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Citric acid and ethylene diamine tetra-acetic acid as effective washing agents to treat sewage sludge for agricultural reuse

Xianghao Ren [a], Rui Yan [a], Hong-Cheng Wang [b], Ying-Ying Kou [a], Kyu-Jung Chae [c], In S. Kim [d], Yong-Jin Park [e], Ai-Jie Wang [b,*]

[a] State Key Laboratory of Urban Storm Water System and Water Environment, Ministry of Education, School of Environment and Energy Engineering, Beijing University of Civil Engineering and Architecture, Beijing 100044, China
[b] Key Laboratory of Environmental Biotechnology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (CAS), Beijing 100085, China
[c] Department of Environmental Engineering, College of Engineering, Korea Maritime and Ocean University, 727 Taejong-ro, Yeongdo-gu, Busan 606-791, South Korea
[d] Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, South Korea
[e] Korea-Europe Environment Energy Expert Forum, 3825 Seodongdae-ro, Pyeongtaek-shi, Gyeonggi-do 450-701, South Korea

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ABSTRACT

This paper presents the effects of different concentrations of citric acid (CA) and ethylene diamine tetra-acetic acid (EDTA) when used as additive reagents for the treatment of sewage sludge for agricultural use. Herein, both the retention of nutrients and removal of metals from the sewage sludge are examined. The average removal rate for the metals after treatment by CA decreased in the order Cu > Pb > Cd > Cr > Zn, while the rates after treatment by EDTA decreased in the order of Pb > Cu > Cr > Cd > Zn. After treatment with CA and EDTA, total nitrogen and total phosphorus concentrations in the sludge decreased, while the content of available nitrogen and Olsen-P increased. In addition, a multi-criteria analysis model-fuzzy analytic network process method (with 3 main factors and 12 assessment sub-factors) was adopted to evaluate the effectiveness of different treatment methods. The results showed that the optimal CA and EDTA concentrations for sewage sludge treatment were 0.60 and 0.125 mol/L, respectively.

1. Introduction

Sewage sludge is a nutrient-rich material that normally contains high concentrations of carbon, nitrogen, phosphorous, organic matter, and mineral elements. Nutrients are essential for plant growth (Hanay et al., 2009; Singh and Sinha, 2004; Zhang et al., 2008), and the use of sewage sludge in agriculture to ameliorate the physicochemical deficiencies of degraded soil is a practice that is growing worldwide (Gupta and Sinha, 2006; Singh and Agrawal, 2007). Moreover, land application is considered one of the most economic and effective ways to dispose of sludge and supply plants with nutrients (Zhu et al., 2013). However, there are toxic metals in sewage sludge that necessitate restrictions on its use for certain land applications because of the potential for environmental and human health risks (Wang et al., 2012; Zhu et al., 2013). Therefore, there is need for sludge treatment methods that can reduce toxic metals while preserving nutrients, especially if the sludge is to be reused for farmland. Over the past few decades, many methods for sewage sludge treatment and disposal have been developed. These include chemical treatments (Lo and Chen, 1990; Stylianou et al., 2007), thermal treatments (Zorpas et al., 2001), ion exchange methods (Dabrowski et al., 2004; de Villiers et al., 1995), chlorination methods (Fraissler et al., 2009), electrochemistry methods (Hanay et al., 2009), membrane separation methods (Chaudry et al., 1998), and bioleaching methods (Chen et al., 2005; Pathak et al., 2009). Chemical treatments have received extensive attention due to the simplicity of operation processes, short operation times, and high efficiency for metal removal (Deng et al., 2009). Various inorganic acids, organic acids, and strong complexing reagents have been proposed as effective additives to remove toxic metals from sludge or soil.

Citric acid (CA) and ethylene diamine tetra-acetic acid (EDTA) are the most widely used chemical additives because they have high efficiencies for metal extraction (Di Palma and Ferrantelli, 2005; Liu and Lin, 2013; Sun et al., 2001). Moreover, EDTA has been reported to have low aquatic toxicity and it is does not bioaccumulate in living organisms throughout the food chain. However, its

* Corresponding author.
E-mail address: ajwang@rcess.ac.cn (A.-J. Wang).

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application may lead to nutrient deficiencies in the re-claimed sewage (Zhang et al., 2008). There are also other problems associated with the use of EDTA in remediation. For example, EDTA is recalcitrant in the environment and buildup of EDTA can lead to potential toxicity issues (Anupa et al., 2008; Peters, 1999). EDTA is biodegraded in soil under aerobic conditions at an estimated half-life of 120–300 days. Compared to EDTA, CA is more readily biodegradable (Römkens et al., 2002).

In this study, different concentrations of CA and EDTA were employed to treat sewage sludge to a level that would be sufficient for landfill requirements. As shown in previous studies, large doses and frequent applications of additives are typically needed to remove high concentrations of metals from sewage sludge (Deng et al., 2009; Zhu et al., 2009, 2013). However, such a large number of washings results in high processing costs and can even be detrimental to the environment because of the loss of nutrients (e.g., total nitrogen (TN), total phosphorus (TP), available-N, Olsen-P, and organic matter). Thus, it is necessary to determine optimal dosages and application frequencies for the additives to eliminate most of the toxic metals while simultaneously retaining most of the nutrients in the sludge.

The analytic network process (ANP) technique was proposed by Saaty (1996) to overcome the problem of interrelation among criteria or alternatives, and it has been successfully applied in many multi-criteria decision-making problems (Karsak et al., 2003; Yüksel and Dağdeviren, 2010). However, for problems such as the one posed by this study, i.e., those associated with incomplete information and subjective uncertainties, it can be difficult to quantify the precise ratio of weights for the different criteria used in each area. The concept of fuzzy sets has been incorporated into the ANP technique to deal with the problem of uncertainty. Hence, such a technique was applied in this study.

The primary objective of this research was to investigate the performance of different concentrations of CA and EDTA for treating sewage sludge to remove toxic metals and retain nutrients. In addition, the optimal conditions needed to maximize heavy-metal removal while minimizing nutrient loss were determined through the use of a fuzzy ANP (FANP) model.

2. Material and methods

2.1. Chelants

All the reagents used were of analytical grade. Additionally, the EDTA (ethylenediamine tetraacetic acid disodium salt dihydrate) and CA ($H_3C_6H_5O_7$, Sinopharm Chemical Reagent Beijing Co., Ltd) that were used in the laboratory experiments were of analytical grade. Deionized water was obtained from a Millipore Milli-Q system. All the standards, reagent solutions, and samples were stored in polyethylene containers pre-cleaned with 4.0 M HNO_3 and rinsed with deionized water.

2.2. Sampling of sewage sludge and soil

The sewage sludge used in the experiments was obtained from a two stage anaerobic sludge digester at a wastewater treatment plant (WWTP) located in Beijing, China. A total of 92.0% of the wastewater from the WWTP was domestic wastewater that was collected from a population of 800,000; 8.0% of the wastewater was industrial wastewater. The WWTP is operated as an extended aeration system. The sludge was air-dried, ground up, and passed through a 0.15 mm sieve. Sludge samples were then stored in polyethylene containers for further analyses and experiments.

The soil samples used in the experiments were collected from a fallow rice paddy in Yanglin City, Shanxi, China; these samples were used to represent unpolluted soil. Adequate amounts of soil were collected from the topsoil (0–20.0 cm) and subsoil (20–40.0 cm) layers by use of an auger. The soil was also air-dried, ground up, and passed through a 0.15 mm sieve prior to being stored in polyethylene containers for further analyses and experiments.

The sewage sludge and soil samples that were collected were stored at 4 °C during transportation. After air drying the samples in the laboratory, physical and chemical characteristics of the samples were measured immediately. The physicochemical characteristics of the original sludge (OS) and soil are summarized in Table 1.

2.3. Sewage sludge and soil chemical analyses

Sludge and soil physical and chemical characteristics before and after washing treatments were respectively termed "original physicochemical characteristics" and "final physicochemical characteristics" in this study. Physicochemical characteristics measured included pH, relative humidity, total alkalinity, organic matter, TN, TP, available nitrogen, available P (Olsen-P), total suspended solids (TSS), volatile suspended solids (VSS), soluble chemical oxygen demand (SCOD), Cd, Pb, Cu, Zn, and Cr. These parameters were determined according to standard methods (APHA, 1998), except for available nitrogen, Olsen-P and metals. Available nitrogen was extracted from the soil at a soil solution ratio of 1:5 using 1.0 M KCl for 1 h. Afterward, Devarda alloy was added into the extracted solution to reduce the NO_3^- into NH_4^+. The ammonia concentration was then determined by a titrimetric distillation method (EPA Method 350.2, U.S.) and the content of available nitrogen was obtained (Liu and Lin, 2013). Olsen-P was extracted using the Bray-1 method and quantified by the molybdenum blue colorimetric method (Olsen and Sommers, 1982). Soil and sludge samples were digested with a mixture of HCl/HNO_3 (Wu et al., 2004) and total concentrations of metals in soils and sludge were determined using an atomic absorption spectrometer (AAS, PERKIN ELMER Analyst 300).

A modified BCR-sequential extraction procedure (Aydin et al., 2013; Pan, 2009) was employed to study the partitioning of metals in the original sludge and treated sludge. This was done by separating the metals into fractions, namely, the exchangeable fraction, reducible fraction, oxidizable fraction, and residual fraction. After sequential washings, the sludge was air-dried and metal concentrations in the sludge samples were estimated for mass balance determination. Simultaneously, TN, TP, available-N, Olsen-P, and

Table 1
Physical and chemical characteristics of sludge and soil used in the experiment.

Parameters	Sewage sludge[a]	Soil[a]
pH	7.3 ± 0.1	6.8 ± 1.1
Relative humidity (%)	87.4 ± 0.30	78.8 ± 0.20
Total alkalinity (mg/kg)	81.2 ± 2.6	–
Organic matter (g/kg)	257.4 ± 12.8	10.6 ± 0.08
Total nitrogen (g/kg)	32.5 ± 0.47	1.1 ± 0.03
Total phosphorus (g/kg)	23.7 ± 0.21	5.1 ± 0.22
Available-N (mg/kg)	394.9 ± 8.9	116.7 ± 8.4
Olsen-P (mg/kg)	453.5 ± 44.4	26.4 ± 2.1
TSS (g/kg)	27.7 ± 0.12	–
VSS (g/kg)	20.8 ± 0.08	–
SCOD (mg/kg)	121.7 ± 18.3	–
Cd (mg/kg)	3.3 ± 0.58	0.16 ± 0.05
Pb (mg/kg)	54.7 ± 6.2	17.7 ± 2.3
Cu (mg/kg)	1735.4 ± 286.3	19.7 ± 0.69
Zn (mg/kg)	2110.3 ± 78.5	46.0 ± 3.3
Cr (mg/kg)	372.8 ± 23.6	9.3 ± 0.40

[a] All these values are the means of four replicates. – no detect.

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