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A new insight into resource recovery of excess sewage sludge: Feasibility of extracting mixed amino acids as an environment-friendly corrosion inhibitor for industrial pickling

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ABSTRACT

HIGHLIGHTS

GRAPHICAL ABSTRACT

- A value-added product was extracted from the municipal excess sludge.
- The effective components contained in the product were mixed amino acids.
- The product could provide a reliable protection to the steel from the acid medium.
- A new insight into the resource recovery of excess sewage sludge was provided.

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1. Introduction

In the past decade, a number of WWTPs have been constructed and successfully operated around the world. While having a positive effect in terms of water quality improvement, WWTPs also generate large volumes of excess sewage sludge (ESS), which has

http://dx.doi.org/10.1016/j.jhazmat.2014.06.053 0304-3894/© 2014 Elsevier B.V. All rights reserved. The work mainly presented a laboratory-scale investigation on an effective process to extract a valueadded product from municipal excess sludge. The functional groups in the hydrolysate were characterized with Fourier transform infrared spectrum, and the contained amino acids were measured by means of an automatic amino acid analyzer. The corrosion-inhibition characteristics of the hydrolysate were determined with weight-loss measurement, electrochemical polarization and scanning electron microscopy. Results indicated that the hydrolysate contained 15 kinds of amino acid, and their adsorption on the surface could effectively inhibit the corrosion reaction of the steel from the acid medium. Polarization curves indicated that the obtained hydrolysate was a mixed-type inhibitor, but mainly restricted metal dissolution on the anode. The adsorption accorded well with the Langmuir adsorption isotherm, involved an increase in entropy, and was a spontaneous, exothermic process.

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aroused increased concern in many metropolitan cities [1]. ESS, as a by-product of WWTPs, has become a major limiting factor for determining the success of a WWTP operation. The costs relating to treatment, transportation, storage and final disposal of ESS may account for more than 50%, in terms of building and operating a WWTP [2]. Traditional methods for disposing ESS include application to cropland [3], landfill [4], incineration [5], and ocean dumping [6], which have been operated in some countries for many years, and are still adopted in many European countries [7]. The negative environmental effects of these methods have gradually been









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reflected by the transfer of pollutants from ESS to the soil, the atmosphere and the ocean [6–9]. The demand for effective safe disposal of ESS, without causing secondary pollution, is therefore a matter of urgency. In many countries the priority sequence, in terms of treating and disposal of ESS, is reduction, reuse and, finally, detoxification (neutralization) [7].

ESS has long been regarded as a potential source of bioenergy [10,11], since it can be converted to a combustible gas and other bio-fuels through processes such as anaerobic digestion, fermentation, hydrolysis, gasification and pyrolysis. The residual solids, after extracting bio-fuel, contain inorganic substances such as SiO₂, CaO, Al₂O₃, Fe₂O₃ and other metal oxides, which may be used as building materials [12], The abundant proteins contained in ESS could also possibly be used as a raw material for producing organic fertilizer [13] or animal feed [14]. Other bio-products, such as biological surfactants and adsorbents, have also been be extracted from ESS [15,16].

Corrosion-inhibition is important in terms of material protection and industrial pickling. Amino-containing substances are very effective for inhibiting acid corrosion, and some conventional corrosion inhibitors, such as organic amines, thiourea and urotropine, are widely used for industrial pickling [17–19]. In recent years investigations have mainly focused on corrosion inhibitors that are highly efficient and have a good environmental safety rating. Suitable candidates for such agents include extracts from plant seeds, fruits, leaves, peels and flowers [20-25], which are used as corrosion inhibitors. Amino acids are widely-available natural compounds that contain amino and carboxyl group as part of their molecular structure. This special structure suggests that they would be suitable candidates as corrosion inhibitors. The application of amino acids, as effective inhibitors to control corrosive reactions in a number of different metals in acidic media has been verified by a series of investigations [26–29].

ESS has a rather complex and variable chemical composition in its solid part. However, in the past several years, the chemical compositions in the solid part of ESS have been measured by some researchers [30-32], their results indicated that proteins, carbohydrates and lipids were the major organic compositions, which were determined to be about [33]: $2602 \pm 134 \text{ mg L}^{-1}$, $497 \pm 66 \text{ mg L}^{-1}$, $233 \pm 13 \, mg \, L^{-1}$, respectively. Proteins can be easily biodegraded to small-molecule organics, such as amino acids, under suitable conditions. For extracting the amino acids from ESS, hydrolysis is generally the first step. Nevertheless, the specific network formed by extracellular polymeric substances (EPS) and some divalent cations, as well as the protection of cell membrane, often present a physico-chemical barrier that resists hydrolysis. Thus, the hydrolysis of ESS is generally a rate-limiting step in the process of biological treatment. In conventional anaerobic digestion, hydrolysis, which is the first step, is a very slow process that can prolong anaerobic digestion for more than 20 days. It has been indicated that the destruction of the floc of sludge and the cell membranes is an effective way to accelerate the anaerobic digestion of ESS [34]. Certain physical methods, such as ultrasound [35] and microwave irradiation [36], have recently been used to pre-treat ESS, so as to decrease the time taken for the anaerobic digestion process and other biological treatments.

To the best of our knowledge, there are no similar reports on the extraction of value-added product from ESS, for use as an environment-friendly corrosion inhibitor in acidic media. The purpose of the present investigation was to develop a rapid method for the effective hydrolysis of proteins in ESS, and to confirm the feasibility of using ESS as a cheap raw material for extracting valueadded product as an environment-friendly corrosion inhibitor. Two aspects were considered: (1) proposing an ultrasound-assisted hydrochloric acid-hydrothermal method as well as optimizing the conditions in order to achieve rapid volume-reduction of excess sludge and extract value-added product; (2) using Fourier transform infrared spectrum (FTIS), amino acid analyzer, weight-loss measurement, electrochemical polarization and scanning electron microscopy (SEM) to characterize the product, and elucidating its corrosion-inhibition characteristics on mild steel in acid solution. Ultimately, we hoped that the results of these tests would provide a new insight into the utilization of ESS.

2. Material and methods

2.1. ESS samples

ESS samples were obtained from the secondary sedimentation tank of Lijiao municipal wastewater treatment plant (located in Haizhu District, Guangzhou, China). Sludge samples were collected once a week from September 2012 to May 2013 and stored in a refrigerator at 4°C for maximum 3 days during the experiments. The characteristics of ESS samples were measured immediately after sampling from the secondary sedimentation tank. Their characteristics were determined by the standard method [37], and are listed below: pH: 6.36-6.49; settling velocity (SV): 78.0–88.3%; total suspended solid (TSS): $9.12-12.93 \text{ gL}^{-1}$; total volatile solid substance (TVSS): $6.66-9.11 \text{ gL}^{-1}$; total COD (TCOD): 10149–11235 mgL⁻¹; soluble COD (SCOD): $94-120 \text{ mgL}^{-1}$; water content: 98.71-99.09 wt.%.

2.2. Methods of extraction

After having finished measuring all of the basic characteristics, the thoroughly mixed samples were centrifuged (TDL-60B, Anke Scientific Instrument Factory, Shanghai) for a number of different time periods, so as to obtain variable samples in terms of water content. Samples with different water content were then placed into an ultrasonic reactor (KQ2200DE, Kun Shan Ultrasonic Instruments Co., Ltd, China). After sonolysing for 90 min at 100 W and 40 kHz, all of the suspended sludge was divided equally into five conical beakers, after which a certain volume (2, 4, 6, 8, 10, 12 mL) of HCl (37.0 wt.%) was added to adjust the concentration of hydrochloric acid (0.65, 1.30, 1.95, 2.60, 3.25, 3.90 mol L^{-1}). The samples were then sealed and placed in a thermostatically controlled water bath (Light brand digital temperature type, Yaxing Instrument and Meter Co., Ltd., Yuyao, China) at a range of different temperatures $(60, 70, 80, 90, 100 \pm 0.5 \,^{\circ}\text{C})$ for hydrolysis which lasted for variable time periods (2, 6, 10, 14, 18, 22 h). Each extracting experiment was repeated 3 times with the same procedure with the average value as the final result. Single factor extraction experiments were designed by fixing three of the four above-mentioned parameters while varying one parameter, to assess the influence of different operational conditions on the solubilization of the organic solid in ESS. A parameter, defined by Eq. (1), was used to assess the extraction efficiency.

$$SS_I(\%) = \frac{\text{TVSS}_0 - \text{TVSS}_1}{\text{TVSS}_0} \times 100\%$$
(1)

where SS_t is the solubilization index of organic solids, TVSS₀ and TVSS_t are the contents of TVSS in ESS before the experiment, and after hydrolysis, for time *t*, respectively. This definition was used to quantitatively describe the degree of extraction of the TVSS in ESS.

The liquid–solid mixture was then filtered, using qualitative filter paper (Whatman-Xinhua Filter Paper Co., Ltd., Hangzhou, China) and some of the red-brown transparent liquid filtrate was sampled for characterization with the Fourier transform infrared spectrum (FTIR, Nicolet 6700, Thermo Fisher Scientific Inc., U.S.) under the spectrum conditions of 400–4000 cm⁻¹. The remaining filtrate was used for subsequent experiments. The pH was measured using a pH meter (PHS-25, Shengci instrument Co., Ltd., Shanghai, China). Download English Version:

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