CITY UNIVERSITY OF HONG KONG
香港城市大学

The Performance and Mechanism of Removal of Heavy Metals from Water by Water Hyacinth Roots as a Biosorbent Material
利用水葫芦根系去除水中重金属的效率和机理研究

Submitted to
Department of Biology and Chemistry
生物及化学系
in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy
哲学博士学位

by

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August 2010
二零一零年八月
Abstract of Thesis Entitled

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For the Degree of Doctor of Philosophy at City University of Hong Kong & University of Science and Technology of China

May 2010

Abstract

Water hyacinth roots was evaluated as a biosorbent material for the removal of Cu(II), Cd(II), and Cr(VI) in aqueous media. N2 adsorption analysis revealed that the biosorbent possesses a small surface area of 4.5 m² g⁻¹. Water hyacinth roots have a \( \text{pH}_{\text{PZC}} \) of 6.6.

Mono-metal biosorption was carried out for Cu(II), Cd(II), and Cr(VI), respectively. The data demonstrated a considerable sorption capacity of Cu(II) and Cd(II) with sorption amount up to 22.7 and 27.6 mg g⁻¹, respectively. However, water hyacinth roots had no attractive sorption capacity of Cr(VI). The equilibrium experimental data was modeled by Langmuir and Freundlich equation, and results revealed that Langmuir model fitted Cu(II) biosorption isotherm much better than Freundlich model; however, both Langmuir and Freundlich model fitted Cd(II) biosorption rate well. The fitted parameters also revealed that the water hyacinth
roots have a high affinity and large sorption capacity for Cu(II) and Cd(II). The pseudo-second-order kinetics model revealed a rapid biosorption rate for both Cu(II) and Cd(II) biosorption, which increased with increasing temperature. This suggests the endothermic characteristics of the Cu(II) biosorption, which was consist with evaluated thermodynamic parameters. The activation energy of biosorption of Cu(II) and Cd(II) was calculated to be 28.35 and 23.45 kJ mol\(^{-1}\) respectively, which are comparable to chemisorption processes and is consistent with the \(S_{\text{BET}}\).

The pH effect on extent of adsorption, pH reduction and calcium release during sorption suggest that ion exchange is involved in the removal of Cu(II) and Cd(II) by water hyacinth roots. The changes of relative content of oxygen and shifts of carbon and oxygen binding energy are consistent with the formation of complex between Cu(II) and surface functional groups on the biosorbent. This is further supported by the shift of the FTIR peaks of the –OH and C=O functionalities in the water hyacinth roots after Cu(II) adsorption. Our findings suggest that ion exchange and complex formation are the major mechanisms for the activated chemisorption of Cu(II) and Cd(II) by the biosorbent.

Binary-metal biosorption was carried out in Cd(II) – Cu(II) and Cr(VI) – Cu(II) system respectively. Although water hyacinth roots possess high sorption capacity for both cadmium and copper ions, the biosorption of Cd(II) was found to be strongly inhibited by the co-exist Cu(II) ions in the pH range of 3 - 5. The release of light metal ions such as Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\) and H\(^+\) confirmed the ion exchange mechanism of the binary-metal biosorption processes and the difference in binding
active site. Revealed by XPS analysis, chelation with amine and oxygen-containing functionalities was also found to contribute to the sorption of Cd(II) and Cu(II). Binding sites taken up by Cd(II) were snatched by copper ions. This confirms that water hyacinth roots possess a higher affinity for copper ions than cadmium ions even at high temperature.

When temperature increases, the increased fold in sorption rate of Cd(II) is larger than that of Cu(II), which is attributed to the larger activation energy of Cd(II) biosorption (28.35 vs. 23.45 kJ mol\(^{-1}\)), and this can abate the inhibition effect posed by Cu(II) in some sort. However, the higher affinity of water hyacinth roots to Cu(II) ensures the strong inhibition on Cd(II) removal. Moreover, sorption of Cu(II) not only occurred on neat roots but also on Cd-sorbed roots.

Our study calls for special consideration of the presence of copper ions in the application of live water hyacinth roots for remediation of cadmium contaminated water, as it can significantly inhibit cadmium uptake.

Contrary to Cd(II) – Cu(II) system, synergic biosorption effect was found in Cr(II) – Cu(II) system. Cu(II) was found to exert cooperative effect on Cr(VI) uptake by water hyacinth roots at pH 3.5-5.5 without diminishment in copper ions uptake. Additionally, this cooperative effect became stronger as temperature increases, resulting in an increase in chromium uptake rate.

XPS high resolution spectra of N1s and O1s of water hyacinth roots with and without metal uptake have shown significant differences. Uptake of metal caused a shift of binding energy, which confirms the main contribution of electrostatic
attraction between hydrogen chromate and protonated amine groups to the removal of chromium. In the single Cr(VI) system, peak corresponding to C-O in carboxyl groups disappeared due to the oxidation by Cr(VI), and the increase in the amide groups induced a decline of protonated amine groups.

In the presence of Cu(II), the rapid occupation of amine and carboxyl groups by copper ions hindered the transformation of amine to amide groups and the consumption of carboxyl groups by Cr(VI) reduction, which extend the contribution of direct electrostatic attraction to chromium removal.
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