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Effect of immobilization on growth and organics removal of chlorella in fracturing flowback fluids treatment

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ABSTRACT

In this paper, fracturing flowback fluids were biologically treated by immobilized chlorella. The individual and interactive effects of three variables (sodium alginate concentration, $CaCl_2$ concentration, and crosslinking time) on growth of immobilized algal were optimized by response surface methodology combined with Box-Behnken design. The results showed that the SA (sodium alginate) concentration most significantly affected algal density and treatment efficiency. The interaction between SA concentration and crosslinking time was weak, the interaction between $CaCl_2$ concentration and crosslinking time was modest, while the interaction between SA concentration and $CaCl_2$ concentration was significant. The immobilized chlorella performed the best when the SA concentration, $CaCl_2$ concentration and crosslinking time were 2.42%, 2.69% and 16.76 h, respectively, and the COD removal rate of fracturing flowback fluids was significantly higher than that of the free algal (34.70% vs. 8.96%), indicating immobilization could improve growth and organics removal of chlorellas for processing fracturing flowback fluids.

1. Introduction

The fracturing process is capable of efficiently improving the conductivity of hydrocarbon reservoirs and is a major measure for production increment in low-permeability and extra-low-permeability oil-gas wells. Fracturing liquids are usually composed of water (98%–99.2%), multiple chemical additives (0.5%–2%) and the proppant, and the discharge onto ground surfaces becomes fracturing flowback fluids (Luek and Gonsior, 2017). Along with the exploitation of low- and extra-low permeability oil fields and the intensified shortage of water resources, growing attention has been paid to deep processing and recovery of fracturing wastewater. The commonly used flowback fluid treatment methods include physical methods, chemical methods and biological methods. In particular, biological methods are highly efficient and do not produce secondary pollution (Coday et al., 2014; Estrada and Rao, 2016; He et al., 2016), and thus are environmental-friendly and sustainable techniques for treatment of flowback fluids.

Chlorellas are a type of unicellular organisms featured by diversity, fast growth, fat and protein richness, and strong adaptability (Wijffels and Barbosa, 2010). Chlorellas can either autotrophically grow with the use of optical energy and CO_2, or heterotrophically grow with the use of organic carbon sources (Gessler et al., 2015; Liu et al., 2014). Thus, chlorellas are the most potential for industrialization in the world and become a biomass renewable source that can substitute traditional sources. Traditional feedstock for algal cultivation can be replaced with a variety of wastewater. (Passos and Ferrer, 2015; Salama et al., 2017; Sutherland et al., 2015). In recent years, chlorellas for wastewater treatment have been extensively studied, but most studies are focused on wastewater rich in N and P (e.g. monosodium glutamate wastewater, brewery wastewater) (Boelee et al., 2011; Ji et al., 2014; Farooq et al., 2013). However, there is little research on chlorella-based treatment of fracturing flowback fluids that are compositionally complicated and highly concentrated.

Response surface methodology (RSM) is the most popular statistical technique for optimizing complex processes. It will reduce the number of experimental trials and cost for operating and design. (Alwan, 2015; Giovanni, 1983). Box–Behnken design (BBD), one of RSM, is more efficient and easier to arrange and interpret experiments (Zhong and Wang, 2010).

In this study, fracturing flowback fluids were biologically treated by immobilized chlorellas. RSM-BBD was used to investigate how immobilized conditions (sodium alginate concentration, $CaCl_2$ concentration and crosslinking time) would affect algal density and treatment efficiency. Thereby, the algal immobilizing process was optimized to improve the treatment efficiency.

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Table 1
Process variables, their coded values and limits.

Variable	Unit	Code	−1 level	0 level	+1 level
SA concentration	%	X_1	2	3	4
$CaCl_2$ concentration	%	X_2	2	3	4
Crosslinking time	h	X_3	12	16	20

2. Materials and methods

2.1. Materials

The reagents used here included SA, $CaCl_2$, sodium citrate, hydroxypropyl guar gum (commercial), Na_2CO_3, KCl, sodium tetraborate, ammonium persulfate, H_2SO_4, Na_2SiO_3, $AlCl_3$, and $Fe_2(SO_4)_3$. All reagents were analytically pure. *Chlorella vulgaris* was purchased from institute of hydrobiology, Chinese academy of sciences.

The instruments used here included a UV-5800 ultraviolet–visible (UV–vis) spectrophotometer (Shanghai Metash Instruments Co., Ltd), a 5B-3A COD Colorimeter (Lianhua Scientific corporation), an HI93703 turbidimeter (HANNA, Italy), a pHS-3C precision pH meter (Shanghai Leici Instruments Factory), an HB-1 multifunctional digestion device (Guangdong Medical Equipment Industrial Co.), a 85-2 temperature control magnetic stirrer (Jiangsu Danyang Science Instrument Factory), and a TD5A-WS centrifuge (Changzhou Jintan High-tech Instrument Factory).

2.2. Preparation of fracturing flowback fluids

0.35% hydroxypropyl guar gum, 0.12% Na_2CO_3, and 4% KCl were successively added into clean water under high-speed stirring to get base fluid. The sodium tetraborate was added at the crosslinking ratio of 100:2.4 into base fluid, forming fracturing fluid gels. After ageing for 24 h, 0.02% ammonium persulfate was added to the gels and heated at 80 °C for 1 h, forming a fracturing flowback fluid.

2.3. Immobilized culture of chlorellas

The chlorella fluid at the logarithmic phase was centrifuged at 4000 r/min for 10 min, and then was cleaned, centrifuged and diluted with sterile water, forming an algal suspension. The algal suspension was added into an SA solution (at a certain concentration) under uniform mixing. Then a $CaCl_2$ solution (at a certain concentration) was slowly dripped via a burette to the above mixture, forming algal gel balls with diameter of ~4 mm. After placement for a certain period of crosslinking, the algal gel balls were washed and soaked with distilled water and stored until used. Blank gel balls were prepared in the above steps except that the alga fluid was replaced by distilled water. A BG11 (Singh et al., 2015) medium was prepared by replacing the fracturing flowback fluid with distilled water. The algal gel balls and blank gel balls were separately thrown into the medium under the culture

Table 3
ANOVA table for algal density by immobilizing process.

Source	Sum of squares	d.f.	Mean square	*F* value	*P* value	Remarks[a]
Model	5.30	9	0.59	5.39	0.0185	Significant
X_1	0.74	1	0.74	6.75	0.0355	Significant
X_2	0.40	1	0.40	3.66	0.0971	–
X_3	0.04	1	0.04	0.33	0.5817	–
X_1X_2	0.48	1	0.48	4.36	0.0753	–
X_1X_3	0.03	1	0.03	0.25	0.6330	–
X_2X_3	0.22	1	0.22	1.98	0.2024	–
X_1^2	0.48	1	0.48	4.40	0.0741	–
X_2^2	2.42	1	2.42	22.14	0.0022	Significant
X_3^2	0.24	1	0.24	2.23	0.1791	–
Error	0.77	7	0.11	–	–	–
Lack of fit	0.70	3	0.23	13.73	0.0143	Significant
Pure error	0.07	4	0.02	–	–	–
Total	6.07	16	–	–	–	–

[a] $R^2 = 0.8739$, adjusted $R^2 = 0.7118$.

Table 4
The significance test for algal density by immobilizing process.

Factor	Coefficient estimate	d.f.	Standard error	95% CI low	95% CI high
Intercept	2.01	1	0.15	1.66	2.36
X_1	−0.30	1	0.12	−0.58	−0.03
X_2	−0.22	1	0.12	−0.50	0.05
X_3	0.07	1	0.12	−0.21	0.34
X_1X_2	0.35	1	0.17	−0.05	0.74
X_1X_3	0.08	1	0.17	−0.31	0.47
X_2X_3	−0.23	1	0.17	−0.62	0.16
X_1^2	−0.34	1	0.16	−0.72	0.04
X_2^2	−0.76	1	0.16	−1.14	−0.38
X_3^2	−0.24	1	0.16	−0.62	0.14

Table 2
BBD matrix with three independent variables (coded values) and corresponding experimental and predicted algal density.

Std.Run Order	Coded value			Actual value			Algal density (g/L)		
	X_1	X_2	X_3	SA concentration (%)	$CaCl_2$ concentration (%)	Crosslinking time (h)	Expt.[a]	Pred.[b]	ε
1	−1	−1	0	2	2	16	1.88	1.78	0.10
2	1	−1	0	4	2	16	0.89	0.49	0.41
3	−1	1	0	2	4	16	0.24	0.65	−0.41
4	1	1	0	4	4	16	0.63	0.73	−0.10
5	−1	0	−1	2	3	12	1.88	1.75	0.13
6	1	0	−1	4	3	12	0.80	0.97	−0.17
7	−1	0	1	2	3	20	1.89	1.72	0.17
8	1	0	1	4	3	20	1.14	1.27	−0.13
9	0	−1	−1	3	2	12	0.70	0.93	−0.23
10	0	1	−1	3	4	12	1.22	0.95	0.27
11	0	−1	1	3	2	20	1.26	1.53	−0.27
12	0	1	1	3	4	20	0.85	0.62	0.23
13	0	0	0	3	3	16	1.99	2.01	−0.02
14	0	0	0	3	3	16	1.84	2.01	−0.17
15	0	0	0	3	3	16	2.19	2.01	0.18
16	0	0	0	3	3	16	1.95	2.01	−0.06
17	0	0	0	3	3	16	2.06	2.01	0.05

[a] Expt. means experimental.
[b] Pred. means model predicted.