



Diatomite-assisted sorption of humic acid from environmental waters: Kinetics and interparticle diffusion in a highly porous material

Aoi Tachibana^a, Shoji Yoshioka^{b,*}, M. Mehedi Hasan Rocky^{c,*}, Shengbin Ni^d,
Idha Y. Ikhsani^e, Farah A. Idrus^f, Kuo H. Wong^c, Asami S. Mashio^c, Hiroshi Hasegawa^{c,*}

^a Kanazawa University Senior High School, 1-1-15 Heiwamachi, Kanazawa, Ishikawa, 920-1180, Japan

^b Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa, Ishikawa, 920-1192, Japan

^c Institute of Science and Engineering, Kanazawa University, Kakuma, Kanazawa, Ishikawa, 920-1192, Japan

^d Graduate Faculty of Interdisciplinary Research, University of Yamanashi, 4-4-37 Takeda, Kofu, 400-8510, Japan

^e Research Center for Oceanology, National Research and Innovation Agency (BRIN), Jl. Pasir Putih No.1, Ancol 14430, Jakarta, Indonesia

^f Faculty of Resource Science and Technology, Universiti Malaysia Sarawak (UNIMAS), Kota Samarahan, Sarawak, Malaysia

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ABSTRACT

Humic acid (HA), a major fraction of natural organic matter, is a persistent contaminant that impairs water quality and contributes to the formation of disinfection byproducts. In this study, natural, unmodified diatomite was investigated as a cost-effective sorbent for HA removal, with particular emphasis on diffusion limitations within its hierarchical meso-macroporous structure derived from diatom frustules. Equilibrium data (2.5–30 mg L⁻¹, pH 7) were described by the Langmuir and Freundlich models, indicating the coexistence of monolayer and heterogeneous sorption behavior. The uptake kinetics showed rapid initial removal, followed by a diffusion-limited regime. The pseudo-first-order model captured early-stage uptake, whereas the pseudo-mixed-order fractional (PMOF) model best represented the full kinetic profile. HA removal decreased from pH 4 to 9 owing to enhanced electrostatic exclusion above the point of zero charge and increased HA ionization. Divalent cations (Ca²⁺, Mg²⁺) enhanced removal through charge neutralization and cation bridging, while phosphate strongly inhibited uptake via site-specific competition. A comparative evaluation identified high-performing diatomite, and integrated evidence from BET, FT-IR, FE-SEM, and zeta potential analyses elucidated diffusion- and surface-controlled sorption pathways. Application to natural water (containing an HA-equivalent concentration of 9.4 mg L⁻¹) achieved up to 87% removal at practical dosages. These results demonstrate that unmodified diatomite is a low-cost, environmentally benign sorbent for HA removal, providing a mechanistic basis for scaling up diatomite-based sorption in column or filtration-assisted configurations for practical water treatment.

1. Introduction

Global freshwater scarcity is intensifying, with nearly 1.8 billion people experiencing absolute water shortages and almost 4 billion facing severe seasonal scarcity [1]. Beyond this limited availability, water quality is increasingly compromised by natural organic matter, industrial effluents, and agricultural inputs, thereby exposing large populations to contaminants above health-based limits [2]. Among these pollutants, humic substances (HS) constitute the dominant fraction of dissolved organic carbon in many natural waters and play a critical role in controlling aesthetic quality, light penetration, and the formation of

regulated disinfection by-products [3]. Their highly aromatic and polydisperse structures render HS recalcitrant to biodegradation, enabling their long-term persistence in rivers, lakes, and groundwater systems [4].

Humic acid (HA), the major component of HS, further complicates treatment by forming strong complexes with metal ions and mineral surfaces, thereby enhancing the solubility and mobility of heavy metals [5]. Conventional HS removal methods, including coagulation, flocculation, membrane filtration, sorption, and oxidation, are widely applied; however, each exhibits intrinsic limitations, including excessive sludge generation, high operational costs, and energy-intensive operation

* Corresponding authors.

E-mail addresses: yoshioka2652@stu.kanazawa-u.ac.jp (S. Yoshioka), mmhrocky@se.kanazawa-u.ac.jp (M.M.H. Rocky), hhiroshi@se.kanazawa-u.ac.jp (H. Hasegawa).

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