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Treating urban dredged silt with ethanol improves settling and solidification properties

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Abstract−The organic matter content in urban dredged silt is high for the indraft of municipal sewage, and it seriously influences the utilization of urban dredged silt. It is necessary to find a method to solve this problem. This paper presents a method of treating the silt with ethanol (STE), considering that ethanol is a good organic solvent which can dissolve many kinds of organic matter, and optimizes the treatment conditions through Box-Benhnken design (BBD) experiment with organic matter removal efficiency as the response. The ideal conditions were as follows: action time, 47 min; ethanol concentration, 41%; ratio of ethanol to silt, 54 : 1 ml/g with organic matter removal efficiency of 51.12%. Then, settling and solidification properties of raw silt and STE were explored through laboratory experiments. The results show treating urban dredged silt improved the settling and solidification properties of silt.

Key words: Urban Dredged Silt, Organic Matter, Ethanol, Settling, Solidification

INTRODUCTION

Bottom silt in urban lakes gathers much organic matter because of the amount of municipal wastewater discharged into lakes. It would promote the nutrient over-enrichment of water bodies, when the organic matter is released into lakes under certain conditions [1]. Besides, CO_2, CH_4, volatile halogenated organic compounds and other ozone-depleting gases are produced in the mineralization of organic matter [2]. The vast deposition of silt is disadvantageous to the flood prevention and storage ability of lakes. Therefore, dredging bottom silt regularly plays an important role on the health of urban lakes. But dredged silt treated in simple ways occupies a large amount of land and causes secondary pollution, so determining how to deal with urban dredged silt has become a serious concern. Used as bricks and fillers after dehydration and solidification is the main use of dredged silt at the present stage [3-5].

Because of high organic matter content of urban dredged silt, the concentration efficiency is poor and the compressive strength is small [6-10]. Although the needed strength could be reached by adding a large quantity of cement, excessive cement leads to loss of use value of the silt solidification technology. So how to reduce the impact of organic matter on the properties of urban dredged silt has become an important research issue. Formerly, methods, such as hydrogen peroxide method, cement-gypsum solidification method and high-temperature calcination were used to remove the organic matter in dredged silt [11-13]. But the first method is dangerous because of the strong oxidizing of hydrogen peroxide; the second is only applicable to solidification stage, and the last one could cause secondary pollution for producing ozone in the treatment. Therefore, it is essential to find a safe and comprehensive method.

Ethanol is a good organic solvent that can dissolve various substances. It is widely used to separate and purify material besides being used as fuel and sterilization [14,15], but few reports state its application on the disposal of dredged silt. We first treated urban dredged silt with ethanol, optimized the conditions through BBD experiment, and analyzed the settling and solidification properties of raw silt and STE by laboratory experiments. It was also stressed that the ethanol used in the treatment could be recovered and recycled. The results could provide a new approach for the practice of urban dredged silt treated with ethanol.

MATERIALS AND METHODS

1. Sample Collection and Processing

The silt used in this study was taken from Nanhu Lake in Wuhan, China. First, it was mixed fully in a plastic bucket to ensure same organic matter content. And then some sample was seasoned in a cool and well-ventilated place, the sundries such as weed and conch were wiped off, and it was ground to the wanted mesh. The rest was stored at 4 °C for solidification use. Table 1 shows the physical properties of the silt sample.

2. Ethanol Treatment

The ethanol used in this study was bought from Wuhan Chemical Reagent Factory in Hubei, China, of which the initial volume

Table 1. Physical properties of silt sample

Initial water content (%)	Liquid limit (%)	Plastic limit (%)	Plasticity index	Content of organic matter (%)	PH value
180.0 (±3.5)	92.6 (±1.2)	40.6 (±0.7)	52 (±1.9)	7.64 (±0.15)	7.2 (± 0.2)

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concentration was 95%. It was prepared with different volume concentration before being used.

The ethanol treatment was in a glass flask. In each experiment, 1.0 g silt was placed in the flask and ethanol solution was added. And then the flask was put into a thermostatic water bath at a fixed temperature of 40 °C for a certain time, while the mixture was stirred at a certain speed. After the soaking was a solid/liquid separation operation. The silt from the solid/liquid separation operation was washed with deionized water to remove the residual ethanol on it, and then the content of organic matter was tested through external heating potassium dichromate oxidation method [16]. The wash water and the liquid from solid/liquid separation operation both entered an evaporator where ethanol was evaporated and recovered for recycle.

Response surface method (RSM) was used to determine the influence of major operating variables on organic matter removal and to optimize the treatment conditions. The BBD with three factors and three levels, including three replicates at the center point for estimation of errors, was adopted to evaluate the main and interaction effects of the factors and to fit a second-order model with quadratic terms. For ethanol treatment, ethanol concentration (C), action time (T) and ratio of ethanol to silt (L) were chosen as three independent variables through single-factor test, while organic matter removal efficiency was considered as the response (R1). The ethanol concentration (C) varied between 30 and 50%, while the action time (T) ranged from 35 to 55 min, and the ratio of ethanol to silt (L) ranged from 40 to 60 ml/g. The low, middle and high levels were designated as −1, 0 and +1, respectively. Table 2 shows the coded and actual values of the three independent variables with the response for BBD. The software Design Expert 7.0 was used for the experimental design, determination of the coefficients and the data analysis.

3. Silt Settling

Settling performance of silt is not only the main reason of estuarine sedimentation, but also closely related to the dehydration of silt. So we studied the settling performance of raw silt and STE through pipette method, taking a concentration of 10 g/L as an example. The experiment was performed in a measuring cylinder of 1,000 ml. 10 g silt was put into the cylinder and water was added. After full mixing we started the timer. 20 ml suspension was extracted from the place under 20 cm of the surface at fixed time, while the silt was settling in the cylinder. And then the suspension was dried in an air-dry oven until constant weight. Finally, we could get a solid concentration of the suspension.

4. Unconfined Compression Experiment

In this study, solidification properties of raw silt and STE were analyzed through unconfined compression experiment. First, we mixed the samples well with the cement, and the dosages of the cement were 40, 50, 60, 80, 100 and 125 kg/m^3. Then the mixture was filled into a mold layer by layer, while vibration was carried out between two layers to eliminate air. The mold was taken out from the mold and put into a curing room for curing 24 hrs later. Lastly, the unconfined compression strength was measured after the samples were maintained to the designated age (7, 14 and 28 days).

All experiments were done three times in parallel, and data were expressed as mean±standard deviation.

Table 2. Programs and results of BBD experiment

Run	T (min)	C (%)	L (ml/g)	R1 (%)
1	−1 (35)	−1 (30)	0 (50)	32.50 (±0.78)
2	+1 (55)	+1 (50)	0 (50)	42.20 (±1.37)
3	0 (45)	−1 (30)	+1 (60)	41.50 (±1.21)
4	−1 (35)	0 (40)	+1 (60)	43.80 (±1.55)
5	0 (45)	0 (40)	0 (50)	50.10 (±2.35)
6	0 (45)	+1 (50)	−1 (40)	43.40 (±1.49)
7	0 (45)	0 (40)	0 (50)	50.00 (±2.55)
8	0 (45)	−1 (30)	−1 (40)	38.70 (±1.47)
9	0 (45)	0 (40)	0 (50)	51.20 (±2.81)
10	+1 (55)	0 (40)	+1 (60)	47.30 (±1.71)
11	0 (45)	+1 (50)	+1 (60)	45.10 (±1.70)
12	−1 (35)	0 (40)	−1 (40)	40.50 (±1.18)
13	−1 (35)	+1 (50)	0 (50)	39.10 (±1.15)
14	+1 (55)	−1 (30)	0 (50)	42.30 (±1.41)
15	+1 (55)	0 (40)	−1 (40)	44.50 (±1.50)

RESULTS

1. Ethanol Treatment

A regression model of ethanol treatment was obtained through quadratic regression analyzing the experiment results as shown in Table 2:

$$R1 = -248.791 + 5.226T + 6.242C + 1.762L - 0.017TC - 0.048T^2 - 0.066C^2 - 0.016L^2 \quad (1)$$

Where R1 is the organic matter removal efficiency (%), T is the action time (min), C is the concentration of ethanol (%), and L is the ratio of ethanol to silt (ml/g).

Table 3 shows the statistical significance of linear, cross and square terms through variance analysis. It can be seen from the table that *P* value of the model, linear terms, cross terms and squared terms were 0.0001, 0.0048, 0.0073 and 0.013, respectively. All of them were smaller than the standard value of 0.05, which indicates that

Table 3. ANOVA results of regression model for ethanol treatment

	df	Sum of squares	Mean square	F	P-value
Regression	7	337.10	48.16	59.96	0.0001
T	1	52.02	52.02	64.78	0.0001
C	1	27.38	27.38	34.09	0.0006
L	1	14.05	14.05	17.49	0.0041
TC	1	11.22	11.22	13.97	0.0073
T^2	1	84.33	84.33	105.01	<0.0001
C^2	1	162.26	162.26	202.05	<0.0001
L^2	1	9.80	9.80	12.20	0.0101
Residual	7	5.62	0.80		
Lack of fit	5	4.73	0.95	2.14	0.3489
Pure error	2	0.89	0.44		
Total	14	342.72			
Std. Dev		0.90	R^2		0.9836
Mean		43.48	Adj-R^2		0.9672
C.V. %		2.06	Pred-R^2		0.8680
Press		45.23	Adeq precision		26.7140

this second-order regression equation is at 95% condence level. In addition, the high value of regression coefficient (R^2=0.9836) and adjusted regression coefficient (Adj-R^2=0.97) show the model predictions fit satisfactorily with the experimental observations. Thus this model can be used to predict the organic matter removal efficiency for ethanol treatment and has high accuracy. Further, the *F* value for ethanol concentration of 34.09 and for action time of 64.78 were much larger than that of 17.49 for ratio of ethanol to silt, which reveals the ethanol concentration and action time played more important roles in the treatment.

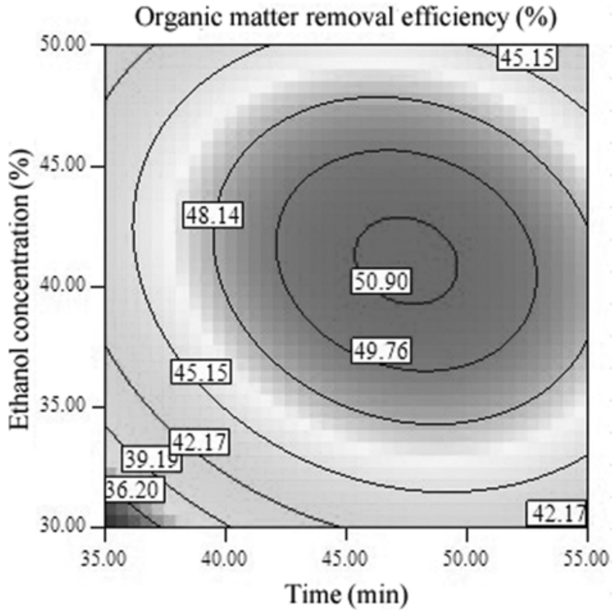

Fig. 1. Contour graph for response R1 as T and C variable at L=54.06.

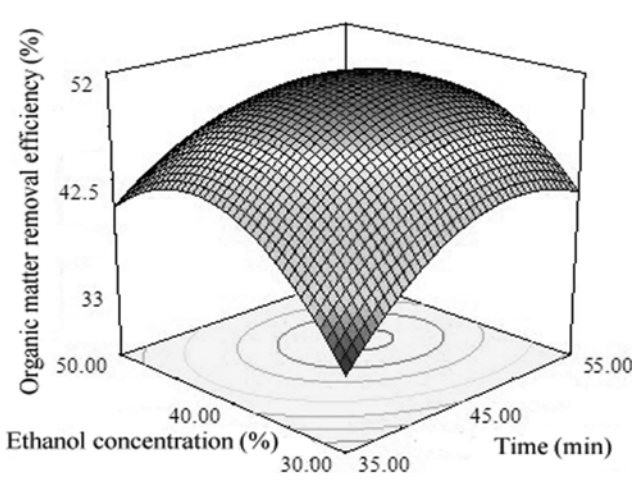

Fig. 2. 3-D surface graph for response R1 as T and C variable at L=54.06.

Ideal conditions were obtained through the derivation of the three variables of the model in a given interval. The conditions were: action time, 47.47 min; ethanol concentration, 41.09%; ratio of ethanol to silt, 54.06 : 1, while organic matter removal efficiency was 51.12%. Fig. 1 and Fig. 2 show the contour and 3D surface graph of response R1 as T and C variable at L=54.06. Taking actual situation into consideration, the optimal conditions were finally defined as: action time, 47 min; ethanol concentration, 41%; ratio of ethanol to silt, 54 : 1 ml/g. The contrast between proof experimental result of 50.9% and predicted data shows the difference between them was small.

2. Silt Settling

Fig. 3 shows the changes of suspended solid concentration below 20 cm of the surface with time between raw silt and STE. It can be seen that the changes were small within 15 min and became greater with the increase of time. After settling about 60 min, the suspended solid concentration of STE was 2.57±0.16 g/L, while that of raw silt was 3.01±0.17 g/L.

Because we focused on whether treating silt with ethanol improves the settling performance or not, paired-samples T test was performed with SPSS 13.0 to detect the statistical differences of settling performance between raw silt and STE. Data were first checked for normality and transformed when necessary to meet the assumption of normal distribution. Table 4 shows the paired-samples T test results of the settling experiment. *P* value of less than 0.05 was considered as statistically significant difference of settling performance after washing with ethanol.

Median settling velocity was calculated based on second floccu-

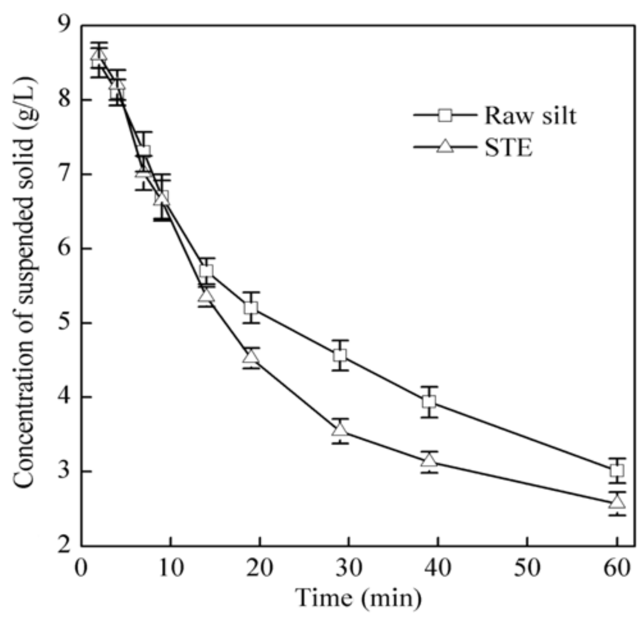

Fig. 3. Changes of suspended solid concentration below 20 cm of the surface between raw silt and STE.

Table 4. Paired-samples T test results of settling experiment

Mean	Std. deviation	Std. error mean	95% Confidence interval of the difference		t	df	P-value
			Lower	Upper			
0.38	0.40	0.13	0.076	0.69	2.88	8	0.0206

lation and sedimentation dynamical model to further study the changes of settlement performance after treated with ethanol. The calculation is as follows:

$$dc/dt=-kc^2 \quad (2)$$

where c is the suspended solid concentration (g/L), t is the settling time (min) and k is the attenuation coefficient. By integrating on both sides of Eq. (2), the equation can be written as

$$1/c=kt+1/c_0 \quad (3)$$

where c_0 is the initial concentration (g/L). By multiplying c_0 on both sides of Eq. (3), the equation changes into

$$c_0/c=ktc_0+1 \quad (4)$$

When c_0/c equals to two, the half-period is

$$t_{0.5}=1/(kc_0) \quad (5)$$

where $t_{0.5}$ is the half-period, and the median settling velocity is

$$\omega_{50}=h/t_{0.5}=khc_0 \quad (6)$$

Where ω_{50} is the median settling velocity (mm/min) and h is the sampling height (cm).

Fig. 4 shows the relationship between 1/c and t was approximately linear. The correlation coefficients were greater than 0.99 in both circumstances, which indicates the calculation of median settling velocity based on second flocculation and sedimentation dynamic model was available. So the median settling velocity of raw silt and STE was obtained through Eq. (6). They were 7.4 mm/min and 10.0 mm/min, respectively, and the results reveal the settling performance of silt was improved after treated with ethanol.

3. Unconfined Compression Experiment

The utilization of dredged silt largely depends on the compressive strength after solidification, so we studied the unconfined compression strength of raw silt and STE mixed with cement in different curing periods. Fig. 5 shows the unconfined compression experiment results of raw silt and STE mixed with different doses of cement, while the curing periods were 7 and 14 days. The figure shows that the unconfined compression strength of STE was larger than that of raw silt, such as, when the content of cement was 125 kg/m^3 and the curing period was 7 days, the strength of STE and raw silt was 193.48±10.80 and 125.40±5.77 kpa, respectively. So treat-

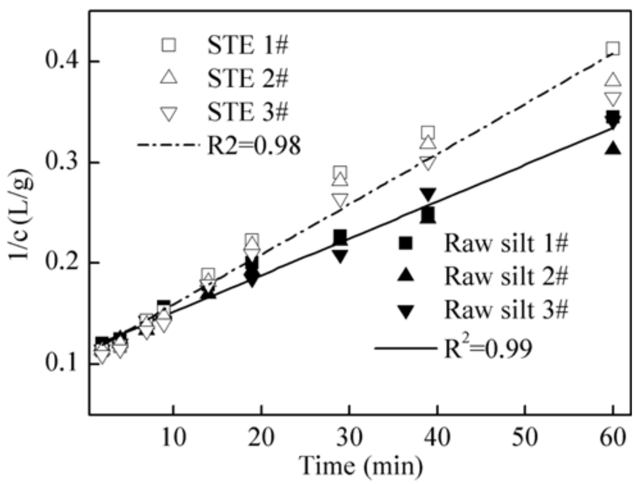

Fig. 4. Curve fitting between 1/c and t of raw silt and STE.

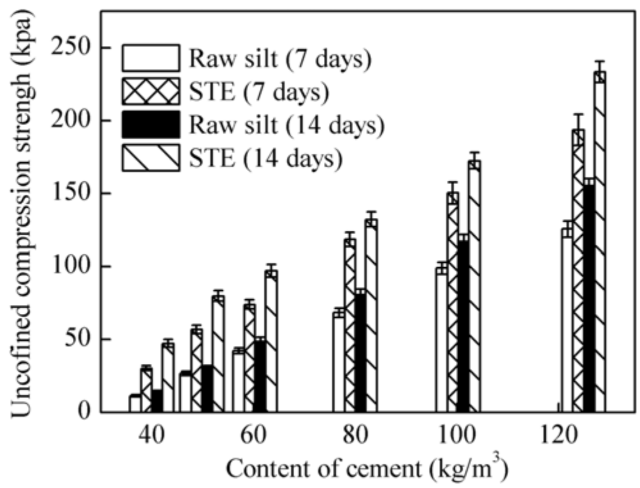

Fig. 5. Variation of unconfined compression strength of raw silt and STE.

Table 5. Univariate results of unconfined compression experiment

	Sum of squares	df	Mean square	F	P-value
Model	752746.34	35	21507.04	882.66	<0.0001
Intercept	1296861.77	1	1296861.77	53223.93	<0.0001
CP	73780.81	2	36890.41	1514.00	<0.0001
CC	471758.80	5	94351.76	3872.25	<0.0001
ET	109641.73	1	109641.73	4499.76	<0.0001
CP*CC	46554.63	10	4655.46	191.06	<0.0001
CP*ET	15373.49	2	7686.74	315.47	<0.0001
CC*ET	23010.68	5	4602.14	188.87	<0.0001
CC*ET*CP	12626.20	10	1262.62	51.82	<0.0001
Error	1754.36	72	24.37		
Total	2051362.47	108			
Corrected total	754500.70	107			

R^2=0.9982 (Adjusted R^2=0.9971)

ing urban dredged silt with ethanol can improve the solidification property.

Univariate was adopted with SPSS 13.0 to detect the statistical impact of fixed factors on dependent variable. In this study, curing period (CP), content of cement (CC) and ethanol treatment (ET) were considered as three fixed factors, while unconfined compression strength was taken as the dependent variable. Table 5 shows the univariate results of unconfined compression experiment. *P* values of CP, CC and ET were much smaller than 0.05, which indicates the unconfined compression strength was statistically significantly influenced by CP, CC and ET. In addition, *F* values of ET and CC far outweigh that of CP, which demonstrates ethanol treatment and cement content played more important roles on the unconfined compression strength of urban dredged silt.

DISCUSSION

1. Residue and Recycling of Ethanol

The ethanol dose, as discussed earlier, has a striking influence on the organic matter removal. However, residual ethanol after treatment not only influences the measurement accuracy of organic matter content, but also pollutes the environment and harms our health, if not well treated [17]. So it must be taken into consideration in the ethanol treatment. Previous studies put forward some methods for the recycling of ethanol, such as sedimentation and membrane retention [18-20]. In this study, water solubility and volatility of ethanol were used to remove the residual ethanol and recycle the ethanol after ethanol treatment. The details of the methods are described in the Materials And Methods.

2. Possible Mechanisms

Generally speaking, organic matter in silt can form a network because of its high molecular weight. So there is usually an organic coating on the surface of the sediment particle, and it affects charge properties and makes sediment particles own negative charge [21, 22]. When organic matter content of silt is high, the electric repulsion caused by organic matter is strong and the hydrophilic group of organic matter is exposed outside as shown in Fig. 6(a). So the flocculation among cohesive fine sediment is reduced and the drag force is large, and all of these give rise to poor settling performance of silt with high organic matter content. In addition, complex compound formed by fulvic acid and cation can hinder the process of cement hydration, and calcium ion formed in hydration reaction of cement would be depleted by humic acid [23], which affects the solidification of silt and results in low strength.

When the silt was washed with ethanol, some organic matter dissolved in ethanol was removed. The flocculation of cohesive fine sediment strengthened for the weak electric repulsion and short distance between particles [24]. Moreover, some hydrophobic groups of organic matter may be exposed outside as shown in Fig. 6(b); therefore, the settling velocity of STE accelerated. Fig. 3 shows this phenomenon. Otherwise, the impact on hydration reaction of cement was minimized with lower organic matter content, which makes the compression strength dramatically increase. However, due to the complex composition of dredged silt, further mechanism remains to be studied.

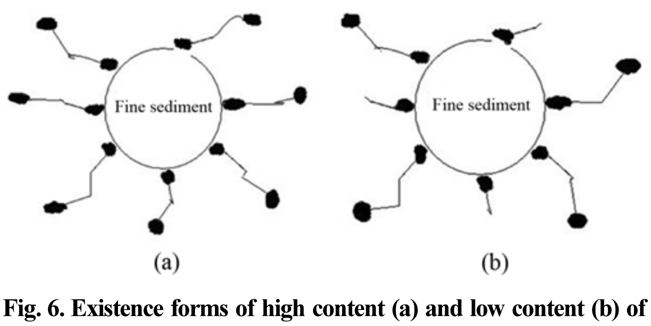

Fig. 6. Existence forms of high content (a) and low content (b) of organic matter on the surface of fine sediment particle.

CONCLUSIONS

Urban dredged silt was treated with ethanol to remove organic matter and improve settling and solidification properties. The ideal conditions of the treatment were obtained through BBD experiment: action time, 47 min; ethanol concentration, 41%; ratio of ethanol to silt, 54 : 1 ml/g, while the organic matter removal efficiency was 51.12%. In addition, action time and ethanol concentration played important roles in the treatment. The experimental and statistical analysis results reveal the settling and solidification performances of urban dredged silt were improved after being treated with ethanol. Possible mechanisms were as follows: After being treated with ethanol, organic matter content of silt became lower, electric repulsion among particles turned weaker, and existing form of organic matter on particle surface changed. All of these promoted the settling performance of urban dredged silt. The increase of unconfined compression strength was attributed to the reduction of impact of organic matter on the reaction of cement hydration.

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