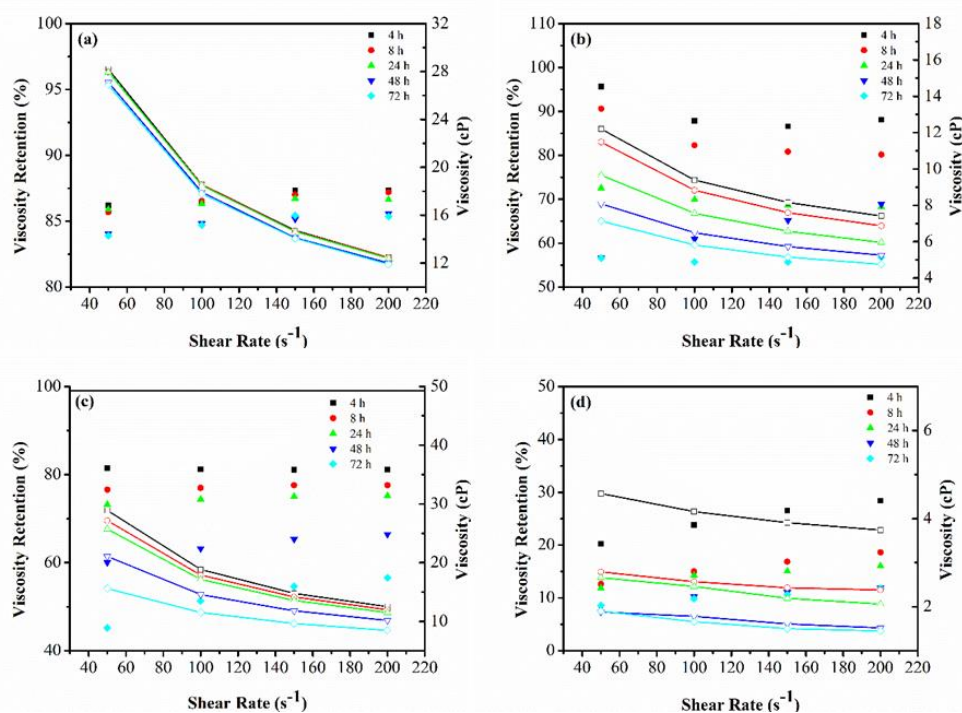


Figure A3. Viscosity retention and shear thinning behavior of the polymer–oxidant mixtures with time: (a) xanthanKMnO₄; (b) HPAMKMnO₄; (c) xanthanNa₂S₂O₈; (d) HPAMNa₂S₂O₈. The concentration of polymer is 3.2 g/L. The filled symbols indicate “Viscosity Retention” and the white symbols indicate “Viscosity”.

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