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Decolorization Kinetics of Sludge Protein Solution by ^{60}Co γ-Ray Irradiation/H_2O_2 Oxidation*

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Abstract: In order to carry out decolorization, sludge protein solution, a dark brown close to black solution from activated sludge, was subjected to ^{60}Co γ-ray irradiation in the presence of hydrogen peroxide. UV/Vis spectrophotometric method was used to investigate the effect of H_2O_2 on the coloration apparent kinetics and rate constants of sludge protein solution under γ-ray irradiation. In addition, the effects of irradiation dose, initial sludge protein solution concentration, and pH value on the decolorization efficiency of sludge protein solution were studied. Results showed that the decolorization apparent kinetics of sludge protein solution was a first-order reaction. The solution decolorization percentage increased with the increase of irradiation dose or the decrease of initial sludge protein solution concentration. The examination results of pH value showed that the sludge protein solution could be more efficiently decolorized in alkaline media than in acid media. Moreover, sensory evaluation and foamability analysis indicated that irradiated samples under H_2O_2 oxidation showed better sensory score and foamability.
Keywords: sludge protein solution; decolorization kinetics; irradiation; hydrogen peroxide; sensory evaluation; foamability

Sludge protein solution obtained from activated sludge can be applied in the areas of foam concrete and foam fire extinguishing agent because of its good foaming properties. However, the color of sludge protein solution is too dark, which has restricted its wide application.

Nowadays, there are many approaches to decolorization, such as biodegradation[1], activated carbon adsorption[2], membrane separation[3], ultrasonic synergistic degradation[4], chemical coagulation[5], electrical chemistry[6], TiO_2 photocatalytic oxidation[7], UV/H_2O_2 process[8], Fenton oxidation[9]. These decolorization processes are all popular methods to dispose colored solution, and a great amount of energy and chemical will be consumed in the processes[10,11].

Irradiation has been shown to be a promising alternative for contaminant destruction[12]. The applicability of irradiation technique to efficient degradation/decolorization of biorefractory substances has been confirmed for a variety of pollutants, such as chlorinated benzaldehydes[13], methyl tertbutyl ether[14], calcium lignosulfonate[15], acetochlor[16], and polyvinyl alcohol[17]. However, information regarding the degradation/decolorization of sludge protein solution under γ-ray irradiation/H_2O_2 oxidation is still sparse, especially in kinetics analysis.

This study aimed at the decolorization of sludge protein solution under ^{60}Co γ-ray irradiation and H_2O_2 oxidation. The data were interpreted in terms of kinetic parameters. The effects of initial sludge protein solution concentration, solution pH value and irradiation dose on the decolorization of sludge protein solution were also investigated. In addition, the foamability, sensory quality, and appearance of sludge protein solution after decolorization treatment were analyzed by using Ross Miles method and sensory evaluation.

1 Materials and methods

1.1 Preparation of sludge protein solution

Sludge samples were collected from a wastewater treatment plant in Tanggu district, Tianjin, China. Experiments were carried out under alkaline conditions in a reactor. The effective reactor volume was 1 L, working pressure 9.8 MPa and operating temperature 140 ℃. For the alkaline treatment, the pH value of activated sludge was adjusted to 12 with an adequate intake of CaO and

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the sludge was stirred for 2 h. Soluble protein in the supernatant was obtained by centrifuging the disintegrated sludge at 3 000 r/min for 30 min at ambient temperature of 21—25 ℃. Supernatant was condensed into 20% protein solution, and the pH value of obtained protein solution was approximately 9.

1.2 Irradiation and decolorization studies

Sludge protein solution was prepared in a 250 mL flask. Necessary dilution of the original solution was done with deionized water to obtain a series of protein solution with varying concentrations. The diluted solution was mixed with a given amount of H_2O_2 and the mixture was irradiated with a ^{60}Co irradiator (dose rate 70 Gy/min). The mixture was turned 360° continuously during the irradiation process to achieve uniform target doses. After a certain time interval, the absorbance of the solution was measured at a wavelength corresponding to the maximum absorbance by means of a UV/Vis spectrophotometer. Distilled water served as a reference[18]. Decolorization percentage D was calculated by comparing the absorbance value of sludge protein solution after treatment with that of the original solution and was determined by

$$D = \frac{A_0 - A_t}{A_0} \times 100\% \tag{1}$$

1.3 Foamability analysis

200 mL of sludge protein solution was taken in a pipette with an orifice of internal diameter (i.d.) 0.002 9 m and length 0.010 m. The solution in the pipette was allowed to fall from a height of 0.90 m onto 50 mL of the same solution present in a cylindrical vessel (i.d. 0.05 m) surrounded by a water jacket. All measurements were performed at 40℃. The foam height in the receiver was measured immediately after the last drop of the solution fell from the foam pipette. Foamability of the samples was described in terms of foam height (cm)[19].

2 Results and discussion

2.1 UV/Vis spectra evolution of sludge protein solution

Sludge protein solution with an initial concentration of 20% (v/v) was irradiated at a dose rate of 4 kGy in the presence of 0.6% (v/v) hydrogen peroxide, and pH was natural value (approximately 9). Fig.1 illustrates the evolution of UV/Vis spectra of the solution as a function of irradiation time. The maximum absorbance of the solution appeared at wavelength of 400 nm. It decreased during the irradiation, indicating the decomposition of colored compound and the decolorization of the solution. A new band at wavelength of 281 nm appeared, suggesting the formation of radiolytic products.

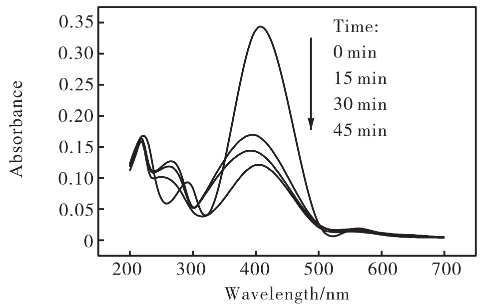

Fig.1 UV/Vis spectra evolution of sludge protein solution as a function of irradiation time

2.2 Time-dependent decolorization of sludge protein solution

The change in decolorization percentage D of sludge protein solution *versus* irradiation time is shown in Fig.2. According to Eq.(2), the kinetics of the solution decolorization with respect to its change in absorption value is fitted well into a first-order rate equation (see Fig.3).

$$\ln(A_0 / A_t) = \ln\left(\frac{1}{1-D}\right) = kt \tag{2}$$

The decolorization of sludge protein solution is due

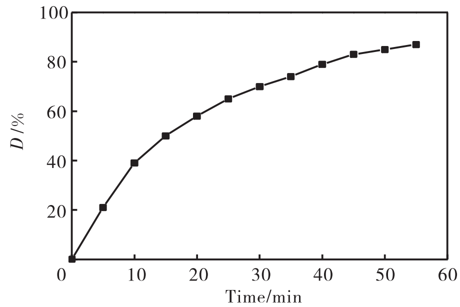

Fig.2 Decolorization data of sludge protein solution *versus* time using ^{60}Co γ-ray irradiation/H_2O_2 oxidation

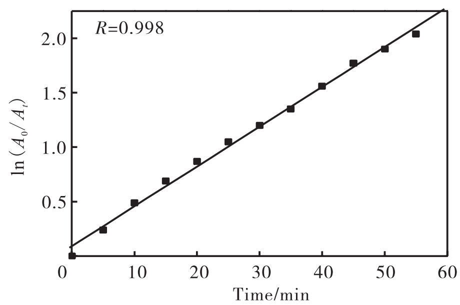

Fig.3 First-order curve fitting of decolorization data of sludge protein solution

to the reaction of hydroxyl radicals generated by H_2O_2 and H_2O in solution under ^{60}Co γ-ray irradiation[20]:

$$H_2O \xrightarrow{\gamma\text{-rays}} \cdot OH, \cdot H, H_2, e_{aq}^-, H_2O_2$$

$$\cdot H + H_2O_2 \rightarrow \cdot OH + H_2O$$

$$H_2O_2 + e_{aq}^- \rightarrow \cdot OH + OH^-$$

$$H_2O_2 \xrightarrow{\gamma\text{-rays}} 2 \cdot OH$$

Wang *et al*[21] reported that the colored compound was sensitive to hydroxyl radicals. Since hydroxyl radicals are strong oxidizing reagents, they can react with the colored compound (R) to produce intermediates (P) which can cause the decolorization of the original solution.

$$R + \cdot OH \rightarrow P$$

Assuming that a majority of the hydroxyl radicals generated in solution remain in the vicinity of R during their short lifetime, they are probably the main source of initiating the decolorization reaction of sludge protein solution.

2.3 Effects of initial concentration and γ-ray dose

Under initial pH value (approximately 9), the decolorization efficiency of sludge protein solution with initial concentrations of 20%, 40% and 60% and γ-ray dose of 2, 4 and 6 kGy is illustrated in Fig.4. Decolorization percentage D rapidly increases with the increase of irradiation time, and also increases with the increase of irradiation dose and decrease of initial sludge protein solution concentration. At an initial concentration of 20% and irradiation dose of 6 kGy, decolorization percentage of sludge protein solution reaches approximately 92% after 40 min irradiation.

As illustrated in Fig.4, decolorization percentage of sludge protein solution exponentially ascends with the increase of irradiation time, indicating that decolorization of sludge protein solution follows pseudo first-order kinetics. Thus, apparent degradation rate constant k could be estimated through linear regression analysis of the log-transformed data according to Eq.(2), and the results are shown in Tab.1. The k value increases with the increase of irradiation dose and decrease of initial sludge protein solution concentration. The high values of correlation coefficient R in Tab.1 suggest that the decolorization of sludge protein solution follows pseudo first-order kinetics.

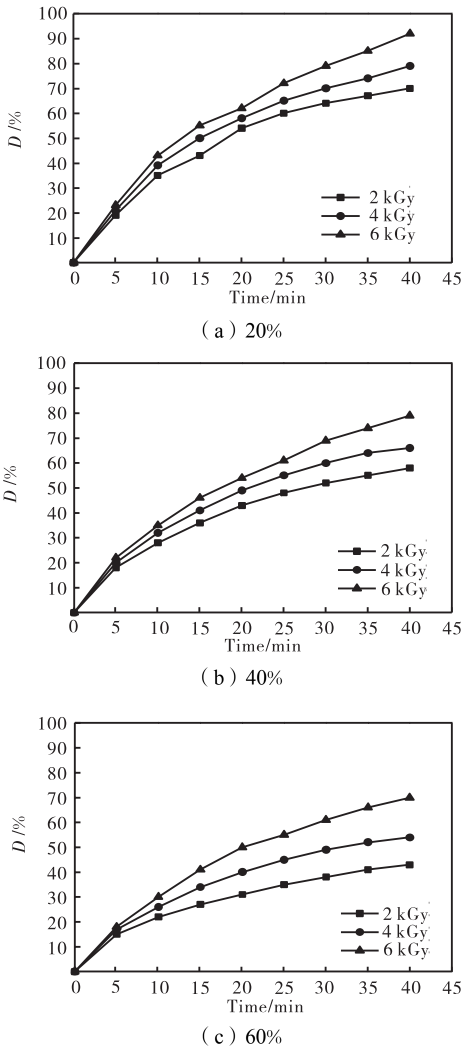

Fig.4 Decolorization percentage of sludge protein solution *versus* time using irradiation / H_2O_2 oxidation
(Initial sludge protein solution concentration: 20%, 40%, 60%; H_2O_2: 0.6%)

Tab.1 Pseudo first-order apparent decolorization rate constants of sludge protein solution

Initial protein solution concentration/%	Dose/kGy					
	2		4		6	
	k/min^{-1}	R	k/min^{-1}	R	k/min^{-1}	R
20	3.013×10^{-2}	0.987	3.656×10^{-2}	0.998	5.837×10^{-2}	0.988
40	2.093×10^{-2}	0.986	2.683×10^{-2}	0.990	3.780×10^{-2}	0.999
60	1.136×10^{-2}	0.993	1.850×10^{-2}	0.994	2.843×10^{-2}	0.998

2.4 Effect of pH value

The pH value plays an important role in decolorization of protein solution in the presence of ^{60}Co γ-ray irradiation/H_2O_2 oxidation, but decolorization percentage was lower, and a mass of depositions was produced at lower pH values, and odor was produced at higher pH values. The effect of pH value was studied by adding incremental amount of either concentrated HCl or NaOH to sludge protein solution under ^{60}Co γ-ray irradiation and H_2O_2 oxidation. Tab.2 lists the changes in decolorization percentage and rate constant of sludge protein solution at three pH values (5, 7 and 9), respectively.

Tab.2 Effect of pH value on decolorization percentage and rate constant of sludge protein solution
(Initial sludge protein solution concentration: 20%; dose: 4 kGy; H_2O_2: 0.6%; irradiation time: 30 min)

pH	Decolorization percentage *D*/%	Rate constant *k*/min^{-1}
5	51.17	2.39×10^{-2}
7	57.02	2.81×10^{-2}
9	74.08	4.50×10^{-2}

Decolorization percentage appears to be higher in alkaline media and lower in acidic media. Decolorization rate constants in acidic and neutral media are only slightly influenced by the solution pH value, but decolorization rate constant significantly increases in alkaline media. This enhancement in solution decolorization in alkaline conditions is most likely due to the fact that in alkaline media, peroxide anions (HO_2^-) are produced by ^{60}Co γ-ray irradiation, which in turn can generate more hydroxyl radicals[22]:

$$HO_2^- \xrightarrow{\gamma\text{-rays}} \cdot OH + \cdot O^-$$

However, the decolorization percentage and constant *k* are limited in acidic media because the hydroxyl radical is likely consumed by the excessive hydrogen ion.

$$\cdot OH + H^+ + e^- \rightarrow H_2O$$

2.5 Sensory evaluation and foamability changes

To examine changes in the foamability and sensory quality as well as appearance of sludge protein solution, two groups of experiments were designed. The total volume of solution was 250 mL, and pH was 8.0 for each of the two groups of experiments. The correlative conditions are given in Tab.3.

Tab.3 Conditions of two groups of experiments

Condition	Experiment group No.	
	①	②
Initial sludge protein solution concentration	40%	40%
H_2O_2	0	0.6%
Irradiation dose/kGy	0	6

Significant differences in sensory quality attributes, such as color and odor, were observed during storage. The original color of sludge protein solution was dark brown close to black, but after γ-ray irradiation and H_2O_2 oxidation, the color changed to weak yellow. The color of the samples turned dark during storage. However, the irradiated samples had better acceptance than the non-irradiated control. After 14 weeks, the irradiated and oxidized samples had still better acceptance than that without ^{60}Co γ-ray/H_2O_2 treatment.

The initial odor scores of irradiated and oxidized samples were significantly higher than samples without ^{60}Co γ-ray irradiation/ H_2O_2 oxidation (Tab.4). During storage, the odor scores of irradiated and oxidized samples were still significantly higher than the contrast samples. It was shown that the fecal odor was reduced in the irradiated and oxidized samples. ^{60}Co γ-ray/H_2O_2 treatment improved the odor of sludge protein solution.

The foamability of sludge protein solution without ^{60}Co γ-ray/H_2O_2 treatment was 17.63 cm. The foamability of irradiated and oxidized samples increased to 20.22 cm. And the foamability decreased during storage. However, the foamability of the irradiated and oxidized samples was still higher. Therefore, the foamability of sludge protein solution can also be improved by γ-ray irradiation and H_2O_2 oxidation. This is because the degradation of some proteins might occur in the case of γ-ray irradiation and H_2O_2 oxidation[20]. Foaming properties of proteins are often improved by moderate degradation, which may be caused by an increase in surface hydrophobicity and flexibility of degraded proteins. Surface hydrophobicity is one of the most important factors determining the foaming capability of proteins[23]. In a protein, degradation is carried out by the action of selected ways and

Tab.4 Changes in sensory evaluation and foamability of sludge protein solution during storage at room temperature

Item	Experiment group No.	Storage period/week							
		0	2	4	6	8	10	12	14
Sensory scores	①	2.61	2.60	2.59	2.50	2.81	2.49	2.42	2.21
	②	3.83	3.75	3.91	3.55	3.65	3.52	3.47	3.65
Foamability/cm	①	17.63	17.65	17.56	17.51	17.49	17.40	17.00	16.50
	②	20.22	20.20	20.21	20.15	20.18	20.10	19.86	19.90

Note: Values within a column are not significantly different at the 95% confidence level.

means to split specific groups-surface hydrophobicity groups. Therefore, foaming capability of proteins was enhanced when protein molecules were degraded and more surface hydrophobicity groups were exposed to solvent after ^{60}Co γ-ray / H_2O_2 treatment.

2.6 Cost analysis

As the previous study[24] showed, the decolorization percentage of irradiation process alone was very low and less than 15%. A comparison of operating cost just for H_2O_2 alone and ^{60}Co γ-ray /H_2O_2 was studied. And 51% of decolorization percentage, the highest one achieved by H_2O_2 alone under more favorable foamability conditions (if the amount of H_2O_2 was further increased, though the decolorization percentage increased, the foamability was destroyed), was selected as the final removal efficiency. The results showed that the operating cost of ^{60}Co γ-ray/H_2O_2 process was 0.200 7 $/L when 51% of decolorization percentage was achieved for 40% sludge protein foaming solution, which was less than the operating cost of H_2O_2 alone, 0.263 7 $/mL. Therefore, ^{60}Co γ-ray/H_2O_2 appeared to be more cost-effective than H_2O_2 alone in terms of operating cost.

3 Conclusions

^{60}Co γ-ray radiolytic decolorization of sludge protein solution was carried out in the presence of H_2O_2. The decolorization of sludge protein solution was investigated by monitoring the absorption values of the solution. It was found that pseudo first-order kinetics was fitted well into the decolorization scheme of sludge protein solution. The apparent degradation rate constant increased with the increase of irradiation dose and decrease of initial sludge protein solution concentration. And the decolorization rate constants in alkaline media were significantly higher than those in acidic and neutral media. After γ-ray irradiation and H_2O_2 oxidation, the color of the sludge protein solution changed from dark brown to weak yellow and had better acceptance than that without ^{60}Co γ-ray/H_2O_2 treatment. Furthermore, the irradiated and oxidized samples showed higher sensory scores and foamability, and the qualities were sustained during storage.

Nomenclatures

A_0 — absorbance values before decolorization for the original solution;

A_t — absorbance values after decolorization for the original solution;

D — decolorization percentage, %;

k — apparent degradation rate constant, min^{-1};

t — irradiation time, min.

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