PHYSICAL CHEMISTRY 2022

16th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume I

September 26-30, 2022
Belgrade, Serbia

Title: PHYSICAL CHEMISTRY 2022, 16th International Conference on Fundamental and Applied Aspects of Physical Chemistry (Proceedings) **ISBN** 978-86-82475-41-5
Volume I: ISBN 978-86-82475-42-2
Editors: Željko Čupić and Slobodan Anić
Published by: Society of Physical Chemists of Serbia, Studentski Trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: ″Jovan″, <Printing and Publishing Company, Ilije Đuričića 19, Belgrade, 200 Copies
Number of pages: 6+320, Format A4, printing finished in December 2022.

Text and Layout: ″Jovan″

200 - *Copy printing*

CONTENT

PHYSICAL CHEMISTRY 2022

16th International Conference on Fundamental and Applied Aspects of Physical Chemistry

Organized by

The Society of Physical Chemists of Serbia

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

Boreskov Institute of Catalysis Siberian Branch of Russian Academy of Sciences

and

University of Belgrade, Serbia:

Faculty of Physical Chemistry
Institute of Chemistry, Technology and Metallurgy
Vinča Institute of Nuclear Sciences
Faculty of Pharmacy

and

Institute of General and Physical Chemistry, Belgrade, Serbia

International Organizing Committee

Chairman:	S. Anić (Serbia)
Vice-chairman:	M. Gabrovska (Bulgaria) A. A. Vedyagin (Russia) S. N. Blagojević (Serbia)
Members:	N. Cvjetićanin (Serbia), S. M. Blagojević (Serbia), M. Daković (Serbia), J. Dimitrić-Marković (Serbia), T. Grozdić (Serbia), Lj. Ignjatović (Serbia), A. Ivanović-Šašić (Serbia), D. Jovanović (Serbia), N. Jović-Jovičić (Serbia), M. Kuzmanović (Serbia), S. Maćešić (Serbia), D. Marković (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Pejić (Serbia), M. Petković (Serbia), A. Popović Bijelić (Serbia), B. Simonović (Serbia), B. Šljukić (Serbia), G. Tasić (Serbia), S. Veličković (Serbia), N. Vukelić (Serbia),

International Scientific Committee

Chairman:	Ž. Čupić (Serbia)
Vice-chairman:	V. Bukhtiyarov (Russia) S. Todorova (Bulgaria) B. Adnađević (Serbia)
Members:	S. Anić (Serbia), A. Antić-Jovanović (Serbia), A. Azizoğlu (Turky), R. Cervellati (Italy), A. Clayton (Australia), A. Cristina Silva (Portugal) G. Ćirić-Marjanović (Serbia), V. Dondur (Serbia), R. Faria (Brasil), M. Fronczak (Poland), I. Grinvald (Russia), P. Humpolíček (Czech), M. Jeremić (Serbia), I. Kiss (USA), E. Kiš (Serbia), A.V. Knyazev (Russia), Lj. Kolar-Anić (Serbia), T. Kowalska (Poland), G. Kyzas (Greece), G. Lente (Hungary), Z. Marković (Serbia), S. Mentus (Serbia), K. Novaković (UK), N. Ostrovski (Serbia), V. Parmon (Russia), J. Pérez-Mercader (USA) Z. Petkova Cherkezova-Zheleva (Bulgary), M. Plavšić (Serbia), J. Savović (Serbia), G. Schmitz (Belgium), I. Schreiber (Czech), L. Schreiberova (Czech), D. Stanisavljev (Serbia), N. Stepanov (Russia), Zs. Szakacs (Romania), Z. Šaponjić (Serbia), Á. Tóth (Hungary), M. Trtica (Serbia), H. Varela (Brasil), V. Vasić (Serbia), Nadezda Vasilyeva (Russia), D. Veselinović (Serbia), V. Vukojević (Sweden), A. De Wit (Belgium)

Local Executive Committee

Chairman:	S. N. Blagojević
Vice-chairman:	A. Ivanović-Šašić
Members:	M. Ajduković, I. N. Bubanja, D. Dimić, J. Dostanić, D. Drakulić, S. Jovanović, Z. Jovanović, D. Lončarević, J. Krstić, B. Marković, J. Maksimović, S. Marinović, D. Milenković, T. Mudrinić, M. Pagnacco, N. Potkonjak, B. Stanković, I. Stefanović, A. Todorović, M. Vasić, F. Veljković, M. Pejčić, G. Stevanović, H.Šalipur.K. Milošević, S. Pavlović, V. Kostić, B. Milovanović.

SPONSORS

Ministry of Education, Science and Technological Development of the Republic Serbia

Institute of General and Physical Chemistry, Belgrade

University of Belgrade, Institute of Chemistry, Technology and Metallurgy, National Institute of Republic of Serbia, Belgrade

University of Belgrade, Faculty of Physical Chemistry, Belgrade

REMOVAL EFFICIENCY OF Pb(II), Zn(II) AND Cu(II) IN MONO- AND MULTIMETAL SYSTEMS BY ALKALI TREATED APRICOT SHELLS BIOSORBENT

T. Šoštarić[1], J. Milojković[1], J. Avdalović[2], N. Lugonja[2], V. Adamović[1], A. Antanasković[1] and Z. Lopičić[1]

[1]*Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Franchet d'Esperey St. 86, Belgrade, Serbia*
[2]*University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia. (jelena.avdalovic@ihtm.bg.ac.rs)*

ABSTRACT
The mutual interaction of metal ions (lead, zinc and copper) on removal efficiency in binary and ternary systems, by biosorbent based on alkali treated apricot shells (*Prunus armeniaca* L.) was examined. The evaluation was done in batch system at two metals concentrations: 0.2 and 0.5mmol/dm^3. Tested biosorbent exhibited preferential uptake of lead in a multimetal systems. It is evident that mutual inhibition exists in all multimetal systems, but systems containing lead ex-hibited extreme inhibition toward copper and zinc ions. Process of sorption depends not only on specific chemistry of each metal, their affinity toward binding sites and the type of metal binding onto biosorbent, but also on sorbent chemical and morphological characteristics. In multimetal systems, tested sorbent showed preferential sorption orders: Pb (II)>Cu (II)>Zn (II).

INTRODUCTION
Research focusing on biosorption offers a stepping stone for developing a whole new environmental technology aiming to the removal or the recovery of various pollutants from water systems. It's not surprising that many papers have been published about this topic in the past decades [1,2]. Although, biosorption is a technology that has been seen with great potential for wastewater treatment, it has to be commercialized [3]. The number of published papers for single metal removal by biosorption is many times higher compared to multi-metal removal [4]. Considering that wastewater contains a mixture of metal ions, it is necessary to study and understand multicomponent sorption under competitive conditions by using low-cost biosorbents [5]. It is well known that when several different metal ions are in solution a few possible interactions can be expected: synergism (resulting in an increase in sorption efficiency), antagonism (resulting in a decrease in sorption of individual ions from the mixture) or no interactions [6]. This work focuses on the removal efficiency of Pb(II), Zn(II) and Cu(II) in mono- and multimetal systems by alkali treated apricot shells.

METHODS
The apricot stones were obtained from Juice Factory "Vino Župa" Aleksandrovac. Seeds were manually separated from shells and for further experiments only apricot shells were used. Dried shells were grounded (KHD Humbolt Wedag AG) at fraction less than 1.0 mm. Furthermore, modification was performed by mixing of 50 g of dried/grinded/sieved biomass sample with 1.0 dm^3 of 1.0 mol/dm^3 NaOH on a magnetic stirrer (at 250 rpm) for 3h. Afterwards, the suspension was filtered and residue was repeatedly washed with distilled water until stable pH value was observed. Subsequently, it was dried at 50°C until reaching a constant mass. It was labeled as SHM.

The mutual interaction of the examined metals on the removal efficiency by SHM was investigated in solutions of binary and ternary mixtures of metals. The following binary solutions of metal ions were tested: Pb(II) and Cu(II); Pb(II) and Zn(II); Zn(II) and Cu(II), at each metal concentration of 0.2

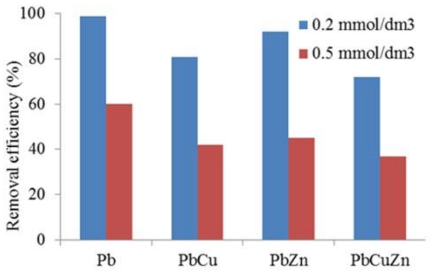
and 0.5 mmol/dm^3. At the same concentrations, the ternary solution of metal ions: Pb(II), Cu(II) and Zn(II) were tested, too. The experiments were performed at sorbent concentration of 2.0 g/dm^3, the initial pH value 5.0 (adjusted by 0.1 mol/dm^3 HNO_3 or KOH solution). The suspensions were stirred on orbital shaker at 250 rpm for 120 minutes. After this time the suspensions were filtered and the filtrates were analyzed by using atomic adsorption spectrophotometer (Perkin Elmer AAnalyst 300). Stock solutions were prepared by dissolving precise amount of $Cu(NO_3)_2 \times 3H_2O$; $ZnSO_4 \times 7H_2O$ and $Pb(NO_3)_2$ (p.a. grade) in distilled water. Metal solutions of specific concentrations were prepared by dilution of the stock solution. Using pH meter (SensIon MM340), pH value was adjusted to the required values with 0.1 M HNO_3 and 0.1 M NaOH solutions.
The biosorption efficiency of SHM was calculated using the following equation:

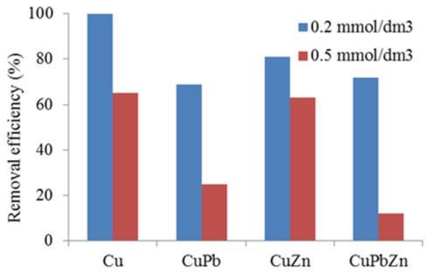
$$R\ (\%) = \frac{(C_i - C_{eq})x100}{C_i}$$

where: C_i and C_{eq} (mg/dm^3) are the initial and final equilibrium metal ion concentration, respectively.

RESULTS AND DISCUSSION
Previous study confirmed that alkaline treatment of apricot shells had successfully improved adsorption capacity by 154, 61 and 90% for Cu(II), Zn(II) and Pb(II), respectively [7]. In order to determine the efficiency of SHM in complex systems simulating the real effluents, biosorption experiments in binary and ternary systems, with Cu(II), Zn(II) and Pb(II) were investigated and the results of testing are presented in Figure 1. As can be seen, sorption efficiency of lead ions in a mixture with copper ions decreases by 18 % at both concentrations, while with zinc ions decreases by 7% and 15% at initial concentration 0.2 and 0.5 mmol/dm^3, in comparison to the sorption efficiency from solution which contains only lead ions. However, the sorption efficiency of lead ions in the ternary system decreases more by 28 and 23%, at same initial concentrations. Sorption efficiency of SHM toward copper ions in a mixture with lead ions decreases even more by 30% and 40% and with zinc ions by 19% and 2% at same initial concentrations, in comparison to the sorption efficiency from solutions where copper ions were individually present. The sorption efficiency of copper ions in the ternary system decreases by 28% and 53%, at same initial concentrations. However, SHM sorption efficiency of zinc ions in the mixture with lead ions decreases drastically by 63% and 46% and with copper ions by 60% and 47% at initial concentration 0.2 and 0.5 mmol/dm^3 in comparison to the sorption efficiency from the solution where zinc ions were individually present. The sorption efficiency of zinc ions in the ternary system decreases by 83% and 49% at same initial concentrations. It is evident that the efficiency of heavy metals removal from solutions containing individual ions is significantly higher in relation to the efficiency of metals removal from multimetal solutions. Evidently, there is antagonism between ions as a consequence of competition for available active sites on the SHM surface. Suppression of sorption by other metal ions is most pronounced with lead ions and least pronounced with zinc ions present in solution. The complexity of the process is reflected in interaction between sorbent and metals, which is related to sorbent chemical and morphological characteristics and to the chemical and physical properties of metals. According to authors previous research alkaline treatment causes an increase in porosity (by 20%), total pore volume (by 24%), specific surface area (by 33%) and average pore diameter (by 20%) in comparison to untreated apricot shells [7,8]. Metal ion characteristic parameters: ionic radius, electronegativity, hydrated radius, covalent index, hydration enthalpy, charge-to-radius ratio are listed in Table 1/Figure 1. Metals with higher electronegativity adsorb more readily because metal ions with larger ionic radius have lower charge density and lower electrostatic attraction that limits the interaction of the metal ions with the adsorption sites [9]. Also, the higher the electronegativity, the stronger the bond that is established between metal ions and oxygen atoms from functional groups on the surface of the SHM and experimental results showed that SHM affinity followed the order Pb(II)>Cu(II)>Zn(II) which is

consistent with the electronegativity values. Hillel [10] explained that the smaller the ionic radius and the higher the valence, the closer and stronger the ion is adsorbed. However, on the other hand, the higher the hydration of the ion, the further it is from the surface of the adsorbent and the weaker the adsorption. Since the attraction of water molecules around ions depends on the charge density of ions, smaller ions will attract more water molecules leading to an inverse relationship between the ionic radius and the hydrated ionic radius. The ionic radius grows in the following order: Cu(II)>Zn(II)>Pb(II), while the radius hydrated ions decrease in the following order: Zn(II)>Cu(II)>Pb(II) (Table 1). With an increase of the ionic size, the absolute value of enthalpy of hydration decreases. According to the values of enthalpy of hydration Pb(II) ions will have greater accessibility to the SHM surface. The results of these experiments showed that in multimetal systems, tested sorbent exhibited preferential sorption order: Pb(II)>Cu(II)>Zn(II). Similar results were obtained by Milojković [11] examining the removal of Pb(II), Cu(II), Cd(II), Ni(II), and Zn(II) ions from aqueous solution by application of the *Miriophylum spicatum* compost. According to that study the biosorbent showed the highest affinity for Pb(II) and Cu(II), while the biosorption capacity decreased in the order Pb(II)>Cu(II)>Cd(II)>Zn(II)>Ni(II), at pH 5.0.





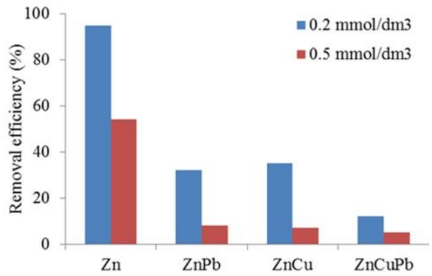


Table 1 Metal ion characteristic parameters and their trends

Metal	**Ionic radius (pm) [12]**	**Hydrated radius (pm) [13]**	**Electronegativity (Pauling) [12]**	**Covalent index, Ci = X_m^2 (r + 0.85) (pm)**	**Hydration enthalpy (kJ/mol) [12]**
Pb(II)	120	401	2.33	1,113	−1,480
Cu(II)	73	419	1.9	578	−2,100
Zn(II)	74	430	1.65	433	−2,044
Ionic radius (pm)			Pb(II) > Zn(II) > Cu(II)		
Electronegativity (Pauling)			Pb(II) > Cu(II) >Zn(II)		
Hydrated radius (pm)			Zn(II) > Cu(II)> Pb(II)		
Covalent index (pm)			Pb(II) > Cu(II) > Zn(II)		
Hydration enthalpy (kJ/mol)			Pb(II) > Zn(II) > Cu(II)		
Charge-to-radius ratio (electrostatics effect on ionic bonding)			Cu(II) > Zn(II) > Pb(II)		

Figure 1. SHM removal efficiency of lead, copper and zinc ions in binary and ternary systems

CONCLUSION

In this study, the application of the biosorbent based on alkali treated apricot shells was tested for removal of Pb(II), Cu(II) and Zn(II) ions from multimetal solution. SHM showed the highest affinity for Pb(II) and the lowest affinity for Zn(II). Antagonism between metal ions as a consequence of competition for available active sites on the SHM surface has been evident. The resulting biosorption efficiency decreased in the order Pb(II)>Cu(II)>Zn(II), at pH 5.0.

Acknowledgment
This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grant no 451-03-68/2022-14/200023 and grant no 451-03-68/2022-14/200026).

REFERENCES

[1] M. Abdulaziz, S. Musayev, Pol J Environ Stud, 26 (2017) 1433–1441.
[2] H. I. Syeda, I. Sultan, K. S. Razavi, P.-S. Yap, J Water Process Eng, 46 (2022) 102446.
[3] M. Fomina, G. M. Gadd, Bioresource Technol, 160 (2014) 3–14.
[4] M. Long, H. Jiang, X. Li, Sci Rep 11 (2021) 11527.
[5] H. E. Reynel-Avila, D. I. Mendoza-Castillo, V. Hernández-Montoya et al., Chapter 5: Multicomponent removal of heavy metals from aqueous solution using low-cost sorbents In: Water Production and Wastewater Treatment Editor: B. Antizar-Ladislao et al., 2010 Nova Science Publishers
[6] D. L. D. Mitić, Uklanjanje teških metala iz vode bosorbentom na bazi *Lagenaria vulgaris*, Univerzitet u Nišu, Prirodno-matematički fakultet. Doktorska disertacija, Niš, 2012.
[7] T. D. Šoštarić, M. S. Petrović, F. T. Pastor, D. R. Lončarević, J. T. Petrović, J. V. Milojković, M. D. Stojanović, J Mol Liq, 259 (2018) 340-349.
[8] T. Šoštarić, M. Petrović, J. Stojanović, M. Marković, J. Avdalović, A. Hosseini-Bandegharaei, Z. Lopičić, Biomass Convers Biorefin (2020) https://doi.org/10.1007/s13399-020-00766-2
[9] M. Minceva, , L. Markovska, V. Meshko, Maced J Chem Chem En, 26 (2) (2007) 125–134.
[10] D. Hillel, Environmental Soil Physics. Academic Press, San Diego, CA, 1998.
[11]J. V. Milojković,, M. D. Stojanović, M. L. Mihajlović, Z. R. Lopičić, M. S. Petrović, T. D. Šoštarić, M. Đ. Ristić, Water Air Soil Poll 225 (2014) 1927.
[12]G. Wulfsberg, Principles of descriptive chemistry. Monterey CA:Brooks/Cole Publishing, 1987.
[13]E. R. Nightingale, J Phys Chem, 63 (1959) 1381–1387.

CIP - Каталогизација у публикацији - Народна библиотека Србије, Београд

544(082)
66.017/.018(082)
502/504(082)

INTERNATIONAL Conference on Fundamental and Applied Aspects of Physical Chemistry (16 ; 2022 ; Beograd)
Physical Chemistry 2022 : proceedings. Vol. 2 / 16th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 26-30, 2022, Belgrade, Serbia ; [editors Željko Čupić and Slobodan Anić]. - Belgrade : Society of Physical Chemists of Serbia, 2022 (Belgrade : Jovan). - VI str., str. 323-640 : ilustr. ; 30 cm

Tiraž 200. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-82475-43-9
ISBN 978-86-82475-41-5 (niz)

a) Физичка хемија - Зборници b) Наука о материјалима - Зборници c) Животна средина - Зборници

COBISS.SR-ID 82228745