University of Belgrade
Technical Faculty in Bor and
Mining and Metallurgy Institute Bor

49th International October Conference on Mining and Metallurgy

PROCEEDINGS

Editors:
Nada Štrbac
Ivana Marković
Ljubiša Balanović

IOC 2017
International October Conference

Bor Lake, Serbia
October 18-21, 2017

PROCEEDINGS,

49th INTERNATIONAL OCTOBER CONFERNCE

on Mining and Metallurgy

Editors:

Prof. dr Nada Štrbac

Doc. dr Ivana Marković

Doc. dr Ljubiša Balanović

University of Belgrade, Technical Faculty in Bor

Technical Editor:

M. Sc. Uroš Stamenković

University of Belgrade, Technical Faculty in Bor

Publisher: University of Belgrade, Technical Faculty in Bor

For the publisher: Dean Prof. dr Nada Štrbac

Circulation: 200 copies

Printed by "Happy trend DOO", Zaječar, 2017

ISBN 978-86-6305-066-2

CIP - Каталогизација у публикацији - Народна библиотека Србије, Београд

622(082)
669(082)

INTERNATIONAL October Conference on Mining and Metallurgy (49 ; 2017 ; Bor Lake)
Proceedings / 49th International October Conference on Mining and Metallurgy - IOC 2017,
Bor Lake, Serbia, October 18-21, 2017;
[organized by] University of Belgrade, Technical Faculty Bor and Mining and Metallurgy Institute Bor;
editors Nada Štrbac, Ivana Marković, Ljubiša Balanović. - Bor : University of Belgrade, Technical Faculty,
2017 (Zaječar : Happy trend). - XXIII, 664 str. : ilustr. ; 25 cm

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

ISBN 978-86-6305-066-2

a) Рударство - Зборници b) Металургија - Зборници

COBISS.SR-ID 246349324

Bor Lake, Serbia, October 18-21, 2017

Conference is financially supported by
The Ministry of Education, Science and
Technological Development of the
Republic of Serbia

SCIENTIFIC COMMITTEE

ORGANIZING COMMITTEE

TABLE OF CONTENTS

ENHANCED Cu^{2+} ADSORPTION ABILITY OF GRAPE POMACE HYDROCHAR UPON ALKALI MODIFICATION

Jelena Petrović, Marija Mihajlović, Mirjana Stojanović, Marija Petrović, Marija Kojić, Jelena Milojković

Institute for Technology of Nuclear and Other Mineral Raw Materials, 86 Franchet d'Esperey St., 11000 Belgrade, Serbia

Abstract

Grape pomace hydrochar was evaluated as potential adsorbent of Cu^{2+} from aqueous solution. In order to enhance the adsorption ability, obtained hydrochar was alkali modified using KOH and characterized by Fourier Transform Infrared spectroscopy and Scanning Electron Microscopy. Preliminary tests showed that adsorption capacity of hydrochar increased from 8.0 to 38.2 mg/g after alkali modification. It was found that KOH treatment increased the aromatic and oxygen-containing functional groups on hydrochar surface, which might affect the improvement of the Cu^{2+} removal. The results suggest that KOH-modified hydrochar could be an effective adsorbent of Cu^{2+} from wastewaters.

***Keywords**: Hydrothermal carbonization, grape pomace, copper removal, alkali modification*

1. INTRODUCTION

In recent years, contamination of water by toxic heavy metals caused by spillage of industrial wastewater into watercourses has become a worldwide environmental problem [1,2]. Heavy metal ions in water pose a potential threat to humans and other living organisms due to their accumulation in tissues of various organisms, causing numerous diseases and disorders [2]. For that reason, polluted wastewater must be depurated and returned to water receptors or to land [3,4].

Copper is a widely used material and one of the toxic metals commonly found in industrial effluents. Although it is an essential micro-nutrient, its excessive levels in waters can be detrimental [5]. Therefore, it is necessary to remove copper from contaminated water prior to discharge into water bodies or irrigation.

So far, a numerous techniques, such as coagulation/flocculation, chemical oxidation, membrane filtration, adsorption on activated carbon and electrochemical treatment, have been applied for removal of inorganic pollutants from wastewater. However, many of them are usually expensive, polluting, time consuming and mostly ineffective at low concentrations of contaminants [1,2]. Among these techniques, adsorption is currently considered as a simple, effective, efficient, and economic method for wastewater purification [3]. In recent years, along with traditional material, like activated carbon, different biological materials (e.g. biomass), were considered as potential adsorbents [5,6].

Besides biosorption, development of novel methods for conversion of waste biomass into multifunctional products is on the increase. One of such technologies is hydrothermal carbonization (HTC) [7-9]. This method offers significant advantages relative to other conversion technologies, such as mild reaction conditions and high conversion efficiency of wet biomass load [10]. The resulting product – hydrochar (HC), is hydrophobic, porous, solid material with high carbon and oxygen-containing functional groups (OFGs) (e.g., hydroxyl and carboxylic) content [1,7,9]. These characteristics make hydrochar a convenient low-cost adsorbent of heavy metals from polluted waters [1]. In order to enhance the adsorption capability of hydrochar, it might be required to modify/activate the hydrochar surface [9]. Recently, Regmi et al. (2012) and Sun et al. (2015) have demonstrated that KOH modification significantly enhances the adsorption capacity of hydrochar because it increased OFGs content that interact with metal ions [1,7].

The aim of this research was to investigate the ability of grape pomace hydrochar (GP-HC) to remove copper ions (Cu^{2+}) from aqueous solution. Particular interest of this study was to evaluate the suitability of GP as a precursor for preparation of biosorbent, because this type of biomass is largely available in Serbia. In order to improve adsorption capacity produced hydrochar was alkali modified using 2M KOH solution.

2. EXPERIMENTAL

2.1 Biomass

The used GP was randomly collected from landfill sites, from a test plot Radmilovac. Biomass was air-dried to constant weight and grinded in order to obtain homogeneity of sample. Fraction of 0.5 mm was used in further HTC experiments.

2.2 Hydrochar preparation and activation

Preparation of GP-HC at 220 °C was described in our previous works [2,11]. To make the modified GP-HC (GP-HCA), 5 g of the obtained HC were mixed with 500 mL of 2 M KOH solution for 1 h at room temperature. Obtained GP-HCA was neutralized, rinsed with distilled water, filtered and dried overnight in an oven at 105 °C.

2.3 Chemicals

Copper solutions and standards were prepared using analytical grade copper nitrate salt ($Cu(NO_3)_2$, Sigma-Aldrich). A stock copper nitrate solution (100 mg/L $Cu(NO_3)_2 \times 3H_2O$) was prepared with deionized water.

2.4 Preliminary adsorption test

Removal of Cu^{2+} ions using GP-HC and GP-HCA were performed at batch adsorption test. Adsorbent mass of 0.025 g of each HC was added to 100 mL volumetric flasks containing 50 mL of standard Cu^{2+} solution, and shaken at room temperature for 60 min at 250 rpm. The content of Cu^{2+} ions in the resultant filtrates were measured using Atomic Absorption Spectrophotometer (AAS) (Analytic Jena Spekol 300).

The amounts of metal ion adsorbed on hydrochars in mg/g at equilibrium q_{eq} were calculated using following equation:

$$q_{eq} = \left(\frac{C_0 - C_{eq}}{m} \right) \times V \qquad (1)$$

where V, is the volume of the Cu^{2+} solution (L), m is the amount of adsorbent (GP-HC or GP-HCA) (g); C_0 and C_{eq} are the initial and equilibrium concentrations of the Cu^{2+} ions (mg/L) respectively.

2.5 Scanning electron microscopy

Scanning electron microscopy (SEM) was performed using a JSM-6610 (JEOL Inc., USA) in order to analyze the surface structure of GP-HC and GP-HCA. All samples were coated with gold, placed on the adhesive carbon disc and recorded.

2.6 FTIR spectroscopy

FTIR analysis of GP-HC and GP-HCA was performed in transmission mode using Thermo Scientific Nicolet iS50. The spectra were obtained in the spectral range of 4000-400 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1 Preliminary adsorption test

The obtained results showed (Figure 1) that the GP-HCA displayed enhanced ability for Cu^{2+} removal in relation to non-activated HC. The amount of Cu^{2+} adsorbed by the GP-HC was 8.0 mg/g, whereas for the GP-HCA was 38.2 mg/g. This is in agreement with literature data stating that the alkali modification of HC may increases porosity, surface area and causes the change of surface functional groups of HC [1].

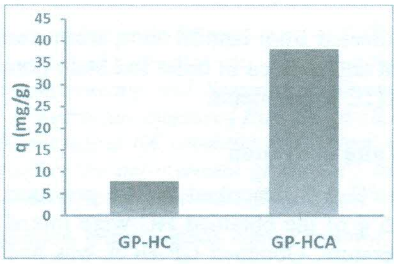

Figure 1 - Cu^{2+} removal using HC and AHC

3.2 Scanning electron microscopy

SEM images of GP-HC and GP-HCA are presented in Figure 2. Figure shows that the surface of the GP-HCA was rougher compared to the GP-HC, presumably because the activation with KOH caused an increase of surface cracks due to the removal of impurities from the partially blocked pores [2].

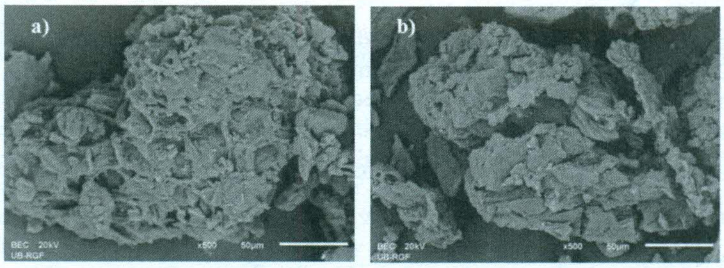

Figure 2 - SEM images of hydrochars before (a) and after (b) alkali modification

3.3 FTIR spectroscopy

FTIR spectrums of GP-HC and GP-HCA before and after alkali modification are presented in Figure 3. As can be seen, after alkali treatment the peaks attributed to O-H and C-O vibrations (3385 cm^{-1}, 1617, 1058 and 1033 cm^{-1}) become more apparent. This suggests that GP-HCA have more OFGs than GP-HC, i.e. more electron donating sites for Cu^{2+}, and thus increased adsorption ability. The obtained result is in agreement with previous studies that investigated alkali modification of different hydrochars [1,2,7].

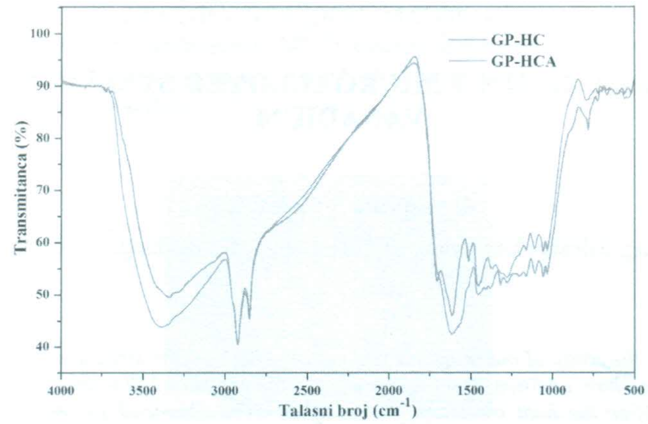

Figure 3 - FTIR spectra of hydrochars before (GP-HC) and after (GP-HCA) alkali modification

4. CONCLUSION

Our study showed that the GP-HCA exhibited almost fivefold higher capacity of Cu^{2+} removal than the GP-HC. From SEM analysis can be concluded that KOH activation increases surface cracks which provide a larger contact surface i.e. more binding sites for Cu^{2+} removal. The differences in FTIR spectra of GP-HC samples before and after KOH treatment showed structural changes which might affect the increase of the Cu^{2+} sorption ability. Overall findings suggest that the GP is a promising precursor for production of quality adsorbents for Cu^{2+} removal from wastewaters using HTC.

ACKNOWLEDGEMENTS

The authors are grateful to the Serbian Ministry of Education, Science and Technological Development for the financial support of this investigation included in the project TR 31003.

REFERENCES

[1] P. Regmi, J. Moscoso, S. Kumar, X. Cao, J. Mao, G. Schafran., J. Environ. Manage., 109 (2012) 61-69.
[2] J. Petrović, M. Stojanović, J. Milojković, M. Petrović, T. Šoštarić, M. Laušević, M. Mihajlović., J. Environ. Manage., 182 (2016) 292-300.
[3] I. Anastopoulos, I. Massas, C. Ehaliotis., Chem. Eng. J., 231 (2013) 245-254.
[4] O.E. Abdel Salam, N.A. Reiad, M.M. Elshafei., J. Adv. Res., 2 (2011) 297-303.
[5] H. Jin, M.U. Hanif, S. Capareda, Z. Chang, H. Huang, Y. Ai., J. Environ. Chem. Engin., 4 (2016) 365-372.
[6] M. Petrović, T. Šoštarić, M. Stojanović, J. Milojković, M. Mihajlović, M. Stanojević, S. Stanković., J. Taiwan Inst. Chem. Eng., 58 (2016) 407-416.
[7] K. Sun, J. Tang, Y. Gong, H. Zhang., Environ. Sci. Pollut. Res., 22 (2015) 16640-16651.
[8] D. Mohan, P. Singh, A. Sarswat, P.H. Steele, C.U. Pittman Jr., J. Colloid Interface Sci., 448 (2015) 238-250.
[9] Y. Xue, B. Gao, Y. Yao, M. Inyang, M. Zhang, A.R. Zimmerman, K.S. Ro., Chem. Eng. J., 200 (2012) 673-680.
[10] X. Tan, Y. Liu, G. Zeng, X. Wang, X. Hu, Y. Gu, Z. Yang, Chemospher., 125 (2015) 70-85.
[11] J. Petrović, N. Perišić, J. Dragišić Maksimović, V. Maksimović, M. Kragović, M. Stojanović, M. Laušević, M. Mihajlović., J. Anal. Appl. Pyrol., 118 (2016) 267-277.