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Systematic assessment of dredged sludge dewaterability improvement with different organic polymers based on analytic hierarchy process

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ABSTRACT

Organic polymeric flocculants are commonly used in improving dredged sludge dewaterability, but less attention has been paid to residual water quality. In this paper, the effects of cationic etherified starch (CS) and poly-dimethyl diallyl ammonium chloride (PDDA) on dredged sludge dewatering efficiency and residual water quality of Baiyangdian lake were comprehensively investigated and evaluated by analytic hierarchy process (AHP). The results indicated that PDDA had stronger electrical effect and flocculation performance compared with CS, resulting in more efficient dewatering performance. PDDA can reduce the pollutants of discharged residual water, while CS significantly promoted the increase of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the residual water. The increase of $\text{NH}_4^+\text{-N}$ in the residual water of CS was due to the release of dredged sludge, while the increase of $\text{NO}_3^-\text{-N}$ was introduced by CS leaching. AHP showed that PDDA performed better in flocculation treatment of dredged sludge than other organic polymers. This work provides a method for optimization of flocculation treatment for dredged sludge dewaterability.

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Introduction

Sediment is the carrier of water pollution and the source of second pollution (Forshay and Stanley, 2005; García-Ordiales et al., 2016). Baiyangdian lake is the largest inland lake in north China, which is characterized by interlacing and fragmentation of land and water. With the development of

the local industry and agriculture, sewage from up-stream and surrounding regions is discharged into the lake, and the closed state made it difficult for the pollutants to be exported and entered the sediment. Dredging is considered as an effective means to control the internal pollution of rivers and lakes (Zhang et al., 2014). Dredged sludge has the features of large amount and high-water content (Huang et al., 2016), so dewatering is a crucial aspect of dredged sludge treatment and disposal (He et al., 2001).

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Organic polymeric flocculant is a common and effective way to improve dredged sludge dewatering performance (Thomas et al., 1999; Yang et al., 2016b). Poly dimethyl diallyl ammonium chloride (PDPA) and cationic etherified starch (CS) are cationic organic high polymer, with the advantages of safety, nontoxic, wide pH range of application, and now there have been relevant reports on dewatering study, which mainly focus on the dewatering efficiency of flocculants (Chen et al., 2007; Mishra et al., 2011; Wang et al., 2013). In practical engineering application, the residual water produced by dewatering process is generally discharged into natural water bodies without treatment or simple treatment, which requires that the residual water quality can meet the requirements of discharge. On the other hand, pollutants from the dredged sludge may enter the residual water during the dewatering process, causing the deterioration of residual water quality. Therefore, dewatering efficiency and residual water quality during dredged sludge flocculation process should be studied comprehensively. However, it has not been given sufficient attention at present.

Additionally, there is no evaluation system for flocculant selection in dredged sludge dewatering. It is of great practical significance to construct a comprehensive evaluation system for guiding practical projects to select appropriate flocculants. The analytic hierarchy process (AHP) is an effective tool for dealing with complex decisions (Saaty, 1980), as well as a systematic and hierarchical analysis method combining qualitative and quantitative analysis, which can help decision maker determine priorities and make the best decisions. By simplifying a complex decision into a series of pairwise comparisons and synthesizing the results. Moreover, it includes an effective technique to check the consistency of the decision maker's evaluation in order to reduce bias in the decision-making process. AHP is valid to capture the subjective and objective aspects of decision and widely used in the fields of management science and operations research (Vaidya and Kumar, 2006; Ishizaka and Labib, 2011; Rezaeisabzevar et al., 2020).

To sum up, there are few studies on the residual water quality of dredged sludge dewatering, and the comprehensive evaluation system of flocculant is also urgently needed in practice. Therefore, the main purpose of this study is to (1) assess the influence of organic polymeric flocculant on dewatering efficiency of Baiyangdian dredged sludge; (2) understand the effect of flocculation on the residual water quality; (3) es-

tablish comprehensive evaluation model for dredged sludge dewatering flocculants by AHP modeling analysis.

1. Materials and methods

1.1. Source and characteristics of dredged sludge

Raw dredged sludge was sampled from Baiyangdian lake (115°56' 43.42" E, 38°53' 59.31" N), located in Xiongan New Area, China. Petersen grab sampler (Wuhan Hengling Tech. Co., China) was used to collect surface sediment sample (0–10 cm), and then placed in clean sealed plastic bucket to be transported to the laboratory. Mesh sieve (1.7 mm) was adopted to filter the samples. Samples were kept in a refrigerator at 4 °C. Table 1 shows the properties of dredged sludge and Table 2 shows the properties of pore water.

1.2. Chemical agents

Poly dimethyl diallyl ammonium chloride solution (PDPA, $(C_8H_{16}NCl)_n$), with relative molecular mass of 100,000–200,000, the mass percentage of 20%, viscosity (mPa·s) of 400–1000 (25 °C), was diluted to 2% of the mass content during the experiment; Cationic etherified starch (CS), quaternary ammonium type, spot (per cm^2) ≤ 0.5 , the solubility is 21%, viscosity (mPa·s) (6%, 95 °C): 460–1200, whiteness $\geq 88\%$. The other reagents used were analytical grade and came from Sinopharm Chemical Reagent Co., Ltd.

1.3. Dredged sludge conditioning procedures

Dredged sludge dewatering experiment was carried out by using a six-line agitator machine. The flocculant was added according to the amount of dry sludge. 300 g of dredged sludge sample was put into a beaker for each of different doses of PDPA (5, 10, 20, 30, 40, 60 mg PDPA $\cdot g^{-1}$ TSS, respectively) and CS (20, 40, 60, 80, 100 mg CS $\cdot g^{-1}$ TSS, respectively) were added to the dredged sludge. Then the samples were stirred at 400 r/min for 2 min and at 40 r/min for 8 min subsequently. The effects of PDPA and CS with different dosage on the dewatering performance, flocculation characteristics and residual water quality of the dredged sludge were investigated after standing for 30 min.

Table 1 – Physical and chemical properties of dredged sludge.

Index	zeta (mV)	pH	floc size (μm)	Moisture content (%)	CST _n (s·L·g ⁻¹)	TP (mg·kg ⁻¹)	TOC (%)
Value	–16.85	7.49	24.50	87.10	2.75	1084	3.10

Table 2 – Physical and chemical properties of pore water (mg·kg⁻¹).

Index	NH ₄ ⁺ -N	NO ₃ ⁻ -N	NO ₂ ⁻ -N	DON	TDN	TDP	DIP	DOP	DOC
Value	12.84	0	0.003	1.03	13.87	3.57	1.80	1.77	25.53

TDP: Total dissolved phosphorus; DIP: Dissolved inorganic phosphorus; DOP: Dissolved organic phosphorus.

1.4. Dewaterability assessment

Capillary suction time (CST) (Niu et al., 2013) was performed by a CST tester (Model 319, Triton, 151 UK) with Whatman No. 17 chromatography grade paper. The CST results were normalized using the initial TSS value ($\text{s} \cdot \text{L} \cdot \text{g}^{-1}$ TSS) (Merlo et al., 2007), and recorded as CST_n .

Specific resistance to filtration (SRF) was calculated by (Cao et al., 2016):

$$\text{SRF} = \frac{2PA^2b}{\mu\omega} \quad (1)$$

where P ($\text{kg} \cdot \text{m}^{-2}$) is content of vacuum filtration pressure; A (m^2) is the filter area; b is the time-to-filtration ratio; μ ($\text{kg} \cdot \text{s} \cdot \text{m}^{-2}$) represents the coefficient of viscosity; ω ($\text{kg} \cdot \text{m}^{-3}$) is the dry filter cake mass per volume filtrate (Niu et al., 2013).

The compressibility of the dredged sludge cake was evaluated by the compactness of the dredged sludge cake under regular pressure (Qi et al., 2011). The specific calculation formula of compressible coefficient (CC) was introduced as:

$$\frac{\text{SRF}_1}{\text{SRF}_2} = \left(\frac{P_1}{P_2} \right)^s \quad (2)$$

Where s is the value of CC; P_1 (Pa) and P_2 (Pa) represent different pressures applied to the dredged sludge; SRF_1 and SRF_2 are specific resistance of the dredged sludge at pressures P_1 and P_2 respectively.

1.5. Residual water analysis

Residual water was filtered through a $0.45 \mu\text{m}$ membrane before analysis. Ammonia nitrogen (NH_4^+ -N), nitrate nitrogen (NO_3^- -N) and total dissolved nitrogen (TDN) were determined using alkaline potassium persulfate digestion ultraviolet spectrophotometry. Total dissolved phosphorus (TDP) and orthophosphate phosphorus (PO_4^{3-} -P) were obtained using ammonium molybdate spectrophotometry. Dissolved organic carbon (DOC) was investigated using a TOC analyzer (TOC-V CPH, Shimadzu, Japan). Dissolved organic matter (DOM) composition was analyzed using a three-dimensional excitation–emission matrix (3D-EEM) spectroscopy (Thermo FisherF-4700, USA). Actual fluorescence spectra were separated from EEM fluorescence spectra by Parallel factor analysis

(PARAFAC). Then MATLAB 8.6 software (MathWorks Inc., USA) was conducted to process EEM data.

Pretreatment and determination procedure for turbidity was as follow: after flocculation treatment, the samples were left standing for 1 hr, and 50 mL supernatant was extracted with a syringe and added to the sample bottle, shading cap was covered and placed in the turbidimeter (HACH2100Q, USA), and the value was recorded after the instrument reading was stable.

The residual water was extracted by a $0.22 \mu\text{m}$ membrane for high-performance size exclusion chromatography (HPSEC) determination. Changes of organic matter molecular weight was studied by Waters liquid chromatography system composed with a Waters 2487 Dual λ Absorbance Detector (Zhang et al., 2015), using sodium polystyrene sulfonate as the standard molecular weight substance.

1.6. Dredged sludge suspension analysis

Dredged sludge pH was tested using a pH meter (M97574, Mettler Toledo, Switzerland). A certain amount of homogenized dredged sludge was weighed accurately and dried at a temperature of 105°C for 4 hr, then the final weight was measured by an electronic analytical balance to obtain the moisture content. The above method was also used for the analysis of dredged sludge cake moisture content. The concrete operator was repeated for 3 times, and the results were averaged. The effect of flocculation dosage on the zeta potential of the dredged sludge was investigated using a Zetasizer Nano ZS90 (Malvern Panalytical, UK). Meanwhile, the floc size of dredged sludge used in this study was measured by a Malvern Zetasizer Nano (ZS 900) instrument.

1.7. Statistical analysis

The results were analyzed by SPSS 25 software for correlation analysis and presented in Table 3.

1.8. Dewatering evaluation of dredged sludge in Baiyangdian Lake based on AHP

Through qualitative analysis, AHP can determine the factors affecting the selection of flocculant for dredged sludge dewatering. Firstly, evaluation indicators were selected and ranked

Table 3 – Correlation between dewatering properties and residual water quality of dredged sludge.

	DOC	Turbidity	C1	C2	TDN	NH_4^+ -N	NO_3^- -N	TDP	PO_4^{3-} -P
CST_n	0.841**	0.786**	0.119	0.865**	−0.180	−0.253	−0.182	0.840**	0.543
SRF	0.825**	0.850**	0.217	0.842**	−0.253	−0.377	−0.267	0.699*	0.431
Cake water content	0.702*	0.888**	0.227	0.717*	−0.369	−0.369	−0.363	0.758**	0.383
CC	−0.342	0.101	0.648*	−0.395	−0.645*	−0.517	−0.661*	0.041	−0.201
Zeta	−0.455	−0.662*	−0.492	−0.428	0.471	0.618*	0.526	−0.198	0.089
Floc size	−0.843**	−0.632*	0.100	−0.852**	−0.084	0.097	−0.081	−0.492	−0.402
DOC	1	−0.200	0.958**	0.579	0.226	0.052	0.216	0.738**	0.710*
C1	−0.200	1	−0.282	0.204	−0.905**	−0.961**	−0.941**	0.030	−0.217
C2	0.958**	−0.282	1	0.590	0.289	0.134	0.282	0.729*	0.688*

** Correlation is significant at 0.01 levels (two-tailed).

* Correlation is significant at 0.05 levels (two-tailed).

Table 4 – Interpretation on the meaning of each factor weight in judgment matrix.

Scale values	Interpretation (B_{ij})
1	Factor B_i and factor B_j are equally important
3	Factor B_i is slightly more important than factor B_j
5	Factor B_i is more important than factor B_j
7	Factor B_i is strongly more important than factor B_j
9	Factor B_i is extremely more important than factor B_j
2,4,6,8,	Intermediate values between the two adjacent judgments-
1/3, 1/5, 1/7, 1/9	If activity i has one of the above numbers assigned to it when compared with activity j , then j has the reciprocal value when compared with i
1/2, 1/4, 1/6, 1/8	Ratios arising from the scale

Table 5 – Judgment matrix and eigenvector.

Factor	CST _n	Dosage	EC	TDN	NO ₃ ⁻ -N	NH ₄ ⁺ -N	W _i
CST _n	1	2	3	5	6	8	0.39
Dosage	1/2	1	2	4	5	7	0.27
EC	1/3	1/2	1	3	4	6	0.18
TDN	1/5	1/4	1/3	1	2	4	0.08
NO ₃ ⁻ -N	1/6	1/5	1/4	1/2	1	3	0.06
NH ₄ ⁺ -N	1/8	1/7	1/6	1/4	1/3	1	0.03

according to its importance, formed a weight for each evaluation criterion and given weight value, constituted a judgment matrix, and the evaluation model was formed by judgment matrix vector. Finally, the merits and demerits of different flocculants were judged by a certain numerical value.

According to the feature of dewatering, the following indicators were selected to comprehensively evaluated the flocculant: (1) dewatering efficiency: CST_n; (2) residual water quality: TDN, NH₄⁺-N and NO₃⁻-N; (3) economic costs: costs, dosage.

The judgment matrix is generally established by the scale method. According to the data of this study and the analysis of the relative importance of each impact factor, 1–9 and its reciprocal were assigned to each factor respectively to establish the judgment matrix. The specific meaning of assignment was shown in Table 4 (Saaty, 1987).

The consistency evaluation of AHP was to test whether the judgment matrix and eigenvector (W_i) can be used as the basis for the comprehensive evaluation criteria of flocculant, and verify whether the evaluation model determined by AHP has satisfactory consistency. The eigenvector of the judgment matrix was shown in Table 5, then the largest eigenvalue (λ_{\max}) was calculated as 6.21. Finally, the consistency of the judgment matrix was verified as follows:

$$\overline{W_i} = n\sqrt{M_i} = n\sqrt{\prod B_{ij}} \quad (3)$$

$$W_i = \frac{\overline{W_i}}{\sum \overline{W_i}} \quad (4)$$

Table 6 – Values of RI.

Matrix order	1	2	3	4	5	6	7	8	9
RI	0	0	0.58	0.90	1.12	1.24	1.38	1.41	1.46

$$\lambda_{\max} = \sum \frac{(BW)_i}{nW_i} \quad (5)$$

where B_i is the values of dimensional column vector of matrix; M_i is the product of the values in each row of matrix; W_i is the weight coefficient of each factor, the greater the W_i , the less important the factor, $\sum W_i = 1$; n is the exponent number of the judgment matrix; λ_{\max} is the largest eigenvalue.

Consistency test of matrix is obtained as:

$$CI = \frac{\lambda_{\max} - n}{n - 1} \quad (6)$$

$$CR = \frac{CI}{RI} \quad (7)$$

where CI is the critical value of combinatorial consistency of judgment matrix; CR is the ratio of random consistency of judgment matrix, When $CR < 0.1$, the judgment matrix has satisfactory consistency; RI is the average random deviation degree of judgment matrix, and RI values were presented in Table 6.

2. Results and discussions

2.1. Effects of flocculation on dewatering performance of dredged sludge

The effects of flocculant dosage on the dewatering behavior of dredged sludge was investigated by using CST_n, SRF, moisture content, and compressible coefficient (CC), as shown in Fig. 1. The values of CST_n, SRF, cake water content and CC in raw sludge were 2.76 s·L·g⁻¹, 46.75 × 10¹¹ m·kg⁻¹, 87.10% and 1.04, respectively. It was obvious that all indexes of samples gradually dropped with the addition of flocculant. When CS dosage increased to 60 mg·g⁻¹ TSS, CST_n, SRF, cake water content and CC were reduced to 0.61 s·L·g⁻¹, 12.49 × 10¹¹ m·kg⁻¹, 45.82% and 0.30, with a decrease of 77.96%, 73.28%, 47.39% and 71.41%, correspondingly. Under PDDA dosage of 20 mg·g⁻¹ TSS, the CST_n, SRF, cake water content and CC were decreased to 0.43 s·L·g⁻¹, 7.54 × 10¹¹ m·kg⁻¹, 50.10% and 0.58, with a decline of 84.49%, 83.87%, 42.48% and 43.97%, correspondingly. The CST_n and SRF showed no obvious change as the dosage of PDDA and CS rose continuously. Nevertheless, CC increased, indicating that dredged sludge has the lowest CC when CS dosage is 60 mg·g⁻¹ TSS and PDDA dosage is 20 mg·g⁻¹ TSS. Then the structure strength of formed sludge cake was the largest and was not easy to be compressed, which was conducive to build up a more porous and permeable structure of the cake (Zhao and Bache, 2001). It was concluded that the optimal dosage of PDDA and CS were 20 mg·g⁻¹ TSS and 60 mg·g⁻¹ TSS, respectively.

Both PDDA and CS improved the dewatering effect of dredged sludge. The CST_n and SRF values of PDDA condi-

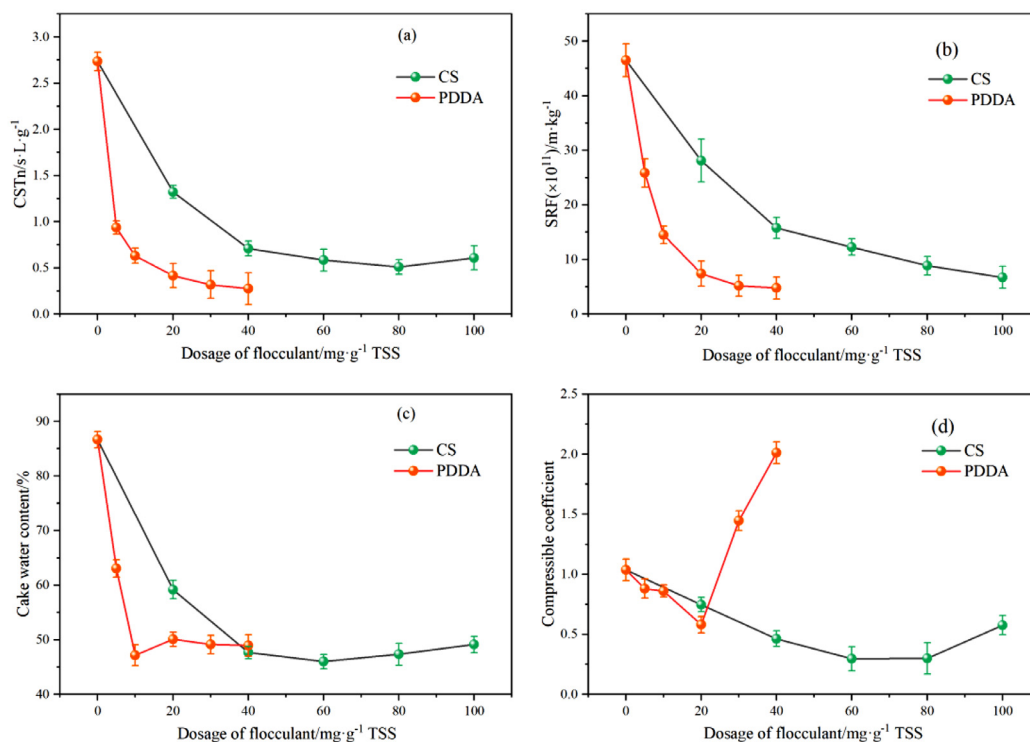


Fig. 1 – Effect of flocculant dosage on dredged sludge dewatering efficiency: (a) CST_n; (b) SRF; (c) cake water content; (d) CC.

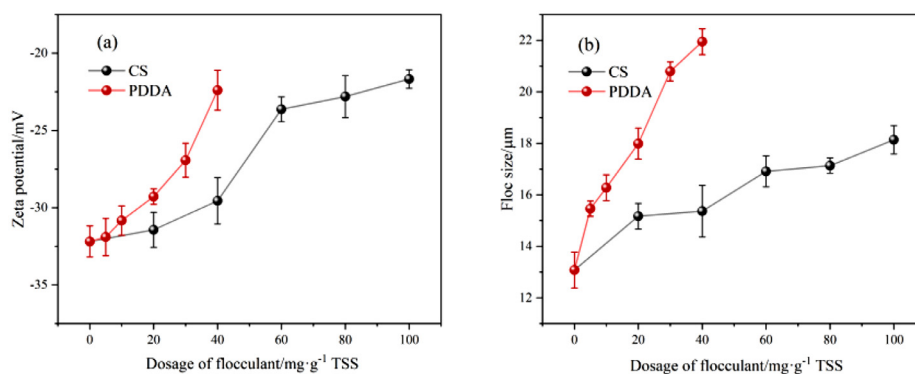


Fig. 2 – Effect of flocculant dosage on (a) zeta potential; (b) floc size.

tioned samples were lower suggested better dewatering performance, compared with CS.

This may relate to the long chain structure of PDDA and CS, which can provide sufficient cationic adsorption sites, prompted strongly adsorption with negatively charged dredged sludge particles through electrostatic interaction and formed large aggregates consequently, and avoided the blockage of water delivery channels by fine particles in filtration process (Chi et al., 2018).

2.2. Effects of flocculation on floc characteristics of dredged sludge

The effect of PDDA and CS with different dosage on zeta potential and flocs size in the dredged sludge was shown in Fig. 2. The value of zeta potential in samples increased with the in-

crease of flocculant dosage. The zeta potential of raw sample was −35.33 mV. Under the optimal dosage, it increased to −26.7 mV (CS) and −31.40 mV (PDDA), respectively. The dredged sludge particles are usually negatively charged, and can be neutralized by quaternary amine groups of PDDA and CS. It works to reduce the mutual repulsion of dredged sludge particles, promote particles agglomeration, and achieve the purpose of dewatering, meaning that PDDA and CS have good performance in charge neutralization. The same zeta potential can be achieved with less PDDA dosage, so PDDA electrical neutralization capacity was better than CS.

Fig. 2b presented that the flocs size increased from 13.08 μm to 16.91 μm when CS dosage was increased to 60 mg·g⁻¹ TSS, and the flocs size was increased to 17.99 μm by increasing PDDA dosage to 20 mg·g⁻¹ TSS. Quaternary ammonium salt linear groups with positively charged was pro-

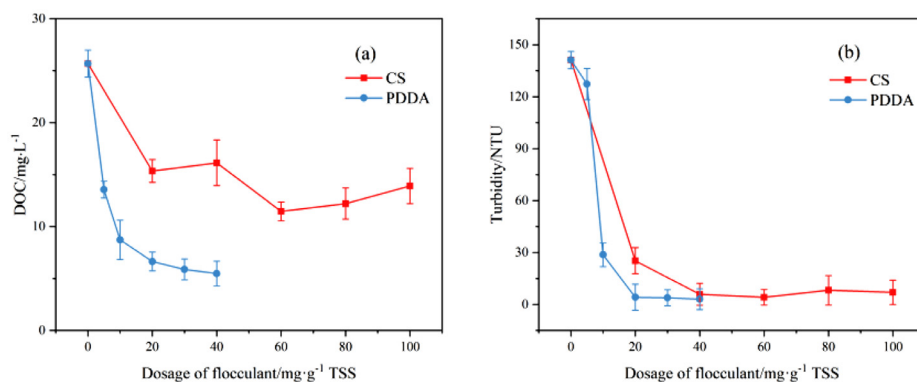


Fig. 3 – Effect of flocculant dosage on (a) DOC; (b) turbidity.

duced when PDDA dissolved and ionized in water. The positively charged groups attracted negatively charged sludge ions and the ion neutralization reaction was acted. Meanwhile, colloidal diffusion layer was compressed leading to make the particles agglomerating and destabilizing. Then flocculation sedimentation was generated because of virtue of the cohesive bridging effect of polymer chain. The destabilized agglomerates rapidly formed network flocs because of the role of electrical neutralization and bridging of chitosan. It was noted that flocs size increased with the addition of flocculant, charge neutralization and bridging simultaneously affect the flocculation process (Zheng et al., 2014), the linear long chain molecular structure provides many sites, which can absorb suspended particles and promote large aggregation to achieve solid-liquid separation (Eriksson, 1993). PDDA has better water-solubility and higher positive charge density (Fig. 2a), it may reduce the repulsion force between flocs and help to form the larger flocs, relatively.

2.3. Effects of flocculation on residual water quality of dredged sludge dewatering

2.3.1. Effects of flocculant on DOC and turbidity in residual water

As shown in Fig. 3a, with the increase of PDDA and CS dosage, DOC values in residual water decreased gradually. DOC of residual water in raw sample was $25.53 \text{ mg}\cdot\text{L}^{-1}$, and then reduced to $11.49 \text{ mg}\cdot\text{L}^{-1}$ (CS) and $6.58 \text{ mg}\cdot\text{L}^{-1}$ (PDDA) under the optimal dosage. Both CS and PDDA showed good removal effect on DOC in residual water, and PDDA performed better than CS comparatively. It is likely that organic matter formed more stable hydrogen bonds with nitrogen atoms in the quaternary amine groups on the CS and PDDA molecular chains, prompting the removal of organic matter from residual water. In addition, PDDA was better soluble in water and occupied higher effective charge density, which was more conducive to the adsorption and removal of organic matter.

Fig. 3b presented that the turbidity of residual water first gradually decreased and then became roughly stable with the increase of the dosage of CS and PDDA. At the optimal dosage, turbidity value decreased from 143.2 NTU (raw residual water) to 4.5 NTU (CS) and 3.8 NTU (PDDA), respectively. The removal efficiency of turbidity by PDDA was better than CS. It indicates

that flocculation destabilizes the negatively charged fine suspended particles in residual water through electrical neutralization and adsorption bridging, and then coalesces into large sized flocs, which can be removed by gravitational settling.

2.3.2. Effects of flocculant on DOM characterization in residual water

Flocculants may have effects on fluorescent components in DOM, which can be readily and fast characterized by 3D-EEM, and then PARAFAC analysis was adopted to resolve the overlapped peaks in EEM spectra. As depicted in Fig. 4, two main fluorescence compounds were detected in residual water including component 1 (C1) - fulvic acid-like substances (FA) and component 2 (C2) - tryptophan proteins-like substances (TPN), and the Ex/Em peaks were centered at 245/420 nm and (225, 280)/330 nm for C1 and C2, correspondingly.

The maximum fluorescent intensities (FI_{\max}) trend of different fractions of DOM in residual water was shown in Fig. 5. It was clear that the fluorescent intensities showed no obvious changes of FA (C1), while that of TPN (C2) decreased with the increase of CS dosage. TPN (C2) decreased by 68.02% at the optimal dosages of $60 \text{ mg}\cdot\text{g}^{-1}$ TSS, indicating that CS had a removing effect on protein-like substances (C2), but had no effect on fulvic acid-like substances (see in Fig. 5a). Unlike the CS treated samples, after PDDA conditioning, the FI_{\max} of FA (C1) and TPN (C2) decreased. Specifically, FA (C1) decreased by 15.86% and TPN (C2) decreased by 39.95% under the optimal dosage, implying that the biopolymers in residual water were flocculated with PDDA.

2.3.3. Effects of flocculant on nitrogen and phosphorus in residual water

Nitrogen and phosphorus measurement aim to determine the potential effect of flocculant on eutrophication of the residual water. As displayed in Fig. 6, the concentrations of TDN, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in raw residual water were $5.21 \text{ mg}\cdot\text{L}^{-1}$, $4.06 \text{ mg}\cdot\text{L}^{-1}$ and $0.28 \text{ mg}\cdot\text{L}^{-1}$, respectively, and significantly increased to $14.04 \text{ mg}\cdot\text{L}^{-1}$, $7.84 \text{ mg}\cdot\text{L}^{-1}$ and $4.8 \text{ mg}\cdot\text{L}^{-1}$ with CS conditioning at optimal dosage, correspondingly. After PDDA conditioning, TDN, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ changed to $5.02 \text{ mg}\cdot\text{L}^{-1}$, $4.60 \text{ mg}\cdot\text{L}^{-1}$ and $0.02 \text{ mg}\cdot\text{L}^{-1}$, respectively. It was obvious that CS promoted the increase of nitrogen ($\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$) in residual water.

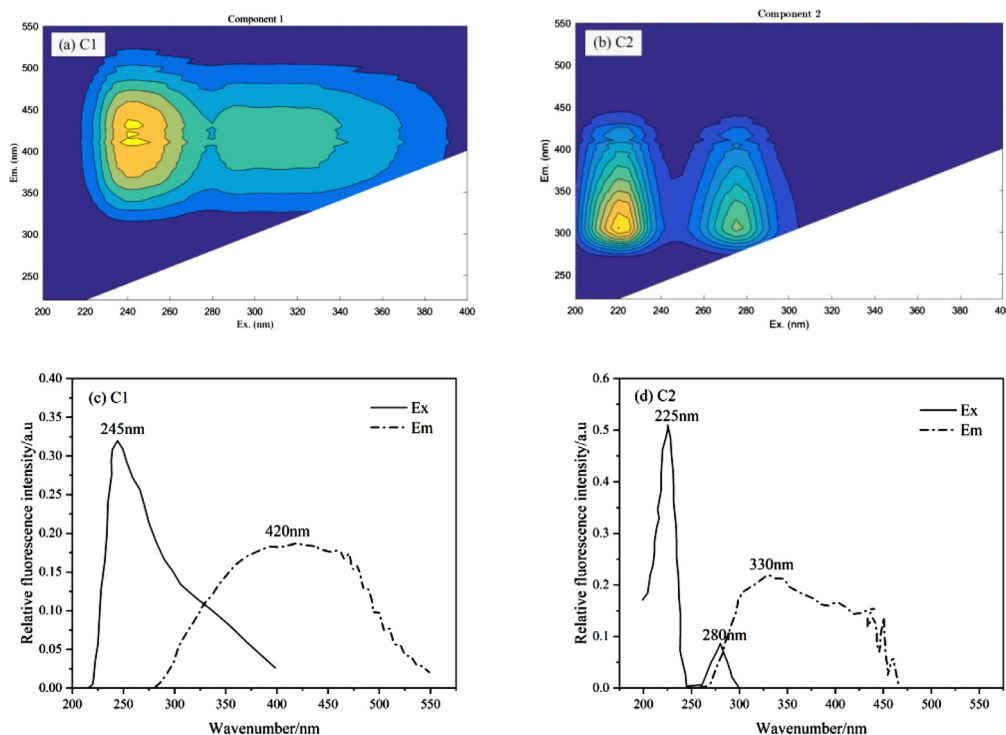


Fig. 4 – EEM-PARAFAC analysis for DOM in residual water of (a) fluorescent C1 in EEM spectra; (b) fluorescent C2 in EEM spectra; (c) C1 peak excitation/emission wavelength location map; (d) C2 peak excitation/emission wavelength location map.

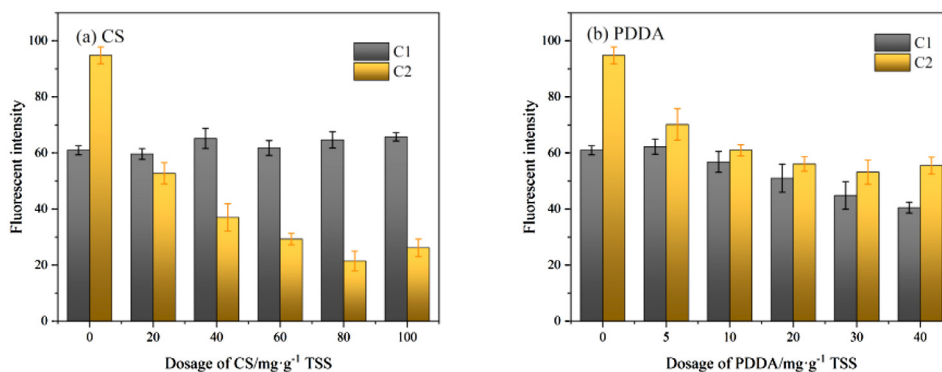


Fig. 5 – Changes in fluorescent components of DOM in residual water under different flocculation dosage.

To further verify the reasons for the increase of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in residual water caused by CS, the CS leaching test (deionized water medium) was conducted to determine the concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the CS leaching solution, and the result was shown in Fig. 6f. With the optimal dosage, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in leaching liquid were $0.22 \text{ mg}\cdot\text{L}^{-1}$ and $4.8 \text{ mg}\cdot\text{L}^{-1}$ respectively. $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the remaining water are $7.84 \text{ mg}\cdot\text{L}^{-1}$ and $4.8 \text{ mg}\cdot\text{L}^{-1}$ respectively, compared with that in CS treated residual water and raw residual water, it can be found that only 5.80% of the increased $\text{NH}_4^+\text{-N}$ in remaining water was caused by CS leaching, indicating that the rest $\text{NH}_4^+\text{-N}$ came from the release of dredged sludge, while the increased of $\text{NO}_3^-\text{-N}$ in remaining water was all from the introduction of CS leaching. This may

be attributed to the cationic groups in CS, which exchange with the amino groups in dredged sludge or the amino groups adsorbed by dredged sludge, thus $\text{NH}_4^+\text{-N}$ in dredged sludge released into residual water, causing the increase of $\text{NH}_4^+\text{-N}$ subsequently.

The values of TDP and $\text{PO}_4^{3-}\text{-P}$ in the residual water of raw sample was $0.056 \text{ mg}\cdot\text{L}^{-1}$ and $0.024 \text{ mg}\cdot\text{L}^{-1}$, respectively. When the optimal dosage was applied, TDP and $\text{PO}_4^{3-}\text{-P}$ decreased to $0.032 \text{ mg}\cdot\text{L}^{-1}$ and $0.022 \text{ mg}\cdot\text{L}^{-1}$ in CS treated residual water, and changed to $0.024 \text{ mg}\cdot\text{L}^{-1}$ and $0.012 \text{ mg}\cdot\text{L}^{-1}$ in PDPA treated residual water. Flocculation reduced TDP and $\text{PO}_4^{3-}\text{-P}$ in the residual water, and PDPA was more effective. PDPA and CS, with positive charge, can adsorb $\text{PO}_4^{3-}\text{-P}$ with negative charge, which can adsorb and capture orthophos-

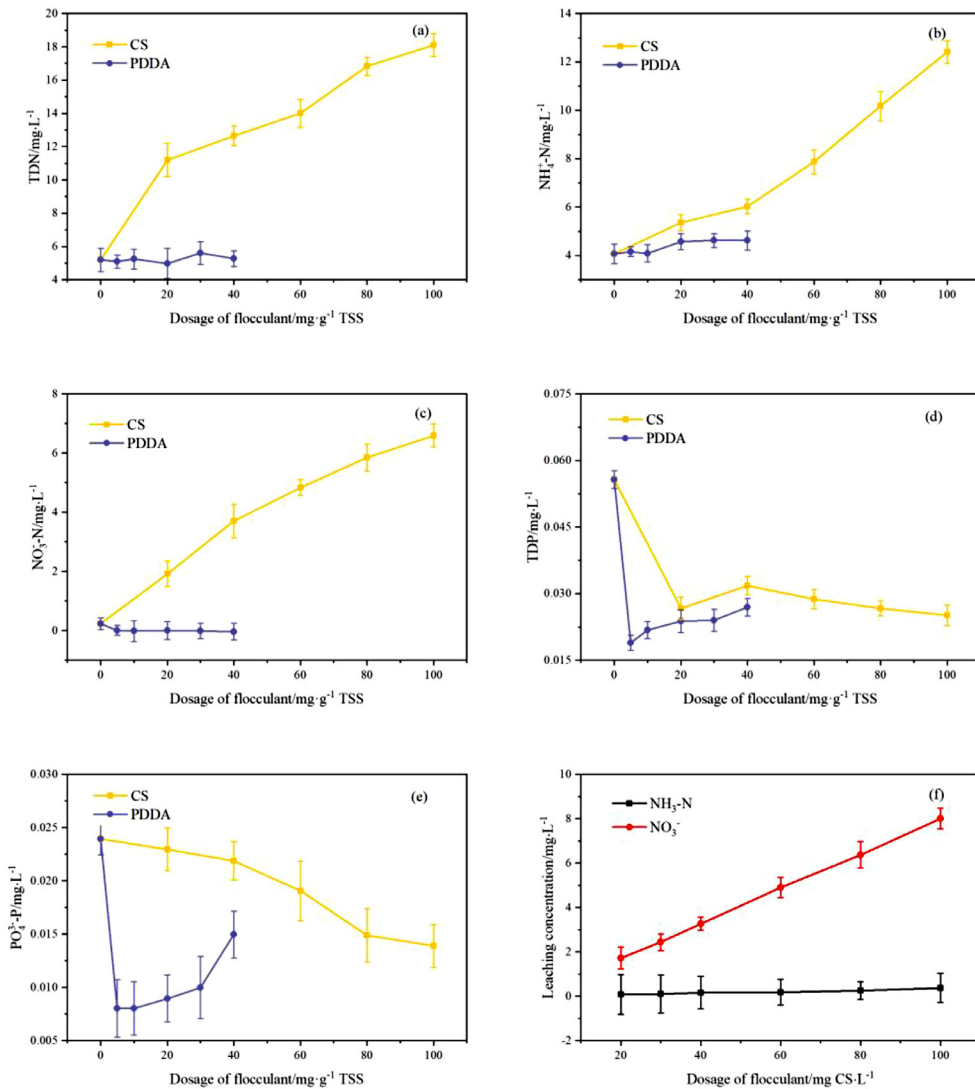


Fig. 6 – Effect of flocculant dosage on residual water quality: (a) TDN; (b) $\text{NH}_4^+\text{-N}$; (c) $\text{NO}_3^-\text{-N}$; (d) TDP; (e) $\text{PO}_4^{3-}\text{-P}$; (f) CS leaching test.

phoric acid phosphorus in flocculation process into dredged sludge to remove TDP and $\text{PO}_4^{3-}\text{-P}$ from residual water.

2.3.4. Factors affecting residual water quality in dredged sludge dewatering

In order to explore the controlling factors of residual water quality in dredged sludge dewatering treatment, Pearson correlation analysis was conducted between the dewatering performance and the residual water quality, to understand the influencing factors of residual water quality. As can be seen from Table 6, DOC, C2, turbidity and TDP were all positively correlated with dewatering indexes (CST_n , SRF and cake water content). Enhanced dewatering efficiency was conducive to reducing the content of DOC, protein-like substances (C2), turbidity and TDP in the residual water. Flocculation promoted the removal of fine particles in residual water and correspondingly removed pollutants attached to fine particles. Meanwhile, there was a strong negative corre-

lation between fulvic acid-like substances (C1) and nitrogen (TDN: $R = -0.905$, $p < 0.01$; $\text{NH}_4^+\text{-N}$: $R = -0.961$, $p < 0.01$; $\text{NO}_3^-\text{-N}$: $R = -0.941$, $p < 0.01$). It can be inferred that the nitrogenous substances in residual water mainly came from the release of fulvic acid-like substances in dredged sludge. In the process of dewatering, the stable binding state of nitrogenous substances and fulvic acid-like substances (C1) was broken by flocculation. CC was positively correlated with fulvic acid-like substances (C1) ($R = 0.648$, $p < 0.05$) and negatively correlated with nitrogen (TDN, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$) (TDN: $R = -0.645$, $p < 0.05$; $\text{NH}_4^+\text{-N}$: $R = -0.517$; $\text{NO}_3^-\text{-N}$: $R = -0.661$, $p < 0.05$). With the compression of the cake, nitrogenous substances released from fulvic acid-like substances (C1) and entered the residual water through the water delivery channel along with the separated water. The better the compression performance was, the less fulvic acid-like substances (C1) and the higher the nitrogenous substances were in residual water. Good compressibility performance aggravated the nitrogen release in the re-

Table 7 – Comprehensive evaluation results of flocculant.

Flocculant	Dosage (kg·ton ⁻¹ TSS)	EC (RMB·ton ⁻¹ TSS)	TDN (mg·L ⁻¹)	NO ₃ ⁻ -N (mg·L ⁻¹)	NH ₄ ⁺ -N (mg·L ⁻¹)	Y
CS	60	336	14.01	4.83	7.87	38.60
PDDA	20	20	4.98	0.01	4.57	7.19
CTS	1.40	154	1.25	0.02	0.35	27.91
CPAM	4.50	31.50	4.33	0.03	0.68	7.59

maining water. Zeta was negatively correlated with turbidity ($R = -0.662$, $p < 0.05$). The electric neutralization promoted the adsorption, aggregation, and settlement of particles in the dredged sludge suspension, thus reducing turbidity. Floc size was negatively correlated with DOC, protein-like substances (C2) and turbidity due to the adsorption and bridging of flocculation, the suspended particles in residual water were reduced, and DOC and turbidity were reduced correspondingly. DOC was significantly positively related with protein-like substances (C2) ($R = 0.958$, $p < 0.01$), showing that DOC mainly originated from the protein-like substances. In addition, protein-like substances (C2) and phosphorus were positively correlated (TDP: $R = 0.729$, $p < 0.05$; PO_4^{3-} -P: $R = 0.688$, $p < 0.05$), implying that phosphorus in residual water mainly existed in the form of protein-like substances. It is inferred that DOC is mainly composed with the phosphorous compound bound with protein-like substances, and phosphorous substances is the main factor affecting DOC in residual water.

2.4. Evaluation system of dredged sludge dewatering

2.4.1. Dewatering target of ecological dredging sludge in Baiyangdian Lake

According to the basic properties of dredged sludge in Baiyangdian lake and the discharge requirements of residual water quality, the flocculant for dredged sludge dewatering should meet the objectives of high dewatering efficiency, little impact on the residual water quality, small dosage, and low cost.

Dewatering efficiency: the basic principle of flocculant selection is to achieve effective dewatering of dredged sludge. In this study, when the CST_n value of dredged sludge was less than $0.6 \text{ s} \cdot \text{L} \cdot \text{g}^{-1}$ and the SRF value was less than $1.4 \times 10^{12} \text{ m} \cdot \text{kg}^{-1}$, the cake water content can reach below 50%, indicating effective dewatering performance. Therefore, the flocculant should meet $\text{CST}_n < 0.6 \text{ s} \cdot \text{L} \cdot \text{g}^{-1}$ and $\text{SRF} < 1.4 \times 10^{12} \text{ m} \cdot \text{kg}^{-1}$.

Residual water quality: the dredged sludge is high water content, the residual water is large quantity, meanwhile, the residual water is generally discharged into the natural water body without treatment or simply treated. Generally, the requirements for residual water quality should be strict and meet the discharge requirements of natural water bodies. Therefore, the selection of flocculant should meet the following requirements: pollutants will not be introduced into the residual water, will not cause the release of pollutants from dredged sludge into the residual water, and the residual water can be discharged without treatment or simple treatment. Based on the above analysis, the indexes that have great in-

fluence on the water quality of the remaining water were selected TDN, NH_4^+ -N and NO_3^- -N.

Economic cost (EC): the selection of flocculant should consider the economic cost as well as the dewatering effect and the effects on the residual water quality. The type and dosage of flocculant have influence on the cost. Based on meeting the above two points, the flocculant with low price and dosage should be selected.

2.4.2. Evaluation model

Since the value of CI and CR was 0.0426 and 0.0343 respectively, both were less than 0.1, the matrix established had approving consistency. Matrix eigenvector (W_i) was suitable for the comprehensive evaluation model of flocculant. The model equation was established according to the weight coefficient in Table 5, and shown in Eq. (8).

$$Y = rm0.3908t + 0.2650m + 0.1760E + 0.0831C_{(\text{TDN})} + 0.0291C_{(\text{NH}_4^+-\text{N})} + 0.0560C_{(\text{NO}_3^--\text{N})} \quad (8)$$

where Y is the comprehensive performance index; t is CST_n , $\text{s} \cdot \text{L} \cdot \text{g}^{-1}$; m is dosage, $\text{mg flocculant} \cdot \text{g}^{-1} \text{ TSS}$; E is EC, $\text{RMB} \cdot \text{ton}^{-1}$; $C_{(\text{TDN})}$, $C_{(\text{NH}_4^+-\text{N})}$, $C_{(\text{NO}_3^--\text{N})}$ are the concentrations of TDN, NH_4^+ -N and NO_3^- -N in residual water respectively, $\text{mg} \cdot \text{L}^{-1}$.

2.5. Evaluation of flocculant in dredged sludge dewatering

In addition to CS and PDDA in this work, the organic polymeric flocculant, chitosan (CTS, 30 kDa molecular weight) and cationic polyacrylamide (CPAM, 12,000 kDa molecular weight) investigated in our previous study was also evaluated (Song et al., 2020). Referring to the market prices of flocculants, the treatment cost of each ton of dry dredged sludge under the optimal dosage of each flocculant was calculated, as shown in Table 7. The smaller comprehensive performance index (Y) means the better comprehensive performance of flocculant.

The organic polymeric flocculant significantly improved the dewaterability of dredged sludge under the optimal dosage, achieving the goal of enhancing dredged sludge dewatering efficiency. However, from the perspective of comprehensive performance index (Y), the value of CS was the largest. CS had a significant impact on nitrogen release, which was not conducive to the realization of residual water quality objectives. PDDA, CTS and CPAM showed no obvious effect on nitrogen release, which favored the reduction of pollution emissions, especially CTS. On the other hand, from the cost analysis, the EC value of CTS was $154 \text{ RMB} \cdot \text{ton}^{-1} \text{ TSS}$, so its economic cost is not competitive relatively. For PDDA and CPAM,

the values of each evaluation index were relatively close. It is difficult to accurately evaluate the flocculants only from the index perspective, which may cause confusion in the selection of flocculant in the application process. With the AHP model, it showed that PDDA was more appropriate than CPAM from the value of the calculated comprehensive performance index Y . The comprehensive performance index can reflect the results of single factor experiment, also verify the rationality of weight index and simulation equation.

3. Conclusions

PDDA was more effective in enhancing the dewaterability of dredged sludge than CS. Likewise, PDDA showed incomparable advantages over CS in residual water quality, which can effectively reduce DOC, turbidity, TP, PO_4^{3-} -P, and remove FA (C1) and TPN (C2). CS promoted the increase of nitrogen (NH_4^+ -N and NO_3^- -N) in residual water. CS leaching test showed that the increase of NH_4^+ -N was due to the release of dredged sludge, while the increase of NO_3^- -N was introduced by CS leaching. It is inferred from correlation analysis that nitrogenous substances in residual water mainly came from the release of fulvic acid-like substances in dredged sludge, and the release of nitrogenous substances was intensified by the compression property. AHP was used to establish the comprehensive evaluation model of flocculants in dredged sludge dewatering. The synthetic performance evaluation indexes (Y) of four kinds of organic polymeric flocculants were calculated according to the equation. The result presented that PDDA had the optimal comprehensive performance, relatively. The comprehensive performance index can reflect the results of single factor experiment, and verify the rationality of weight index and simulation equation.

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