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Green and efficient removal of cadmium from rice flour using natural deep eutectic solvents

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ABSTRACT

Natural deep eutectic solvents (NADESs) constitute a novel class of biodegradable and inexpensive solvents. In this study, twenty choline chloride- and glycerol-based NADESs were prepared and investigated as washing agents in the removal of cadmium (Cd) from rice flour for the first time. Choline chloride-based NADESs demonstrated good Cd removal (51%–96%). A natural, biodegradable surfactant, saponin, was mixed with the NADESs to enhance their efficiency. No increase in Cd removal was observed when glycerol-based NADESs were combined with 1% saponin; however, synergistic effects between saponin and choline chloride-based NADESs were observed during the washing process and > 99% Cd was removed using NADES-saponin mixtures. Moreover, NADESs washing process did not affect the main chemical components or structure of rice flour. The mechanism of Cd removal by NADESs and regeneration of Cd-contaminated NADESs were also explored. The study presents a green and efficient way of removing Cd from contaminated rice.

1. Introduction

Various human activities leaded to Cd pollution of land, ground water and atmosphere such as mining, smelting, fertilization, and so on (Archana & Sharma, 2016; Clemens, Aarts, Thomine, & Verbruggen, 2013; Fu & Wang, 2011). Industrial waste produced by human activities is the main source of Cd pollution of agricultural soils. However, heavy metals which cannot be degraded by microorganisms tend to persist and accumulate in the soils (Archana & Sharma, 2016; Clemens et al., 2013). Rice is easier to accumulate Cd from soil compared with other cereal crops. (Archana & Sharma, 2016; Clemens et al., 2013; Huo, Du, Xue, Niu, & Zhao, 2016; Jorhem et al., 2008; Wu et al., 2016; Zhuang et al., 2016). Rice is an important food commodity in the international market, and is a major staple for about half of the world's population (Gunduz & Akman, 2013; Zhuang et al., 2016). Cd accumulation in rice is a global issue.

The toxicity of Cd is well established, and Cd can accumulate in human kidneys (Archana & Sharma, 2016; Chavez et al., 2015; Clemens et al., 2013). Cd exhibits a long biological half-life of 10–30 years, and is classified as a group 1 carcinogen (Archana & Sharma, 2016; Clemens et al., 2013). Therefore, rice safety has garnered considerable attention in many countries. The Cd concentration in rice should be below accepted limits (0.4 mg/kg as an international standard limit and 0.2 mg/kg in China) (Huo et al., 2016; Jorhem et al., 2008; Wu et al., 2016). Excess Cd should be removed from Cd-polluted rice grains or their products to reduce the risks to the public. To date, several methods, such as breeding low Cd- accumulating rice cultivars, soil remediation, and phytoremediation have been developed to reduce the accumulation of Cd in rice (Archana & Sharma, 2016; Clemens et al., 2013). However, rice containing a high concentration of Cd is still being produced in Cd-contaminated areas in the world every year. Thus, it is imperative to develop simple and efficient decontamination methods for Cd-polluted rice.

Extraction and detection of heavy metals in water, soil, and some agricultural products have been reported by several research groups (Baghban, Shabani, & Dadfarnia, 2012; Behbahani et al., 2013; Behbahani, Abolhasani, et al., 2015; Behbahani, Bagheri, et al., 2015; Moghaddam, Shabani, Dadfarnia, & Baghban, 2014; Mukhopadhyay, Mukherjee, Adnan, et al., 2016; Mukhopadhyay, Mukherjee, Hayyan, et al., 2016; Omidi, Behbahani, Bojdi, & Shahtaheri, 2015; Zarezade, Behbahani, Omidi, Abandansari, & Hesam, 2016). Washing rice grains or soil contaminated with heavy metals and organics is a widely accepted practice (Huo et al., 2016; Mulligan, Yong, Gibbs, James, & Bennett, 1999; Wu et al., 2016), but efficient and environmentally friendly techniques are rare. Recently, natural deep eutectic solvents (NADESs) obtained from natural components have

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emerged as green, versatile solvents for various applications (Huang et al., 2017; Karimi, Dadfarnia, Shabani, Tamaddon, & Azadi, 2015; Paradiso, Clemente, Summo, Pasqualone, & Caponio, 2016; Zhao et al., 2015). Components of NADESs are edible, and NADESs can be classified as "readily biodegradable" solvents (Huang et al., 2017). However, NADESs have not been used as washing agents for contaminant removal from food matrices to date. Therefore, in this study, twenty choline chloride- and glycerol-based NADESs were synthesized and used as washing agents for Cd removal from contaminated rice flour. Moreover, saponin, a natural biodegradable surfactant, is environmentally friendly and has been used in the food and medical industries for many years (Mukhopadhyay, Mukherjee, Hayyan, et al., 2016; Suhagia, Rathod, & Sindhu, 2011). The effect and mechanism of surfactant on heavy metal removal have been reported (Fu & Wang, 2011). So, NADESs were combined with saponin, in order to investigate synergistic effects. The purpose of this study was to develop a novel, inexpensive, and efficient method for removing Cd from rice.

2. Materials and methods

2.1. Reagents and materials

Cd-contaminated rice flour sample (Cd: 2.16 mg kg^{-1}) was purchased from National Standard Material Center Network (Beijing, China). Cadmium nitrate was purchased from Macklin Reagent Co., Ltd. (Shanghai, China). Concentrated nitric acid (Guaranteed reagent) was supplied by Nanjing Chemical Reagent Co., Ltd. (Nanjing, China).

Compounds for NADESs preparation, including choline chloride (≥98.0%), glycerol (≥99.0%), D-(+)-xylose (≥99.0%), Glucose (≥99.0%), fructose (≥99.0%), L-(−)-sorbose (≥99.0%), mannose (≥99.0%), D-(+)-galactose (≥99.0%), sucrose (≥99.0%), L-(+)- arabinose (≥99.0%), L-(+)- rhamnose (≥99.0%), trehalose (≥99.0%), proline (≥99.0%), L-alanine (≥99.0%), glycine (≥99.0%), L-threonine (≥99.0%), L-histidine (≥99.0%), DL-malic acid (≥99.0%), citric acid (≥99.5%), L-(+)-tartaric acid (≥99.5%), xylitol (≥99.0%), sorbitol (≥99.0%), and saponin (biological reagent) were obtained from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Preparation of NADESs

Twenty NADESs were tested in the preliminary study. The compositions of the NADESs are given in Table 1. NADESs were prepared according to a previously published method (Huang et al., 2017).

2.3. Sample treatment

Cd-contaminated rice flour was dried under vacuum at 80 °C for 4 h. For each experiment, 0.30 g of rice flour was washed with 2.0 mL of the washing solution (NADES, surfactant solutions, and NADES-surfactant mixtures) in a 10.0 mL centrifuge tube. The test tubes were heated to 60 °C and shaken at 100 rpm for 1 h. During this period, ultrasound assisted extraction was performed every 15 min for 5 min using an ultrasonicator (20 kHz, 200 W; Type NP-B-400-15; New Power Co., Ltd., Kunshan, China) equipped with a digital timer and a temperature controller. The water bath temperature was maintained within ± 1 °C. The washing solution was then centrifuged (12,000 rpm, 20 min), and the supernatant was discarded. Ultrapure water (2.0 mL) was added to the tube and it was briefly vortexed, and then centrifuged at 12,000 rpm for 10 min. After centrifugation, the precipitate was transferred to polytetrafluoroethylene (PTFE) digestion tubes (60.0 mL inner volume). The rice flour was further digested using a microwave-assisted digestion system. For comparison, ultrapure water was also used as a washing solvent. The concentrations of surfactant saponin aqueous solutions used in this study were 1% (w/w). NADESs -saponin systems consist of 1% saponin aqueous solution and NADESs by mixing.

To minimize the risk of metal contamination, all glass ware was soaked in 5% HNO_3 (v/v) for at least 24 h. PTFE digestion tubes were soaked in 20% HNO_3 (v/v) overnight prior to digestion. The water used in this study was ultrapure water.

2.4. Sample microwave digestion and determination

In the microwave digestion, a conventional acid digestion method was used for the determination of Cd in rice flour. Concentrated nitric acid (8.0 mL) was added to the PTFE digestion tubes containing precipitate. The operating conditions for the MARS6XP1600 microwave-assisted digestion system (USA, CEM) are presented in Table S1. After digestion, a clear solution was obtained. The interior walls of the tube were washed with a minimum amount of ultrapure water. After cooling, the solution was filtered through a 0.45 μm filter and then transferred to a 50.0 mL volumetric flask and diluted with ultrapure water. The concentrations of Cd in rice flour were determined without

Table 1
List of different NADESs prepared from natural products.

NADES Abbreviation	Components			Mole ratio	pH
	Component 1	Component 2	Component 3		
GlyPro	Glycerol	Proline	–[a]	3:1	7.74
GlyAla	Glycerol	L-Alanine	–	3:1	7.34
GlyGly	Glycerol	Glycine	–	3:1	7.27
GlyThr	Glycerol	L-Threonine	–	3:1	6.48
GlyHis	Glycerol	L-Histidine	–	3:1	7.09
ChCit	Choline Chloride	Citric acid	Water	1:1:2	0.09
ChMal	Choline Chloride	DL-Malic acid	Water	1:1:2	0.23
ChTar	Choline Chloride	L-(+)-Tartaric acid	Water	1:1:2	0.56
ChXy	Choline Chloride	Xylitol	Water	5:2:5	6.88
ChSo	Choline Chloride	Sorbitol	Water	5:2:5	6.33
ChXyl	Choline Chloride	D-(+)-Xylose	Water	3:1:3	5.16
ChGlu	Choline Chloride	Glucose	Water	5:2:5	4.97
ChFru	Choline Chloride	Fructose	Water	5:2:5	4.36
ChSor	Choline Chloride	L-(−)-Sorbose	Water	5:2:5	4.55
ChMan	Choline Chloride	Mannose	Water	5:2:5	5.06
ChGal	Choline Chloride	D-(+)-Galactose	Water	5:2:5	5.04
ChSur	Choline Chloride	Sucrose	Water	4:1:4	4.77
ChAra	Choline Chloride	L-(+)-Arabinose	Water	5:2:5	4.60
ChRh	Choline Chloride	L-(+)-Rhamnose	Water	2:1:2	5.09
ChTre	Choline Chloride	Trehalose	Water	4:1:4	4.88

[a] No water was added.