ADSORPTION OF Pb^{2+} IONS ON GAMMA IRRADIATED PLUM POMACE BIOCHAR

Đurica Katnić, Marija Kojić, Julijana Tadić, Bojana Vasiljević, Milena Marinović-Cincović, Aleksandar Krstić, Slavica Porobić

Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, P. O. Box 522, 11001 Belgrade, Serbia
e-mail: djurica.katnic@vin.bg.ac.rs

Abstract
Removal of heavy metals is important because of their toxic effects on living organisms and unwanted anthropogenic effects. Biochar is suitable as an adsorbent of heavy metals due to its advantages such as various sources of biomass, a large number of microporous channels and surface functional groups, as well as due to its economic viability. There is no data about the plum pomace biochar usage as adsorbent for lead removal. In this study, the plum pomace biochar modified with gamma irradiation (IrPP) is used for the removal of Pb^{2+} ions from the aqueous solution. The SEM micrographs revealed that surface morphology of plum pomace is suitable for metal adsorption. The results of adsorption kinetics demonstrated that the removal process of Pb^{2+} ions onto IrPP follows a pseudo-second kinetic model, which is confirmed by a better agreement between $q_{e,cal}$=227 mg g^{-1} and $q_{e,exp}$=224 mg g^{-1}. Therefore, based on preliminary research, it can be concluded that IrPP originating from biowaste is a promising, eco-friendly sorbent of heavy metal from wastewater.

Introduction
Due to the uncontrolled release of toxic substances from various industrial facilities into the environment, the problem of environmental pollution has arisen. A large number of scientific researches are directed towards the protection and preservation of the environment, and thus of human health.

Biomass as a natural mixture of hydrocarbons is an excellent precursor for obtaining carbon materials. The use of biomass has significant economic and technical advantages. Waste lignocellulosic biomass is used as a raw material for fuel production, heat energy, as well as for adsorption of heavy metals and organic pollutants. In many countries, waste biomass is disposed of in open landfills, which pollutes the environment instead of being used as an energy source or adsorbent [1,2].

In this work, high temperature pyrolysis was used to convert plum pomace into carbon materials.

Plum occupies a leading position in fruit growing, and is mostly grown in the western part of Serbia. About 80% of the total production of plums is processed into brandy. Extensive production of plums, and then processing of plums in order to obtain brandies, increases the amount of waste biomass that is generated as a by-product of processing. Uncontrolled disposal of pomace can pose a great risk to the environment [3].

In this paper, pyrolysis of plum pomace was performed to obtain carbon material that can be used as an adsorbent of heavy metals. Surface modification of obtain carbon material was done by irradiating the material at the source of Co^{60} gamma radiation to improve the adsorption capacity. Scanning electron microscopy (SEM) was used to analyse the morphology of plum pomace before and after irradiation.

The irradiated plum pomace biochar was tested as adsorption materials to remove Pb^{2+} ions. In order to define kinetics and adsorption process equilibrium, corresponding kinetic models were applied.

Experimental

Plum pomace biochar (PP) is a carbon-rich material derived from the oxygen-limited pyrolysis of plum pomace waste biomass. PP were produced using pyrolysis at 500 °C. Modification od PP was done using gamma irradiation of 50 kGy at the Co^{60} source. The surface morphology of the PP before and after radiation (IrPP) was observed by SEM method.

Adsorption experiments

An estimate of the kinetic adsorption parameters of IrPP was executed in a batch of Pb^{2+} solutions. The IrPP dose of 0.025 g was added to 25 mL aliquot of 250 mg L^{-1} Pb^{2+} solution. The mixtures were shaken at the different times interval (5, 10, 15, 30, 60, 90, 120, 150 and 180 min). The samples were filtered and the residual number of tested metals in filtrates were detected by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES 7400). The adsorption capacity of the Pb^{2+} ions (q_e) were calculated based on the equations (1):

$$q_e(mgg^{-1}) = \frac{(C_o - C_e)V}{m} \quad (1)$$

where C_0 and C_e - the initial and equilibrium concentration (mg L^{-1}), V- the volume of the metal solution (mL) and m-the amount of sorbent (mg).

The adsorption kinetics was simulated with pseudo-first-order and pseudo-second-order models, respectively:

$$ln(q_e - q_t) = lnq_e - k_1 \cdot t \quad (2)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (3)$$

where q_t (mg g^{-1}) is the amounts of Pb^{2+} adsorbed at time, k_1(min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants of pseudo-first and pseudo-second model, respectively.

Results and discussion

The surface morphology of PP and IrPP was examined by SEM analysis. As can be seen in Figure 1, PP shows a smooth surface with a small number of pores and grooves. On the other hand, the presence of pores and the appearance of small cracks on the surface of IrPP are noticed, which is probably a consequence of PP radiation. Petrović et al. [2] concluded that the formation of pores on the surface of biochar can be useful if this material is used as a sorbent of heavy metals from aqueous solutions, because the pores allow easier internal diffusion of metal ions from wastewater.

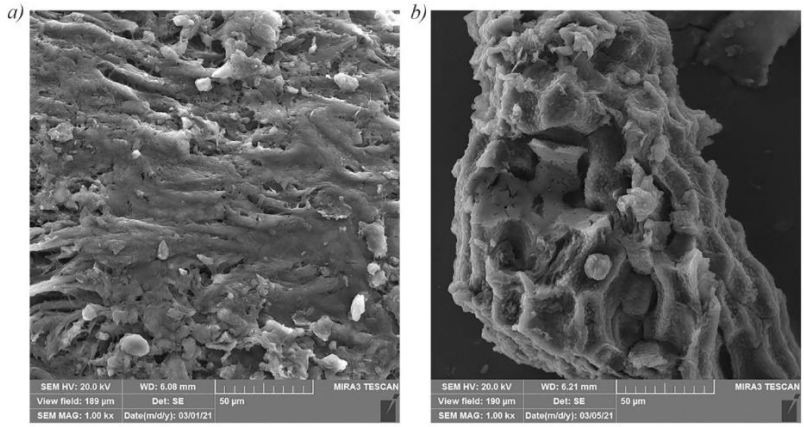

Fig. 1. SEM of PP (a) before and (b) after radiation.

Adsorption kinetics

The adsorption kinetics of Pb^{2+} ions by IrPP were presented in Figure 2 and the kinetics parameters were summarized in Table 1.

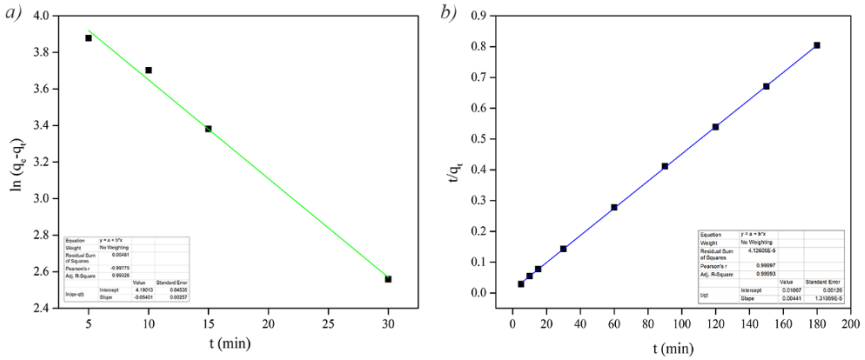

Fig. 2. Pseudo-first-order (a) and pseudo-second-order(a) kinetic adsorption curves of IrPP for Pb^{2+} ions

Although both models described the kinetic data well with all R^2 higher than 0.99, the pseudo-second-order model gave better fits (R^2=0.9999) and compared to pseudo-first-order kinetic model (R^2=0.9933), suggesting that the adsorption of Pb^{2+} by the PP was ascribed to chemical process [4]. Additionally, this was verified with the better agreement of theoretical ($q_{e,cal}$) and experimental results ($q_{e,exp}$) for the pseudo-second model.

Table 1 The kinetic parameters of Pb^{2+} ions adsorption using IrPP

	Contaminant Pb^{2+}
$q_{eq,exp}$ (mg g^{-1})	224
Pseudo-first-order model	
$q_{eq,cal}$ (mg g^{-1})	66
k_1 (min^{-1})	0.124385
R^2	0.9933
Pseudo-second-order model	
$q_{eq,cal}$ (mg g^{-1})	227
k_2 (g mg^{-1} min^{-1})	$8.58 \cdot 10^{-08}$
R^2	0.9999

Conclusion

Based on preliminary research, the SEM analysis demonstrated that radiation significantly changed the structure of the PP. That is, a large number of pores were observed on the surface of PP after radiation, which facilitate the internal diffusion of Pb^{2+} from aqueous solutions. Also, on the basis of kinetic analysis, it was confirmed that Pb^{2+} adsorption is well described by a pseudo-second order kinetic model. These results show that IrPP can be used as a cost-effective sorbent of heavy metals from wastewater.

Acknowledgements

The research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (contract number 451-03-9/2021-14/200017 and 451-03-9/2021-14/200135)

References

[1] C.G. Khoo, M.K. Lam, A.R. Mohamed, K.T. Lee, Environ. Res. 188 (2020) 109828.
[2] J.T. Petrović, M.D. Stojanović, J.V. Milojković, M.S. Petrović, T.D. Soštarić, M.D. Laušević, M.L. Mihajlović, J. Environ. Manage. 182 (2016) 292-300.
[3] Y. Li, H. Yu, L. Liu, H. Yu, J. Hazard. Mater. 420 (2021) 126655.
[4] M. Petrović, Tatjana Šoštarić, Mirjana Stojanović, Jelena Milojković, Marija Mihajlović, Marija Stanojević, Slavka Stanković, J. Taiwan Inst. Chem. Eng. (2015) 1-10.