



# Impact of Montmorillonite Clay on Polysulfone Mixed Matrix Membrane for Heavy Metal Adsorption

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**Abstract** Exposure to high levels of heavy metals exerts serious health hazards to humankind. It is, hence, imperative to limit exposure to heavy metals by avoiding their consumption, direct or indirect, and by appropriately disposing of items that may contain heavy metals. To explore heavy metals removal efficacy, montmorillonite (MMT), a type of clay, was prepared at varying dosages (0.5, 1.0, and 1.5 wt%) to fabricate polysulfone mixed matrix membranes for treating aqueous solution contaminated with cadmium and lead. The mixed matrix membranes are characterized by scanning electron microscope (SEM), Fourier transforms infrared (FTIR), energy dispersive X-rays (EDX), water uptake test, pure water flux calculation, and heavy metal adsorption test. The particle size distribution of MMT is first measured covering the range of 1 to 42  $\mu\text{m}$ . The FTIR spectra of MMT and MMT-filled membranes indicate that the silica functional group dominates the MMT elemental composition. It

is revealed that the modified design improves water uptake by 83% compared to the pristine membrane. The pure water flux of the 1.5 MMM membrane is the fastest among the membrane at  $\sim 2500 \text{ L/m}^2\cdot\text{h}$  and is the most porous membrane with a porosity of 10%. Heavy metal rejection measurement shows that the modified membrane can remove cadmium and lead by 3% and 14%, respectively. Furthermore, all prepared membranes show solute water flux of more than  $500 \text{ L/m}^2\cdot\text{h}$ . The incorporation of MMT has successfully altered the polysulfone mixed matrix membrane to become a high-flux membrane capable of treating cadmium- and lead-rich water. Further study is needed to utilize the membrane to treat heavy metal wastewater.

**Keywords** Montmorillonite · Mixed matrix membrane · Heavy metal · Clay dosage · Adsorption · Polysulfone

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## 1 Introduction

The use of membranes has been at the forefront of water treatment with additional functionality as a part of wastewater treatment systems (Gozali Balkanloo et al., 2020). Its ability to eliminate contaminants is undoubtedly one of the best in the industry. Generally, membranes are made of an ordinary hydrophobic polymer (Alenazi et al., 2017). Hence, to tackle the issue of membrane hydrophobicity, particles, preferably in nano sizes, are introduced as part of the membranes such that the resulting membranes are known as mixed matrix membranes (MMM) (Ali & Ismail, 2021). The purpose of adding nanoparticles to membranes is to impart new abilities, such as anti-fouling and adsorption. Besides the new functionality, adding particles would improve the structural integrity, surface hydrophilicity, porosity, and thermal resistance (Abdel-Karim et al., 2021). One of the outstanding particles to be included in the membrane is clay. Clay is known for its low cost, high surface area, and excellent hydrophilic material, all of which are essential in improving membrane characteristics (Al Kausor et al., 2022; Tran et al., 2012). Montmorillonite (MMT) is a type of clay made up of silica and alumina that exist as an interlayer with a d-spacing of 1 nm (Vaiano et al., 2018). In detail, the structures of silica and alumina in MMT are arranged in quadrilateral and octagonal forms, respectively (Kumar et al., 2014). Despite its advantages, MMT has low aqueous form dispersion and is susceptible to aggregation, which could affect the membrane permeability and structural integrity. There are three phases of MMT dispersion in polymer solution: phase separation, intercalation, and exfoliation (Al Kausor et al., 2022). Intercalation occurs when some particles or foreign molecules are introduced between the MMT interlayers, which causes it to expand or swell (Al-Zaoari et al., 2022; Tran et al., 2012). The structure of MMT normally consists of the alumina octahedral layer placed between the quadrilateral silica layers, while the cation ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) exists across the interlayer for balancing the charges (Miller, 2001). The presence of weak cations as sandwiched by the interlayer means that, at present, MMT has a high potential for cation exchange.

The adsorption mechanism for heavy metal-MMT follows the general step similar to dye adsorption, which starts with the transfer of pollutant particles

from bulk solution towards the adsorbent surface, followed by the diffusion of adsorbate across the boundary layer that encapsulates the adsorbent (Momina et al., 2018). Next, the adsorbate, i.e., dye or heavy metal, would attach to the adsorbent's active site, leading to intraparticle diffusion of adsorbate inside the adsorbent pore (Momina et al., 2018). Due to the unique MMT structure, which consists of cations, upon contact with an aqueous solution, it will release the cations, mainly  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , thus turning the MMT surface to contain a negative charge (Hu et al., 2006). The highly negatively charged surface would attract either dye or heavy metal cation particles, thereby providing the great potential of utilizing clay as a material in fabricating the adsorption membrane. Zhang et al. (2022) investigated the potential of utilizing  $\text{MgFe}_2\text{O}_4$ -MMT with biochar for treating soil contaminated with heavy metals, such as cadmium (Cd), zinc (Zn), and lead (Pb). Based on their findings,  $\text{MgFe}_2\text{O}_4$ -MMT has higher removal performance than  $\text{MgFe}_2\text{O}_4$ -MMT-biochar with Cd, Zn, and Pb removal of 58%, 25%, and 50%, respectively (Zhang et al., 2022). However, besides removing heavy metals, the main purpose of the works is to improve the soil conditions, which can be obtained by mixing  $\text{MgFe}_2\text{O}_4$ -MMT with biochar. Meanwhile, Hao et al. (2022) synthesized graphene oxide (GO)/MMT with sodium alginate aerogels for treating copper (Cu) infested wastewater. The resulting composite has a large surface area of  $266.3 \text{ m}^2/\text{g}$ , with copper removal as high as 95% (Hao et al., 2022). The high removal performance is contributed by the unique slit-shaped pore that selectively rejects any planar molecules, such as hydrated copper. Hao et al. (2022) extended the work by carrying out the adsorption test with several other heavy metal elements, such as Zn, manganese (Mn), and chromium (Cr). The adsorption order of GO/MMT is as follows:  $\text{Cu} > \text{Zn} > \text{Mn} > \text{Cr}$ , in which the radius of Cr is the biggest at  $4.61 \text{ \AA}$  while Cu has the smallest radius at  $4.19 \text{ \AA}$ . Despite Cu having a smaller form factor than other heavy metals, Hao et al. (2022) argued that the reason behind its high removal performance is that the hydration shell encapsulates Cu is much smaller, thus easing Cu to interact with the negative group that exists in sodium alginate.

Having observed the great potential of MMT in discarding polluting substances, the present study aims to examine its influence on the mixed matrix