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Effects of acid/alkaline pretreatment and gamma-ray irradiation on extracellular polymeric substances from sewage sludge

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HIGHLIGHTS

- Effects of acid/alkaline pretreatment and gamma irradiation on EPS were examined.
- Gamma irradiation and alkaline treatment generated remarkable synergistic effects.
- The combined application could promote sludge disintegration and solubilization.

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ABSTRACT

In order to investigate the mechanism of extracellular polymeric substances (EPS) influencing sludge characteristics, variations of extractable EPS from municipal sewage sludge by acid/alkaline pretreatment and gamma-ray irradiation were studied. The changes in constituents of EPS were analyzed by UV–vis spectra and SEM images. The effects of alkaline pretreatment and gamma-ray irradiation on the functional groups in EPS were investigated by Fourier transform infrared (FTIR) spectrometer. Results showed that the extractable EPS increased clearly with increasing irradiation dose from 0 to 15 kGy. UV–vis spectra indicated that a new absorption band from 240 nm to 300 nm existed in all irradiated samples, apart from acid condition. The results of FTIR spectroscopic analysis indicated that, irradiation influenced major functional groups in EPS, such as protein and polysaccharide, and these effects were clearer under alkaline condition. SEM images provided that after alkaline hydrolysis, gamma-ray irradiation was more effective in resulting in the sludge flocs and cells broken, compared with acid pretreatment (pH 2.50).

1. Introduction

Sludge extracellular polymeric substances (EPS) is a predominant sludge flocs component. It accumulates on bacterial cell surfaces and is regarded as “cells′ small house” (Tian, 2010). EPS composes of various organic substances such as protein, polysaccharide and a little humic substance, lipid, nucleic acid, and amino acid, etc. (Kim et al., 2011). EPS could influence many characteristics of sludge, such as surface charge, hydrophobicity, sedimentation property, flocculability, dewatering property and heavy metal absorption property, etc., and it could be used as a degree of sludge solubilization (Pei et al., 2007; Zheng et al., 2007; Zhou, 2010).

There are a few views on the effects of EPS on sewage sludge. Zhou (2010) deemed that EPS was adverse to dewatering property of sewage sludge, while Houghton et al. (2001) believed that EPS could enhance dewatering property. In fact, it is complicated to study the effects of EPS on sewage sludge, because the study results rely on different sludge samples, extraction methods, identification methods, and so on.

^{60}Co gamma-ray irradiation could improve sludge dewatering and sedimentation property, and it could degrade organic and non-biodegradable matters which could effectively reduce sludge solids and inactivate pathogenic microorganisms (Wang and Wang, 2007; Zheng et al., 2011), and EPS plays an important role in these effects (Shin and Kang, 2003; Cuba et al., 2003). In addition, gamma-ray irradiation carry out at ambient temperature and it is an environmental-friendly process without additional chemicals (Mudhoo and Mohee, 2010; Haji-Saeid et al., 2012).

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Acid/alkaline pretreatment makes a great difference to EPS which may influence sludge characteristics (Zheng et al., 2007). In this study, variations of extractable EPS from municipal sewage sludge by acid/alkaline pretreatment and gamma-ray irradiation were investigated. UV–vis spectra was used to analyze the changes in constituents of EPS. FTIR spectrometer was employed to analyze the changes of functional groups in EPS, and these effects were explained by SEM. Increased knowledge on this issue will deepen our understanding of the mechanisms of sewage sludge treatment by acid/alkaline pretreatment and gamma-ray irradiation, and it would be helpful for the practical application.

2. Experimental section

2.1. Sludge source

The sewage sludge was obtained from a municipal wastewater treatment plant with A^2/O process in Hengyang, China. The sludge came from the second sedimentation tank and sieved (10 mm pore size) to remove large particles for experiment. Table 1 shows the physicochemical characteristics of the initial sludge.

2.2. Irradiation

The ^{60}Co-source was supplied by Hunan Provincial Nuclear Agriculture Sciences and Space Mutation Breeding Research Institute. The radioactivity of the source was around 1×10^{16} Bq. The sludge samples were irradiated with a dose rate of around 0.56 Gy/s in anaerobic and sealed plastic bottles with a volume of 200 mL under the condition of atmospheric pressure and ambient temperature (around 10 °C). The absorbed doses were measured by means of silver dichromate gamma-dosimeter. Irradiation was performed in a batch system with absorbed doses from 2 to 15 kGy (about 1–7.5 h of contact time).

2.3. Analytical methods

Acid/alkaline pretreatment: 2 mol/L HCl and 2 mol/L NaOH was used to adjust the pH of sludge samples to 2.50, 9.80, 11.80, and blank samples retained the initial pH 7.52 in parallel in comparison. Then N_2 was filled into bottles in order to expel residual air and keep anaerobic condition.

These samples were cultured at 50 rpm for 3 h in shaking incubators (QYC2112, China) at 25(± 2) °C.

Extraction and analysis of EPS: sewage sludge samples by acid/alkaline pretreatment and gamma-ray irradiation were centrifuged at 3000 rpm for 20 min and filtered through a filter membrane (0.45 μm pore size). The filtrate was heated at 105 °C to measure the concentration of EPS. UV–vis spectra (UVmini-1240, Japan) was used to analyze the constituents of EPS. The functional groups in EPS were investigated by FTIR spectrometer (Nicolet 670, USA) to analyze the effects of gamma-ray irradiation and alkaline treatment on EPS.

SEM analysis: the variations of EPS were provided by Scanning Electron Microscope (SEM, FEI Quanta-200, USA) before and after EPS extraction under different conditions.

Table 1
Characteristics of the initial sludge.

Items	Results
pH	7.52
Water ratio (%)	99.19
TS (mg/L)	7800
VS (mg/L)	4310
TSS (mg/L)	4710
VSS (mg/L)	1730
Alk. (mg/L, as $CaCO_3$)	150.15
ORP (mV)	−30

3. Results and discussion

3.1. Effects of acid/alkaline pretreatment and gamma-ray irradiation on constituents of EPS

After acid/alkaline pretreatment and gamma-ray irradiation, the UV–vis spectra of EPS are shown in Fig. 1. Compared to the initial samples, a new absorption band from 240 nm to 300 nm existed in all irradiated samples (Fig. 1A, C, and D), apart from acid condition (Fig. 1B). Nucleic acid component is the most important goal of microorganisms irradiation inactivation. It is specific substance in organisms′ cells, and normal cells′ extracellular substance seldom contains nucleic acid. Only cells are broken and dead, nucleic acid could release into sludge solution (Wu and Bao, 2002; Zhou, 2010). Protein is known as the most difficult compound to extract (Kim et al., 2011). Pure nucleic acid's absorption peak is at 260 nm, and protein's absorption peak is at 280 nm, so UV–vis spectra of EPS could indirectly reflect the disintegration extent of sludge by irradiation. From Fig. 1, it could be concluded that irradiation could disrupt the complex sludge flocs structure and release extracellular substances such as proteins, nucleic acid from the flocs structure into the soluble phase, which could achieve the biodegradability enhancement of sludge. Moreover, the broken sludge flocs and cells could release more bound-water, leading to the enhancement of sludge dewatering property.

After irradiation, absorption peak in UV–vis spectra of EPS all appeared at 260 nm, and peak value increased with increasing irradiation dose from 0 to 15 kGy (Fig. 2). In the case of EPS concentration, it increased in proportion to irradiation dose and pH (Fig. 3). The same unfavorable trend was also found under acid condition, viz., little increase of EPS concentration could be observed. Under strong alkaline condition (pH 11.8, 15 kGy), the concentration of EPS increased sharply, and the result was higher than that of pH 2.5, pH 7.52 and pH 9.8 by about 715%, 900% and 445% (0 kGy), respectively. These results also suggested that alkaline treatment and irradiation could generate obvious synergetic effects, and irradiation solubilization efficiency of sludge enhanced with increasing alkalinity and irradiation dose. At the same time, it was interesting to note that single alkaline treatment could also achieve desirable results at 0 kGy (Fig. 3).

When pure water or aqueous solutions, such as sewage sludge is irradiated by gamma-ray irradiation, the following chemical species are formed (Eq. (1)) (Meeroff et al., 2004). In aqueous media, the oxidizing hydroxyl radical •OH, the reducing hydrated electron e_{aq}^- and the hydrogen radical •H are the predominant products, which are highly reactive transient species and are responsible for the various irradiation effects including physical chemistry effects (colloform degeneration), chemistry effects (irradiation chemistry disintegration or pollutants oxidation), biology effects (pathogens reduction) (Wu and Bao, 2002), etc., and •OH plays a major role in the biological damage of nucleic acid and bacteria inactivation. Besides indirect effects mentioned above, considerable gamma-ray could directly interact with the pollutants in the sludge, which could eventually result in pollutants disintegration and solubilization (Zheng, 2010). Both direct and indirect effects on microorganisms caused by irradiation may result in genetic materials damage, i.e., DNA and RNA, leading to