

# EFFICIENCY OF RICE (*Oryza sativa*) HUSK BIOCHAR IN THE ADSORPTION OF CADMIUM FROM AQUEOUS SOLUTION

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An Undergraduate Thesis Submitted to the Faculty of the Department of Chemistry,  
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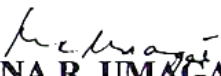
  
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# EFFICIENCY OF RICE (*Oryza sativa*) HUSK BIOCHAR IN THE ADSORPTION OF CADMIUM FROM AQUEOUS SOLUTION<sup>1</sup>

MIKKA GIDDONAH R. LORA

## ABSTRACT

**Background:** Water pollution becomes more serious because of the development of many industries. Heavy metals are one of the major contributors of water pollution. Heavy metal contaminated water can cause risk and adverse effect on human health. Adsorption is an effective technique in removing water contaminants. Biochar derived from rice husk was used as an adsorbent in removing cadmium from aqueous solution. **Methods:** Batch adsorption experiments were conducted. The adsorption parameters (pH, initial metal concentration and contact) were optimized. The solutions were shaken in an automatic shaker with a speed of 200 rpm. The biochar residues were digested using US EPA Method 3050B. Concentration of cadmium adsorbed in the biochar was determined using Microwave-plasma atomic emission spectroscopy. **Results:** The highest removal capacity of cadmium from aqueous solution reached 57.63% and was observed at pH 8, initial metal concentration of 30.0 mg L<sup>-1</sup> and 6 h of contact time. Kinetic study showed that the adsorption process was described by pseudo-second order model. Adsorption isotherm study showed that the adsorption both fit to Langmuir and Freundlich model. **Conclusions:** Result showed that rice husk biochar can be an effective adsorbent in removing cadmium from water.

**Keywords:** adsorption, biochar, cadmium, kinetic studies, adsorption isotherm

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## LITERATURE CITED

- Agrafioti, E., Kalderis, D., & Diamadopoulos, E. (2014). Arsenic and chromium removal from water using biochars derived from rice husk, organic solid wastes and sewage sludge. *Journal of Environmental Management*, 133, 309-314.
- Alemaheyu, E., & Lennartz, B. (2009). Virgin volcanic rocks: Kinetics and equilibrium studies for the adsorption of cadmium from water. *Journal of Hazardous Material*, 169, 396-401.
- Amin, N. K. (2008). Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith. *Desalination*, 223, 152-161.
- Arshadi, M., Mousavinia, F., Amiri, M. J., & Faraji, A. R. (2016). Adsorption of methyl orange and salicylic acid on a nano-transition metal composite: kinetics, thermodynamics and electrochemical studies. *Journal of Colloid and Interface Science*.
- ATSDR. (2011). Cadmium in Drinking Water.
- Azizian, S. (2004). Kinetic models of sorption: a theoretical analysis. *Journal of Colloid and Interface Science*(276), 47-52.
- Balaram, V., Vummiti, D., Roy, P., Taylor, C., Kar, P., Raju, A. K., et al. (2013). Determination of precious metals in rocks and ores by microwave plasma atomic emission spectroscopy for geochemical prospecting studies. *Research Article, Current Science*, 104(9).
- Bennet, J. P., Shiriboga, E., Coleman, J., & Waller, D. M. (2000). Heavy metals in wild rice from northern Wisconsin *Science of Total Environment*(246), 261-269.
- Bogusz, A., Oleszczuk, P., & Dobrowolski, R. (2015). Application of laboratory prepared and commercially available biochars to adsorption of cadmium, copper and zinc ions from water. *Bioresource Technology*, 196, 540-549.
- Bureau, R. G., Kaita, K. Y., Inouye, T. S., & Miller, M. (1973). *Chemical Analysis of Soil Samples from the Salinas Valley, California for Cadmium, Zinc, and Phosphate*
- Chen, T., Zhou, Z., Meng, R., & Wang, H. (2015). Adsorption of cadmium by biochar derived from municipal sewage sludge: Impact factors and adsorption mechanism. *Chemosphere*, 134, 286-293.
- Cheng, Q., Huang, Q., Khan, S., Liu, Y., Liao, Z., Li, G., et al. (2016). Adsorption of Cd by peanut husks and peanut husk biochar from aqueous solutions. *Ecological Engineering*, 87, 240-245.

- Ding, Z., Hu, X., Wan, Y., Wang, S., & Gao, B. (2016). Removal of lead, copper, cadmium, zinc, and nickel from aqueous solutions by alkali-modified biochar: Batch and column tests. *Journal of Industrial and Engineering Chemistry*, 33, 239-245.
- Eccles, H. (1999). Treatment of metal-contaminated wastes. *Trends Biotechnology*, 17, 462-465.
- EFSA. (2009). Cadmium on food, scientific opinion on the panel on contaminants in the food chain. *EFSA Journal*, 980, 3-14.
- Friberg, L., Nordberg, G., & Vouk, V. (1986). *Handbook of the toxicology of metals* (Vol. II). Amsterdam: Elsevier.
- Godt, J., Scheidig, F., Grosse-Slestrup, C., Esche, V., Brandenburg, P., Reich, A., et al. (2006). The toxicity of cadmium and resulting hazards for human health. *Journal of Occupational Medicine and Toxicology*, 1(22).
- Goswami, R., Shim, J., Deka, S., Kumari, D., Katakí, R., & Kumar, M. (2016). Characterization of cadmium removal from aqueous solution by biochar produced from *Ipomoea fistulosa* at different pyrolytic temperatures. *Ecological Engineering*, 97, 444-451.
- Gunatilake, S. K. (2015). Methods of Removing Heavy Metals from Industrial Water. *Journal of Multidisciplinary Engineering Science Studies*, 1(1); 12-18.
- Guzel, F., Yakut, H., & Topal, G. (2008). Determination of kinetic and equilibrium parameters of batch adsorption of Mn(II), Co(II), Ni(II) and Cu(II) from aqueous solution by black carrot (*Daucus carota* L.) residues. *Journal of Hazardous Material*, 153, 1275-1287.
- Hammer, M. R. (2008). A magnetically excited microwave plasma source for atomic emission spectroscopy with performance approaching that of the inductively coupled plasma. *Spectrochimica Acta Part B*, 63, 45-464.
- Hidayu, A. R., & Muda, N. (2016). Preparation and characterization of impregnated activated carbon from pal kernel shell and coconut shell for CO<sub>2</sub> capture. *Procedia Engineering*, 148, 106-113.
- Higashikawa, F. S., Conz, R. F., Colzato, M., Cerri, C. E., & Alleoni, L. R. (2016). Effects of feedstock type and slow pyrolysis temperature in the production of biochars on the removal of cadmium and nickel from water. *Journal of Cleaner Production*, 137, 965-972.
- Hynes, H. B. N. (1960). *The Biology of Polluted Water*. Liverpool, UK: Liverpool University Press.

- IARC (1976). Cadmium, Nickel, some epoxides, miscellaneous industrial chemicals and general considerations on volatile anaesthetics. *Journal*, 11,
- Inyang, M., Gao, B., Yao, Y., xue, Y., Zimmerman, A. R., Pullammanappallil, P., et al. (2012). Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. *Bioresource Technology*, 110, 50-56.
- Jung, M. C., Yun, S., & Lee, J. (2005). Baseline Study on essential and trace elements in polished rice from South Korea *Environmental Geochemistry and Health* (27), 455-464.
- Kolodynska, D., Wnetrzak, R., Leahy, J., Hayes, M., Kwapinski, W., & Hubicki, Z. (2012). Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal*, 197, 295-305.
- Li, W., Simmons, P., Shrader, D., Herrman, T. J., & Dai, S. Y. (2013). Microwave plasma-atomic emission spectroscopy as a tool for the determination of copper, iron, manganese and zinc in animal feed and fertilizer. *Talanta*, 112, 43-48.
- Lima, I. M., Boateng, A. A., & Klasson, K. T. (2010). Physicochemical and adsorptive properties of fast-pyrolysis bio-chars and their steam activated counterparts. *J. Chem. Technol. Biotechnol.*, 85, 1515-1521.
- Liu, Charrua, A. B., Weng, C.-H., Yuan, X., & Ding, F. (2015). Characterization of biochars derived from agriculture wastes and their adsorptive removal of atrazine from aqueous solution: A comparative study. *Bioresource Technology*, 198, 55-62.
- Liu, W.-J., Zeng, F.-X., Jiang, H., & Zhang, X.-S. (2011). Preparation of high adsorption capacity bio-chars from waste biomass. *Bioresource Technology*, 102, 8247-8252.
- Liu, Y. (2006). Some consideration on the Langmuir isotherm equation. *Colloids and Surfaces A*, 274, 34-36.
- Mahmoud, A., Saleh, M., & A., A.-S. (2011). Effect of Rice Husk Biochar on Cadmium Immobilization in Soil and Uptake by Wheat Plant Grown on Lacustrine Soil. *Journal of Agricultural Resources*, 56(2), 117-125.
- Mathialagan, T., & Viraraghavan, T. (2002). Adsorption of cadmium from aqueous solutions by perlite. *Journal of Hazardous Material*, 2002, 291-303.
- Mohan, D., Kumar, S., & Srivastava, A. (2014). Fluoride removal from ground water using magnetic and nonmagnetic corn stover biochars. *Ecological Engineering*, 73.

- Mustafa, H. (1988). Cadmium and zinc concentrations in the potable water of the eastern provinces of Saudi Arabia. *Bulletin of Environmental Contamination and Toxicology*, 40, 462-467.
- Nameni, M., Mghadam, M. R., & Arami, M. (2008). Adsorption of hexavalent chromium from aqueous solutions of wheat brans. *International Journal of Environmental Science and Technology*, 2(5), 161-168.
- Okeola, F. O., & Odebunmi, E. O. (2010). Freundlich and Langmuir Isotherms Parameters for Adsorption of Methylene Blue by Activated Carbon Derived from Agrowastes. *Advances in Natural and Applied Sciences*, 4(3), 281-288.
- Ozbek, N., & Akman, S. (2016). Microwave plasma atomic emission spectrometric determination of Ca, K and Mg in various cheese varieties. *Food Chemistry*, 192, 295-298.
- Page, A. L., Chang, A. C., & El-Amamy, M. (1987). Chapter 10 Cadmium Levels in Soils and Crops in the United States. In T. C. Hutchinson & K. M. Meema (Eds.), *Lead, Mercury, Cadmium and Arsenic in the Environment*: John Wiley & Sons Ltd.
- Pode, R. (2016). Potential application of rice husk ash waste from rice husk biomass power plant. *Renewable and Sustainable Energy Reviews*, 53, 1468-1485.
- Pratiwi, E. P. A., Hillary, A. K., Fukuda, T., & Shinogi, Y. (2016). The effects of rice husk char on ammonium, nitrate and phosphate retention and leaching in loamy soil. *Geoderma*, 277, 61-68.
- Pyrzynska, K. (2010). Sorption of Cd (II) onto carbon-based materials- a comparative study. *Microchimica Acta*, 169, 7-13.
- Qin, Q., Wang, Q., Fu, D., & Ma, J. (2011). An efficient approach for Pb(II) and Cd(II) removal using manganese dioxide formed in situ. *Chemical Engineering Journal*, 172, 68-74.
- Qiu, H., Lu, L., Pan, B., Zhang, Q., & Zhang, W. (2009). Critical review in the adsorption kinetic models. *Journal of Zhejiang University SCIENCE A*, 10(5), 716-724.
- Ramos, N. C., Ramos, R. A., Arcilla, C. A., & Quirit, L. L. (2014). Determination of trace metals in rice using Microwave Plasma Atomic Emission Spectroscopy (MP-AES): Method Validation, Optimization and Application.
- Regmi, P., Moscoso, J. L. G., Kumar, S., Cao, X., Mao, J., & Schafran, G. (2012). Removal of copper and cadmium from aqueous solution using switchgrass biochar produced via hydrothermal carbonization process. *Journal of Environmental Management*, 109, 61-69.

- Zhang, F., Wang, X., Xionghui, J., & Ma, L. (2016). Efficient arsenate removal by magnetite-modified water hyacinth biochar. *Environmental Pollution*, 2-9.
- Zhao, Y., Li, Z., Ross, A., Huang, Z., Chang, W., Ou-yang, K., et al. (2015). Determination of heavy metals in leather and fur by microwave plasma-atomic emission spectrometry. *Spectrochimica Acta Part B*(112), 6--9.