

## REMOVING OF METAL(LOID)S FROM AQUEOUS SOLUTION USING BIOCHAR AND ITS MODIFICATIONS

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### Introduction

Recently, biochar has been used frequently as a suitable biosorbent to remove toxic metals from wastewater (Tan et al., 2015). This removal process consists of three main metal sorption mechanisms: (i) ion exchange, (ii) metal complexation with free functional groups together with physical adsorption, and (iii) surface precipitation (Trakal et al., 2014; Tan et al., 2015). Additionally, as reviewed by Mohan et al. (2014) the biochar removal efficiency usually results in a few milligrams of remediated metal(loid) per gram of activated carbon. Because of that and due to its porous structure, biochar has recently also been modified using various secondary oxides in order to improve its sorption efficiency.

Often, biochar has been modified using Fe-oxides (Mohan et al., 2014). Trakal et al. (2016) showed that metal sorption of the biochars with well-developed structure were significantly improved after the modification, however, the biochars represented by lower BET surface ( $< 100 \text{ m}^2 \text{ g}^{-1}$ ) showed negligible and/or negative effect. Next, biochar could also be modified by Mn-oxides, which usually have had very high immobilization potential for metal(loid)s (Komárek et al., 2013). Specifically, Wang et al. (2015) demonstrated that metal(loid)s sorption was significantly improved for the biochar modified by birnessite and/or other Mn-oxides. Because of that, amorphous manganese oxide (AMO) could also be very suitable candidate for this modification due to its very high efficiency to immobilize various metal(loid)s (Della Puppa et al., 2013).

### Methods

Five different waste agro-materials (nut shells, plum stones, wheat straws, grape stalks and grape husks) were pyrolysed at 600°C in a muffle furnace under 16.7 mL min<sup>-1</sup> nitrogen flow rate at atmospheric pressure and retention time of 30 min. Such prepared biochars were then tested as potential sorbents for Cd(II) and Pb(II). Next, the same biochars were modified by impregnation with magnetic particles in order to enhance the sorption of Cd(II) and Pb(II), respectively. Finally, the selected biochar (from grape stalks) was used for the modification by AMO. Such prepared AMOchar was compared with the pristine biochar for the sorption of As(V), Cd(II) and Pb(II). Next, all prepared/modified biochar samples were analysed for: (i) pH value, pH<sub>ZPC</sub>, CEC; (ii) BET surface (iii) surface functional groups by FTIR; (iv) precipitated phases by XRD; (v) surface structure and composition using SEM-EDX; and (vi) XPS.

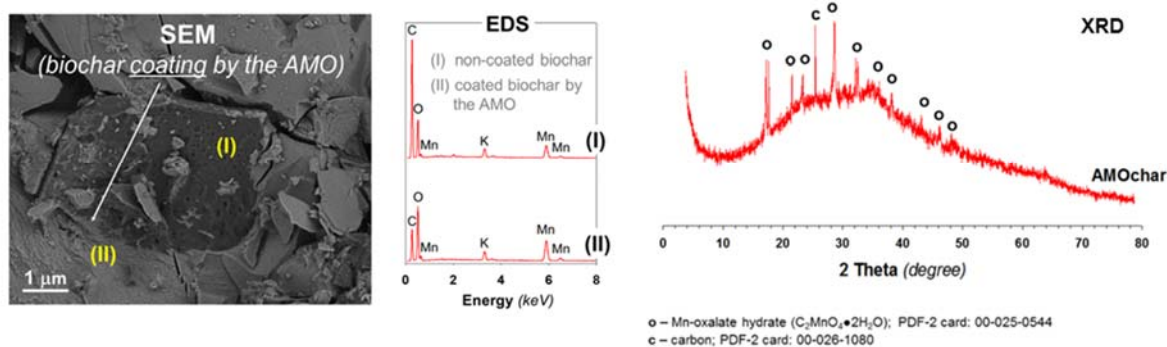
### Results

The removal rate of both metals is the least affected by the biochar morphology and specific surface but this removal efficiency is strongly pH-dependent. The predominant metal sorption mechanism was ion exchange where this mechanism showed very strong binding of sorbed metals as confirmed by the post-desorption of the fully metal-loaded biochars.

Additionally, the cation exchange capacity increased after the magnetic modification, except for grape stalk biochar. The metal loading rate was also significantly improved, especially for Cd(II) sorption on/in nut shell and plum stone biochars (10- and 16-times increase, respectively). The results indicated that cation exchange was strengthened after Fe-oxide impregnation, which limited the desorbed amount of tested metals. In contrast, the magnetization of grape stalk biochar reduced Pb(II) sorption in comparison with that of pristine biochar. Magnetic modification is, therefore, more efficient for biochars with well-developed structure and for more mobile metals, such as Cd(II).

On the other hand, the AMOchar was formed mainly by Mn-oxalates which had coated surface of the pristine biochar (Figure 1). In comparison with the pristine biochar (grape stalks) the AMO-biochar composite was able to remove significantly higher amounts of various metal(loid)s from the solution. Despite the rather high pH of the AMOchar, such modified biochar was able to sorb efficiently not only Pb(II), almost 99%, and Cd(II), 51.2%, but also a very high amount of As(V), 91.4%. Additionally, the AMOchar was able to reduce Mn leaching. This can avoid potential post-contamination caused by the dissolution of less stable Mn-oxalates as observed in the pure AMO.

**Figure 1.** The SEM images with corresponding EDS spectra and X-ray diffraction (XRD) patterns, of the AMOchar.



## Conclusion

Sorption variability was reflected by the origin of the biochar and the most important sorption mechanism is ion exchange. Magnetic modification was able to improve the sorption of those biochars with well-developed structure, nevertheless, the best modification was observed using the Mn-oxide coating.

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