Potassium permanganate modification of hydrochar enhances sorption of Pb(II), Cu(II), and Cd(II)

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Background

Heavy metals including lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), and copper (Cu) have been an increasing ecological and global public health concern associated with environmental contamination by these metals.

The toxic effects of these metals remain present in surface water and drinking water for humans to accumulate in the body and food chain, exhibiting a chronic nature. Various public health measures have been undertaken to control, prevent and treat metal toxicity occurring at multiple levels, such as occupational exposure.

Introduction

Hydrochar is a special biochar that is converted from biomass through hydrothermal carbonization (HTC). It is typically produced at a mild temperature of around 200 °C and at the pressure of the aqueous solution. The production process of hydrochar is convenient and less energy-intensive. Thus, hydrochar was selected for surface functionalization operations to provide sufficient adsorption sites for heavy metal contaminants.

$KMnO_4$ is a commonly used oxidizing agent. Oxidation with $KMnO_4$ creates a hierarchical porous structure of biochar, resulting in a remarkable increase in the oxygen-containing functional groups on the carbon surface. Furthermore, KMnO4 oxidization introduces MnOx to the biochar surface, and heavy metal ions can combine with MnOx via oxidation, adsorption, complexation, or precipitation, thereby significantly improving the removal of heavy metals.

Fig. 1. Hydrochar produced from various biomass

Objective

- To examine the effects of feedstock types and $KMnO_4$ concentrations on the effectiveness of $KMnO_4$ oxidization.
- To study the effect of $KMnO_4$ modification on the physicochemical properties of hydrochar.
- To investigate the kinetics and isotherms equilibrium of heavy metal adsorption by $KMnO_4$-modified hydrochar.

Methods

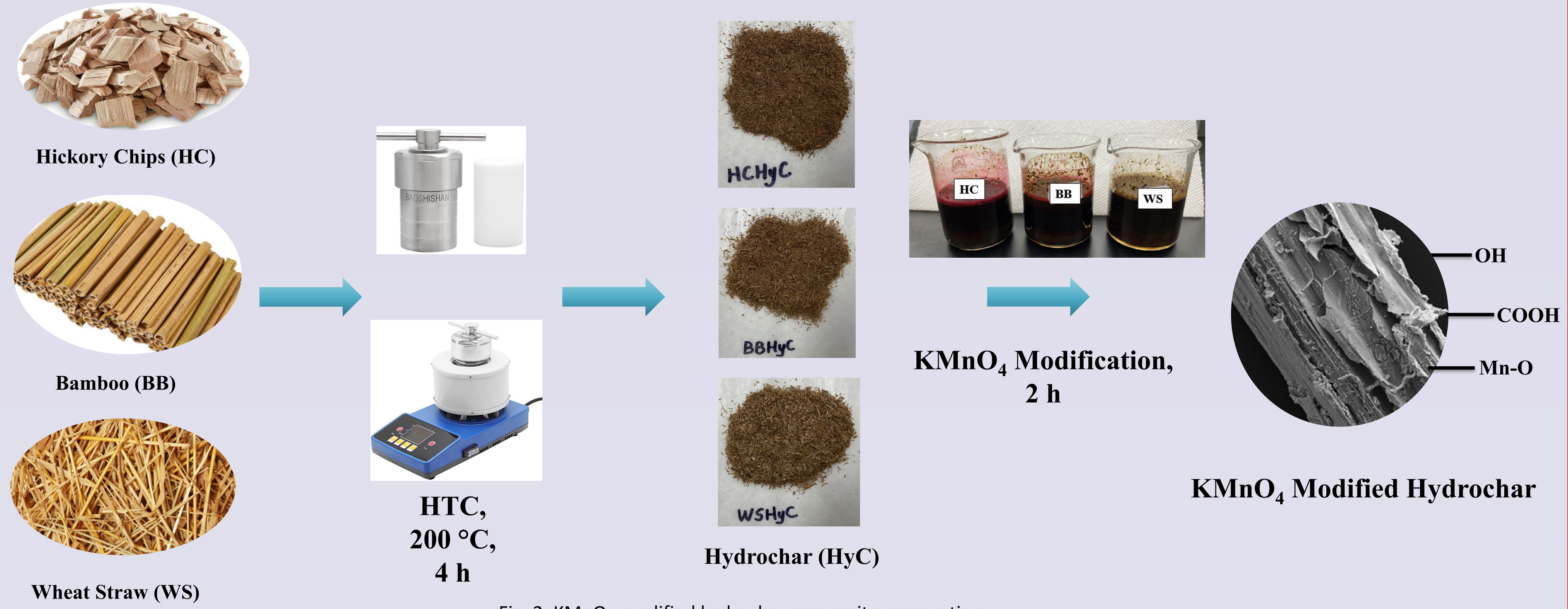

Fig. 2. $KMnO_4$-modified hydrochar composite preparation.

Results

- For each feedstock, Pb, Cd, Cu removal increased with increasing $KMnO_4$ modification concentration. Agricultural biomass WS generally sorbed more heavy metals than woody biomass HC and BB.

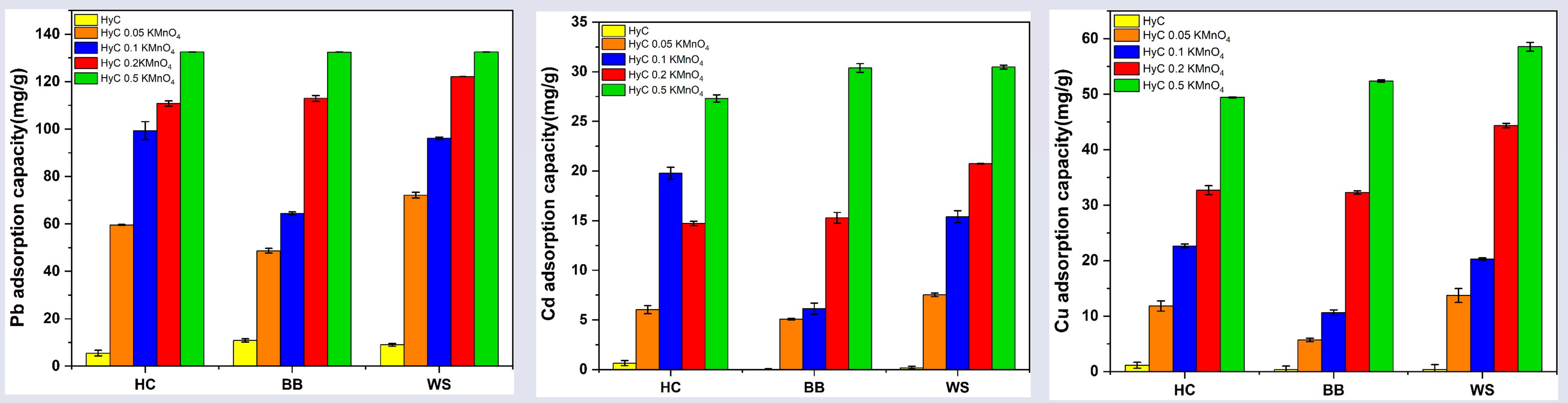

Fig. 3. Effect of feedstock and $KMnO_4$ modification concentrations on heavy metal adsorption by hydrochar (a) Pb, (b) Cd, and (c) Cu.

- Elemental mapping shows that KMnO4 modification increased O and Mn in the hydrochar.
- The C1s spectrum displays three peaks at 284.8, 286.0, and 288.5 eV, corresponding to C=C/C-C, C-O, and O-C=O groups, respectively. After modification with $KMnO_4$, C=C/C-C group decreased (from 60% to 54%) while O-C=O groups increased (from 6% to 13%)

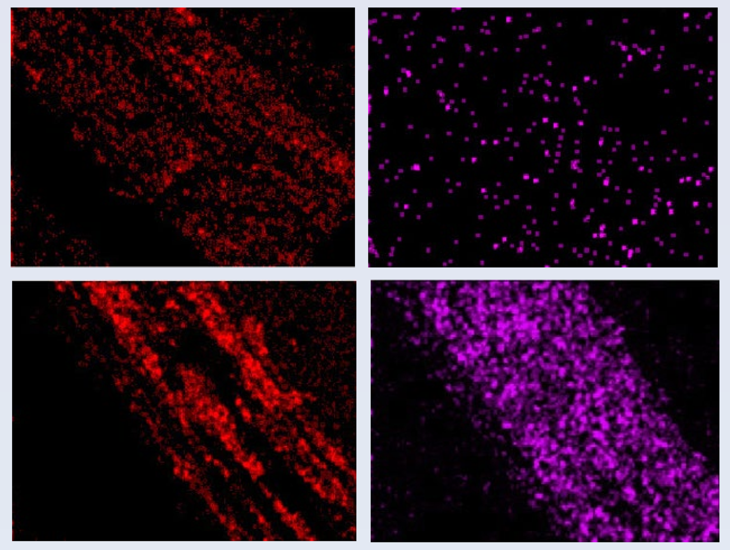

Fig. 4. Elemental mappings of O and Mn of WSHyC (top) and WSHyC-0.2KMnO4 (bottom), respectively.

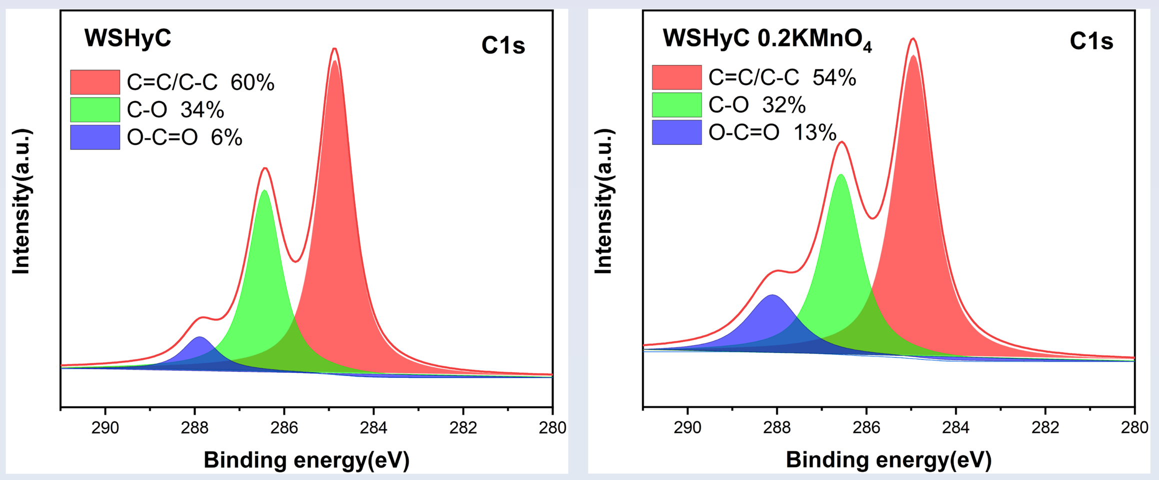

Fig. 5. XPS spectra of C1s of WSHyC and WSHyC-0.2KMnO4.

- The O1s spectrum of WSHyC-0.2 $KMnO_4$ shows a new peak Mn-O bond at the binding energy of 530.1 eV, which accounts for 32%.
- The peak-to-peak separation between the Mn 2p $_{1/2}$ peak and the Mn 2p $_{3/2}$ peak is 11.49 eV, and Mn exhibits an oxidation state between Mn^{3+} and Mn^{4+}.

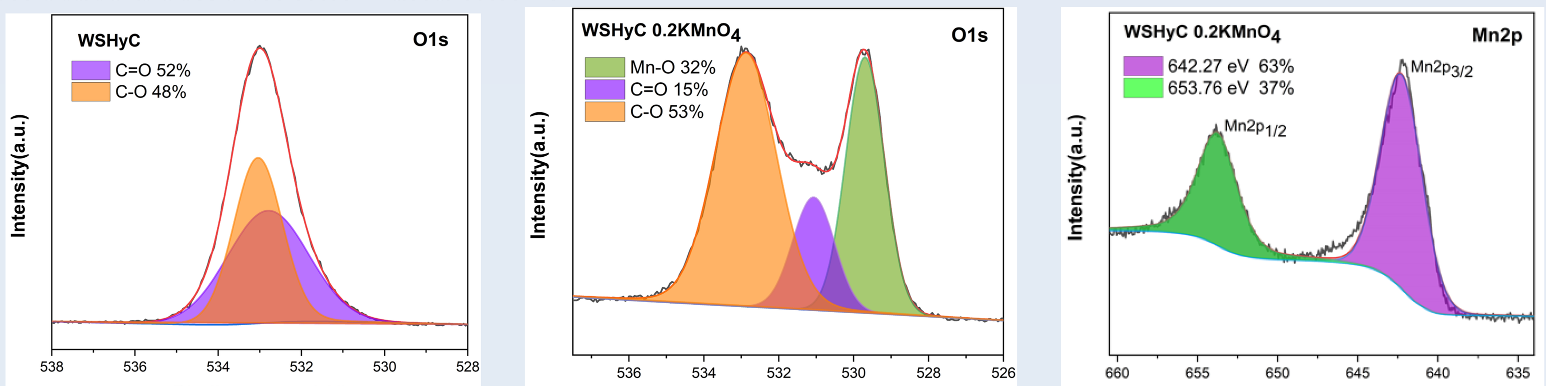

Fig. 6. XPS spectra of O1s and Mn2p of WSHyC and WSHyC-0.2KMnO4.

Results

- Pb, Cd, and Cu adsorption by WSHyC-0.2KMnO4 was much higher and faster than that of WSHyC.
- The initial stage is rapid adsorption with more than 90% of the adsorption accomplished in the first 1-2 h. then the slowing adsorption lasts for about 5 h until reaches equilibrium.

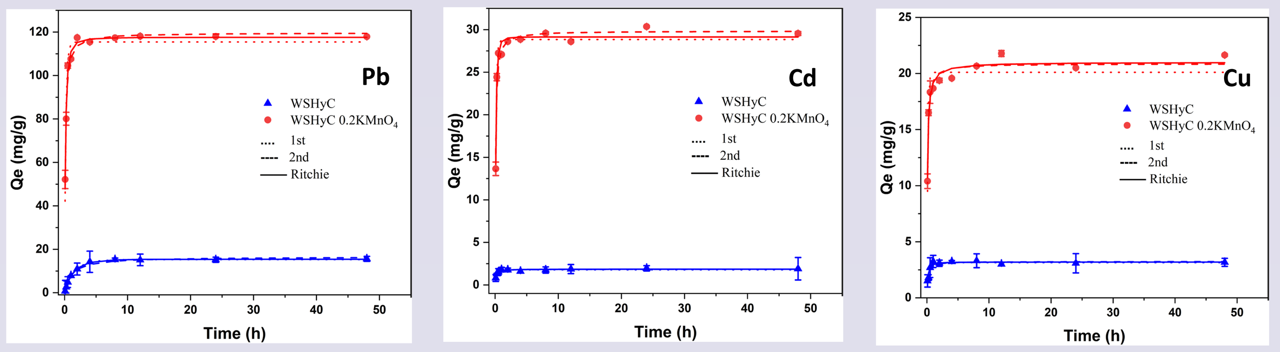

Fig. 7. Sorption kinetics data and fitted models of Pb (II), Cd (II), and Cu(II) onto WSHyC and WSHyC-0.2KMnO4.

- The Langmuir maximum adsorption capacity of WSHyC-0.2KMnO4 were 189.24 mg/g for Pb(II), 29.06 mg/g for Cd(II), and 32.68 mg/g for Cu(II), about 12.46, 17.09 and 12.52 times higher than for the pristine WSHyC.
- Functional groups and MnOx are homogeneously distributed over the hydrochar surface

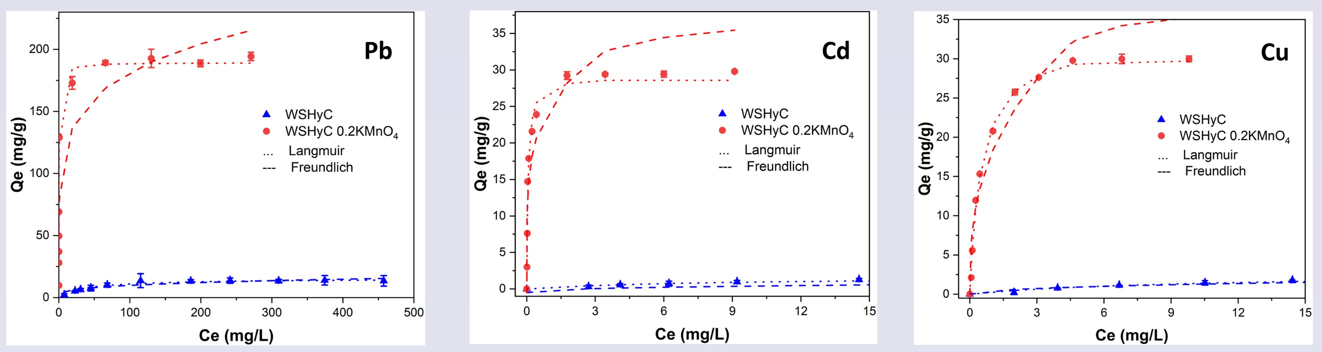

Fig. 8. Sorption isotherm data and fitted models of Pb (II), Cd (II), and Cu(II) onto WSHyC and WSHyC-0.2KMnO4.

Conclusions

- The adsorption capacity of Pb, Cd, and Cu was greatly increased (>12 times higher) for wheat straw hydrochar modified with 0.2 M $KMnO_4$ compared with the pristine hydrochar;
- The $KMnO_4$-modified hydrochar had specific surface area 8 times higher than the pristine hydrochar with increased oxygen-containing functional groups (e.g., hydroxyl and carboxyl) and MnOx on the surface;
- Pb, Cd, and Cu adsorption by WSHyC-0.2KMnO4 involve multiple mechanisms, including electrostatic attraction, ion exchange, and surface complexation;
- The modified hydrochar can be employed in practical applications as a low-cost sorbent.

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