

ULTRASONIC-ASSISTED ADSORPTION OF METHYLENE BLUE ON CYCLODEXTRIN POLYMERS

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An Undergraduate Thesis Submitted to the Faculty of the Department of Chemistry,
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in Partial Fulfillment of the requirements
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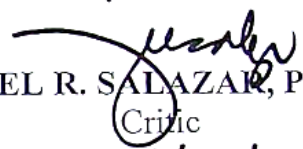
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The undergraduate thesis entitled **ULTRASONIC-ASSISTED ADSORPTION OF METHYLENE BLUE ON CYCLODEXTRIN POLYMERS** prepared and submitted by **RAFFY B. RODRIGUEZ** in partial fulfillment of the requirements for the degree of **BACHELOR OF SCIENCE IN CHEMISTRY** is hereby

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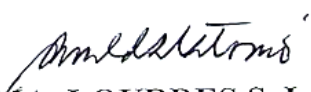

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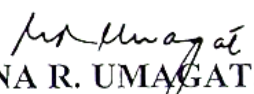

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RAFFY BADIOLA RODRIGUEZ

ABSTRACT

Background: Adsorption using natural polymers is known to remove pollutants from water. To improve the removal, a combination of adsorption and ultrasonic irradiation was introduced. In this study, the ultrasonic-assisted adsorption of methylene blue (MB) on cyclodextrin polymers (CDPs) from aqueous solutions was investigated. **Methods:** Batch adsorption of MB in aqueous solution by CDPs was conducted using a shaker and a sonicator at room temperature. Standard and residual solutions of MB were quantified using UV-Visible spectrophotometer. The effects of contact time and initial dye concentration, sorption kinetics and equilibrium isotherms were evaluated. **Results:** β -CDP showed the highest removal efficiency compared to γ -CDP and α -CDP, the least efficient. Pseudo-equilibrium was reached after approximately 120 min. The sorption of MB on CDPs followed the Ho-McKay's pseudo-second order kinetic mechanism with the liquid film diffusion and intraparticle diffusion as the rate-limiting steps. The amount of MB adsorbed on β -CDP at equilibrium increased with increasing initial MB concentration. The equilibrium data was analyzed using two- and three- parameter isotherm models. It was found that the sorption of MB on CDPs was best described by Sips isotherm. The BET surface area and total pore volume were not the primary factors in controlling the adsorption. The differences in sorption of MB by the CDPs could be credited to the size-matched structure and appropriate hydrophobicity of MB, the size of the CD cavity in the polymer, the average pore radius of the polymer and the amount of CD molecules in the polymer. **Conclusion:** The results showed the potential of ultrasonic-assisted adsorption process using these sorbents in a real wastewater treatment where the cationic dyes like MB is the contaminant.

Keywords: ultrasound, adsorption, methylene blue, cyclodextrin polymers, water, sorption kinetics, sorption isotherms

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LITERATURE CITED

- Ahmad, M. A., Puad, N. A. A., & Bello, O. S. (2014). Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation. *Water Resources and Industry*, 6, 18-35.
- Crini, G., Bertini, S., Torri, G., Naggi, A., Sforzini, D., Vecchi, C., Janus, L., Lekchiri, Y. & Morcellet, M. (1998). Sorption of aromatic compounds in water using insoluble cyclodextrin polymers. *Journal of Applied Polymer Science*, 68(12), 1973-1978.
- Crini, G. (2003). Studies on adsorption of dyes on beta-cyclodextrin polymer. *Bioresource technology*, 90(2), 193-198.
- Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in polymer science*, 30(1), 38-70.
- Crini, G., & Peindy, H. N. (2006). Adsorption of CI Basic Blue 9 on cyclodextrin-based material containing carboxylic groups. *Dyes and Pigments*, 70(3), 204-211.
- Crini, G., Peindy, H. N., Gimbert, F., & Robert, C. (2007). Removal of CI Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. *Separation and Purification Technology*, 53(1), 97-110.
- Crini, G. (2008). Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer. *Dyes and Pigments*, 77(2), 415-426.
- Del Valle, E. M. (2004). Cyclodextrins and their uses: a review. *Process Biochemistry*, 39(9), 1033-1046.
- Djelloul, C., & Housseine, A. (2013). Ultrasound-assisted removal of methylene blue from aqueous solution by milk thistle seed. *Desalination and Water Treatment*, 51(28-30), 5805-5812.
- Fierro, V., Torné-Fernández, V., Montané, D., & Celzard, A. (2008). Adsorption of phenol onto activated carbons having different textural and surface properties. *Microporous and mesoporous materials*, 111(1), 276-284.
- Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 156(1), 2-10.

- Gazpio, C., Sánchez, M., Isasi, J. R., Vélaz, I., Martín, C., Martínez-Ohárriz, C., & Zornoza, A. (2008). Sorption of pindolol and related compounds by a β -cyclodextrin polymer: Isosteric heat of sorption. *Carbohydrate Polymers*, 71(1), 140-146.
- Gutierrez, R., Whangchai, N., & Nomura, N. (2013). Geosmin Sorption on Cyclodextrin Polymers. *International Journal of Geosciences*, 4(05), 24.
- Gülen, J., Akın, B., & Özgür, M. (2016). Ultrasonic-assisted adsorption of methylene blue on sumac leaves. *Desalination and Water Treatment*, 57(20), 9286-9295.
- Ibrahim, M. B., & Sani, S. (2014). Comparative isotherms studies on adsorptive removal of Congo red from wastewater by watermelon rinds and neem-tree leaves. *Open Journal of Physical Chemistry*, 4(04), 139.
- Krause, R. W., Mamba, B. B., Bambo, F. M., & Malefetse, T. J. (2010). Cyclodextrin polymers: synthesis and application in water treatment. *Cyclodextrins: chemistry and physics*, 9, 185-208.
- Kumara, N. T. R. N., Hamdan, N., Petra, M. I., Tennakoon, K. U., & Ekanayake, P. (2014). Equilibrium Isotherm Studies of Adsorption of Pigments Extracted from Kuduk-kuduk (*Melastoma malabathricum* L.) Pulp onto TiO₂ Nanoparticles. *Journal of Chemistry*, 2014.
- Liu, S. (2015). Cooperative adsorption on solid surfaces. *Journal of colloid and interface science*, 450, 224-238.
- Lopes, E. C. N., dos Anjos, F. S. C., Vieira, E. F. S., & Cestari, A. R. (2003). An alternative Avrami equation to evaluate kinetic parameters of the interaction of Hg(II) with thin chitosan membranes. *Journal of Colloid and Interface Science* 263, 542-547
- Mills, A., Hazafy, D., Parkinson, J., Tuttle, T., & Hutchings, M. G. (2011). Effect of alkali on methylene blue (CI Basic Blue 9) and other thiazine dyes. *Dyes and Pigments*, 88(2), 149-155.
- Mohammed, M. A., Shitu, A., & Ibrahim, A. (2014). Removal of methylene blue using low cost adsorbent: a review. *Research Journal of Chemical Sciences ISSN*, 2231, 606X.
- National Center for Biotechnology Information. PubChem Compound Database; CID=6099, <https://pubchem.ncbi.nlm.nih.gov/compound/6099> (accessed Nov. 29, 2016).
- Nethaji, S., Sivasamy, A., & Mandal, A. B. (2013). Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous

particles prepared from *Juglans regia* shell biomass. *International Journal of Environmental Science and Technology*, 10(2), 231-242.

Nunes, C. A., & Guerreiro, M. C. (2011). Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers. *Química Nova*, 34(3), 472-476.

Qiu, H., Lv, L., Pan, B. C., Zhang, Q. J., Zhang, W. M., & Zhang, Q. X. (2009). Critical review in adsorption kinetic models. *Journal of Zhejiang University Science A*, 10(5):716-724

Vadivelan, V., & Kumar, K. V. (2005). Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *Journal of colloid and interface science*, 286(1), 90-100. Secondes, M. F. N., Naddeo, V., Ballesteros, F. J., & Belgiorno, V. (2014). Adsorption of emerging contaminants enhanced by ultrasound irradiation. *Sustainable Environment Research*, 24(5), 349-355.

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Szejtli, J. (1998). Introduction and general overview of cyclodextrin chemistry. *Chemical reviews*, 98(5), 1743-1754.