ADSORPTION AND DEGRADATION BEHAVIOR OF METHANOL IN PRODUCED WATER IN THE SOILS OF NORTHERN SHAANXI GAS FIELD, CHINA

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Abstract. Injection of methanol as a thermodynamic inhibitor is a common approach in the petroleum industry. Due to the volatility and recovery process of methanol, it could be found in natural waters, sediments, soil, and so on. This study focused on adsorption and degradation behavior of methanol in produced water （PW） at northern Shaanxi oil and gas fields soil, China. Through dynamic tests, the results showed that the pH, gas condensate, salinity of PW and temperature have weak influences on methanol adsorption on the soil. Through the simulated degradation experiments, the chemical oxidation, photo and thermal degradation were found not to be the main mechanism of methanol degradation (MD) in nature. The methanol in some soil could not de degraded completely by Nitrate-reducing bacteria (NRB) in the soil within 60 days unless methanol content was less than 600 mg/L with NRB medium. The Griess detection verified that there were NRB in five soils. Even without the NRB medium, there are great differences in MD of the soils. If the concentration of methanol was more than 1000 mg/L, the MD efficiencies were obviously slowing down, nearly 0. The longer the gas development time of the study region, the stronger the MD ability of the region's soil.
Keywords: *methanol, adsorption, degradation, sandy soil, Nitrate-reducing bacteria (NRB)*

Introduction

In economic and safety hazards points of view, it is crucial to avoid the formation of clathrate hydrate of gases in oil and natural gas transportation/production systems (Muromachi, 2019). Injection of methanol as a thermodynamic inhibitor is a common approach in industry to shift the hydrate phase boundary to higher pressures/lower temperatures. Because of its high volatility, methanol is lost in the vapor phase, which lead its toxicity to the environment and human beings (Aziz et al., 2002). Although methanol in aqueous solution was generally treated by biological treatment and advanced oxidation processes (AOPs), in which the most

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commonly used approaches were the up flow anaerobic sludge bed (UASB), supercritical water oxidation (SCWO), bio-filtration and plasma degradation (Ma et al., 2009, 2013; Fujii et al., 2011; Barcón et al., 2012; Zhen et al., 2017; Wu et al., 2019), but few studies focused on adsorption and degradation behavior of the methanol in produced water (PW) in the soil. The northern Shaanxi oil and gas fields is located in Ordos plateau (Semi-arid region), China. The surface layer of the soil is the quaternary aeolian sandy soil or brown desert soil, among which aeolian sandy soil is in the majority. Because of the special soil composition, the methanol will show special adsorption and degradation behavior in the soil. Through temperature oscillation dynamic tests and the simulated degradation of methanol in the five kinds of typical soil, the behavior of adsorption and degradation have been discussed, which lead to a better understanding of the influence of methanol on the north Shaanxi gas field environment.

Material and Method

Soil Sample collection and pre-treatment

The five kinds of soil samples were collected from five different sites located in Northern Shaanxi gas field, respectively is Jingbian gas field (1#), Jingbian farmland (2#), Zizhou gas field (3#), Zizhou farmland (4#) and Wuding river (5#) in Mizhi county, Yunlin city. The map of study area were showed as in *Fig. 1*. The surface layer is the quaternary aeolian sandy soil or brown desert soil, among which aeolian sandy soil is in the majority (Ma et al., 2013). The sampling date was April to May, 2018. The sampling depth is 0 ~ 20 cm. After the soil sample is naturally dried, ground and sifted with a 2 mm sifter, then stored in five bottles at low temperature.

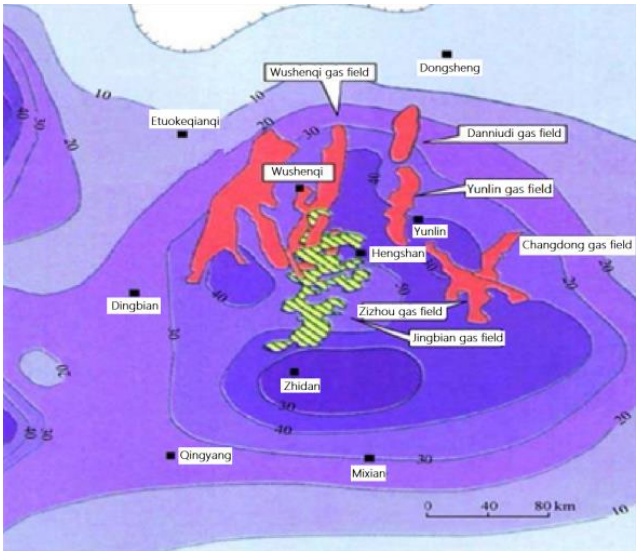

Figure 1. *The map of study area*

Measurement of soil parameters

The physiochemical analysis (pH, moisture, organic matter content and mass size distribution) of five samples was respectively refer to "Soil dry matter and moisture determination - gravimetric method" (HJ 613-2011), "Soil test part II: determination of pH" (NY/T 1121.1 – 2006), "Determination of forest soil organic matter and calculation

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of carbon - nitrogen ratio" (LY/T 1237 – 1999) and the Wu's method (Ghasemy et al., 2019).

Adsorption test

Adsorption of methanol in different soils

Due to the strong adsorption capacity of bentonite and activated carbon, these two materials were selected as the experimental reference in order to facilitate the study of the adsorption capacity of methanol in five soil samples. The seven samples were taken respectively in the experiment and 20.00 g were put into a 250 mL glass bottle, and 100 mL methanol concentration of 1000 mg/L solution with 10000 mg/L salinity and a certain amount of microbial inhibitors were added. Then, the sealed 250 mL bottle were settled in the thermostatic oscillator (TS-200B, Shanghai Tiancheng co. LTD) under the condition of 25℃ for 24 h, later transferred to the soil suspension in the centrifuge tube at 4000 r/min centrifuge for 10 min after taking centrifugal supernatant on 2 mL for methanol concentration. The concentrations of methanol was determined by gas chromatography (Agilent HP 6890). A packed column (Agilent Porapak N G3591-80036) was used. The retention time of methanol was 5.652 min (Ma et al., 2013). The adsorption capacity and samples site were compared, and 3# was selected as the representative for future research.

Adsorption equilibrium and isotherm of methanol in soil

In Adsorption equilibrium test, the 2 mL supernatant was samples after 0.5, 1, 2, 4, 6, 8, 10, 12, 24 h. In Adsorption isotherm test, the methanol concentration, respectively is 0, 20, 40, 60, 80, 100, 200, 500 and 1000 mg/L. Other test conditions are consistent with conditions detailed above.

Affecting factors of methanol adsorption in soil

The range of PW pH , temperature, gas condensate, salinity were according to the quality of gas PW from Northern Shaanxi gas field (The quality of gas PW from North Shaanxi gas field had analyzed by our lab in the past 10 years). Other test conditions are consistent with conditions detailed above.

Degradation behavior of Methanol in soils

Physicochemical factors on degradation of methanol in different simulation conditions

When the gas PW with methanol is treated and injected back into the stratum, it will directly or indirectly enter the soil environment because of evaporation and leakage. According to the possible factors affecting degradation of methanol in the possible environment, ammonium persulfate and hydrogen peroxide (used as oil-field chemicals), high temperature and pressure (reinjection into some formations), strong ultraviolet (direct splar radiation) were selected to make a series of simulation experiments to study the degradation degree of methanol in gas PW under different conditions. A temperature and pressure reactor (Parr 4578, Parr instrument company, USA) was used to stimulate the condition of reinjection formation (200℃ and 15 MPa). The 50 g core powder was added into the reactor, and the methanol equilibrium concentration after 12 hours adsorption in core powder was the baseline concentration for degradation. A UV light (80W, Xinbao Environmental Products Co., Ltd., CHN) was used to stimulate rapid splar

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radiation. The source of radiation was located 25 cm from samples and positioned horizontally. All solution is 1 L and 1000 mg/L methanol, and other experimental temperature is 25℃ unless it is specifically requested.

Stimulated degradation experiment in different soils

Nitrate reducing bacteria (NRB) are very common in nature, most of which are facultative. When methanol (CH_3OH) is used as the carbon source in wastewater treatment, the reaction formula for synthesis of exogenous denitrifying cells was shown in *Eq.1* (Ma and Wei, 2009).

$$NO_3^- + 1.08CH_3OH + 0.24H_2CO_3 \rightarrow 0.06C_5H_7NO_2 + 0.47N_2 + 1.68H_2O + CO_2 + OH^- \quad \text{(Eq.1)}$$

According to the above theory, if methanol is degraded by NRB in nature, the degradation rate would increase. Therefore, the difference between with or without the medium of NRB (M_{NRB}) was compared in different salinity water with different methanol concentration under 25℃ and the proportion of 1# soil to methanol (20%) after 60 days. *Table 1* is the composition of M_{NRB}.

Table 1. *The composition of M_{NRB}*

Composition	KH_2PO_4	$KHCO_3$	$MgSO_4$	$FeCl_3$	$CaCl_2$	CH_3COONa	$(NH_4)_2SO_4$	$NaNO_3$
Concentration (mg/L)	30	500	200	100	30	860	660	850

According above studies, the different soils was respectively soaked in the simulated water containing 200 ~ 2200 mg/L methanol (salinity: 100000 mg/L) for 120 d with the proportion of the soils to methanol (20%). In order to verify the effect of NRB, NRB was enriched, separated and screened form five soils samples, respectively. Two strains in every solid mediums plate were selected, which grow faster, colony moist, roundness, surface smooth, edge tidy, bulging and larger colonies. After many times of separation and purification, a strain was selected out of every two in the soil, which were 1S#, 2S#, 3S#, 4S# and 5S# strain. The five strains of bacteria were tested with Griess reagent (García-Robledo et al., 2014).

Each experiment was performed three times, and the average value is calculated by three parallel experiments.

Results and discussions

Physiochemical analysis results of five samples

The physiochemical analysis results of five samples were shown in *Table 2*. The minimum moisture of five soils was 0.30% (w/w) while the maximum is 1.45% (w/w). The pH values of the tested soil samples were all around 8.0 ~ 9.0, belonging to weakly alkaline soil. The organic content of the tested soil samples was also relatively small, among which the organic matter content of 4# was the highest, 0.655% (w/w) and that of 1# was the lowest, 0.266%(w/w). All soils are sandy soil, except 4# soil is loam sandy soil, which would lead that it was easy for the methanol to infiltrate into the groundwater through them.

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Table 2. *Physiochemical analysis results of five soil samples*

No.	pH	Moisture (w/w%)	Organic matter (w/w%)	Mass size distribution（w/w%）					Type
				2-50μm	50-100μm	100-250μm	250-1000μm	1000-2000μm	
1#	8.34	0.30	0.266	0.0000	0.2413	0.7354	0.2330	0.0000	sandy soil
2#	8.61	0.55	0.307	0.0000	0.1911	0.7616	0.4730	0.0000	sandy soil
3#	8.78	1.10	0.410	0.0000	0.3149	0.4809	0.2042	0.0000	sandy soil
4#	8.88	1.45	0.655	0.0000	0.5623	0.2014	0.2363	0.0000	loam sandy soil
5#	8.66	0.50	0.366	0.0000	0.1659	0.7407	0.9340	0.0000	sandy soil

Adsorption of methanol in different soils

The results of methanol adsorption capacity (MAC) in different soils are shown in *Fig. 2*. The MAC in the five tested soil samples was significantly different from that of activated carbon and bentonite. The largest adsorption capacity of activated carbon was up to 2.38 mg/g, that of bentonite took second place, reached about 1.37 mg/g, and those of five soils are between 0.45 mg/g and 0.60 mg/g. Among five soils, the soil from Zizhou had higher adsorption capacity than those of other soils. The reasons should be that the soil from Zizhou has higher organic content which lead to higher adsorption capacity. The experimental results are consistent with the characteristics of small activated carbon/bentonite particles, large specific surface area of particles and large adsorption capacity. Therefore, it can be concluded that the five soils have a certain adsorption capacity for methanol, but the adsorption amount is relatively small. All that also should lead that most of methanol could infiltrate into groundwater through them easily and not be degraded in the soils.

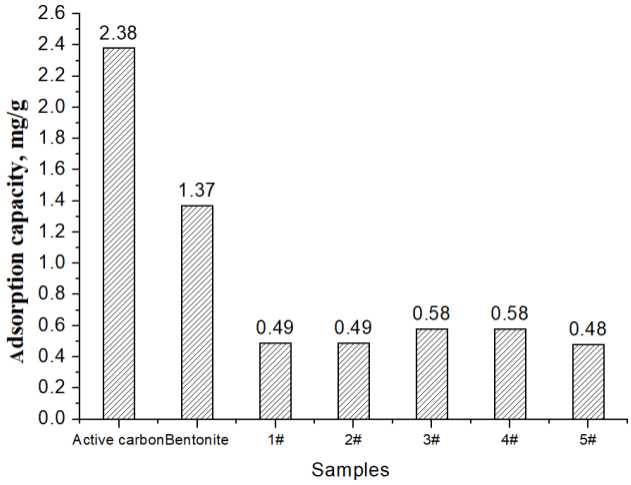

Figure 2. *MAC in different samples and soils*

Adsorption equilibrium and isotherm of methanol in soil

The adsorption equilibrium curve and isotherm curve of methanol in 3# soil respectively was shown in *Fig. 3* and *Fig. 4*.

From *Fig. 3*, when the adsorption time was less than 10 h, the adsorption capacity of methanol in the 3# soil increased rapidly, but when the adsorption time was more than

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10 h, the adsorption capacity tended to be stable, and the maximum adsorption amount was about 0.55 mg/g. This reason is that the opportunity for the soil to fully contact methanol increases with the gradual extension of time, and the amount of methanol adsorption in the soil increases. From *Fig. 4*, when the methanol concentration is samller than 200 mg/L, the adsorption capacity increases sharply with the increase of methanol concentration. When the methanol concentration is higher than 200 mg/L, the adsorption capacity tends to be balanced, about 0.5 mg/g, which indicated that the adsorption capacity of methanol in the soil had reached a saturated state.

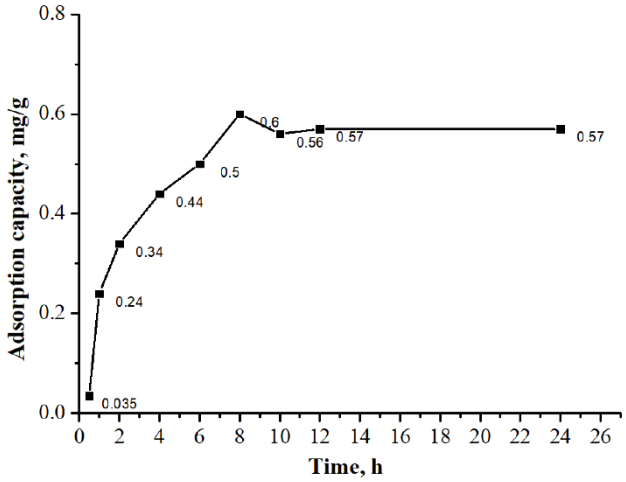

Figure 3. *Adsorption equilibrium curve of methanol in 3# soil*

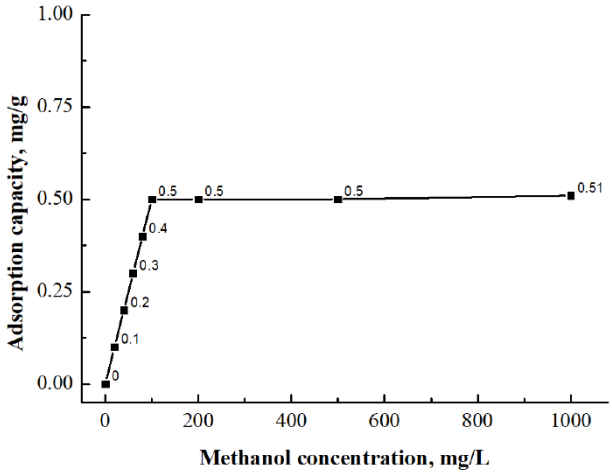

Figure 4. *Isotherm curve of methanol in 3# soil*

Affecting factors of methanol adsorption in soil

pH values

The influence of different pH values on the methanol adsorption amount (MAA) was shown in *Fig. 5*. As can be seen from *Fig. 5*, with the increase of pH value of solution, the MAAin soil gradually decreases from 0.458 mg/g to 0.007 mg/g. In the alkaline environment, the sediments and organic matter in the soil may undergo flocculation

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changes, leading to the fact that methanol molecules cannot be uniformly adsorbed on the soil sediments and organic matter (Viotti et al., 2000). Lopez et al. (1996) believe that at low pH, strong hydrogen bonds are formed between organic pollutants and O, N, and H atoms in some materials in the soil, but they are completely different under alkaline conditions, and the resistance to hydrogen bond formation increases, leading to hydrogen bond dissociation. Some scholars also reached the conclusion that the adsorption amount of an organic compound in alkaline soil was low, while that in acidic soil was high (Ertli and Marton, 2004; Goh and Lim, 2004). With the increase of pH value, the increase of OH^{-1} content on the surface of soil particles leads to the increase of electrostatic repulsion force, the decrease of charge density on the surface of soil, and the decrease of adsorption force on the surface of soil particles. The pH value is an important factor affecting the variable charge, and the change of pH value has an important impact on the electrostatic adsorption of anions. With the decrease of pH value, the positive charge increases, and the amount of electrostatic adsorption of anions increases. In the case of pH > 7, even the variable charge soil with kaolinite and iron and aluminum oxides as the main colloidal substances has a relatively low electrostatic adsorption capacity of anions (Zhang, 2009).

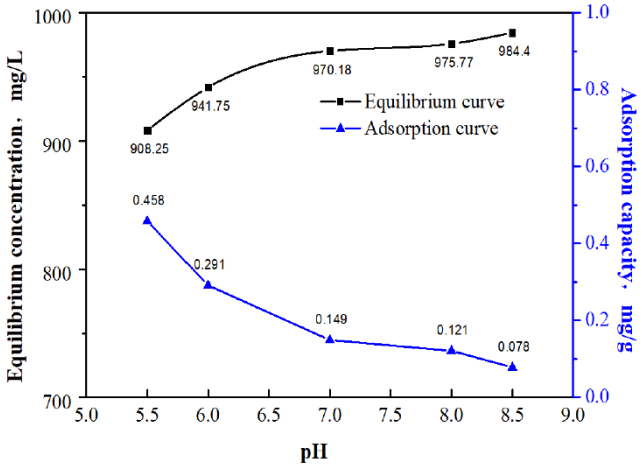

Figure 5. *Influence of different pH values on the MAA in 3# soil*

Salinity

The effects of water quality with different salinity on the adsorption of methanol in soil was shown in *Fig. 6*.

The MAA in soil increases from 0.373 mg/g to 0.487 mg/g with the increase of salinity in solution from 0 mg/L to 100000 mg/L. This was due to the adsorption coefficient (*Kp*) is defined as follows *Eq.2* (Pena et al., 2019):

$$K_p = \frac{\text{Adsorption capacity of organic compounds in the solid phase, mg/g}}{\text{dissolved amount of organic matter in aqueous solution, mg/L}} \quad \text{(Eq.2)}$$

From *Eq.2*, the *Kp* is related to the adsorption amount in solid phase and the solubility of organic matter in water phase. With the increase of salinity in soil solution, the solubility of organic matter in water decreases, which is mainly due to the influence of "salting out". Salting out, in which salts are added to an aqueous solution of a substance, results in a decrease in the solubility of the substance. In this experiment, the soil adsorption increased with the increase

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of salinity, indicating that methanol was affected by "salting out". Since "salting out" reduced the value in the denominator of the above equation, *Kp* value increased (Zhao et al., 2000). The lower the solubility, the higher the solid adsorption. The adsorption capacity is closely related to the hydrophilicity of the adsorbed substance. Although salinity cannot change the nature of the adsorbed substance in the soil, it does change its solubility. Therefore, it is basically the same as increasing its hydrophobic effect, so the solid phase adsorption increases. It can be seen from the above analysis that the adsorption of pollutants by salinity mainly affects the solubility of pollutants (Gennadiev et al., 2015).

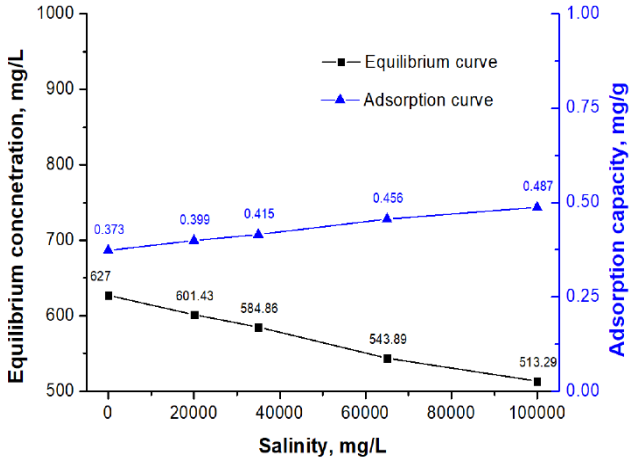

Figure 6. *Influence of different salinity on the methanol adsorption amount in 3# soil*

Condensate oil

The effect of condensate oil content on the methanol adsorption in soil was shown in *Fig. 7*.

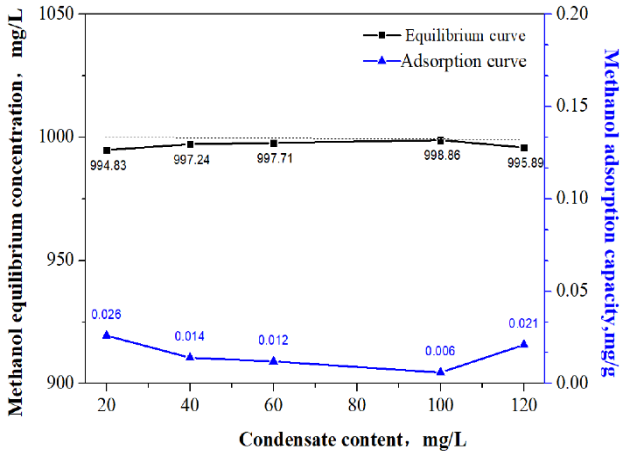

Figure 7. *Effect of condensate oil content on the methanol adsorption in 3# soil*

With the increase of the condensate concentration, the equilibrium concentration of methanol in the soil did not change much, between 994.83 mg/L and 995.89 mg/L, indicating that the condensate could not be adsorbed by the sediments or organic matters

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in the soil after entering the soil environment. Some scholars also found similar phenomena in soil-water system (Jonker et al., 2003, 2006). They called the minimum concentration of oil in sediments or soil in independent form as critical sperate phase concentration (CSPC), and pointed out that this concentration was related to organic matter content. Generally, the higher the organic matter content is, the higher the CSPC is, which is 11% (Khan et al., 2018) or 15% (Li et al., 2019) of the soil organic carbon content. The soil organic matter content of 3# sandy soil is 0.41%, which should be 1100 or 1500 mg/kg according to the theoretical value of CSPC in previous studies. The practical significance of CSPC is that when the condensate oil concentration in the soil is greater than this value, the condensate oil can exist in the soil in the form of free state (independent phase), as a "adsorbent" to enhance the overall adsorption (distribution) ability of the soil to other organic pollutants. When the value is less than that, the condensate oil is absorbed by the soil organic matter in the form of "adsorbent", which may compete with other organic pollutants for the adsorption position on the organic matter. In the study of Jonker et al. (2003, 2006) this competitive adsorption was more obvious.

Temperature

The influence of environmental temperature on the MAA in the soil was shown in *Fig. 8*. With the increase of temperature from 10 ℃ to 35℃ , the MAA in the soil also increases obviously (from 0.330 mg/g to 0.975 mg/g) when the temperature was below 35℃. When the temperature rises to 35℃, the adsorption curve begins to be smooth, methanol adsorption capacity is essentially unchanged. It indicates that the adsorption reaction rate of methanol in soil increases with the increase of temperature. When the adsorption capacity of methanol in soil reaches a balance, the MAA in soil does not increase, indicating that the adsorption of methanol in soil is an endothermic process. Li et al. (2019) believed that soil adsorption is a kind of biphasic adsorption, and mineral as a traditional solid adsorbent, organic matter as a distribution medium. As the temperature rises, water molecules are more affected by molecules than organics, and the relative adsorption competitiveness of organic matters increases, and the adsorption capacity on the mineral surface increases (Pena et al., 2019).

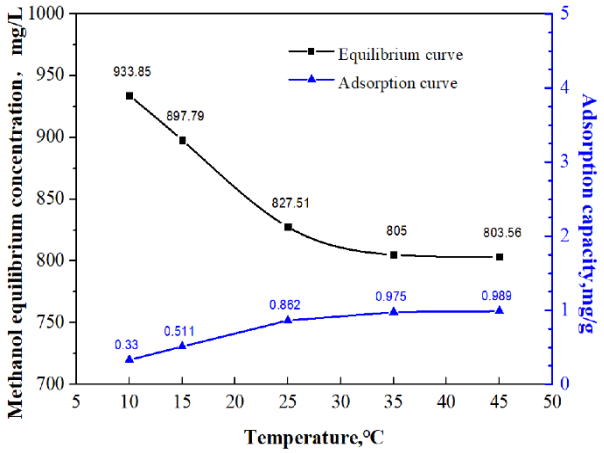

Figure 8. *Influence of environmental temperature on the MAA in 3# soil*

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Degradation behavior of methanol in soils

Physicochemical factors on degradation of methanol in different simulation conditions

Degradation degree of methanol in different simulated extreme environment was shown in *Table 3*. The degradation efficiency (η) of methanol in extreme environment (200℃, 15 Mpa) after 30 days was only 10.18%. The *η* of strong ultraviolet radiation and the chemical oxidation were 23.94%, 21.69% and 11.84%, respectively. The radiation intensity and the concentration of chemical oxidant were usually more than their value in nature. The results showed that among the factors on degradation of organic matter in nature, the physicochemical factors, such as thermal degradation relying solely on temperature, chemical oxidation degradation and photo-degradation could not be found the main factors of methanol degradation (MD).

Table 3. *Degradation degree of methanol in different simulated environment*

Simulated extreme environment (200℃, 15 MPa)			**Strong ultraviolet radiation (Power: 80W)**			**Chemical oxidation (Reaction time: 30 min)**			
Reaction time (day)	Concentration (mg/L)	η (%)	Reaction time (h)	Concentration (mg/L)	η (%)	Reaction dosage (mg/L)		Concentration (mg/L)	η (%)
0	933	0	0	1000	0	Ammonium persulfate ($(NH_4)_2S_2O_8$)	0	1000	0
4	886	5.04	10	942	5.78		300	858	14.21
6	861	7.72	20	901	9.86		500	846	15.39
8	859	7.93	40	827	17.31		800	783	21.69
10	857	8.15	60	803	19.72	Hydrogen Peroxide (H_2O_2)	0	1000	0
12	854	8.47	80	799	20.12		5000	1093	2.51
14	841	9.86	100	781	21.87		10000	1025	6.89
30	838	10.18	120	761	23.94		20000	882	11.84

Nitrate reducing bacteria influence on methanol degradation

NRB influence on (MD) in 1# soil was shown in *Fig. 9*. Obviously, the ability to degrade methanol of 1# soil with M_{NRB} was much higher than that of 1# soil without M_{NRB}, up more than 50%, which indicated that NRB could significantly promoted the degradation methanol ability of the soil.

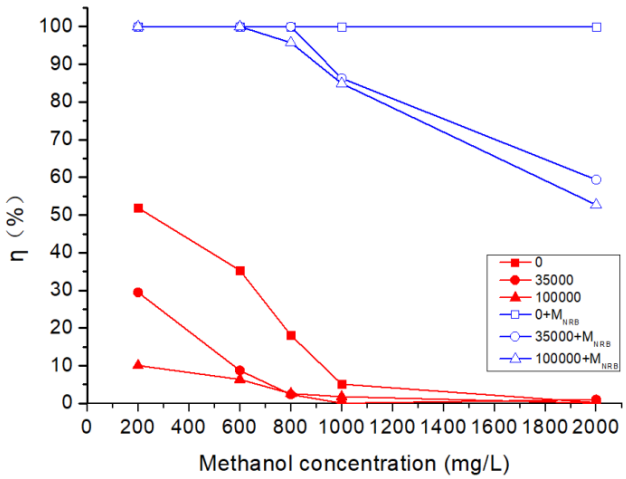

Figure 9. *NRB influence on MD in 1# soil (60 days)*

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In the presence of M_{NRB}, methanol concentration in fresh water was less than 2000 mg/L, the methanol can be completely degraded in 1# soil. In the absence of M_{NRB}, methanol cannot be completely degraded within the range of 200 ~ 2000 mg/L, the highest η was only 51.9% and the lowest one was 0.07%, nearly 0. In the presence or absence of M_{NRB}, the degradation rate began to decline when the salinity increased, and the degradation rate decreased significantly when the methanol concentration was more than 1000 mg/L. The reason should be that both salt and methanol have inhibitory effect on soil microorganisms and affect the biodegradation of methanol.

Methanol degradation in different soils

MD efficiency in different soils was shown in *Fig. 10*.

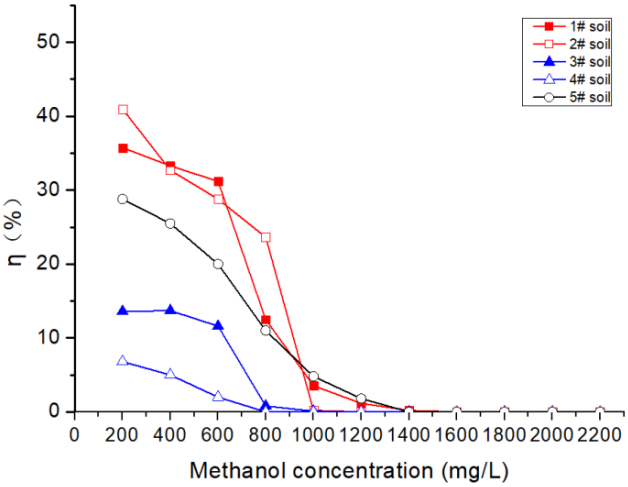

Figure 10. *Different MD in different soils (Salinity: 100000 mg/L, Without M_{NRB} and 120 days)*

When the salinity is 100000 mg/L in the absence of M_{NRB}, the degradation degree of methanol was obviously different when the initial concentrations were different. The highest η was 2# soil, 41.0%. The degradation rate decreased rapidly when the methanol concentration was greater than 1000 mg/L. The lowest one was nearly 0 when the methanol concentration is more than 1400 mg/L. There were great differences existing in degradation rate of different soil. The 1# and 2# soil from Jingbian had the best degradation ability of methanol, followed by the 5# from the Wuding river, the worst were that of 3# and 4# soils from Zizhou. The main reasons should be the Jingbian region had the longest history of developing gas, so it is the earliest blocks where the methanol was first used among the three regions. The microbes in Jiangbian surrounding soil has more superiority strains capable of degrading methanol. The 5# sediments was from Wuding river, so the microbial content in it was relatively high. Therefore, 3# soil and 4# soil had the lower degradation ability of methanol than other's.

The Griess detection result of five strains was showed in *Fig. 11*. Compared with the control, all the bacterial solutions immediately changed from colorless or pale yellow to red after the addition of Griess reagent, which indicated that all strains were NRB. Under the same culture conditions, the color of the reaction between strain 3S# and Griess reagent was lighter than that of other strains, while that of strains 1S# and 4S# was faster and darker. This may be related to the quantity of nitrate reductase and nitrite reductase

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produced by each strain. The higher the concentration of nitrate reductase and nitrite reductase in the bacterial solution, the deeper the color rendering, which indicated that the denitrification ability of each NRB is different (Ma and Wei, 2009). Compared with the degradation results, the denitrification ability of five NRB strains from five soils did not correspond to the MD capacity of five soils. The reason should be that the MD in the soil was not entirely dependent on NRB, but the NRB significantly promoted the degradation methanol ability of the soil.

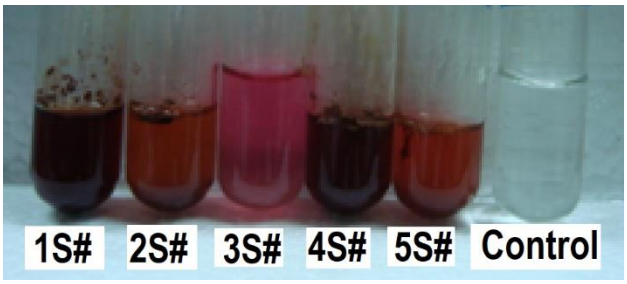

Figure 11. *Griess detection photo of five strains form five soils*

Conclusion

Five kinds of soils in the study region are sandy soil or loam sandy soil, and the MAA of them are relatively small, which would lead that the methanol to infiltrate into groundwater through them easily not be degraded in the soils. The pH, gas condensate, salinity of PW, temperature have the weak influences on methanol adsorption on the soil. Through the simulated degradation experiment of methanol, the chemical oxidation degradation, photo-degradation and thermal degradation are not the main mechanism of MD. But when the methanol comes into contact with the soil, the methanol in some soils could not de degraded completely by NRB in the soil within 60 days unless methanol content is less than 600 mg/L with NRB medium. The NRB significantly promoted the degradation methanol ability of the soil. Even without the NRB medium, there are large differences among the soils although five soils had the certain capability to degrade methanol. When the methanol content increase or the salinity of the water increased without M_{NRB}, the MD rate decreased. The Griess detection verified the there were NRB in five soil. The longer the gas developing time of the studying region, the stronger the methanol degrading ability of the region's soil. If the concentration was more than 1000 mg/L, the MD efficiencies were obviously slow after 120 days. Both salt and methanol have inhibitory effect on soil microorganisms and affect the biodegradation of methanol. The conclusion leaded to a better understanding of the influence of methanol on the north Shaanxi gas field environment, and suggested that the biodegradation of methanol in nature should be considered, especially NRB.

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