Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES www.jesc.ac.cn

Novel cationic polyamidine: Synthesis, characterization, and sludge dewatering performance

Bo Guo[1], *Huan Yu*[1], *Baoyu Gao*[1,*], *Sen Zhang*[2], *Qinyan Yue*[1], *Xing Xu*[1]

1. *Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China. E-mail: guobo751119@163.com*
2. *Shandong Institute of Metrology, Jinan 250014, China*

ARTICLE INFO

Article history:
Received 5 May 2016
Revised 21 July 2016
Accepted 3 August 2016
Available online 13 August 2016

Keywords:
Polyamidine
Synthesis
Characterization
Sludge dewatering

ABSTRACT

In this study, a new and facile route was employed for synthesis of polyamidine with abundant cations and attractive five-membered ringlike structural unit. N-vinylformamide and acrylonitrile copolymerized firstly to form intermediates, and the intermediates were processed with hydrochloric acid to produce polyamidine. A series of polymerization conditions (*e.g.* polymerization time, temperature and dosage of initiator) were optimized through productivity, viscosity and cationic degree as evaluation. SEM analysis illustrated that the amidinization process could reduce the size of spaces between molecular and created compact structure, which would contribute to good flocculation performance and high viscosity. FT-IR, XPS and NMR spectra presented a rather clear structure of polyamidine. 34.3% of sludge was sedimentated through the flocculation of polyamidine in the early stages. In contrast, only 6.8% of sludge was sedimentated by polyacrylamide. The moisture content in dehydrated floc could be reduced to 77.7% when 60 mg/L polyamidine was added. These results demonstrated that the polyamidine showed a great potential in the practical application of sludge dewatering.

Introduction

With the development of urbanization and industrialization, municipal sewage and industrial effluent treatments produced abundant sewage sludges. These sewage sludges can be used to prepare fertilizer, fodder, cement additive, fuel admixture after sludge dewatering and other further processes (Wu et al., 2010; Liang et al., 2014). However, the vast pathogenic bacteria, parasite, and heavy metals, especially the high water content (WC) in the sewage sludge (WC, 95%–98%) resulted in it being more difficult to stack, transport, further treat and re-use (Liu et al., 2015; Wang et al., 2016). Therefore, sludge dehydration should be the primary and emergent task for sludge treatment. In various types of sludge dewatering equipment, dewatering agents are always indispensable additives. Normally, the common dewatering agents are cationic polyacrylamide (PAM), nonionic PAM, anionic PAM and other novel chemical conditioners, like Fe(II)-activated persulfate oxidation (Addai-Mensah, 2007; Lin et al., 2012; Tanaka et al., 2014; Zhen et al., 2012a, 2012b, 2012c, 2013). As far as we know, there are still few reports related to the dewatering of sewage sludge that using polyamidine as flocculant.

As a kind of important intermediate in organic synthesis, amidine is widely used in pesticide and medicine, such as parasiticide, diuretic, antibiotic and anti-inflammatory (Khan et al., 2008). Amidine is an organic compound that the carbonyl oxygen in acylamino is replaced with imidogen. While, polyamidine is an organic compound containing

* *Corresponding author*. E-mail: bygao@sdu.edu.cn (Baoyu Gao).

http://dx.doi.org/10.1016/j.jes.2016.08.002

amidine groups in polymer molecular chain. Generally, polyamidine possesses two typical structures: linear-chain structure with amidine group as polymer backbone and cyclic structure with amidine group as pendant group. It is worth mentioning that this cyclic polyamidine containing five-membered rings is a cationic polymer, which shows exceptional performance such as high charge density, good stability and hypotoxicity. Consequently, polyamidine has recently gained growing interest in different fields–applications including papermaking, dyestuff and water treatment due to its good performance as flocculant.

The research and development of polyamidine have been nearly sixty years. The term polyamidine was first mentioned in 1959 by Grundman et al. (1959). Their work developed the field of polyamidine and resulted in several practical applications. Kurita et al. (1977) used the polyaddition of bisketenimines with various diamines to afford linear polyamidines. And then their structures were confirmed *via* elemental analysis and infrared characterization. Mathias and Overberger (1979) prepared an aromatic polymer containing formamidine groups in the polymer backbone using aromatic diamines, a,a-dichloromethyl ether and triethylformate as monomers. Then these polymers were characterized by viscosity, microanalysis, and nuclear magnetic resonance and infrared spectroscopy (IR). Rillich et al. (1993) synthesized aliphatic polyformamidines by reaction of aliphatic diamines with triethylformate in the presence of catalytic amounts of acetic acid. The polymer structure has been confirmed by IR and nuclear magnetic resonance (NMR) spectroscopy. Sato et al. (1994) synthesized polyamidine with five-membered rings which feeds on N-vinylformamide and acrylonitrile. The products possessed high positive charge density and exhibited improved performance in dehydration, filtration and stability. Sawayama et al. (1995) improved the reaction conditions of polyamidine and studied its application in paper additive.

In addition, many scholars have devoted their efforts to the application of polyamidine (Lin et al., 2002; Sharavanan et al., 2004; Aleksandrova et al., 2004; Guo et al., 2015; Wang and Zhang, 2008; Jin et al., 2009). Lin et al. (2002) prepared a new chelating fiber from a hydrolyzate of poly(N-vinylformamide/acrylonitrile) by a wet-spinning method. The fiber has high binding capacities and good adsorption properties for heavy metal ions, such as Cu^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, and Mn^{2+}. Sharavanan et al. (2004) studied hydrolytic degradation of an aliphatic polyacetamidine at different pH values. The degradation of polyamidine occurred at neutral and basic conditions whereas under acidic conditions the polyamidine was stable. The results showed that aliphatic polyamidines were potential carriers for active compounds which can be released by the hydrolytic degradation of the polymer (Sharavanan et al., 2004). Aleksandrova et al. (2004) studied the photophysical properties and mechanism of charge-carrier photogeneration in supramolecular polyamidine structures. Wang and Zhang (2008) synthesized a ring-like polyamidine, characterized it by Fourier transform infrared spectra (FT-IR) and ultraviolet (UV), and got a good turbidity removal effect in sludge dewatering. Jin et al. (2009) prepared this cationic polymer by acidic hydrolysis of poly(N-vinylformamide-co-acrylonitrile) and used FT-IR and ^{1}H NMR to prove that it contained cationic amine groups, cationic 5-member ring amidine groups and 6-member ring amidine groups. The application of polyamidine is still relatively new and is under development.

Herein, we reported on a novel cationic polyamidine which had five-membered ring-like unit in its structure. N-vinylformamide and acrylonitrile copolymerized firstly to form intermediates, and the intermediates were processed with hydrochloric acid to produce polyamidine. The polyamidine possessed high molecular weight and the amido in five-membered ring-like structural unit contributed to the high charge density. Moreover, this distinctive structure was conducive to extend in aqueous solution to contact more contaminants. All of the above advantages and the hydrophobicity of polymer would be beneficial to the dewatering of sludge. And some characterization methods were used to investigate the properties of cationic polyamidine, *e.g.* scanning electron microscope (SEM), ultraviolet–visible spectrum (UV–vis), FT-IR, thermogravimetric analysis–differential thermal gravimetric analysis (TG-DTG), X-ray photoelectron spectroscopy (XPS) and NMR spectra. Moreover, the prepared product has been successfully applied to sludge dewatering and shows good results, demonstrating its potential use in environmental protection.

1. Materials and methods

1.1. Materials

The chemical used in the polymerization experiment included N-vinylformamide (NVF), acrylonitrile (AN), 2,2′-Azobis(2-methylpropionamidine) dihydrochloride (AIBA, high purity grade, purchased from BioDuly Co., Ltd., Nanjing, China). HCl and NaOH were supplied by Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Acetone, poly(vinylsulfate) potassium salt (PVSK), toluidine blue (T.B.) and other chemicals were of analytical reagent grade. Deionized water was used in the experiment. Sludge was drawn from secondary sedimentation tank of Guangda sewage treatment plant (Jinan, China). The collected sample was stored at 4°C. Within 48 hr of collection, the sludge was prepared for experimentation. The main characteristics of sludge are as follows: temperature 20.5°C, pH 6.7, turbidity 57.3 NTU, water content 99.4%, sludge settling ratio 86%, and mixed liquor suspended solids 5.85 g/L.

1.2. Methods of characterization

The surface morphology was examined using JEOL JSM-6480LV SEM with the magnification of 7000. A GBC Cintra 20 UV–vis spectrophotometer with 1.0 cm quartz cell was used for recording UV–vis spectra of intermediates and polyamidine. The FT-IR of polymer was recorded with Perkin–Elmer "Spectrum BX" spectrometer in the range of 4000–400 cm^{-1}. TG-DTG was carried out with thermo gravimetric analyzer (SHI-MADZU, TGA-50). The samples were heated from 10 to 800°C in N_2 flow at a rate of 10°C/min. XPS was used to analyze the surface binding state and elemental speciation of polyamidine. The measurements were performed by a spectrometer (ESCALAB 250) with MgKα radiation (1486.71 eV of photons) as the X-ray source. And the sample was