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Study on the removal of Cd from dewatered sludge by combined extraction agents: Peel extract and compound chemical extraction agent

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ABSTRACT

The recycling of fruit peel resources is a current research hotspot. This study screened and configured a composite extractant consisting of peel and chemical extractant through extraction experiments and explored the heavy metals(HMs) release effect. The results showed that *citrus reticulata*(CR), *citrullus lanatus* (CL), 0.16 mol·L^{-1} nitrilotriacetic acid(NTA) with 0.04 mol·L^{-1} oxalic acid(NO5), and 0.12 mol·L^{-1}NTA with 0.08 mol·L^{-1}tartaric acid(NT4) had the strongest extraction ability. After the cross-combination was optimized, CR-NO5 (1:50, 6 h, 35 °C) and CL-NT4 (1:50, 36 h, 45 °C) had the highest extraction rates for Cd and Zn, which were 92.6 % and 98.4 %, respectively. The CL series increased the nutrient content of sludge (157.75–177.88 g·kg^{-1}). The four combined extractants increased the proportion of soluble components of HMs in sludge (14–36 %). Therefore, the combined leaching agent will provide a valuable reference for the harmless treatment of HMs in sludge and the resource utilization of peel waste.

1. Introduction

With the rapid development of the social economy, the amount of industrial wastewater and urban sewage generated by various industries is increasing daily. Heavy metal mineral mining, non-ferrous metal smelting, electroplating, pesticide synthesis, machinery manufacturing and processing, leather making, and other industries will inevitably produce a large amount of sludge(Kulkarni et al., 2019). According to survey data in 2019, China produces more than 40 million tons of sewage sludge with a moisture content of about 80 % yearly. It is expected to exceed 60 million tons in 2025(Rao et al., 2019). The large amount of waste sludge generated every year is randomly piled up, which not only occupies land resources but also seriously threatens the average growth and development of humans, animals, and plants with toxic elements(Liu et al., 2022).

There is still a lack of reasonable means to dispose of sludge, and the risk of secondary pollution is relatively high. Based on the reduction, stabilization, and harmlessness principles, sludge disposal is mainly carried out by sanitary landfills, land use, incineration, and construction of raw materials. Sanitary landfills require a large area of land resources, and leachate may also pollute groundwater (Thaiyal Nayahi et al., 2022). Improper incineration will produce polluted gases (Cai et al., 2022) and problems with exposure to pollutants when used as building materials (Brasil et al., 2024). Sewage sludge in the United Kingdom, France, and Denmark is mainly used for agricultural production, in Finland, Hungary, and Slovakia for composting, while in Germany, Austria, and Belgium, sludge treatment is mainly based on incineration (Stunda-Zujeva et al., 2018). In the EU, sewage sludge contains nutrients such as nitrogen, phosphorus, potassium, and organic matter, which can be used as fertilizer to help plant growth (Chojnacka et al., 2023). At the same time, the unique colloidal characteristics of sewage sludge can also improve soil's physical and chemical properties and the intensity of

Abbreviations: CR, *citrus reticulata*; PS, *pyrus spp*; VT, *vitis vinifera* L; CL, *citrullus lanatus*; HMs, heavy metals; E, the leaching rate of heavy metals such as Cd, Zn and so on; NTA, nitrilotriacetic acid; I_R, partition index.

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microbial activity (Lamastra et al., 2018). Sludge's excellent hydroscopicity and viscosity allow nutrients to enter the soil, achieving soil remediation and effective fertility improvement (Jiang, 2020). Land utilization is one of the most promising methods for sewage sludge treatment. However, the "Black Soil Protection Law of the People's Republic of China" stipulates that topsoil is prohibited for garden soil. The bottom soil and organic materials are currently the primary sources of greening soil in China, and sewage sludge can replace organic materials and part of the soil, reducing fertilizer pollution and saving soil resources. This provides a new idea for the problem of large-scale sewage sludge disposal, but there may be pollution risks in actual application. Among them, HMs (accounting for 0.5–2 % of total solids) are one of the main factors restricting the land use of sewage sludge.

Sludge produced in industrial processes such as electroplating, mechanical processing, and leather making contains many HMs. Direct application increases the risk of HMs release (Yong et al., 2021), ultimately harming human health through the food chain. Bioleaching, supercritical fluid extraction, electrokinetic method, chemical extraction, and phytoremediation have been widely used to remove HMs from sludge (Tang et al., 2018). Among them, chemical extraction has attracted more and more attention due to its simple process, high removal efficiency, economy and environmental protection. Its principle is to transfer HMs from the solid phase to the liquid phase through acidification, ion exchange (Kim et al., 2024), micellar solubilization of surfactants and complexation of complexing agents, and then the liquid is recovered and processed. Commonly used extractants are mainly organic acids, inorganic acids, chelating agents, surfactants, and other categories. Ethylenediaminetetraacetic acid (EDTA) has a formidable selective chelating ability for metal ions and is currently the most widely used artificial chelating agent (Yang et al., 2022). However, its biodegradability is limited, it has a long residual time in the environment, and its large-scale use may lead to secondary pollution. Therefore, studying more environmentally friendly and biodegradable chemical extractants is increasingly essential.

When looking for efficient sludge HMs extractants, biodegradability, low environmental risk and minimal damage to sludge fertility are important considerations. Fruits are rich in essential vitamins, dietary fiber, calcium, iron and other minerals, and are part of residents' daily diets. The considerable consumption makes fruit waste a significant part of urban domestic waste, and the rational disposal of fruit residues has become an increasingly severe environmental problem. Fortunately, fruit peel waste is a valuable biomass resource (Ekloh & Yafetto, 2024), containing a variety of polymers that can bind to HMs ions and is expected to become a substitute for EDTA. This type of waste includes residues such as citrus peels, banana peels, grape peels, watermelon peels and pear peels. Studies have shown that fruit peels contain vitamins, pectin, cellulose, protein and citrulline (Ho et al., 2018). These polymers contain functional groups such as carboxyl, amine and hydroxyl, which easily attract metal ions to form soluble complexes. If they are piled up randomly, it will waste resources and cause various environmental pollution. In the past, researchers have found that fruit peel waste has potential applications in environmental pollution control. Mishra et al. (2023) prepared biochar using citrus lemon peel as raw material to remove organic pollutants from polluted wastewater effectively. Letechipia et al. (2023) showed that watermelon peel biosorbent is a potential material for removing arsenic from groundwater. Nitrilotriacetic acid (NTA) is a powerful chelating agent with three carboxyl groups. It has been widely used as a substitute for EDTA due to its low cost and strong biodegradability. Wang et al. (2022) found that the half-life of NTA in highly Zn-contaminated soil is 1–3 days, and it can be completely decomposed within 57 days after high-dose application. Other studies have found that low-molecular organic acids such as tartaric acid and oxalic acid can provide protons to replace HMs ions in the solution, realizing the transfer of HMs from the solid phase to the liquid phase (Shao et al., 2023).

Currently, chemical extractants are mainly single chelating agents, which have poor degradability and remain in the environment, negatively impacting physiological properties. It is urgent to study emerging alternatives. Fruit peel waste residues are mainly used as biochar raw materials to adsorb HMs and very few studies have explored the extraction effect of peel extract on HMs in sludge. In order to improve the extraction efficiency of HMs in sludge, explore new extracting agent combinations, and realize the value-added of waste biomass resources.

In this study, the extracts of *citrus reticulata*(CR), *pyrus spp*(PS), *vitis vinifera* L(VT), and *citrullus lanatus*(CL) were compounded with NTA, oxalic acid, and tartaric acid as a new leaching agent. The sludge from a sewage treatment plant in Changchun City, Jilin Province, was used as the object. The optimal fruit peel waste leaching agent, chemical activator, and peel-chemical activator combined leaching agent were screened by the Cd content in the leaching solution, sludge pH, and organic matter content. The effects of different solid-liquid ratios, leaching time, and temperature on removing Cd and Zn in sludge by combined leaching agents were studied. Under optimal leaching conditions, the changes in soil pH, organic matter, and different forms of HMs were analyzed to provide a practical basis and scientific basis for recycling fruit peel waste and removing HMs from sludge.

2. Materials and methods

2.1. Sample preparation and characterization

The dewatered sludge sample was collected from a sewage treatment plant in Changchun City, Jilin Province, China. The sludge was grounded and sieved, and the pH was measured to be 6.46, the organic matter content was 109.81 $g\cdot kg^{-1}$, and the contents of Cd, Hg, Pb, Cr, As, Ni, Zn, and Cu were 29.84 $mg\cdot kg^{-1}$, 0.93 $mg\cdot kg^{-1}$, 77.16 $mg\cdot kg^{-1}$, 61.34 $mg\cdot kg^{-1}$, 10.72 $mg\cdot kg^{-1}$, 31.89 $mg\cdot kg^{-1}$, 404.02 $mg\cdot kg^{-1}$, and 96.53 $mg\cdot kg^{-1}$, respectively. The Cd content exceeded the pollutant concentration limit specified in the "Agricultural Sludge Pollutant Control Standard" (GB 4284–2018) and was highly toxic. Therefore, Cd was used as an observation indicator to analyze the extraction effect.

The experiment selected fruit peels of CR, PS, VT, and CL obtained from the fruit market. Each waste peel residue was washed with deionized water and then weighed. The peel residue and deionized water were crushed into residue in a blender at a mass ratio of 1:5, and the residue was centrifuged at a speed of 5000 $r\cdot min^{-1}$ for 10 min. After filtering with filter membrane of 0.45 μm, the filtrate was used as the waste fruit peel residue extract, and none of the HMs (Cd, Cu, Pb, Zn, Hg, As, Cr and Ni) were detected in the extract by atomic absorption spectrophotometer (AAS).

2.2. Sludge extraction experiment

The extraction experiment was carried out in a 50 mL polypropylene centrifuge tube. The dewatered sludge sample passed through a 2 mm sieve was placed in a centrifuge tube with different types of extractants at a solid-liquid ratio of 1:20. NTA, oxalic acid and tartaric acid with concentrations of 0.04, 0.08, 0.10, 0.12 and 0.16 $mol\cdot L^{-1}$ were mixed in pairs as chemical extractants (Table S1). Among them, NO1 ~ NO5 are NTA: oxalic acid concentration ratios of 1:4, 2:3, 1:1, 3:2, and 4:1, respectively. Similarly, OT1 ~ OT5 and NT1 ~ NT5 are oxalic acid: tartaric acid and NTA: tartaric acid, respectively, in pairs according to the same concentration ratio. Four fruit peel extracts (CR, PS, VT and CL) with the highest extraction rates of Cd (E_{Cd}) were selected and combined with compound chemical extractants in a volume ratio 3:2 to form a combined extractant. Deionized water was used as a control. After the tube was sealed and mixed, it was shaken in an oscillating incubator at 200 rpm and 25 °C for 24 h, then transferred to a high-speed centrifuge and centrifuged at a speed of 5000$r\cdot min^{-1}$ for 10 min. After filtering with medium-speed filter paper, the Cd contents in the supernatant were determined. Three parallel tests were set for each group. The pH and organic matter of the leached sludge were determined simultaneously, and the leaching agent was selected based on the sludge HMs leaching rate(E), pH and organic matter status. The E of HMs was calculated as follows:

$$E(\%) = \frac{c \times V}{M \times c_0}$$

where c is the HMs concentration in the extraction solution (mg·L^{-1}), V is the volume of chelator solution added (L), M is the dry mass of the dewatered sludge (g), and c_0 is the original content of corresponding HMs in the raw dewatered sludge (mg·kg^{-1}).

2.3. Influencing factor experiment

In order to investigate the effect of the solid-liquid ratio, the experiment was conducted with the solid-liquid ratio ranging from 1:10 to 1:50 for 24 h at 25 °C. The effect of extraction time on the E_{Cd} of solid-liquid ratio 1:20 was investigated at 25 °C. The experiment was conducted at different time intervals(6 h, 12 h, 24 h, 36 h and 48 h). Five different temperature levels(15 °C, 25 °C, 35 °C, 45 °C and 55 °C) were applied to a solid-liquid ratio of 1:20 for 24 h to determine the effects of the leaching rate of Cd(E_{Cd}). Each group was experimented in a 50 mL centrifuge tube and repeated three times. After the extraction, the sludge was centrifuged at 5000r·min^{-1} for 10 min in a high-speed desktop centrifuge, and the supernatant was collected to determine the heavy metal content. At the same time, the sludge's pH and organic matter content after extraction were determined to assess the effect of each factor on the extraction effect.

2.4. Experiment on sequential extraction of heavy metal forms from dewatered sludge

The BCR continuous extraction method modified by the European Community Standard Measurement and Testing Agency was used to determine the content of different forms of Cd and Zn (Kou et al., 2020). The metal components include soluble(Sol), exchangeable (Exc), reducible(Red), oxidizable(Oxi) and residual(Res) forms. The specific determination steps are shown in Table S2. The partition index(I_R) was calculated as follows:

$$I_R = \frac{\sum_{i=1}^{k} i^2 \times F_i}{k^2}$$

where i represents the number of the extraction step, k is 5 for the BCR procedure, and Fi is the percentage of the considered metal in fraction i.

2.5. Analytical methods

The specific steps for determining the organic matter, Cd and Zn content in sludge are shown in the Appendix A (Ministry Agriculture and Rural Affairs of the People's Republic of China, 2012). The determination of pH was conducted following standardized protocols by glass electrode(pH meter, Leici pHS-3C). All tests were conducted in triplicate, where the average results were presented, and the error bars indicated the standard deviations(SD). The data analysis were performed in SPSS Statistics 26 (SPSS Inc. IBM Corporation, Armonk, NY, USA), one-way analysis of variance (ANOVA) was tested to compare whether the E(%) under different experimental conditions was significantly different. Statistical significance ($p < 0.05$) was determined by the least significant difference (LSD). Pearson's correlation coefficient (R), which measures the relationship between two factors, was calculated. The correlation is considered statistically significant with a 95 % confidence interval ($p < 0.05$).

3. Results

3.1. Comparison of the effects of waste peel extracts

3.1.1. Effect of waste peel extract on Cd extraction from dewatered sludge

Using deionized water as the control, the extraction rates of Cd in sludge by the four extracts ranged from 9.87 % to 36.94 % (Fig. 1). The order of Cd extraction capacity from high to low was CR > CL > VT > CK > PS, and the E_{Cd} of CR and CL were statistically different from those of the other treatments ($p < 0.05$). The E_{Cd} of CR and CL were 36.9 % and 32.1 %, respectively, 150.0 % and 117.5 % higher than CK's. It can be seen that CR and CL performed better in extracting Cd from sludge.

3.1.2. Effects of waste peel extract on physicochemical properties of sludge

The pH and organic matter content of the four kinds of leaching sludge ranged from 4.88 to 6.46 and from 106.33 g·kg^{-1} to 146.88 g·kg^{-1}, respectively. They were ranked in order of pH: CL > CK > PS > CR > VT, all of which were acidic sludges (Fig. 2a). The pH and organic matter conditions were quite different. The organic matter content of the four kinds of leaching sludges was ranked as follows: CR > CL > CK > VT > PS (Fig. 2b). There were statistical differences in the pH and organic matter conditions of the sludges treated with different fruit peel waste extracts ($p < 0.05$). Compared with CK, the pH value of the sludge treated with CL increased by 5.6 %, while the pH of CR, PS, and VT decreased by 20.4 %, 10.5 %, and 24.4 %, respectively. The change in organic matter content was that CR and CL treatments increased by 33.8 % and 15.7%, respectively, and PS and VT decreased by 3.1 % and 1.5 %, respectively. Therefore, the treatment with CR and CL waste peel extracts can increase the large amount of organic nutrients in the sludge, and the organic matter content of the sludge treated with the four peel extracts was more significant than 20 g·kg^{-1}, which met the standard requirements (GB 4284-2018). Therefore, CR and CL can be combined with chemical extractants to form excellent sludge Cd extractants.

3.2. Comparison of the effects of compound chemical extractants

3.2.1. Effect of compound chemical extractants on extraction of Cd from dewatered sludge

With deionized water as the control, the extraction rates of 15 chemical extractants for sludge Cd ranged from 3.5 % to 42.3 %(Fig. 3). The top eight extraction abilities from high to low were NO4 > NO5 >

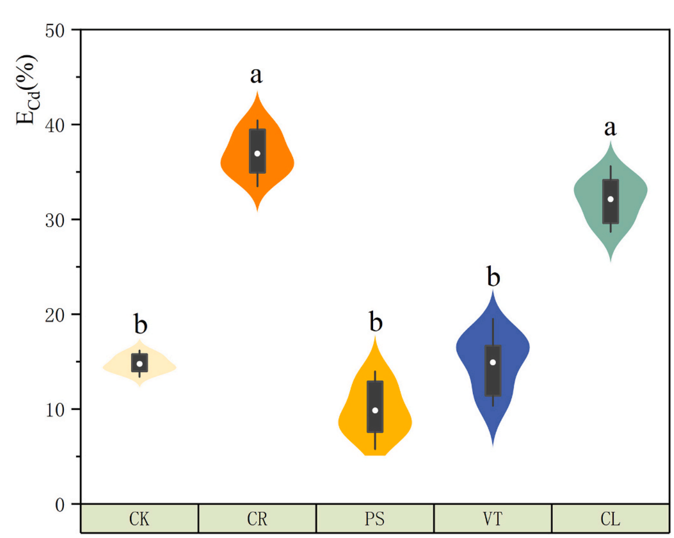

Fig. 1. The E_{Cd} of different peel extraction solution, the dots in the box represent the mean, and the error bars represent 1.5 times the standard error, different lower-case letters indicate significant ($P < 0.05$) differences between treatment means according to the LSD test.

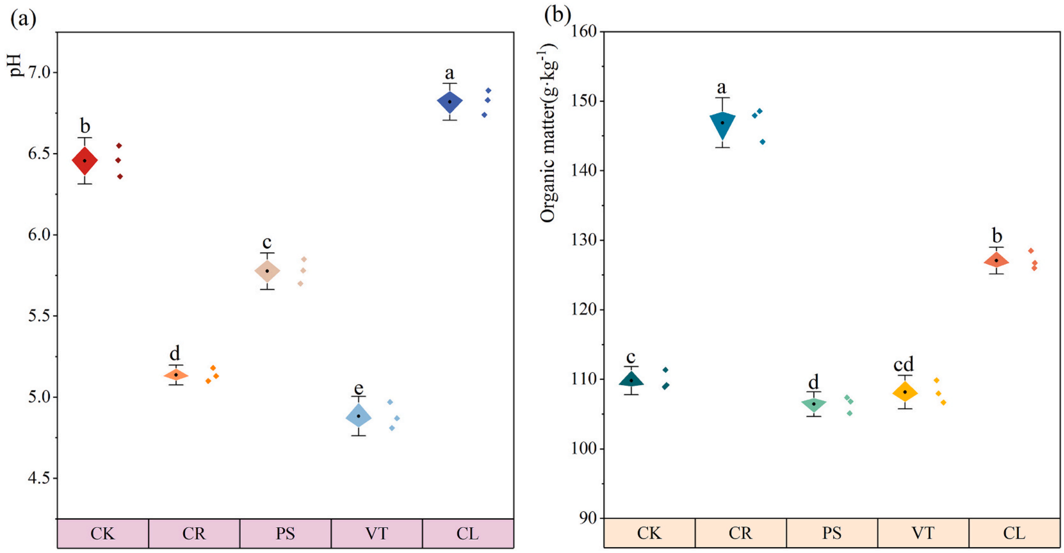

Fig. 2. Effects of different peel extracts on sludge pH and organic matter, sludge pH (a), sludge organic matter(b), the dots in the box represent the mean, and the error bars represent 1.5 times the standard error, different lower-case letters indicate significant ($P < 0.05$) differences between treatment means according to the LSD test.

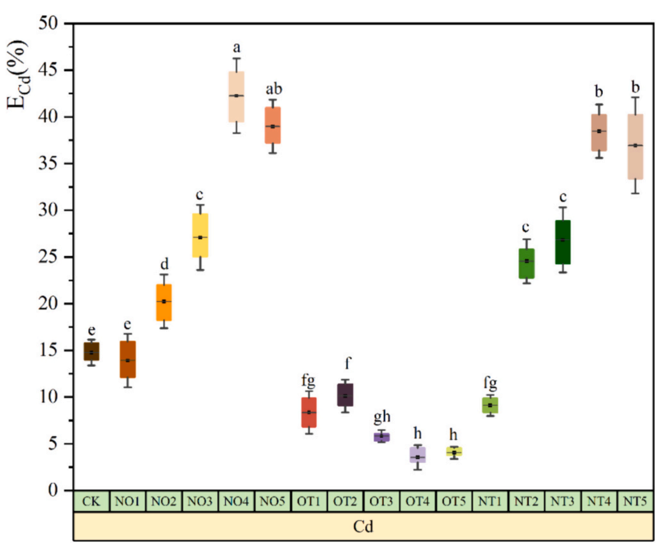

Fig. 3. The E_{cd} changes of different chemical extractants, the dots in the box represent the mean, and the error bars represent 1.5 times the standard error, different lower-case letters indicate significant ($P < 0.05$) differences between treatment means according to the LSD test.

NT4 > NT5 > NO3 > NT3 > NT2 > NO2, which were 186.0 %, 163.7 %, 160.3 %, 150.0 %, 83.2 %, 81.5 %, 66.1 %, and 37.0 % higher than those of CK, respectively. This indicates that the chemical extractants with NTA as the paramount combination have a more substantial extraction effect on Cd in sludge. Among the top four, there is a statistical difference in the extraction effect between NO4 and the other extractants ($p < 0.05$). The data show that NO5 and NT4 have apparent extraction effects, with E_{Cd} of 39.0 % and 38.5 %, respectively.

3.2.2. *Effects of compound chemical extractants on physicochemical properties of sludge*

The leached sludge's pH and organic matter content ranged from 2.35 to 9.10 and from 96.67 g·kg^{-1} to 115.79 g·kg^{-1}, respectively. The sludges treated with NO5 and NT5 were alkaline, with pH values of 8.98 and 9.10, respectively. The pH of the sludges with NO1, NO2, OT1, and OT5 were less than 3, with pH values of 2.36, 2.35, 2.44 and 2.45, respectively. The pH of the sludges treated with the other treatments ranged from 3.39 to 6.46, all acidic sludges (Fig. 4a). Compared with the original sludge organic matter, the sludge organic matter content after NO1, NO5, OT2, and NT4 treatments was higher than that of CK, which were 114.12 g·kg^{-1}, 115.79 g·kg^{-1}, 113.96 g·kg^{-1}, and 112.85 g·kg^{-1}, respectively (Fig. 4b), which were 3.9 %, 5.4 %, 3.8 %, and 2.8 % higher than that of CK, respectively. In addition to the NT4 treatment, the organic matter content of the sludge in the other treatments was statistically different from that of CK ($p < 0.05$). Therefore, chemical extractants easily affect the acidity and alkalinity of sludge. However, the organic matter content of sludge is still greater than 20 g·kg^{-1}. Therefore, NO5 and NT4 have sound sludge Cd removal effects, can improve sludge nutrients, and have higher application values.

3.3. *Effect of extraction conditions on extraction effect of combined extraction agents*

CR, CL, NO5 and NT4 were cross-combined to form CR-NO5, CR-NT4, CL-NO5 and CL-NT4 respectively. As the solid-liquid ratio decreases, the four combinations have inconsistent trends in the leaching rate of Cd in sludge. However, when the solid-liquid ratio is 1:50, the E_{Cd} is the highest, and the leaching effect 1:20 is second (Fig. 5a), the order of different combinations from high to low is CR-NT4 (88.5 %) > CL-NT4 (87.3 %) > CR-NO5 (86.0 %) > CL-NO5 (84.1 %). Compared with the rest, there is a statistical difference in the solid-liquid ratio's E_{Cd} ($p < 0.05$), and there is no significant difference in the highest E_{Cd} between combinations.

It can be seen from Fig. 5b that CR-NT4, CL-NO5 and CL-NT4 achieve the best leaching effect when the leaching time is 36 h, and the E_{Cd} are 90.6 %, 88.8 % and 89.7 %, respectively. CR-NO5's highest E_{Cd} is 88.3 % at 6 h, which is statistically different from the E_{Cd} at other extraction times in the group ($p < 0.05$), and there is no significant difference between the highest E_{Cd} of the four extraction agents.

When the extraction temperature is 35 °C, CR-NO5 (85.2 %) and CL-NO5 (78.9 %) have the best extraction effect on sludge Cd, and CR-NT4 (88.0 %) and CL-NT4(82.5 %) achieve the best extraction effect at 45 °C (Fig. 5c). There were statistical differences in the extraction effects produced by different extraction agents ($p < 0.05$).

Therefore, after a comprehensive comparison, Table 1 shows the optimal leaching conditions of the four combined agents.

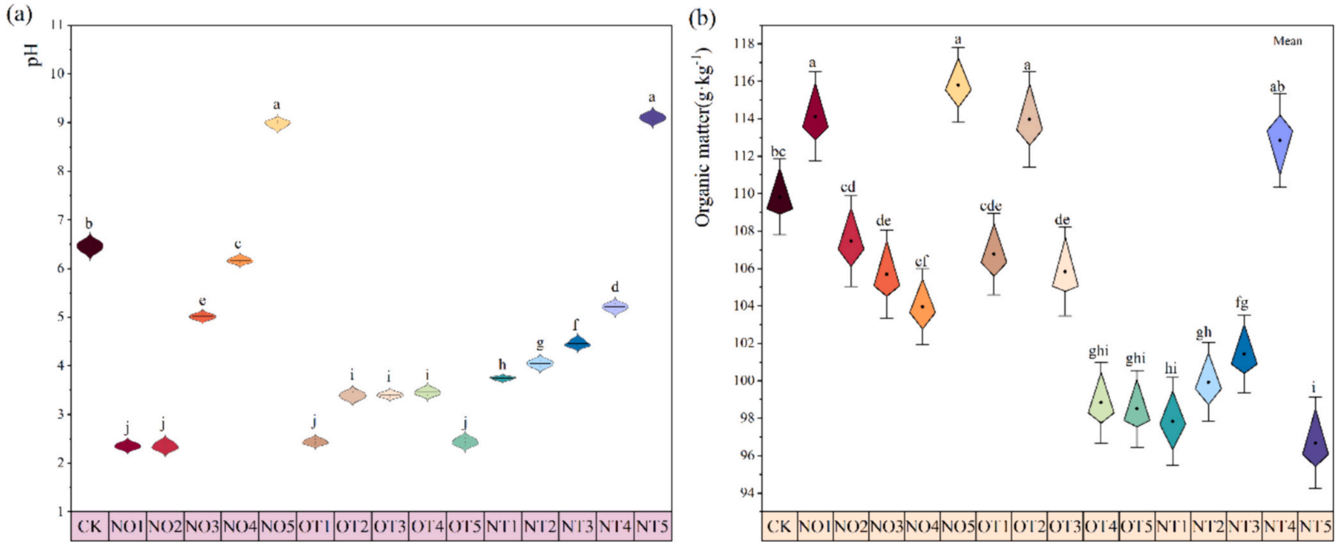

Fig. 4. Effects of different chemical extractants on sludge pH and organic matter, sludge pH (a), sludge organic matter(b), the dots in the box represent the mean, and the error bars represent 1.5 times the standard error, different lower-case letters indicate significant ($P < 0.05$) differences between treatment means according to the LSD test.

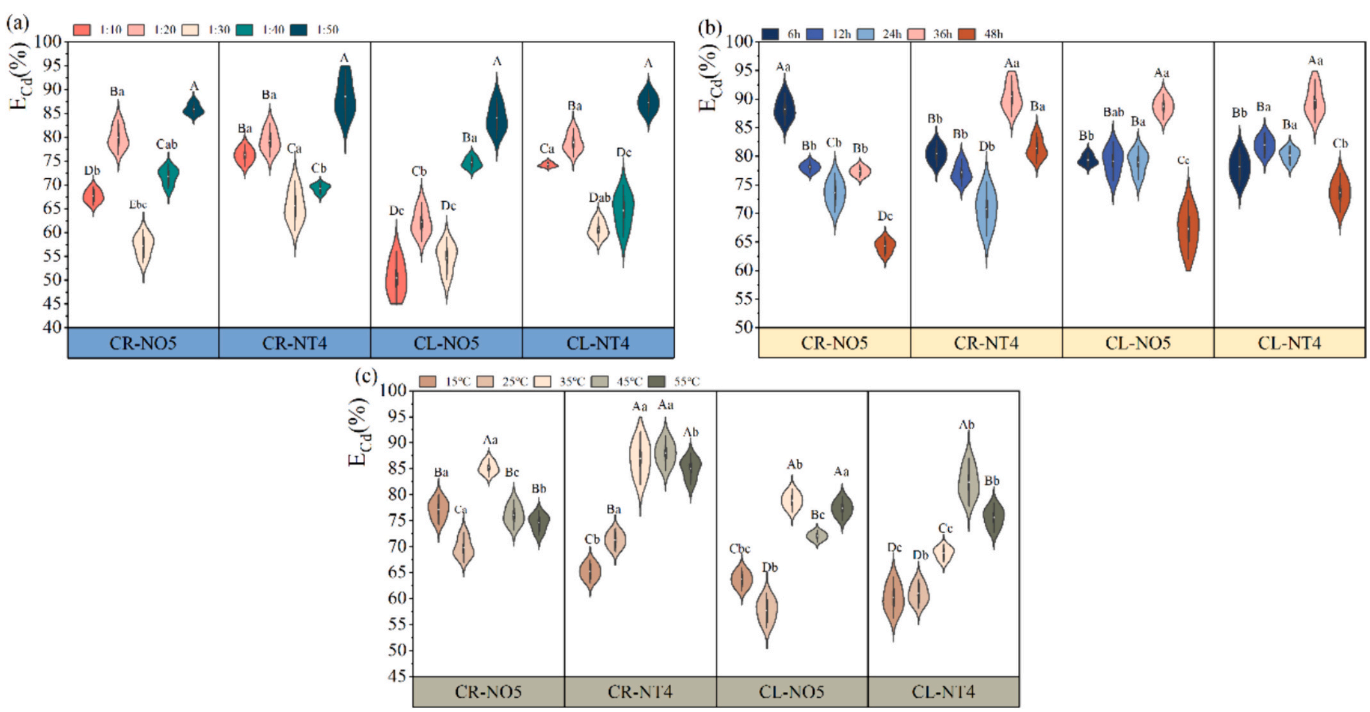

Fig. 5. Changes in the E_{cd} of leaching conditions, solid-liquid ratio(a), extraction time(b), extraction temperature(c), the dots in the box represent the mean, and the error bars represent 1.5 times the standard error, different lower-case letters indicate significant ($P < 0.05$) differences between treatment means according to the LSD test.

Table 1
Optimal extraction conditions of combined extraction agents.

Extracting agent	Solid-liquid ratio	Time/h	Temperature/°C
CR-NO5	1:50	6	35
CR-NT4	1:50	36	45
CL-NO5	1:50	36	35
CL-NT4	1:50	36	45

3.4. Comprehensive extraction effects of different combined extractants under optimal extraction conditions

The E_{Cd} of the four extractants were within 72.4 % ~ 92.6 %, in the order of CR-NO5 > CR-NT4 > CL-NT4 > CL-NO5 (Fig. 6a), and the extractant effects were significantly different ($p < 0.05$). Notably, the extractants also have a specific extraction effect on sludge-associated metals, and the extraction effect of Zn is particularly prominent (the E_{Zn} is 90.9 % ~ 98.4 %). The combined extractants have very different effects on sludge pH and organic matter. Analysis of Fig. 6b shows that the pH range of the four combined extractants is 5.92–9.07. CR-NO5 and

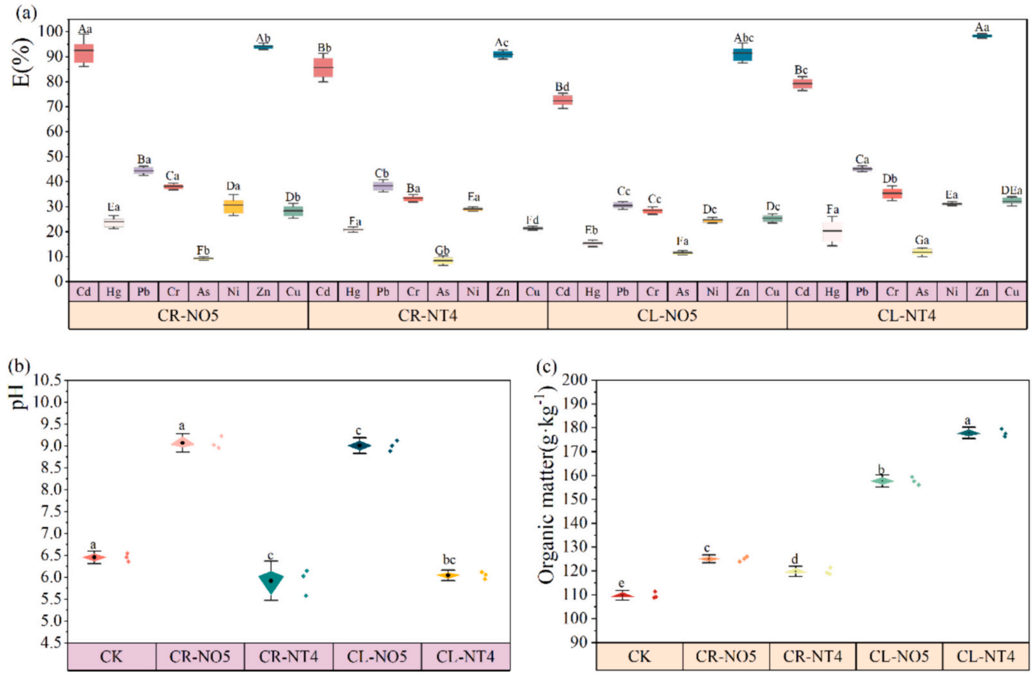

Fig. 6. Comprehensive extraction effect of combined extractants, the E_{Cd} changes(a), sludge pH(b), sludge organic matter(c), the dots in the box represent the mean, and the error bars represent 1.5 times the standard error, different lower-case letters indicate significant ($P < 0.05$) differences between treatment means according to the LSD test.

CL-NO5 belong to alkaline sludge. Compared with CK, the pH of CR-NT4 and CL-NT4 decreased by 8.36 % and 6.35 %, respectively, and belong to acidic sludge. Statistical differences exist in the acidity and alkalinity of the four combined leaching sludges ($p < 0.05$). All four extractants can promote the improvement of sludge nutrients, and the order is CL-NT4 (177.88 $g \cdot kg^{-1}$) > CL-NO5 (157.75 $g \cdot kg^{-1}$) > CR-NO5 (125.10 $g \cdot kg^{-1}$) > CR-NT4 (119.87 $g \cdot kg^{-1}$). They increased by 62.0 %, 43.7 %, 13.9 % and 9.2 %, respectively, compared with CK (Fig. 6c). There were statistical differences in the organic matter conditions of different leached sludges ($p < 0.05$). In a comprehensive comparison, CR-NO5 had the best Cd extraction effect but significantly impacted the sludge pH. Although CR-NT4 had a better Cd extraction effect, the sludge nutrient increment was the smallest. CL-NO5 positively affected the improvement of sludge nutrients, but the HMs extraction effect was the worst and pH > 9 greatly impacted the environment. CL-NT4 had the largest increase in sludge organic matter content, and weakly acidic sludge had a negligible impact on the environment and had a higher E_{Cd} and E_{Zn}. Therefore, appropriate extractants can be selected according to sludge utilization requirements in actual production applications.

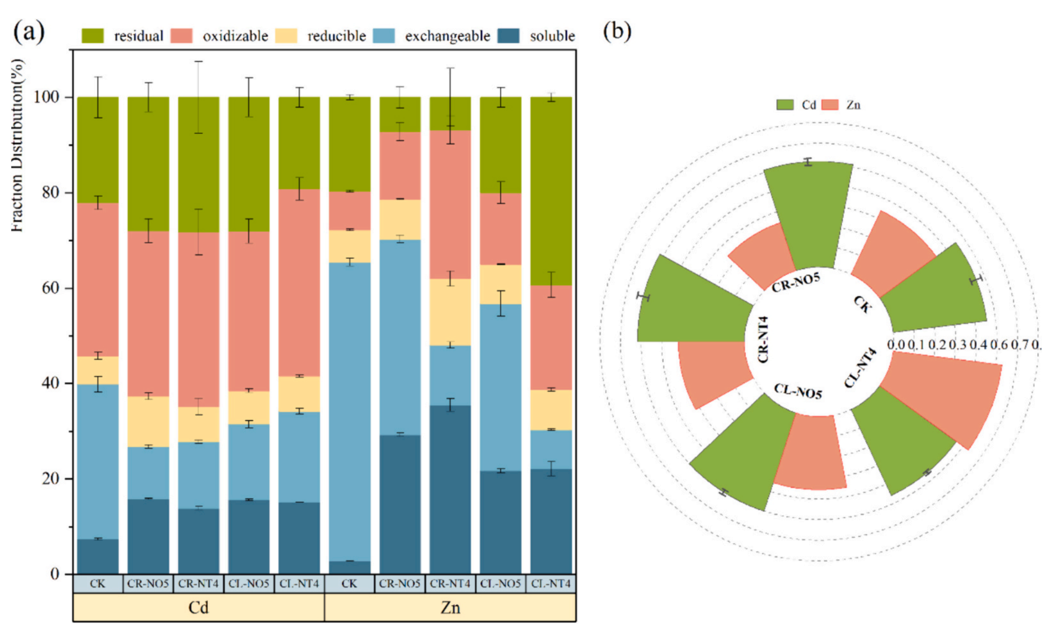

Fig. 7. Effects of different combined extraction agents on the distribution of HMs forms and the partition index (I_R), distribution of HMs forms in sludge(a), the change of the partition index(b), and the error bars represent 1.5 times the standard error.

3.5. Morphological changes of Cd and Zn in dewatered sludge and potential ecological risk assessment

Because the extracting agent has the best extraction effect on Cd and Zn, the heavy metal forms of different treated sludges were graded. Compared with the original sludge, after CR-NO5, CR-NT4 and CL-NO5 extraction, the exchangeable(Exc)-Cd was transformed into soluble (Sol), reducible(Red), oxidizable(Oxi) and residual(Res), and the proportion of Sol and Res increased significantly(Fig. 7a). Among them, CR-NO5 and CR-NT4 promoted the conversion of Exc and Res Zn into Sol, Red and Oxi, and the proportion of Sol-Zn was more significant than that of Red. CR-NT4 extraction greatly increased the proportion of Red-Zn in sludge. CL-NO5 mainly affects the Exc-Zn in the sludge, converting it into Sol, Red and Oxi states. It is worth noting that CL-NT4 has a significant difference in the morphological transformation of Cd and Zn in sludge. After extraction, the proportion of Exc and Res Cd in the sludge decreased, and the proportion of Sol, Red and Oxi Cd increased. The Sol, Oxi and Res Zn proportions increased after extraction, and the Res had the most prominent change.

According to the partition index(I_R) calculation results, the stability and fluidity of Cd and Zn in sludge were evaluated. When the I_R value is close to 1.0, the metal mainly exists as residual components, and the potential pollution risk is low (Yang & Hodson, 2019). As shown in Fig. 7b, the risk of Cd in the original sludge is lower than that of Zn, indicating that Cd is more stable than Zn in sludge. The four combined extractants have a stabilizing effect on Cd in sludge, and the I_R are higher than CK, which are 0.56, 0.57, 0.55 and 0.51, respectively. Among them, after CR-NO5, CR-NT4 and CL-NO5 extraction, the I_R of Cd changed statistically ($p < 0.05$), and CR-NT4 had the most substantial stabilization effect on sludge Cd. In addition, after CR-NO5 and CR-NT4 extraction, the I_R of Zn decreased, which was 28.05 % and 6.03 % lower than those of CK, respectively. CL-NO5 and CL-NT4 transformed Zn in sludge into a stable form, and the I_R increased by 4.37 % and 56.13 % compared with CK, respectively. Therefore, the combined extractant transformed the residual Cd in sludge into a stable form, effectively reducing the potential ecological risk. The combined extractant of the CR series mainly activated the residual Zn in the sludge, and the potential ecological risk increased. On the contrary, the combined extractant of the CL series mainly played a stabilizing role.

4. Discussion

4.1. Comparison of the effects of peel extract and chemical extractants

Our study found that the Cd leaching ability of sludge derived from different types of fruit peel waste extracts is significantly different. The reason may be that different peels contain different functional groups and low molecular organic acid contents. The leaching capabilities of CR and CL are outstanding (Fig. 1). The excellent HMs extraction effect and the peels of the two contain functional groups such as carboxyl, amino and ester groups (Jeong et al., 2021; Liu et al., 2021), which can the generation of coordination atoms is related to metal ion reactions. The chemical substances of PS and VT are mainly flavonoids and phenolic chemicals (Cui et al., 2024), and the coordination reaction with metal ions is weaker than that of functional groups such as carboxyl groups. Some research results are similar to this. The unique organic acid of orange peel is a crucial HMs ion chelating agent, which can extract HMs ions through dissolution and complexation (Zhao et al., 2023). Watermelon peel contains a large amount of Carbohydrates that can be used as biochar raw materials to adsorb HMs ions in water (Letechipia et al., 2023), which also shows that peel residue is an ideal material for adsorbing heavy metal ions in sludge extracts.

Since the peel extract easily affects the sludge's physical and chemical properties, one-time extraction is challenging to meet the needs of actual production applications. Much research data has found that degradable chemical eluants can significantly improve the elution rate of HMs in sludge. Deng et al. (2022) used 70 mM EDTA and 10 mM citric acid to achieve a leaching rate of Cu in electroplating sludge of 85 %. This paper uses a combination of NTA, oxalic acid and tartaric acid as a chemical leaching agent. It is found that the NO5 and the NT4 have better leaching efficiency for HMs in sludge. NTA is a degradable chelating agent containing three carboxyl groups, which can provide more coordination atoms for metal ions. The carboxyl content of tartaric acid and oxalic acid is lower than that of NTA, so their extraction effects are slightly weaker.

Therefore, from the perspective of extraction efficiency and waste value addition, we considered combining CR and CL with the outstanding NO5 and NT4 extraction agents, respectively, and using peel extract as the joint activator's primary material to remove toxic sludge efficiently elements while reducing the environmental pollution caused by chelating agents.

4.2. Changes in the physical and chemical properties of sludge after extraction

Many studies have proven that pH and organic matter are key factors affecting the morphology of HMs. The results of this study showed that the pH of the sludge was less than 7 after extraction with four kinds of peel extracts (Fig. 2a). The degree of sludge acidification is closely related to the organic acid content and the number of functional groups such as carboxyl and hydroxyl in different peels. The CR and VT contained a large amount of low molecular organic acids and hydroxyl structures in flavonoids. Functional groups such as hydroxyl groups and organic acids undergo ion exchange reactions with metal ions, releasing a large amount of H^+ that combines with vacant adsorption sites in the sludge, lowering the pH. Antonkiewicz et al. (2018) also found that low molecular organic acids can reduce soil pH. CR contains more low molecular organic acids that undergo more exchange reactions with HMs, and acidic extracts contribute to removing HMs from sludge, indicating that low pH may be the main reason CR has a higher extraction rate than VT and PS. CL increased the pH of sludge, presumably because the primary groups of glycoproteins combined with metal ions to form alkaline complexes. The weakly alkaline groups combine with HMs and release weakly alkaline ions to occupy the sludge adsorption sites. Since CL has high sugar content and a large number of alkaline groups in glycoproteins, the E_{Cd} of CL is higher than that of PS and VT, and the groups are weakly alkaline, which also explains why the pH of the sludge is still less than 7 after CL extraction. The acidic environment still has a specific activation effect on HMs ions, further improving the extraction rate. The composite chemical extractant of high concentration NTA, oxalic acid and tartaric acid caused a significant change in sludge pH (Fig. 4a). In both composite chemical extractants, pH increased with NTA proportion. NTA and oxalic acid contain five carboxyl groups, which release H^+ after reacting with HMs ions. When the proportion of oxalic acid is high, H^+ is the primary reaction ion, and the pH drops rapidly. When the proportion of NTA increases, it is easy to react with alkaline salts such as potassium, calcium, and chloride in the sludge, and the pH of the sludge increases (Feng et al., 2023). The extraction rate results in Fig. 3 show that in the composite extractant of NTA and oxalic acid, HMs are more sensitive to NTA, and the extraction rate increases with the increase of NTA concentration. This is related to the chemical structure of NTA containing three carboxyl groups. The increase in reaction sites is the main reason for enhancing the extraction effect of the extractant on sludge HMs removal. Yu et al. (2020) also observed that applying NTA enhanced the effectiveness of Pb because functional groups such as carboxyl and hydroxyl groups complexed with HMs ions in the sludge, allowing the sludge to adsorb more H^+. In addition, the OT1 ~ OT5 series reduced the sludge pH, related tartaric acid containing two carboxyl groups and a hydroxyl group. More H^+ reduced the pH to a greater extent. The nutritional status of sludge is greatly affected by the extractant. When CR, CL and high-concentration composite chemical extractants are used to extract sludge, the fertility can be improved after the residue is mixed with the sludge. The research of Xie et al. (2023) supports this view. The analysis found that CR, CL, NO5 and NT4 changed the sludge's the physical and chemical properties to a more ideal state.

4.3. Effect of extraction conditions on sludge extraction results

The results show that the solid-liquid ratio significantly affects the leaching effect of HMs in sludge. The best effect is when the leaching agent is 1:50. This shows that increasing the amount of leaching agent can enhance the leaching effect because the increase of low molecular organic acids and functional groups such as carboxyl and hydroxyl groups provides more adsorption sites, greatly enhancing the complexation of ions in the sludge. Zhang et al. (2019) also believed that increasing the concentration of the leaching solution could provide more adsorption sites to bind metal ions. However, the effect of extraction time and temperature on the extraction rate was not a simple positive slope function relationship but a repeated fluctuating sawtooth change. In the initial stage of leaching (0-6 h), various functional groups in the combined leaching agent quickly combine with metal ions on the sludge surface to increase the leaching rate. As the leaching time increases, the electrostatic repulsion between metal cations prevents more metal cations from migrating into the leaching agent. However, in the middle stage of leaching (12-36 h), this repulsion weakens, the binding force between metal ions and the adsorption sites of the leaching agent increases, and the E_{Cd} increases significantly (except CR-NO5). Subsequently, as time went on, the leaching rate dropped again due to the re-adsorption and sedimentation of the sludge. CR-NO5 has many carboxyl groups and organic acids, which rapidly undergo replacement reactions with metal ions in the sludge at the initial leaching stage (0–6 h), and the extraction rate rises rapidly. However, the unique chemical structure creates a strong repulsive force between metal cations. Therefore, as the extraction time increases, the metal ions are separated from the extractant and returned to the sludge, and the extraction rate decreases. As the temperature increases, the thickness of fine particles on the sludge surface becomes smaller, the mass transfer resistance of the reaction between surface metal ions and the leaching agent decreases (Xu et al., 2020), the metal ions are transferred to the leaching agent by complexation, and the leaching rate increases accordingly. In addition, studies have shown that the dissolution and diffusion rates of HMs ions increase with increasing temperature (Shaker, & Albishri, 2014), indicating that as the temperature increases, the ions move faster in the liquid phase and the reaction rate increases, which is beneficial to the removal of HMs in sludge. However, high temperature means high energy consumption, high fuel or other power systems demand, and increased sewage system costs. Modern development requires low-energy, high-efficiency extraction processes.

4.4. Effect and mechanism analysis of combined extraction agent

The extraction effects of the four combined extractants were significantly enhanced after changing the extraction conditions. The extractants not only have excellent extraction effects on Cd but also can remove associated metals such as Zn and Pb in sludge with different contents and have apparent extraction effects of Zn. We found that low molecular organic acid substances have a significant extraction effect on Cd in sludge, which also explains that the E_{Cd} of the combined extractant composed of CR is higher than that of the CL combination (Fig. 6a) because CR contains more low molecular organic acids than CL. Compared with the E_{Cd}, CL-NO5 and CL-NT4 showed excellent Zn extraction ability, which may be because the organic matter structure, such as carbohydrates of CL, is more stable when combined with Zn. It is worth noting that when H^+ increases in the extraction system, Cd will have a unique advantage when competing with Zn for adsorption sites. However, the combined extractant of NO5 combination enhances the alkalinity of sludge, which is speculated to be mainly caused by NO5 causing the reaction of sludge base ions to produce alkaline salts adsorbed on the sludge.

On the other hand, reducing nutrient loss during sludge production and application is the key to resource reuse. The organic matter content of sludge treated with combined extractants has increased, and the positive effect of CL on sludge nutrients is more prominent. The organic matter remaining after chemical extractants treat sludge also plays a specific role in nutrient retention. Previous research results also proved that combining chelating agents and low molecular organic acids increases the organic matter content of sludge (Kou et al., 2020). Therefore, from the extraction effect, sludge pH, and nutrient status, it can be observed that after the combined application of peel extract and chemical extractant, the activation amount, chelation degree, and nutrient content of HMs ions have increased. This shows that the combination of the two is mainly synergistic, which significantly enhances the extraction effect of sludge Cd and Zn.

Fig. 8 shows the HMs extraction mechanism in sludge by combining peel extract and chemical extractant into a new combined extractant. NO5 and NT4 are composite chemical extractants with functional groups such as hydroxyl and carboxylic acid. The combined extractants formed with CR and CL increase functional groups, for instance, ester, amino, NH_3^+, and carbonyl, which provide more coordinating atoms for HMs ions in sludge. Not only can the HMs ions free on the sludge surface undergo replacement, coordination, and complexation reactions with functional groups, but a large number of H^+ are generated to change the pH conditions in the extraction system. The activity of HMs ions in the sludge is enhanced, and they migrate to the surface to transform the HM's form of the sludge into a soluble form. Subsequently, multiple extractions can be performed to release HMs ions from the sludge and migrate them into the solution, thereby achieving harmless treatment of the sludge.

4.5. Changes of heavy metal speciation in sludge and analysis of ecological risk

The morphological distribution of HMs in sludge can further reflect the extraction capacity of the composite leaching agent. The proportion of Sol-HMs in the sludge increased with the four combined leaching agents, showing a solubilizing effect on both Cd and Zn in the sludge. Many low molecular organic acids in the extractant converted the exchangeable HMs in the sludge into soluble ones. CR-NO5 and CR-NT4 had a dual effect of activation and passivation on Cd of sludge, and the activation effect on Zn was more prominent, manifested in the inconsistency of the residual of Cd and Zn (Fig. 7a). The small molecular organic acid of CR and the carboxyl group of chemical leaching agents accelerate the migration process of Cd and Zn in sludge. However, after compounding with CL, the difference between NO5 and NT4 was more obvious. CL-NO5 has both activation and passivation effects on Cd and only has a more significant activation effect on Zn. CL-NT4 only has an activation effect on Cd and has both activation and passivation effects on Zn. We speculated that tartaric acid may have amplified the chelation effect of NTA on Zn, and the formed metal-ligand complex was re-adsorbed by the sludge surface, and the ligand formed a bridge between the sludge surface and the metal cation. On the other hand, the alkaline groups in CL and the increase in NTA concentration produced an activation effect on Cd and Zn in the sludge, specifically manifested as the conversion of HMs from exchangeable to soluble states.

The component distribution of HMs determines the ecological risk. When the I_R is close to 1, the surface HMs exist in stable forms such as residual, and the potential risk is low (Yang & Hodson, 2019). All combined leaching agents reduced the potential ecological risk of Cd. However, the CR series composite leaching agents increased the environmental risk of Zn (Fig. 7b). We speculate that the reason for this phenomenon is that Cd and Zn are in a competitive relationship during the leaching process, jointly occupying the adsorption sites and functional groups provided by the leaching agent, an active state of

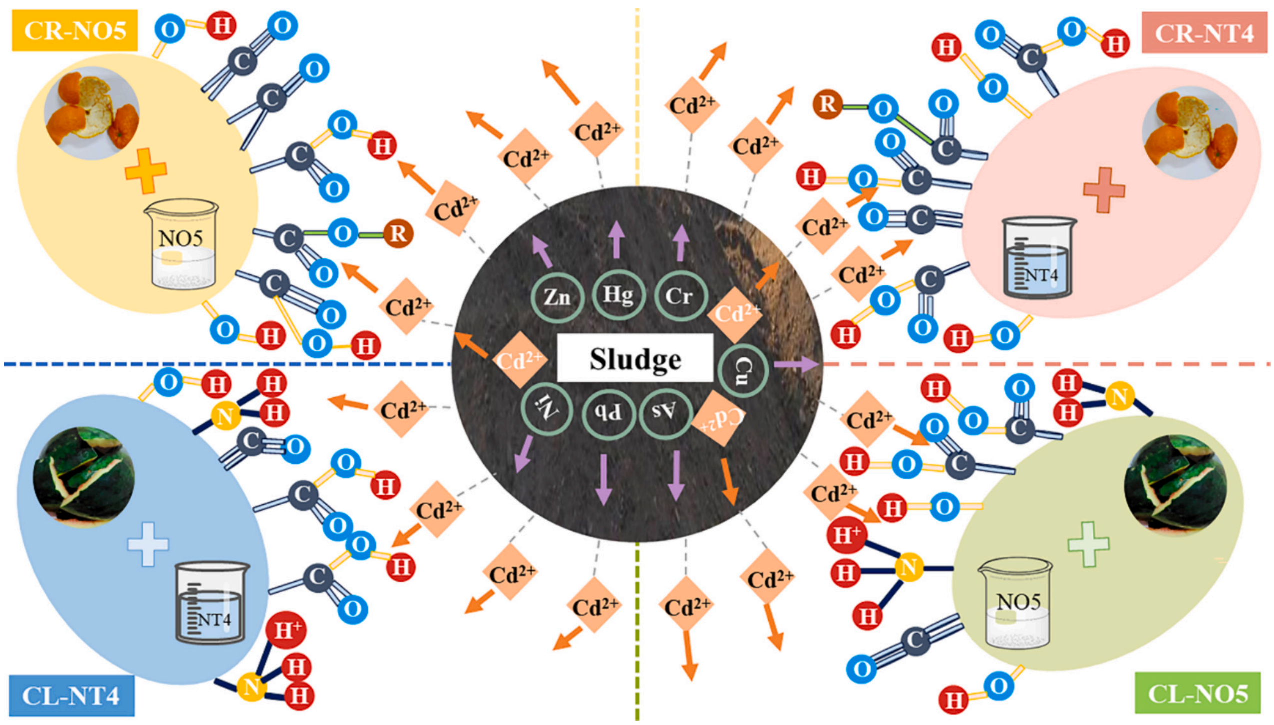

Fig. 8. Mechanism of action of combined extractants on HMs in sludge.

antagonistic coexistence. Low molecular organic acids and many carboxyl groups react with Cd first, and the remaining coordinating atoms and H^+ react with Zn. Therefore, the active Cd in the sludge is leached and discharged into the wastewater. The release risk of Cd is lower than that of Zn. We speculate that the pollution risk can be reduced after multiple extractions. The residual HMs in the sludge are stable and have low risks. The passivation effect of the leaching agent on Zn reduces the risk of sludge leaching, which is consistent with the research results of Wang et al. (2022). In general, multiple extractions can solve the problem of enhanced Zn^{2+} activity, further reduce the active Cd content, and stabilize the residual form of Cd^{2+}. The increase in the extraction rate also shows that the four extractants reduce the risk of secondary sludge pollution.

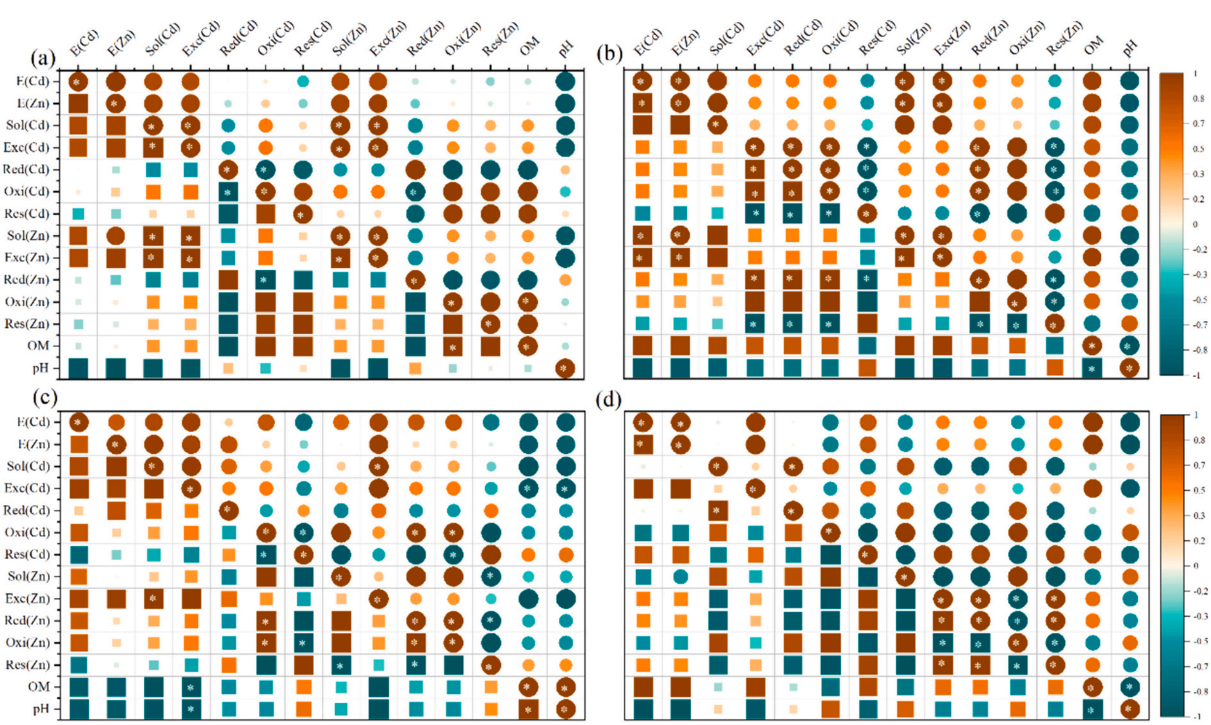

Fig. 9. Pearson correlation analysis between the extraction effect of Cd and Zn by combined leaching agent and environmental factors($p < 0.05$), CR-NO5(a).CR-NT4 (b), CL-NO5(c), CL-NT4(d).

4.6. Correlation analysis between extraction effect and environmental factors

Organic matter(OM) and pH were negatively correlated with the HMs extraction rate in the four extraction systems, consistent with most research results(Fig. 9). In the NT4 extraction system, OM had a significant negative correlation with pH ($p < 0.05$). In the NO5 extraction system, a strong positive correlation existed between the active forms of Cd and Zn. In short, when using CR-NO5 as an extractant, attention should be paid to the effect of OM content on Zn and whether the extractant is sufficient to absorb the activated HMs. In the other three extraction systems, sludge pH and organic matter are the key influencing factors of Cd and Zn extraction rates.

4.7. Comparison with other extraction agents

The extraction capacity of the four combined extractants for HMs was compared with other extractants (Table 2). Chemical extraction is often used to remove HMs from solid waste, and the removal efficiency is closely related to the extractant type. Analysis shows that the combined extractant has an excellent HMs extraction capacity similar to other chelating agents and acid extractants. The E_{Cd} by the four combined extractants is higher than that of *Fatsia japonica*, Hovenia acerba and *Pterocarya stenoptera*, and N, N-bis (carboxymethyl) glutamic acid (Xu et al., 2020), and the extraction effect of Zn is lower than that of IA-AA (Z. Yang et al., 2021). This difference is related to the synthesis conditions of the extractant. IA-AA is a polymer composed of multiple carboxyl-based alkanes, which provides more coordination bonds for metal ions, but the synthesis cost is relatively high. Therefore, the combined extractant of peel and chemical extractant is an environmentally friendly and economical high-efficiency extractant for HMs in sludge.

Table 2
Comparison of HMs extraction capacity of different extractants in sludge.

Extraction agent	Solid waste	Leaching efficiency (%)	Reference
Citric acid(CA)	dewatered sewage sludge	Zn(66.00 %), Cu (73.00 %), Ni (71.00 %), Cr (75.00 %).	(Suanon et al., 2016)
Saponin and sophorolipid	sludge	Cu(55.80 %), Pb (51.60 %), Ni (60.80 %), Mn (56.00 %), Zn (73.80 %), Fe (41.00 %), Hg (35.00 %), Cr (64.00 %).	(Tang et al., 2018)
Fatsia japonica, Hovenia acerba and *Pterocarya stenoptera*	industrial sludge	Cu(75.81 %), Pb (63.42 %), Ni (27.52 %), Cd (56.99 %)	(Xu et al., 2020)
Caboxyethylthiosuccinic acid (CETSA) and itaconic-acrylic acid copolymer(IA-AA)	industrial sludge	CESTA:Pb(59.59 %), Zn(69.48 %), Ni(70.10 %) and Cr(57.14 %). IA-AA: Pb(74.15 %), Zn(99.86 %), Ni(75.69 %) and Cr(54.33 %).	(Z. Yang et al., 2021)
N, N-bis (carboxymethyl) glutamic acid	sewage sludge	Zn(11.72 %), Mn (37.62 %), Cd (0.38 %), Cr(3.16 %).	(Guo et al., 2022)
methyl glycine diacetic acid (MGDA)	dewatered sewage sludge	Zn(94.10 %), Cu (36.90 %), Ni (78.30 %), Cr (54.60 %).	(Hu et al., 2022)
CR-NO5, CR-NT4, CL-NO5, CL-NT4	dewatered sludge	CR-NO5: Cd (92.60 %), Zn (94.18 %). CR-NT4: Cd(85.69 %), Zn(90.94 %). CL-NO5: Cd (72.36 %), Zn (91.46 %). CR-NT4: Cd(79.25 %), Zn(98.35 %).	this study

5. Conclusion

This study found that *citrus reticulata* and *citrullus lanatus* peel extracts have good extraction capacity for sludge Cd. Cd in the environment is highly toxic, and peels are low-cost and usually treated as kitchen waste. Therefore, using peels as extractants can help solve their disposal problems. The extraction rates of peel extracts and compound chemical extractants for sludge Cd were 9.9 % ~ 36.9 % and 3.5–42.3 %, respectively. The pH were 4.88–6.82 and 2.35–9.10, respectively, and the organic matter content was within 106.33 $g \cdot kg^{-1}$–146.88 $g \cdot kg^{-1}$ and 96.67 $g \cdot kg^{-1}$–115.79 $g \cdot kg^{-1}$. Among the combined extractants composed of the two, CR-NO5 (*citrus reticulata* peel, 0.16 $mol \cdot L^{-1}$ NTA with 0.04 $mol \cdot L^{-1}$ oxalic acid) had the best extraction effect on Cd when the extraction process was 1:50, 6 h, and 35 °C, with E_{Cd} of 92.60 %. The highest organic matter content of sludge extracted by CL-NT4 (*citrullus lanatus* peel, 0.12 $mol \cdot L^{-1}$NTA with 0.08 $mol \cdot L^{-1}$tartaric acid) was 177.88 $g \cdot kg^{-1}$. The NT4 (0.12 $mol \cdot L^{-1}$NTA with 0.08 $mol \cdot L^{-1}$tartaric acid) series extractants had little effect on the sludge pH (5.58–6.15). The combined extractants mainly converted the acid-extractable HMs in the sludge. The I_R change trend showed that the CR-NO5 and CL-NT4 extractions reduced the potential risks of Cd and Zn in the sludge. In summary, this paper believes that the extraction of *citrullus lanatus* peel, 0.12 $mol \cdot L^{-1}$NTA, and 0.08 $mol \cdot L^{-1}$tartaric acid can improve the nutrient and acid-base conditions of sludge, and the extraction rates of Cd and Zn are 79.2 % and 98.4 %, respectively. It has an excellent removal effect on other HMs and can be used as an extractant for sludge. Therefore, the use of combined extractants can provide a new direction for the resource utilization of peel waste and the harmless treatment of HMs in sludge. We believe that the extraction effect of Cd and Zn in sludge can be further enhanced by increasing the concentration of peel extract and the number of extractions. The potential application prospects of improving the extraction ability of low-cost extractants for sludge pollutants and their residues as extract adsorbents need further research.

CRediT authorship contribution statement

Hanyu Li: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Shuai Jiao:** Writing – review & editing, Methodology, Data curation. **Lili Tian:** Writing – review & editing. **Yujun Wang:** Writing – review & editing, Visualization, Supervision, Funding acquisition, Conceptualization. **Fei Li:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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