Purification of Heavy Metal Polluted Water by Using Economically Accessible Ceramic Materials

July 2021

Zhu Dirui

Purification of Heavy Metal Polluted Water by Using Economically Accessible Ceramic Materials

A Dissertation Submitted to
the Graduate School of Life and Environmental Sciences,
the University of Tsukuba
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Environmental Studies
(Doctoral Program in Sustainable Environmental Studies)

Zhu Dirui

Abstract

Heavy metal pollution in water is one of the serious environmental issues in the world. Mercury (Hg), cadmium (Cd), chromium (Cr), lead (Pb), and copper (Cu) are the main heavy metals that pollute water quality. Among them, Hg is the most toxic, followed by Cd. In addition, although arsenic (As) is a non-metallic substance, it is also classified as heavy metal pollution because of its similar toxicity with heavy metals. The sources of heavy metal pollutants in water bodies are extensive, usually from mining and mineral processing, smelting industry, fossil fuel combustion, electroplating, coating, glass, chemical, and other enterprises. Heavy metal pollution caused by wastewater discharging is challenging the wastewater treatment plants and the environmental as well. This research for the first time used plateau laterite ceramic (PLC) and plateau laterite sediment ceramic (PLSC) to simultaneously adsorb six heavy metals in wastewater through both batch and fixed-bed studies. The objective of this study was to develop efficient adsorbents from economic and locally available ceramic materials to solve heavy metal pollution caused by several local mineral industries. In this study, PLC and PLSC are comprehensively studied with respect to adsorbent development, adsorption mechanisms, and their practical application.

This dissertation is divided into 5 chapters. In Chapter 1, the author introduced the research background and literature review. The technologies of heavy metals removal from water were introduced, and the development of adsorbents was emphasized. Then the adsorbent materials used in this study were specifically introduced. At last, the author arrived at the objectives and the framework of this research. In Chapter 2, the author investigated the adsorption of heavy metals by PLC. The Langmuir model, pseudo-first-order, and pseudo-second-order kinetic models were applied to fit the experimental data. Results show that the adsorption process was monolayer adsorption, and both physisorption and chemisorption were involved. The pH at the point of zero point charge (pH_{zpc}) of the prepared PLC was 6.8, and its best adsorption efficiencies were 97.38% (As), 96.55% (Cr), 95.62% (Pb), 89.85% (Cu), 87.14% (Cd), and 81.08% (Hg), respectively. The crystalline morphology along with new and enhanced X-ray diffraction (XRD) peaks revealed that heavy metals were successfully adsorbed onto the PLC. In the fixed-bed study, the breakthrough occurred at 270 bed volumes (BV). The prepared PLC could be regenerated at least three times. The adsorption capacity of PLC followed a descending order of As > Cr > Pb > Cu > Cd > Hg in both batch and fixed-bed experiments. The best As removal efficiency obtained in this study may attribute to that As ion has a broader reaction pH

range, which may involve in ligand exchange and formation of an As–Fe shell besides the dominant complexation and precipitation reaction. In Chapter 3, the author researched the adsorption of heavy metals using the prepared PLSC. The XRD spectra and morphology of PLSC show that the crystals are mainly composed of Ca, Mg, Fe, Al, and -OH compounds of heavy metals. The FTIR spectra suggest that C=N, C=O, and O-H bonds have been introduced into PLSC due to the addition of lake sediment (biochar); the existence of these carbon bonds and aromatic compounds can provide practical support for the adsorption of heavy metals. The experiments on pH effect illustrated that Ca^{2+} and Mg^{2+} in the lake sediment contributed most to the adsorption capacity during the adsorption process, and Ca^{2+} took the advantages of all the released ions (33.03 - 91.30 mg/L) when solution pH varied from 5 to 8, achieving the largest release of ions in total amount, which is consistent with the change of adsorption efficiency. PLSC exhibited a solid ability to buffer and improve pH. After adsorption, the final pH maintained around 9.0 when the initial pH varied between 3 and 6, with the equilibrium time about 1 – 8 h. The Langmuir adsorption capacity was estimated as 15.96 mg/g, which is very close to the experimental data (15.85 mg/g). In Chapter 4, the practical application possibility of PLC and PLSC were studied. The mass loss ratio after calcination was 42.56 % for PLC and 18.36 % for PLSC. The PLC breakthrough in the three cycle tests occurred at 270 BV (12.72 L), 210 BV (9.89 L), and 150 BV (7.07 L), with the maximum adsorption capacity in each cycle being 12.38 mg/g, 11.23 mg/g, and 9.50 mg/g, respectively. The PLSC breakthrough BV in three cycle tests were 560 BV (26.88 L), 510 BV (24.48 L), and 450 BV (21.6 L), with the maximum adsorption capacity in each cycle being 19.97 mg/g, 18.52 mg/g, and 15.40 mg/g, respectively. When applied for the actual smelter wastewater treatment, PLC and PLSC showed comparably efficient heavy metal removal capacity. For instance, the adsorption capacity was 19.12 mg/g for PLC and 19.45 mg/g for PLSC when treating the wastewater from smelter 1. Results from safety evaluation tests indicate that the prepared PLC and PLSC are safe and reliable in practical application as construction materials. In Chapter 5, the author summarized the major conclusions and proposed the future research directions.

Keywords: Adsorption; Heavy metals; Plateau laterite ceramic; Sediment biochar; Smelting wastewater; Safety disposal.