



Activated recovery of PVC from contaminated waste extension cord-cable using a weak acid

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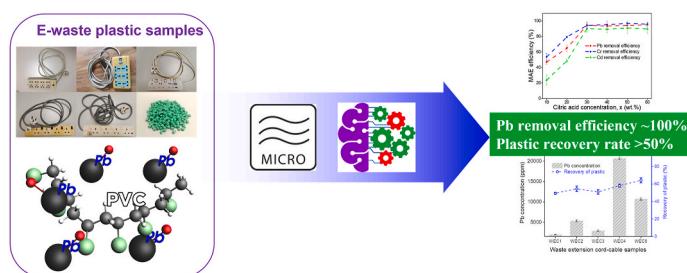
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HIGHLIGHTS

- High level of toxic metal (lead) was found in waste extension cord-cable samples.
- Microwave-assisted extraction was demonstrated to completely remove toxic metal.
- Diluted citric acid was found to be more effective than strong acids.
- Accurate process optimization prediction was generated using machine learning.
- More than 50 wt% plastic recovery was achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Waste electronic and electrical equipment are complex mixtures of valuable and/or toxic materials, which pose serious challenges in their recycling or disposal, for example, electrical transmission wires insulated in polyvinyl chloride materials. These materials are frequently found contaminated with toxic chemical elements, such as Pb, Hg, Cr, or Cd, and are discarded without decontamination. To resolve this problem, we developed a microwave-assisted extraction process to remove toxic metals from plastic e-waste. We processed diluted (30 wt%) citric acid at 210 °C for 1 h inside a pressurized vessel heated by microwave, and found it was suitable not only for the extraction of the toxic metals (~100%) but also for a significant plastic recovery (>50 wt%). To predict an optimized process window, the support vector regression machine learning algorithm was applied, which reduced the amount of experimentation required while still giving accurate results. Conditions optimized for the reference sample also led to maximum extraction of toxic metals from real-life extension cord waste. We also report that the recovered plastic's properties remained intact after the extraction.

1. Introduction

Insulating materials of electrical power cables in waste streams are

often overlooked because of their low market value once separated from the conducting metals. There are many studies on the separation of conducting metals and the insulating material (Sheih and Tsai, 2000; Bedekovic and Trbovic, 2020) as well as new developments on the

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Nomenclature table

Abbreviation Full name

PVC	Polyvinyl chloride
TM	toxic metal
WEEE	waste electronic and electrical equipment
RoHS Directive	Restriction of Hazardous Substances Directive
ML	Machine learning
WEC	Waste extension cord
RM-PVC	Reference material based on the virgin resin PVC
std	standard deviation
DOE	design of experiment
svr	support vector regression
FV	factory value
DTG	derivative thermogravimetry

considered that these compounds tend to form a suspension within polymers rather than being chemically bonded to the polymer macromolecules (Brydson, 1999; Piorek, 2004; Chauhan and Upadhyay, 2015). Furthermore, the presence of TMs in printed circuit boards (PCBs) and associated disposal techniques have been studied extensively over the years (Bi et al., 2010; Jha et al., 2011; Ghosh et al., 2015; Li et al., 2018). Nevertheless, the removal of TMs from waste electronic and electrical equipment (WEEE) plastics, such as the insulation of power cables, has received little attention.

Informal and unregulated recycling or disposal of these plastics may cause pollution to underground water and soil, thus to our daily water and diet. Toxic metals are not biodegradable and tend to accumulate in living organisms, causing various diseases to our nervous, skeletal, circulatory, enzymatic, endocrine, pulmonary, and immune systems, as well as lung cancer, adenocarcinomas, prostatic proliferative lesions, bone fractures, and kidney dysfunction hypertension (Florea et al., 2011; Quan et al., 2014; Tang et al., 2017). Especially, lead compounds are cost-effective and commonly used for stabilizer in PVC. However,

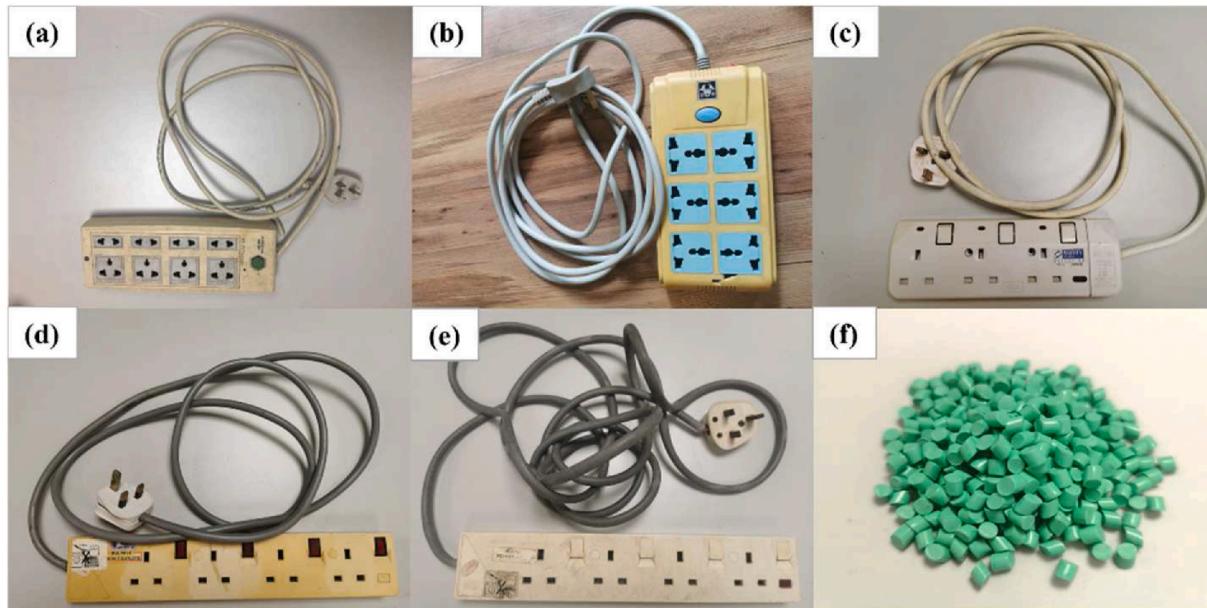


Fig. 1. (a–e) The waste extension cords 1–5 collected in a residential area of Singapore, (f) RM-PVC that was used to screen out the optimization extraction method.

recycling of power cable insulating materials (Yang et al., 2011; Green et al., 2013; Huang et al., 2020). Most of the latter are made of polyvinyl chloride (PVC), the world's third most synthesized thermoplastic material. The cost of PVC resin ranges between US\$ 308 – US\$ 1300 per ton depending on its grade and purity. PVC represents ~3 wt% of the total plastic contained in electronic/electrical waste (e-waste) and in the range of 2–5 wt% of municipal plastic waste (Areeprasert et al., 2017; Das et al., 2021). One of the major hurdles in the recycling of PVC insulators is the presence of toxic metals (TMs), such as lead (Pb), chromium (Cr), and cadmium (Cd). These metals were added to the polymer as additives, such as pigments or stabilizers (Pritchard, 2005; Dimitrakakis et al., 2009; Duarte et al., 2010). Lead oxide (PbO) and its compounds (such as 3PbO·PbSO₄·H₂O and 2PbO·PbHPO₃·H₂O) are commonly used as heat stabilizers for PVC. Cd in its sulfide form (CdS) has been used as a colorant for engineering plastics because it is stable under elevated temperature (Kutz, 2016). In addition, Cd and Barium (Ba) composite stabilizers are also typically incorporated in PVC. Finally, chromium yellow (PbCrO₄) and chromium red (PbCrO₄·Pb(OH)₂) have been extensively used as plastic pigments (Charvat, 2005). Although the physical and chemical interactions between toxic metal compounds and polymers are difficult to identify, it is generally

the common applications in the electronic and electrical equipment can cause high toxicity to the environment and human. The harmfulness of Pb to children is more severe than adult. The lead exposed to pregnant women can be migrated to unborn baby. Even with low-level lead exposures, it can damage the development of baby's nervous system, behaviour, and intelligence. The source of lead poison to children includes the lead containing toys, lead dust, etc. (National Institute for Occupational Safety and Health, 2021). For example, the presence of TMs in many plastic products in recent years, including children's toys and decorative items, has been reported (Maas et al., 2005; Kawamura et al., 2006; Chehade et al., 2012; Zhou et al., 2013; Kang and Zhu, 2015). With its RoHS Directive (2002/95/EC), the European union restricted toxic content in WEEE. The restricted TMs include Pb (<1000 ppm), Hg (<1000 ppm), Cd (<100 ppm), and Cr(VI) (<1000 ppm) (Cusack and Perrett, 2006).

The leaching of these metals from plastics, either when they are in the environment, or once the plastic is degraded into micro/nano particles, can carry the toxins into our food chain causing health issues (Bejgarn et al., 2015; Paul-Pont et al., 2016). A recent study by Xu et al. (Xu et al., 2020) reported the leaching of toxic metals from discarded plastic wastes into the water of Shenzhen and Honghuatao town areas.

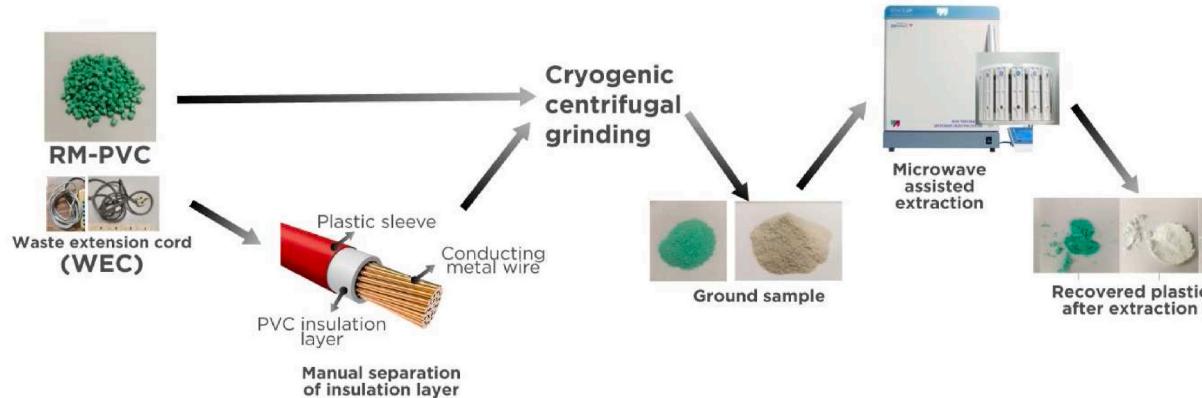


Fig. 2. Detoxification steps for the recovery of PVC from e-waste.

The metal concentrations were found to exceed limits of Chinese national drinking water standards. Furthermore, migration of these TMs from e-waste plastics into secondary recycled products was reported by Mao et al. (Mao et al., 2020). To avoid the latter issue, one can propose the removal of TMs, but ideally this must be done without destroying the polymer matrix, which is a complicated task. Indeed, simple digestion with strong acids or alkaline solutions has been found efficient in the determination of the metal concentration (Kim et al., 2011). For example, Kim et al. (Kim et al., 2011) reported an alkaline extraction method to remove Cr with high extraction efficiency ($100 \pm 6\%$) and a short extraction time (30 min). To date, various inorganic acids and oxidants, including nitric acid, hydrogen peroxide, sulfuric acid, and tetrafluoroboric acid, have been extensively used to digest plastic and other wastes (Pan et al., 2020; Jia et al., 2021). In Nnorom's research, the acid mixture of H_2SO_4 and HNO_3 was used to analyze the metals in mobile phone plastic, and the results show that the metal concentration of Cd is from 4.6 to 1005 mg kg^{-1} , Pb is $5.0\text{--}340 \text{ mg kg}^{-1}$, etc. (Nnorom and Osibanjo, 2009). HNO_3 was used in a microwave to digest parts of personal computers, in order to analyze their metal concentrations, and the TM concentration in the plastic parts were found to be under the RoHS limit. In addition, Ernst et al. investigated the effect of H_2SO_4 , HNO_3 , H_2O_2 and HBF_4 on electrotechnical goods, such as personal computers and TV-sets, and the recovery rate of Pb, Cd and Sb were around 100% when digested by a mixture of HNO_3 and HBF_4 in the microwave system (Ernst et al., 2000). To determine heavy metal concentrations in small electric and electronic waste, HNO_3 and H_2O_2 were applied and the results revealed that only a small percentage contained a higher Pb, Cr, Cd, Hg concentration than the RoHS limit (Dimitrakakis et al., 2009). However, most of these studies failed to report any significant recovery of the polymer. Here, we report on what we believe to be the first microwave assisted extraction of such TMs from e-waste plastics using weak acids (citric acid), plastic compatible temperature ($<210^\circ\text{C}$), in a minimal amount of time, with a high recovery of clean plastic. Extraction conditions were optimized using machine learning (ML) (Zeng et al., 2021) and predicted optimized conditions were tested on real-life samples.

2. Experimental procedure experimental procedure

2.1. Material resources

Five waste extension cords (WEC) were collected from a residential area in Singapore. These extension cords were from different brands made in China, including Ming Ye, Bull, TAIYO, Xin Chao and NGI (see Fig. 1). The original metal content in the WEC samples was unknown and needed to be confirmed. The WEC were dismantled into cables, boards and sockets, called WEC-cables, WEC-boards, and WEC-sockets, respectively. A reference material based on virgin resin PVC (RM-PVC)

with concentrations of Pb, Cr and Cd of 1080 ± 36 , 1110 ± 43 and $70.7 \pm 2.2 \text{ ppm}$ (supplied factory values) respectively, was purchased from the National Institute of Metrology, China. The RM-PVC was supplied as pellets of cylindrical shape (diameter and length of 3 mm).

The acids solutions (HCl , H_2SO_4 , HNO_3 , H_3PO_4 , and citric acid) were purchased from Sigma-Aldrich, and the units of the concentration of acids mentioned in this work are wt%. Demineralized water (DI water)/ ultrapure water was prepared using a Labconco Water Pro BT water purification system. The system uses carbon filtration, deionization, reverse osmosis, and ultraviolet oxidation to produce $>0.5 \text{ L min}^{-1}$ of DI water (Type 1, TOC $<5 \text{ ppb}$).

2.2. Methods

The WEC and the RM-PVC samples were frozen separately in liquid nitrogen (to avoid aggregation induced by the heat of the grinding process), then ground into a smaller size using a high-rotation-rate grinding machine, for the purpose of sample homogeneity and operation convenience. The flow chart of the experimental detoxification process is shown in Fig. 2.

2.2.1. Microwave assisted extraction (MAE)

An Ethos Up microwave oven from Milestone (Italy) equipped with high-pressure 100 mL vessels made of polytetrafluoroethylene (PTFE) was utilized for the extraction of TMs from the plastic powder samples. The microwave oven was temperature-controlled and maintained an airtight closed system during the process. The closed system allows the MAE to maintain the liquid phase of the solvent at high temperatures. The typical procedure was to load 0.1 g of dry powder sample to a clean and dry vessel, then to add 10 mL of solvent, then all vessels were sealed and placed in the microwave oven. The heating program cycle consisted of a first ramp from room temperature to 210°C in 20 min, followed by a plateau for a target time prior to a cooling ramp back to room temperature. Resulting liquid samples were transferred out of the vessel, diluted, and filtered by a $0.45 \mu\text{m}$ pore diameter membrane before analysis. A blank test (only solvent added to the vessel) was also carried out in the same way. To recover the residue from the metal extraction process, the obtained solid-liquid mixture was separated by vacuum filtration, then washed several times with DI water until the pH value of filtrate reached 7 ± 0.5 . In this work, all experiments were performed in triplicate to ensure accuracy and reproducibility, and the metal concentration reported is the average value of the three results shown with standard deviation (std).

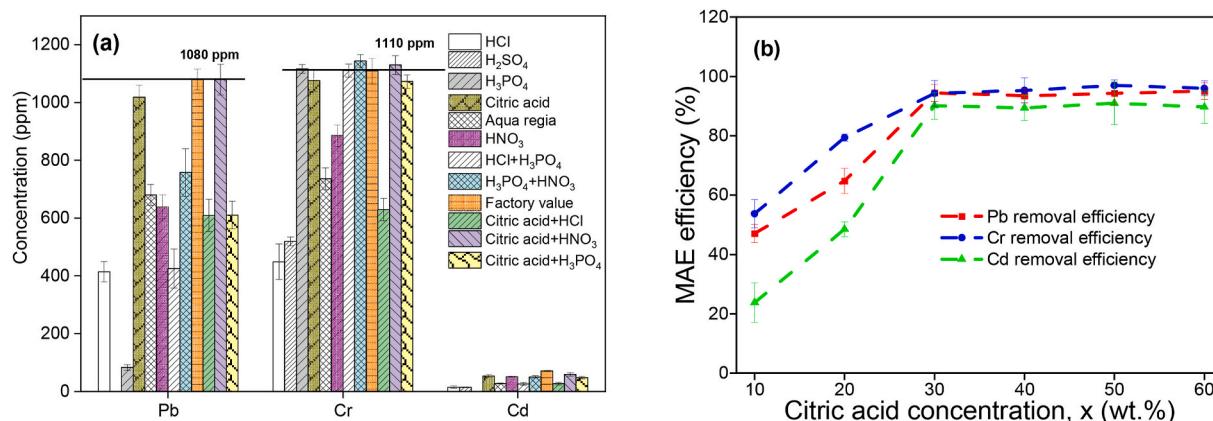
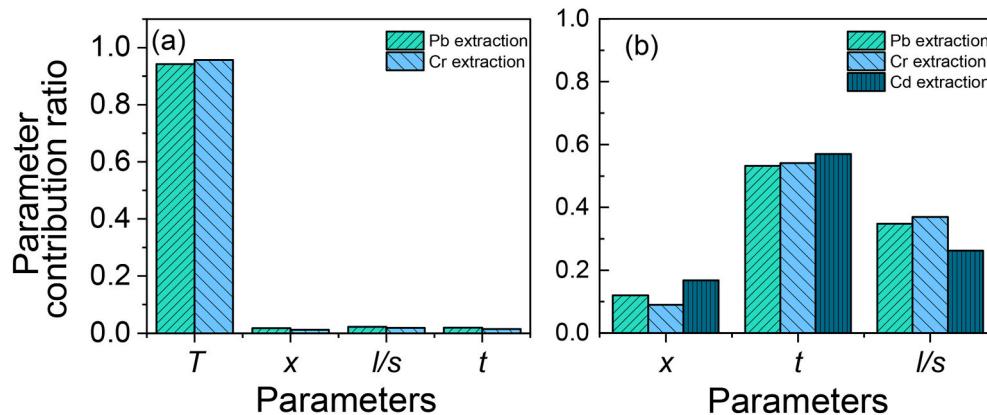
2.2.2. Characterization

Before and after extraction, plastic samples were characterized for their elemental composition by an inductively coupled plasma-optical emission spectrometer (ICP-OES) from PerkinElmer Optima 8000 and

Table 1

Elemental composition of the RM-PVC and five WEC-cable samples measured by XRF.

Elements	RM-PVC	WEC 1-cable	WEC 2-cable	WEC 3-cable	WEC 4-cable	WEC 5-cable
	Conc. ± std	Conc. ± std	Conc. ± std	Conc. ± std	Conc. ± std	Conc. ± std
Cl	33.2 ± 0.3 wt%	21.7 ± 0.6 wt%	22.9 ± 0.6 wt%	21.2 ± 0.7 wt%	45.3 ± 0.3 wt%	43.5 ± 0.6 wt%
Ca	11.8 ± 0.5 wt%	31.7 ± 0.9 wt%	28.5 ± 0.1 wt%	34.9 ± 0.2 wt%	7.7 ± 0.05 wt%	7.1 ± 0.1 wt%
Ti	0.4 ± 0.002 wt%	0.1 ± 0.007 wt%	N.A. ^a	N.A.	N.A.	N.A.
Cr	0.1 ± 0.01 wt%	N.A.	N.A.	N.A.	N.A.	N.A.
Br	1431.1 ± 1.9 ppm	6.3 ± 5.5 ppm	33.7 ± 2.3 ppm	30.6 ± 1.1 ppm	79.4 ± 12.3 ppm	76.6 ± 5.8 ppm
Sr	63.6 ± 2.7 ppm	87.4 ± 7.3 ppm	131.5 ± 10.2 ppm	72.5 ± 1.4 ppm	45.8 ± 4.6 ppm	44.1 ± 4.2 ppm
Zr	16.5 ± 4.2 ppm	N.A.	N.A.	2.7 ± 4.6 ppm	4.6 ± 7.9 ppm	4.2 ± 7.2 ppm
Ag	N.A.	6.5 ± 5.6 ppm	4.2 ± 0.2 ppm	6.5 ± 5.7 ppm	3.7 ± 6.4 ppm	8.8 ± 7.3 ppm
Cd	72.3 ± 0.5 ppm	21.4 ± 18.8 ppm	N.A.	N.A.	N.A.	N.A.
Sn	N.A.	76.2 ± 7.5 ppm	N.A.	55.2 ± 9.3 ppm	43.8 ± 3.7 ppm	39.5 ± 8.9 ppm
Sb	0.9 ± 0.01 wt%	20.5 ± 17.3 ppm	0.5 ± 0.01 wt%	N.A.	12.7 ± 22.5 ppm	N.A.
Ba	0.3 ± 0.007 wt%	371.3 ± 32.5 ppm	346.6 ± 21.5 ppm	304.9 ± 86.6 ppm	296.9 ± 49.8 ppm	270.2 ± 48.9 ppm
Hg	0.1 ± 0.0017 wt%	N.A.	N.A.	N.A.	N.A.	N.A.
Pb	1441.9 ± 18.5 ppm	2066.1 ± 20.1 ppm	5301.6 ± 200.2 ppm	2722.2 ± 92.1 ppm	29651.9 ± 223.6 ppm	28494.6 ± 391.5 ppm

^a Not Applicable (N.A.), as the element could not be detected by XRF.**Fig. 3.** (a) concentrations of TMs in RM-PVC tested by MAE under the conditions of temperature 210 °C, liquid/solid ratio 100 mL g⁻¹, extraction time 15 min in different solvents, measured by ICP-OES and compared with factory values; (b) removal efficiency of TMs using different concentrations of citric acid in the MAE process under the conditions of temperature 210 °C, liquid/solid ratio 100 mL g⁻¹ and extraction time 15 min.**Fig. 4.** The statistically significant MAE parameters for (a) 4 levels x 4 factors DOE matrix and (b) 3 levels × 3 factors DOE matrix (without Temperature).

an X-ray fluorescence (XRF) spectrometer (Olympus Vanta C Series XRF Analyzer). The instruments were pre-calibrated with standard samples such as known metal concentration solutions for ICP-OES, and reference plastics for XRF. The polymers of the e-waste plastics were identified, and their chemical structure was followed using an attenuated total reflection Fourier-transform infrared spectrometer (ATR-FTIR) from PerkinElmer, in the wavenumber range 4000–600 cm⁻¹. Materials' thermal properties were investigated using a thermogravimetric

analyzer (TGA) TGA 4000 from PerkinElmer, in the temperature range of 30–800 °C at a heating rate of 10 °C min⁻¹ under the inert atmosphere of purging N₂ flow at 100 mL min⁻¹.

2.2.3. Process parameter optimization using machine learning (ML)

Machine learning (ML) with support vector regression (SVR) was used to optimize the extraction conditions, using Python coding and the Scikit-learn tool (Cao et al., 2018; Wei et al., 2019). The ML calculation

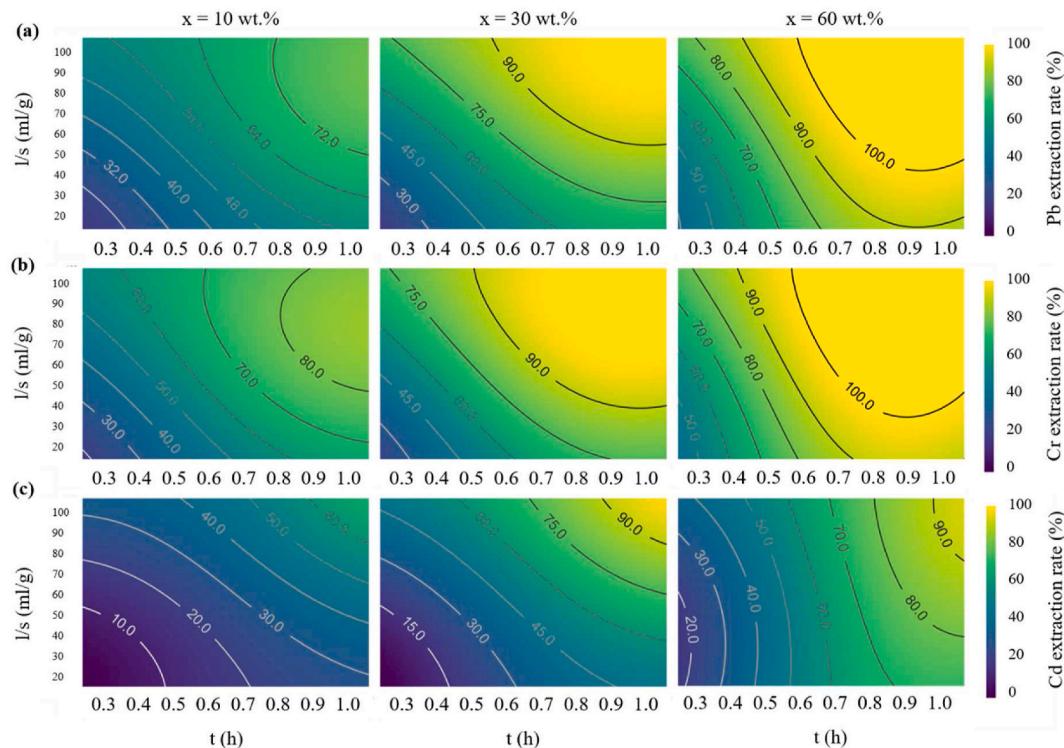


Fig. 5. The contour plots of the predicted heavy metal extractions by MAE from RM-PVC for (a) Pb extraction, (b) Cr extraction, and (c) Cd extraction at constant temperature of 210 °C.

is based on experiment results, so an experiment based on Box-Behnken design was conducted, which requires fewer tests. Each result (responses) corresponded to a parameter group (factors). ML-SVR was used to conduct the regression between the responses and factors. In this experiment, four factors were investigated, namely temperature (T , °C), time (t , h), liquid to solid ratio (l/s , mL g⁻¹), and solvent concentration (x , wt.%). The fitting process was elaborated in the reference (Wei et al., 2019).

The 2D contour curves were plotted for each component. Accordingly, the optimal values or target values were returned, and experimental optimization was performed. A comprehensive elucidation of the design of experiment (DOE) and the prediction of efficiency values in different conditions using ML are detailed in the supplementary information.

3. Results and discussion

3.1. Solvent selection and MAE

A microwave oven is a common tool in acid digestion of any material including soil (Sandroni et al., 2003), plastic (Ernst et al., 2000), and biomass (Liu et al., 2013). MAE is efficient in several extraction applications, in the biological (Kaufmann and Christen, 2002; Proestos and Komaitis, 2008), pharmaceutical (Routray and Orsat, 2011) and metallurgical sectors (Filgueiras et al., 2000). In e-waste treatment, MAE has been reported for the separation of brominated flame retardants (BFR) from e-waste plastics using organic solvents (Vilaplana et al., 2008; Xia et al., 2021). However, to the best of our knowledge, the leaching of TMs from e-waste plastics using MAE has not yet been reported. Hence, we investigated the influence of the extraction process parameters: temperature (T), time (t), liquid to solid ratio (l/s), and acid concentration (x).

The elemental concentrations in TMs within the RM-PVC and WEC-cable samples measured by handheld XRF are reported in Table 1. Furthermore, the FTIR-ATR spectra (Fig. S1) of the WEC-cable plastic

samples matched those of RM-PVC. We observed that all WEC-cable samples had high Pb contents, which were above the permissible limit and in one instance the Pb concentration reached up to 2.8 wt%. We also observed a small discrepancy between the factory values and measured XRF values, that remained within the overall error margin of this method. Pb was used as stabilizer in the WEC samples, which were all made in China several decades ago, before regulations existed. We also tested WEC samples made in recent years, and their Pb content was under the regulatory limit. Nowadays, research on stabilizers focuses on the Ba-Zn, Ca-Zn composite stabilizer as well as organic tin and organic antimony stabilizers (Wang et al., 2013; Wang et al., 2016). The lixiviating power of various acids on the metals within the RM-PVC was then investigated. Metal concentrations measured by ICP-OES along with the factory values and the XRF analysis are shown in Fig. 3. The scattered concentration values measured (and plotted in Fig. 3(a)) prove that different solvents have different interactions with the materials. Hence, not all acids were able to fully extract all the TMs (for example, H₂SO₄ failed to dissolve Pb and H₃PO₄ failed to dissolve Cd). Fig. 3(a) indicates that citric acid is more effective than other tested inorganic strong acids for extracting all the TMs from the PVC matrix at the same time. In addition, mixed acid mixtures were also investigated for the TMs removal. H₂SO₄ was excluded from the mixed acids as it was not able to remove TMs, effectively. In detail, the acid mixtures of HCl and H₃PO₄ (volume ratio = 1:1), H₃PO₄ and HNO₃ (volume ratio = 1:1), aqua regia, citric acid and HCl (volume ratio = 1:1), citric acid and HNO₃ (volume ratio = 1:1) as well as citric acid and H₃PO₄ (volume ratio = 1:1) were used to test their performance on extraction efficiency (see Fig. 3(a)). These mixed solvents were not able to dissolve the plastic sample and most of the mixed solvents did not show high Pb extraction efficiency, except the mixture of citric acid and HNO₃. In addition, because H₃PO₄ can remove Cr completely when it was mixed with HCl or HNO₃, the Cr removal efficiencies were improved compared to the solvents using only HCl or HNO₃. Among all the investigated organic and inorganic acid mixtures, only the mixture of citric acid and HNO₃ increased the Cr removal efficiency slightly. Therefore, citric acid is the most suitable

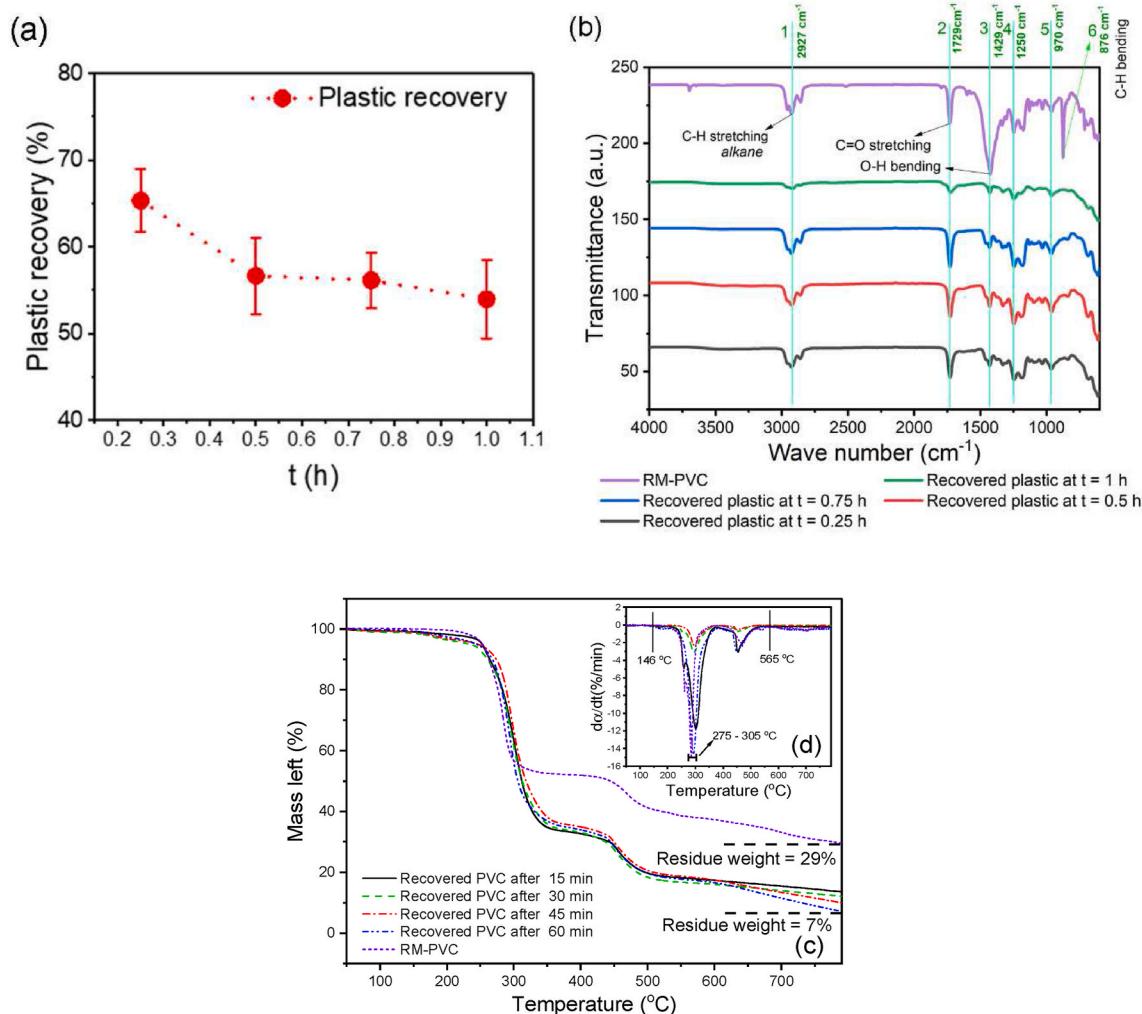


Fig. 6. (a) Recovery of plastic and extraction time (post MAE) at 30 wt% citric acid. (b) FTIR-ATR spectra of RM-PVC (before extraction) and the recovered plastics extracted after different periods; (c) TGA and (d) DTG (insert) analysis of RM-PVC and recovered RM-PVC extracted after different periods.

solvent for extracting Pb, Cr and Cd from the overall consideration of extraction efficiency, corrosiveness, and simplicity.

Indeed, all the values obtained for citric acid are comparatively close to the factory values of the RM-PVC. Hence, all further extraction studies in this work were conducted using citric acid.

In further extraction studies, diluted citric acid solutions (concentration ranging between 10 and 60 wt%) were used to extract the TMs from RM-PVC. In Fig. 3(b), the extraction rates of TMs all reach a steady-state value (~90%) at a concentration of 30 wt%. Increasing citric acid's concentration beyond 30 wt% doesn't show increased extraction efficiency. Past studies have reported the effectiveness of citric acid in the removal of TMs from sandy soil (Bassi et al., 2000; Ke et al., 2020), smelter soil (Ke et al., 2020), contaminated clay loam soil (Wasay, 2000), lithium-ion batteries (Chen and Zhou, 2014), industrial and municipal mixed sludge (Wang et al., 2015), sewage sludge (del Mundo Dacera and Babel, 2006; Ma et al., 2020), plants and leaves (do Nascimento et al., 2020). Citric acid is indeed an excellent chelating agent leading to high stability constant values for metal-citric acid coordination complexes, which therefore favors the solubility of metal oxides (Ma et al., 2020). However, there is limited research into the mechanism of the extraction process of heavy metal from plastic by citric acid using MAE. Firstly, the microwave heats the plastic sample rapidly and the polymer melts and transforms to a fluid state under the hydrothermal conditions. Phase separation of Pb-containing compounds with the polymer occurs easily and the inner Pb compound in the polymer matrix

diffuses quickly to the outside. The proton in the acid solution attacks the Pb compounds and breaks the chemical bonds between the Pb compound and polymer matrix. Then, the citrate chelates with the Pb ions in the solution and forms several soluble complexes via its carboxylate groups (Camel, 2000; Ke et al., 2020; Ma et al., 2020) with $\log_{10}K$ in a range of 4.4–24, which is much higher than other Pb compounds (For example, PbSO_4 has a $\log_{10} K$ of only – 6.2) (Zárate-Gutiérrez and Lapidus, 2014). This is the main reason for the high extraction efficiency of citric acid.

3.2. Optimization of MAE parameters

In another part of our study, we used an ML-SVR to further optimize the process parameters and study the effectiveness of the different parameters in the extraction process. Indeed, we anticipate that such information should be useful for the future design of commercial plants for the sustainable recovery of value-added products from contaminated e-waste plastics. To obtain the most significant process parameters among T , t , l/s and x , the DOE was designed for a 4 level \times 4 factors matrix (Table S1). The corresponding values of the extraction of Pb, Cr and Cd in all the DOE points were listed in Table S2. A variance analysis (ANOVA) was performed, and the resulting contributions of each factor were obtained, as shown in Fig. 5(a). The high contribution ratio measured for temperature indicates that it is the most statistically significant parameter, which constitutes more than 95% of the extraction

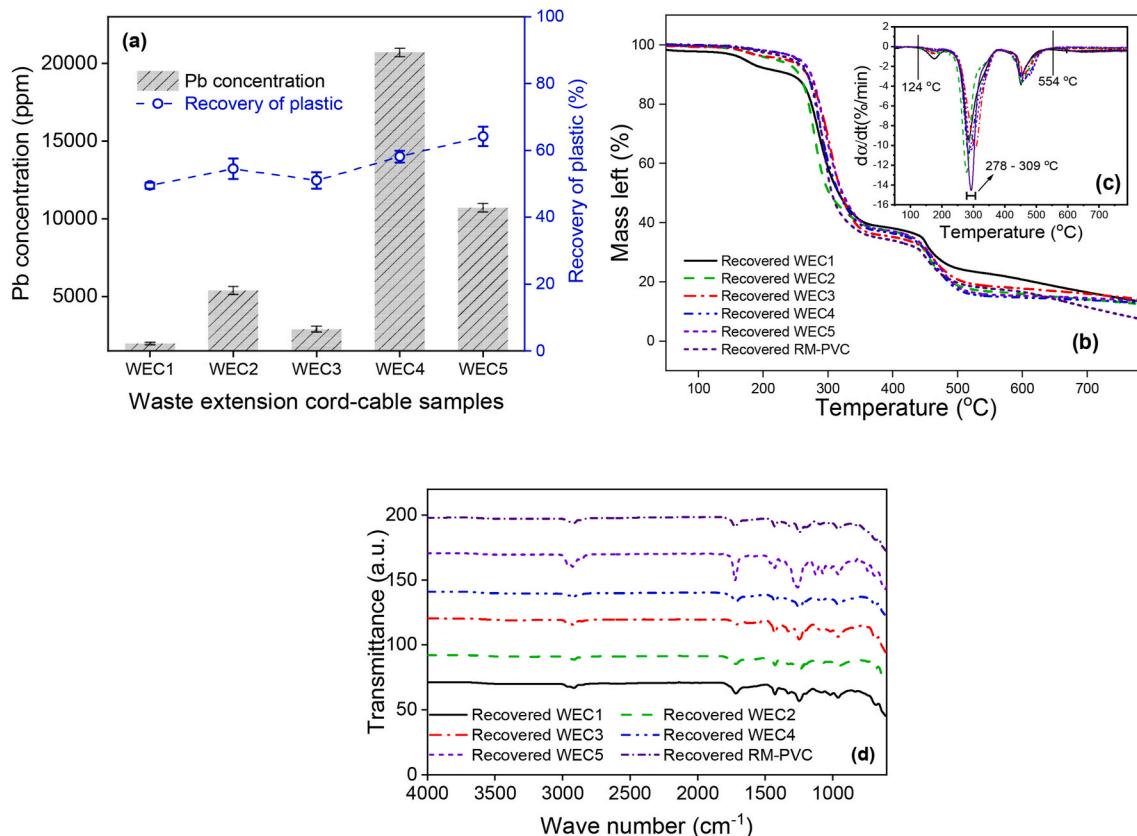


Fig. 7. (a) The metal Pb concentration in the waste extension cord-cable samples tested under the optimal extraction condition: Temperature = 210 °C, solvent = 30 wt% citric acid, liquid/solid ratio = 100 mL g⁻¹ and extraction time = 15 min; (b) TGA, (c) DTG and (d) FTIR-ATR profiles of the recovered plastics from MAE process.

process efficiency. This is mainly because the melting point of PVC materials is in the range of 100–260 °C. A relatively higher temperature is needed to melt the PVC in the acidic solution; thus, the phase separation of additives and polymers can occur, and the metal compounds can react with acid. Since the reaction of metal compounds with acid is very fast at high temperatures, the effect of reaction time and acid concentration on extraction efficiency is not obvious. In addition, the total metal content in the plastic sample is much less than the amount of acid, thus the solid to liquid ratio also has a minor effect on extraction efficiency. It should be noted that the influence of temperature on Cd extraction could not be estimated as it could only be extracted at the highest temperature point of 210 °C. To determine the significance of the other three parameters (t , l/s and x), a similar DOE was designed for a level 3 × factor 3 matrix (Table S3), and the resulting extraction efficiencies can be found in Table S4. The parameter contribution for the second ANOVA analysis is shown in Fig. 4(b). From the results we can see that when temperature is constant, time is the most statistically significant of the three remaining parameters.

Based on the DOE above, response surfaces were constructed through SVR with the selected hyperparameters. Accordingly, the contour plots of the predicted extraction efficiency for Pb, Cr and Cd are shown in Fig. 5. Complete removal of each metal can be obtained in the yellow areas. From the overall consideration, the optimal extraction conditions for Pb, Cr and Cd are selected as: $T = 210$ °C, $l/s = 100$ mL g⁻¹, x of citric acid solution = 30 wt% (or above), and $t = 1$ h.

3.3. Post-extraction characterization of RM-PVC

The recovery rates of the plastics after MAE were found to be more than 50% when using 30 wt% citric acid. However, the recovery decreased as the extraction time increased (Fig. 6(a)). The ATR-FTIR

spectra of fresh and the recovered RM-PVC collected after different extraction times are shown in Fig. 6(b). Two types of additives were observed in RM-PVC. The first one was CaCO₃, which is a common inorganic filler added to the polymer resin to enhance its physical properties, such as toughness, stiffness, and heat resistance (Jiang et al., 2017). Presence of Ca was measured by XRF analysis (Table 1). Hence, in Fig. 6(b), the peaks at 1425 cm⁻¹ and 874 cm⁻¹ can be assigned to CaCO₃. The other type of additive was a plasticizer containing phthalic ester to which one can assign the peaks at 1729 cm⁻¹ (C=O stretching), 1429 cm⁻¹ (O–H bending) and 1250 cm⁻¹ (C–O stretching). Peak 3 in Fig. 6(b) can be assigned to both CaCO₃ and phthalic ester. Since CaCO₃ is dissolved during the extraction process, it results in the disappearance of peak 6 in the FTIR spectra of recovered RM-PVC samples. However, since peak 3 remains in all the spectra of recovered samples, it confirms that only CaCO₃ was dissolved during MAE but not the organic phthalic ester. All IR spectra collected at different extraction times for recovered PVC samples remain consistent with this analysis. The thermal properties of the recovered RM-PVC samples were characterized using TGA. The TGA and the derivative thermogravimetry (DTG) plots of fresh RM-PVC and the recovered RM-PVC collected at various intervals are shown in Fig. 6(c). The degradation initiation temperature (T_i) and the end degradation temperature (T_{end}) were consistent for all samples. The small changes in the peak degradation temperatures (T_{peak}) in Fig. 6(d) are probably due to the removal of inorganic content (such as CaCO₃, metal oxides) during extraction. A reduction in the wt.% (29 wt% to ~7 wt%) of residue left after complete degradation at 800 °C is also due to removal of CaCO₃.

3.4. MAE for real-life waste extension cords

All the five WEC-cables were made of PVC similar to RM-PVC. High

Chlorine concentrations (Table 1) were also confirmed from the comparison of ATR-FTIR spectra (Fig. S1).

The optimal extraction conditions for PVC materials (210 °C for 60 min, 100 mg sample, 10 ml 30 wt% citric acid) obtained from ML was applied to the WEC-cable, and the concentrations of Pb were measured using ICP-OES and were reported as 1970.33 ± 76.26 ppm, 5383.33 ± 254.28 ppm, 2905.5 ± 183.99 ppm, 20713.33 ± 268.23 ppm, 10719.17 ± 272.42 ppm for WEC 1-cable, WEC 2-cable, WEC 3-cable, WEC 4-cable and WEC 5-cable, respectively (see Fig. 7(a)). As the optimal conditions predicted from machine learning can extract 100% of the toxic metals Pb, Cr and Cd, the Pb concentration obtained under these conditions should be referred to as the original metal content in the WEC-cables. The Pb concentrations in the WEC-cables were much higher than the RoHS limit (1000 ppm). Meanwhile, for the WEC-board and socket samples, the heavy metal contents were tested under the limit. The weight recovery of plastic was more than 50 wt% in all the cases (see Fig. 7(a)). To confirm the polymer quality after the extraction, the FTIR-ATR and TGA curves are presented in Fig. 7(b-d). The recovered plastics were consistent with the recovered RM-PVC in terms of thermal (Fig. 6(a)) and chemical properties (Fig. 6(b)).

4. Conclusion

In this work, we demonstrated that a weak citric acid with concentration of 30 wt% is suitable for the complete extraction of major toxic metals (Pb, Cd, Cr) at an optimized MAE condition of 210 °C, extraction time of 1 h and liquid/solid ratio of 100 mL g⁻¹ in one pot. In addition to the extraction of toxic metals, the recovery of plastics with yields of more than 50 wt% of the feedstock was also achieved. Machine learning based optimization reduced the need for experimental optimization and provided accurate predictions. These optimized extraction conditions are also applicable for the determination of other metals in waste extension cord cables. In the future, more machine learning based process optimization can be performed, including at the microfluidic level to save time, energy and follow kinetics, (Maurice et al. 2020, Maurice et al. 2022) which may have a significant impact on the process design, development speed and the optimization of such processes, especially to further reduce the liquid/solid ratio. Such sustainable technology to recover clean plastic from the contaminated plastic stream will greatly improve the goal of achieving a circular economy model in the future.

Author contribute statement

Chunmiao Jia: Conceptualization, performed experimental investigations; data collection and together with all other authors performed data interpretation; Writing original draft and revising. Pallab Das: Writing – review & editing. Qiang Zeng: Programming, Calculation Methodology. Jean-Christophe P.Gabriel: Writing – review & editing. Dalton Chor Yong Tay: Writing – review & editing. Jong-Min Lee: Supervision and together with JCG Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.134878>.

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