Supporting information

Reliability treatment of silicon in oilfield wastewater by electrocoagulation

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Analysis method:

According to GB/T 12149-2017 "Determination of silicon in Industrial circulating Cooling Water and boiler Water", under the condition of (27±5) ℃, silicate reacted with molybdate to produce molybdate yellow (molybdate heteropoly acid), molybdate yellow was reduced to silicomolybdate blue by 1-amino-2-naphthol 4-sulfonic acid, the concentration of silica in this experiment was determined by silico-molybdenum blue-ray method.

In order to draw the calibration curve of silica, standard solution of silica was measured with pipette at 0.00mL (blank), 1.00mL, 2.00mL, 4.00mL, 6.00mL, 8.00mL and 10.00mL, respectively, and placed them in 50mL colorimetric tube and diluted to scale with water. The corresponding amounts of silica were 0.00mg, 0.01 mg, 0.02mg, 0.04 mg, 0.06 mg, 0.08 mg and 0.10 mg, respectively. The absorbance was measured with a 1cm cuvette at 640nm wavelength using an ultraviolet spectrophotometer and reagent blank as reference. With the measured absorbance as the ordinate and the amount of silica as the abscissa, the calibration curve was drawn and the regression equation was calculated.

Secondly, the wastewater sample is filtered with a slow filter paper, and a certain amount of filtered water is absorbed with a pipette. As for the 50mL colorimetric tube, water is added and diluted to the scale. Adding 1.00 mL hydrochloric acid solution and 2.00mL ammonium molybdate solution, mixing and leaving for 5min. Adding 1.50mL of oxalic acid solution and adding immediately 2.00 ml1-amino-2-naphthol 4-sulfonic acid solution after 1min, mixing and leaving for 10min. The absorbance was measured with a 1cm cuvette at 640nm wavelength using an ultraviolet spectrophotometer and reagent blank as reference. The concentration of silicon in the solution to be measured can be obtained by substituting the absorbance of the solution to be measured into the regression equation.

In the experiment, we use a constant current power supply mode, so the voltage is constantly changing during this process. In order to express more clearly, we label the optimal reaction condition in the Figure 5, and the average conductivity value of wastewater was around 1200 μS/cm. As for the electric energy consumed for electrocoagulating a ton of oilfield wastewater should be around 1 kW·h, it would consume around 1 W·h electric energy per liter.

Table S1. Specific data of orthogonal experiment

Test number	pH	Error column	Current density	Reaction time (min)	Waste water temper	Post-experimental	Silica removal rate	Anode mass loss (g)

			(mA/c m^2)		ature(℃)	silica content (mg/)		
1	6	1	27	20	40	27.08	67.93%	0.0194
2	6	2	21	14	45	67.44	14.65%	0.0110
3	6	3	24	17	35	42.09	44.37%	0.0144
4	6	4	18	23	50	72.48	14.03%	0.0138
5	8	1	21	17	50	65.47	28.22%	0.0086
6	8	2	27	23	35	28.53	64.02%	0.0220
7	8	3	18	20	45	60.33	27.58%	0.0134
8	8	4	24	14	40	78.92	10.71%	0.0089
9	5	1	24	23	45	76.03	8.32%	0.0192
10	5	2	18	17	40	77.52	11.65%	0.0098
11	5	3	27	14	50	82.12	3.42%	0.0180
12	5	4	21	20	35	71.75	17.50%	0.0161
13	7	1	18	14	35	66.85	20.44%	0.0086
14	7	2	24	20	50	62.13	27.42%	0.0144
15	7	3	21	23	40	31.58	57.81%	0.0176
16	7	4	27	17	45	60.89	20.79%	0.0159

Ki, ki and range R were calculated respectively according to the results of orthogonal experimental data in Table S1. Especially, Ki is the sum of all experimental results with level i for different columns and ki is equal to Ki divided by the number of factor levels, while range R is the maximum value of Ki minus the minimum value of Ki in either column. In general, the greater the range, the greater the influence of the factors in this column on the experimental indicators, which means a small change could cause the change of the experimental results. Therefore, the primary and secondary factors can be judged by the value of the range, and if the range of the blank column is smaller than that of any factor group, it is proved that there are no interacted factors in this experiment, and all major factors have been taken into account. The determination of the optimization level of each factor is related to the evaluation index. If the bigger the better the evaluation index, the largest Ki or the factor level corresponding to ki should be selected; otherwise, the opposite is true.

According to the detailed rules of selecting optimal scheme of the orthogonal experiment, which is illustrated in the supporting information. As for the silica removal rate (Table S2), the influencing factors from main to secondary were pH, reaction time, current density and wastewater temperature, the optimal scheme of the orthogonal experiment were pH=6, reaction time=23 min, current density=27 mA/cm^2, and wastewater temperature=40°C. Concerning the post-experimental silica content (Table S3), the influencing factors from main to secondary were same as those of silica removal rate, the optimal scheme of the orthogonal experiment were pH=6, reaction time=23 min, current density=27 mA/cm^2, and wastewater temperature=35°C. In relation to anode mass loss (Table S4), the influencing factors from main to secondary were pH, reaction time, current density and wastewater temperature, the optimal scheme of the orthogonal experiment were pH=8, reaction time=14 min, current density=18 mA/cm², and wastewater temperature=50°C. The optimal wastewater temperature was 40℃ according to the silicon removal rate, and 35℃ according to the silicon content after the experiment. It was found that there was no significant difference in the silicon removal effect between the two temperatures. Considering energy consumption, the scheme was optimized as pH=6, reaction time=23min, current density=27mA/cm², and wastewater temperature=35℃. Besides, there are great differences of schemes when we considering the silicon removal effect and the anode mass loss separately. In order to ensure the efficient silicon removal effect and optimize the anode mass loss at the same time, two factors affecting the anode mass loss, reaction time and current density, are adjusted appropriately. Therefore, the theoretical optimal scheme of the orthogonal experiment is pH=6, reaction time=20min, current density=27mA/cm², and wastewater temperature=35℃ (Table 3).

Table S2. Silicon removal rate analysis after electrocoagulation

	pH	Error column	Current density (mA/cm²)	Reaction time (min)	Wastewater temperature(℃)
K_1	1.410	1.249	1.562	1.404	1.481
K_2	1.305	1.177	1.182	0.492	0.713
K_3	0.409	1.332	0.908	1.050	1.463
K_4	1.265	0.630	0.737	1.442	0.731
k_1	0.352	0.312	0.390	0.351	0.370
k_2	0.326	0.294	0.295	0.123	0.178
k_3	0.102	0.333	0.227	0.263	0.366
k_4	0.316	0.158	0.184	0.360	0.183
Range R	0.250	0.175	0.206	0.237	0.192
Factor: major→minor	pH Reaction time Current Density Wastewater temperature				
Optimal scheme	pH=6 Reaction time =23min Current density =27mA/cm² Wastewater temperature =40℃				

Table S3. Silicon content data analysis after electrocoagulation

	pH	Error column	Current density (mA/cm²)	Reaction time (min)	Wastewater temperature(℃)
K_1	209.083	235.434	198.629	221.288	215.091
K_2	233.251	235.622	236.242	295.329	264.694
K_3	307.427	216.115	259.171	245.969	209.217
K_4	221.450	284.040	277.169	208.625	282.208
k_1	52.271	58.858	49.657	55.322	53.773
k_2	58.313	58.906	59.060	73.832	66.174
k_3	76.857	54.029	64.793	61.492	52.304

k_4	55. 362	71. 010	69. 292	52. 156	70. 552
Range R	24. 586	16. 981	19. 635	21. 676	18. 248
Factor: major→minor	pH	Reaction time	Current Density	Wastewater temperature	
Optimal scheme	pH=6 Reaction time=23min Current density=27mA/cm² Wastewater temperature= 35℃				

Table S4. Anode mass loss analysis after electrocoagulation

	pH	Error column	Current density (mA/cm²)	Reaction time (min)	Wastewater temperature(℃)
K_1	0. 059	0. 056	0. 075	0. 063	0. 056
K_2	0. 053	0. 057	0. 053	0. 047	0. 060
K_3	0. 063	0. 063	0. 057	0. 049	0. 061
K_4	0. 057	0. 055	0. 046	0. 073	0. 055
k_1	0. 015	0. 014	0. 019	0. 016	0. 014
k_2	0. 013	0. 014	0. 013	0. 012	0. 015
k_3	0. 016	0. 016	0. 014	0. 012	0. 015
k_4	0. 014	0. 014	0. 011	0. 018	0. 014
Range R	0. 003	0. 002	0. 007	0. 007	0. 002
Factor: major→minor	Current density	Reaction time	pH	Wastewater temperature	
Optimal scheme	pH=8 Reaction time=14min Current density=18mA/cm² Wastewater temperature=50℃				

Table S5. Verified experiment for theoretical optimal scheme.

Chemicals	**Value**
Pre-experimental silicon content (mg/L)	81.51
Temperature (℃)	35
pH	6.0
Reaction time (min)	20
Current Density (mA/cm²)	27.6
Pole plate pitch (cm)	2.5
Anode mass loss (g)	0.0189
Post-experimental silicon content (mg/L)	21.88
Silicon removal rate	73.16%