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. KMnO₄ is a commonly used oxidizing agent. Oxidization with KMnO₄ creates a hierarchical porous structure of biochar, resulting in a remarkable increase in the oxygen-containing functional groups on the carbon surface. Furthermore, KMnO₄ oxidation 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.

Objective
- To examine the effects of feedstock types and KMnO₄ concentrations on the effectiveness of KMnO₄ oxidation.
- To study the effect of KMnO₄ modification on the physicochemical properties of hydrochar.
- To investigate the kinetics and isotherms equilibrium of heavy metal adsorption by KMnO₄-modified hydrochar.

Methods
For each feedstock, Pb, Cd, Cu removal increased with increasing KMnO₄ modification concentration. Agricultural biomass WS generally sorbed more heavy metals than woody biomass HC and BB.

Results
- 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 KMnO₄, C=C/C=C group decreased (from 60% to 54%) while O-C=O groups increased (from 6% to 13%).
- 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 the oxidation state of MnIV and MnVI.

Conclusions
- The adsorption capacity of Pb, Cd, and Cu was greatly increased (>12 times higher) for wheat straw hydrochar modified with 0.2 M KMnO₄ compared with the pristine hydrochar.
- The KMnO₄-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.

Selected References

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Fig. 1. Hydrochar produced from various biomass

Fig. 2. KMnO₄-modified hydrochar composite preparation.

Fig. 3. Effect of feedback and KMnO₄ modification concentrations on heavy metal adsorption by hydrochar (4 h, HTC, and HTC-1 KMnO₄).

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

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

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

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

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