УНИВЕРЗИТЕТ У БАЊОЈ ЛУЦИ
UNIVERSITY OF BANJA LUKA
ТЕХНОЛОШКИ ФАКУЛТЕТ
FACULTY OF TECHNOLOGY

PROCEEDINGS

OCTOBER 21-22, 2022

ACADEMY OF SCIENCES AND ARTS
OF THE REPUBLIC OF SRPSKA,
BANJA LUKA, REPUBLIC OF SRPSKA, B&H

INTERNATIONAL SCIENTIFIC CONFERENCE

XIV CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA

XIV CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA

BOOK OF PROCEEDINGS

Publisher:
University in Banjaluka, Faculty of Technology

Editorial board:
Borislav Malinović, PhD, dean

Design and computer processing
Pero Sailović, PhD
MSc Marina Rakanović
MSc Đorđe Vujčić

CIP - Каталогизација у публикацији
Народна и универзитетска библиотека
Републике Српске, Бања Лука

66(082)
661:663/664(082)
502(082)

CONFERENCE of Chemists, Technologists and Environmentalists of Republic of Srpska (14 ; 2023)
[Book of proceedings] : international scientific conference / XIV Conference of Chemists, Technologists and Environmentalists of Republic of Srpska ; [editorial board Borislav Malinović]. - Banja Luka : University in Banjaluka, Faculty of Technology, 2023 ([S.l : s.n.]). - 313 стр. ; 24 cm

Библиографија уз сваки рад.

ISBN 978-99938-54-98-2

COBISS.RS-ID 137637377

NOTE:

The authors have full responsibility for the originality and content of thier own papers

УНИВЕРЗИТЕТ У БАЊОЈ ЛУЦИ
UNIVERSITY OF BANJA LUKA
ТЕХНОЛОШКИ ФАКУЛТЕТ
FACULTY OF TECHNOLOGY

International scientific conference

"XIV CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA"

under the auspices of

MINISTRY OF SCIENTIFIC AND TECHNOLOGICAL DEVELOPMENT, HIGHER EDUCATION AND INFORMATION SOCIETY

MINISTRY OF AGRICULTURE, FORESTRY AND WATER MANAGEMENT

ACADEMY OF SCIENCES AND ARTS OF THE REPUBLICA OF SRPSKA

Original scientific article

UTILIZATION OF CONSTRUCTION MATERIAL AND UNSATURATED RESIN FROM WASTE PET AS A STABILIZER FOR DESORBED METAL ION Pb^{2+}

Nataša Knežević[1], Jovana Bošnjaković[2], Aleksandar Jovanović[3], Mladen Bugarčić[3], Srećko Manasijević[2], Aleksandar Marinković[1]

[1]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia
[2]Research and Development Institute Lola L.T.D., Kneza Višeslava 70A, 11030 Belgrade, Serbia
[3]Institute for Technology of Nuclear and Other Raw Materials, Bulevar Franše d'Eperea 86, 11000 Belgrade, Serbia

Abstract

Wastewater management covers various techniques developed to provide purified water that would do minimum harm to the environment. Applying adsorption leaves a saturated adsorbent that should be regenerated or stabilized so it can't release pollutants into the environment. Lead, one of the most toxic pollutants, can be efficiently removed utilizing the adsorption process. After the consecutive adsorption and desorption processes, the lead must be processed to significantly reduce and prevent the risk to human health and environmental pollution. As one of the most efficient technologies for treating this toxic pollutant, stabilization has been tested by converting a desorbed lead to its salt lead-phthalate (LP). Obtained LP is used as a component in the production of construction materials and composites with unsaturated polyester resins (UPR). A standard leaching test (Toxicity Characteristic Leaching Procedure - TCLP) was performed to determine the toxicity of the waste material used as an additive. The concentration of leached lead from the construction material with the addition of $Ca(OH)_2$ can be as high as 54 mg/L, which significantly exceeds the permitted limits. After adding cement, lead concentration is lower - 13 mg/L. The acquired results from the sample with UPR show that the concentration of released lead is as low as 0.01 mg/L. Such results indicate complete crosslinking of the UPR and strong binding of the lead ions. Applying the S/S technique together with the utilization of UPR would be an environmentally friendly operation and easily applicable procedure for stabilizing Pb^{2+}.

Keywords: lead, construction materials, (re)valorization of waste material, TCLP, resin composites.

Introduction

The removal of pollutants from wastewater, such as heavy metals, is attracting a lot of attention from scientists because of their negative impact on the environment and human health (Schwarzenbach et al., 2010). The most frequently present heavy metals and metalloids in wastewater are mercury, cadmium, lead, chromium, zinc, copper, nickel, cobalt, arsenic, antimony, etc. Their toxicity, persistence, high prevalence, and mobility are some of the obstacles that can be overcome by stabilization/solidification (S/S) technology (Yaashikaa et al., 2021). The stabilization process is used as the final step in the treatment of hazardous waste before it is landfilled. This chemically stabilizes and physically modifies the waste, in this case, desorbed lead, into a low-permeability solid matrix. In addition to waste disposal, the quality of the obtained composites is easier to handle and transport (Wiles, 1987).

The subject of this study is the stabilization of desorbed lead metal in the form of a very stable lead-phthalate salt ($C_8H_4O_4Pb$) (Stewart et al., 1947; Liming He et al., 2019) by adding calcium hydroxide ($Ca(OH)_2$), cement, and unsaturated polyester resins synthesized from the products of catalytic depolymerization of PET more than bifunctional alcohols (diol component) and maleic anhydride (MA) (Rusmirovic, 2016; Knežević et al., 2022). The possibility of applying the desorbed pollutant as an addition to construction material and polymer matrixes was tested by the standard toxicity characteristic leaching procedure (TCLP) (USEPA, 1990).
The aim of the research is the simultaneous disposal of waste material (desorbed lead) (Moon, 2022) which acquires a useful value, first in saving natural resources for the production of building materials and as a filler when using the newly created UPR composites for the production of floors in vehicles. As a novelty, the TCLP results obtained indicate an environmentally acceptable and health-safe disposal of desorbed metals by a composite UPR stabilization process.

Materials and Methods

1. Materials

Construction material samples were made in the form of a cube with dimensions of 25x65x135 mm by mixing $Ca(OH)_2$ (Carmeuse, "Jelen Do" a.d., Serbia) and portland cement ("Lafarge", Beocin, Serbia) with the addition of sand ("Tr Gravel", Serbia), distilled water and synthesized lead-phthalate salts (as a substitute for TOCell with bound lead ions). The resin-based composites were homogenized by mixing UPR, methyl ethyl ketone peroxide (MEKP, ″Sigma-Aldrich″, Germany) as the initiator and cobalt octoate (Co-oct, ″Sigma-Aldrich″, Germany,) as the accelerator with the addition of the recycling component, salt lead-phthalate.
Leaching fluids were prepared using glacial acetic acid (CH_3COOH, ″Fluka AG″, Switzerland) and 1N sodium hydroxide (NaOH, ″Lachema ″, Czech,) with the addition of deionized water.

2. Methods

By mixing $Ca(OH)_2$/cement, lead-phthalate, sand, and water in a ratio of 2:1:8:2, building material samples were made and thermostated for 7 days at a temperature of 24 °C. UPR-based composites were prepared by the emulsion mixing method by dispersing lead-phthalate in the UPR matrix. The created molds were cross-linked using MEKP (3 wt.%) as an initiator and Co-oct (3 wt.%) as the accelerator in standard polytetrafluoroethylene molds for uniaxial tensile tests (ASTM D882 test standard dimension 60x10x4 mm with narrowed neck area – 15x4x4 mm) and flammability measurements.
The leaching experiment (Leaching experiment - Toxicity Characteristic (TCLP)) was performed in order to confirm the disposal of the desorbed lead after adsorption-desorption cycles (Moon, 2022). One of the reasons for applying the solidification/stabilization method is to reduce the amount of hazardous waste that is disposed of in landfills, as it converts potentially hazardous waste into non-hazardous waste and recycles it while meeting the maximum allowable concentration after the leaching test. It is a standard batch leaching test developed by the US EPA (Method 1311) for waste classification (USEPA, 1990).
The solution used for the toxicity test was made up of 0.300 mL CH_3COOH and 3.500 mL 1N NaOH with the addition of deionized water to a normal beaker volume of 50 mL. The pH value of the obtained solution was 4.75. 25 g of the sample was placed in the extraction vessel and 50 mL of the prepared solution was added. The suspension was mixed on a rotary extractor for 1 day (24 h). After extraction, the solutions were filtered and the resulting filtrate was used to determine the metal concentration (As, Se, Pb, Cr, Cd, Ba) using the ICP-OES technique. As pH values affect the content of heavy metals and their leaching, increased metal leaching is expected in an acidic environment (Brunauer et al., 1938).

Material characterization

Fourier transforms infrared (FTIR) spectra were recorded in absorbance mode with a Nicolet™ iS™ 10 FT-IR Spectrometer (ThermoFisher SCIENTIFIC) equipped with Smart iTR™ Attenuated Total Reflectance (ATR) Sampling accessories.

Results and discussion

1. FTIR analysis

Fourier transform infrared spectra (FTIR) was used to identify the functional groups present in the newly formed building material and their changes after the extraction of heavy metals. Figure 1 shows the FTIR spectrum of the cement/lead-phthalate composite before and after the leaching experiment.

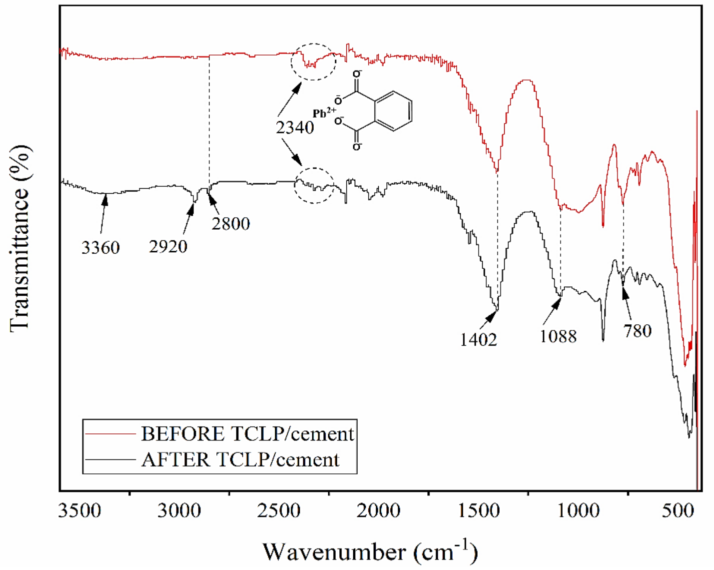

Figure 1. FTIR spectrum of cement/lead-phthalate sample

When examining the FTIR spectra of complexes –OH absorption bands of aqua ligands present at 3360 cm^{-1} correspond to the asymmetric and symmetric stretching vibration of water molecules. Small peaks at 2920 cm^{-1} and 2800 cm^{-1} originate from C-H stretching vibrations in the aromatic methoxy groups and the methyl and methylene groups of the side chain. The presence of lead in the sample before TCLP indicates a peak at 2340 cm^{-1} whose intensity decreased after the removal of heavy metals. The band at 1402 cm^{-1} can be attributed to the C–H bending of the methylene group. The intensity change was recorded at 1088 cm^{-1}, a characteristic peak for valence vibrations of C-O groups in carboxyl groups. The reduced intensity of the band at the wavelength of 780 cm^{-1} indicates the release of heavy metals after the completion of the leaching test (Dursun et al., 2009).

2. Production and testing of construction materials

The concentration of leached heavy metal ions was determined by optical emission spectrometry with inductively coupled plasma - ICP-OES (Thermo ScientificTM iCAP 7200 system).

By using glacial acetic acid as an agent in the leaching experiment, it was determined that significantly higher concentrations of lead ions are released from the analyzed samples with $Ca(OH)_2$, which is considered a health-unsafe method of lead-phthalate stabilization. Low metal concentrations after treating the sample with cement can be attributed to better stability of the crystal structure and lower solubility of cement in the prepared TCLP solution. Of all the results of the TCLP test as the main criterion for the manipulation of the generated waste, the cross-linking of heavy metal with a polymer matrix (UPR), indicate that lead can be safely disposed of as an environmentally acceptable material and the obtained composites can be further used for industrial purposes. The results of the leaching test of the samples (Figure 2) are shown in Table 1.

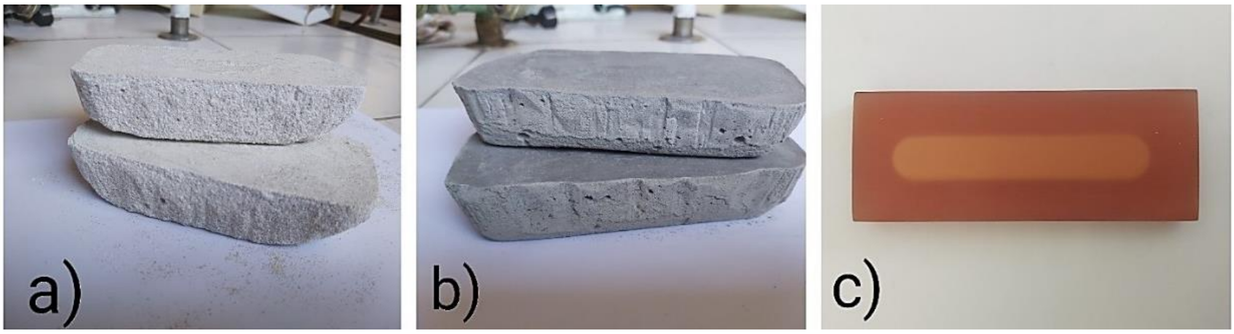

Figure 2. Laboratory samples for testing the release of heavy metals: a) with $Ca(OH)_2$, b) with cement, c) with UPR

Table 1. Concentrations of released metals from formed composites

Element	The concentration of elements after leaching, mg L^{-1}			Limit
	$Ca(OH)_2$	Cement	UPR	
Pb	54	13	0.1	5.0
As	< 0.02	< 0.02	Not Detected*	5.0
Se	< 0.02	< 0.02	Not Detected	1.0
Cr	< 0.01	< 0.01	Not Detected	5.0
Cd	< 0.005	< 0.005	Not Detected	1.0
Ba	0.19	0.22	0.002	100

*Not Detected (< 0.001 mg L^{-1})

The results of the TCLP test show that the leaching of Pb^{2+} ions (54 mg L^{-1}) with the addition of $Ca(OH)_2$ is far greater than the maximum allowed value, which is close to 5 mg L^{-1}, according to national regulations (U. S. EPA, 1992). A drastically lower degree of leaching of desorbed metal (13 mg L^{-1}) was recorded in materials with the addition of cement as a stronger binding agent. The lowest level of leaching of lead ions occurs in the composite made with unsaturated polyester resin and lead-phthalate (0.1 mg L^{-1}). The results obtained by the leaching of UPR composites give the possibility of using a stabilized pollutant for the construction of trains, floors in warehouses, buildings, etc., with improved non-combustible properties and proof of eco-safety. In this way, a process has been developed to remove polluting substances without any additional pollution.

Conclusion

This study presents the results of the immobilization procedure of previously desorbed lead using building materials and resins made from waste PET. The results of the stabilization test showed that the most effective use of unsaturated polyester resins as a matrix for the stabilization of lead-phthalate salts, which meets the regulations on hazardous waste disposal and environmental protection. While the stabilizer $Ca(OH)_2$ was the least effective.

FTIR spectroscopy used to characterize the produced modules with $Ca(OH)_2$ and cement before and after the leaching test shows the changes occurring in the structure of the synthesized composites. The presence of lead in the sample before TCLP indicates a peak at 2340 cm^{-1}, the intensity of which decreased after the removal of heavy metals, which further confirms the effectiveness of the applied stabilization method.

The presented study is part of the contemporary trend related to polemics about energy or other methods of exploitation of waste material, i.e. hazardous waste, to achieve economic benefits, i.e.

marketable products, while satisfying the current legislation. The proposed technology must be a good achievement in the treatment of hazardous waste that produces non-hazardous stabilized materials. The developed methodology fulfills the principles of waste management, material recycling, resource conservation, and environmental protection.

Acknowledgments: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract Nos.., 451-03-1270/2022-14/2685, 451-03-68/2022-14/200066, 451-03-68/2022-14/200023, 451-03-68/2022-14/200135).

References

Yaashikaa, P. R., Senthil Kumar, P., Saravanan, A. & Dai-Viet N. Vo. (2021). Advances in biosorbents for removal of environmental pollutants: A review on pretreatment, removal mechanism and future outlook. *Journal of Hazardous Materials*, *420*, 126596 https://doi.org/10.1016/j.jhazmat.2021.126596

Wiles, C. C. (1987). A review of solidification/stabilization technology. *Journal of Hazardous Materials, 14*, 5–27.

Stewart, A., Pitrot, A. R., Leonard, M. & Kebrich, L. M. (1947). Complex salts are containing lead phthalate and lead salts of aliphatic acids. *United States Patent Office*, 2, 415,917.

He, L., Zhou, J., Dai, S. & Ma, Z. (2019). Influence of Combustion Modifiers on the Cure Kinetics of Glycidyl Azide Polymer Based Propellant-Evaluated through Rheo-Kinetic Approach. *Polymers*, *11*, 637. https://doi.org/10.3390/polym11040637

Rusmirovic, J. (2016). *Dynamic-mechanical and thermal properties of composites based on unsaturated polyester resins and modified silicon-dioxide and cellulose nanoparticles*, (Doctoral dissertation). University of Belgrade, Faculty of Technology and Metallurgy, Belgrade.

USEPA. (1990). Toxicity Characterization Leaching Procedure (TCLP), EPA Method 1311. USEPA, Washington, DC, USA.

Brunauer, S., Emmett, P. H. & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American chemical society*, *60*(2), 309–319. https://doi.org/10.1021/ja01269a023

Dursun, A. K., Ibrahim, U. & Gokce, S. (2009). Bis(N, N-diethylnicotinamide) p-chlorobenzoate complexes of Ni(II), Zn(II) and Cd(II). *Journal of Thermal Analysis and Calorimetry*, *95*(1), 247–251.

USEPA (US Environmental Protection Agency). (1992). Toxicity Characteristic Leaching Procedure. Method 1311, Rev.0. In SW-846: test methods for evaluating solid waste, physical/chemical methods. Washington, DC: Office of Solid Waste.

Schwarzenbach, R. P., Egli, T., Hofstetter, T. B., Von Gunten, U. & Wehrli, B. (2010). Global Water Pollution and Human Health. *Annu. Rev. Environ. Resour.*, *35*, 109–136. https://doi.org/10.1146/annurev-environ-100809-125342

Knežević, N., Jovanović, A., Bošnjaković, J., Milošević, M., Rančić, M., Marinković, A., Gržetić, J. & Gamoudi, H. (2022). Fire-resistant composites based on acrylic-functionalized lignin and polyester resin obtained from waste poly(ethylene terephthalate). *Scientific Technical Review*, *72*(2), 32–37. https://doi.org/10.5937/str2202032K

Moon, D. H. & Koutsospyros. A. (2022). A. Stabilization of Lead-Contaminated Mine Soil Using Natural Waste Materials. *Agriculture*, *12*, 367. https://doi.org/10.3390/agriculture12030367