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Regular Article

# Zirconium-based metal organic frameworks loaded on polyurethane foam membrane for simultaneous removal of dyes with different charges

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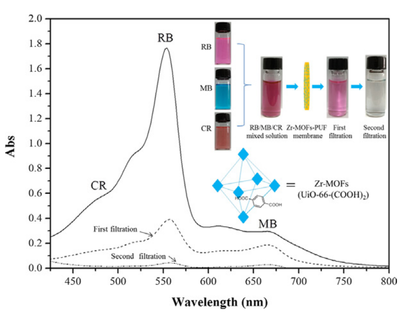
## GRAPHICAL ABSTRACT

The Zr-Based metal-organic frameworks combining polyurethane foam membrane can simultaneously remove RB, MB and CR from RB/MB/CR ternary solution.

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## ABSTRACT

Treating dye wastewater by membrane filtration technology has received much attention from researchers all over the world, however, current studies mainly focused on the removal of singly charged dyes but actual wastewater usually contains dyes with different charges. In this study, the removal of neutral, cationic and anionic dyes in binary or ternary systems was conducted by using zirconium-based metal organic frameworks loaded on polyurethane foam (Zr-MOFs-PUF) membrane. The Zr-MOFs-PUF membrane was fabricated by an in-situ hydrothermal synthesis approach and a hot-pressing process. Neutrally charged Rhodamine B (RB), positively charged Methylene blue (MB), and negatively charged Congo red (CR) were chosen as model pollutants for investigating filtration performance of the membrane. The results of filtration experiments showed that the Zr-MOFs-PUF membrane could simultaneously remove RB, MB, and CR not only from their binary system including RB/MB, RB/CR, and MB/CR mixtures, but also from RB/MB/CR ternary system. The removal of dyes by Zr-MOFs-PUF membrane was mainly attributed to the electrostatic interactions, hydrogen bond interaction, and Lewis acid-base interactions between the membrane and dye molecules. The maximum removal efficiencies by Zr-MOFs-PUF membrane were 98.80% for RB at pH ≈ 7, 97.57% for MB at pH ≈ 9, and 87.39% for CR at

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pH ≈ 3. Additionally, when the NaCl concentration reached 0.5 mol/L in single dye solutions, the removal efficiencies of RB, MB, and CR by Zr-MOFs-PUF membrane were 93.08%, 79.52%, and 97.82%, respectively. All the results suggested that the as-prepared Zr-MOFs-PUF membrane has great potential in practical treatment of dye wastewater.



## 1. Introduction

In recent years, dyes are widely used as the colorant in printing, cosmetic, leather, plastic, food, textile, and other industries [1]. The wastewater containing dyes will cause serious threat to human health and the environment once being discharged without proper treatment. Some organic dyes are toxic, carcinogenic, and teratogenic [2–4]. Thus, it is significant to treat dye effluent before releasing them into the environment.

To date, a variety of chemical, physical and biological approaches have been developed for separation and removal of dyes from wastewater, such as adsorption [4–7], precipitation and coagulation [8–10], photocatalytic degradation [11,12], ion-exchange [13], and membrane filtration [14,15]. Among these methods, membrane filtration technology plays a crucial role in meeting the requirements for wastewater treatment due to its relatively simple operation, low cost, and high efficiency [16,17]. Currently, one of the most attractive aspects in the field of membrane filtration is the innovation of membrane materials.

Polyurethane foam (PUF) is a three dimensional porous material which is commercially available. The material has been used as the support substrate in various applications due to its highly mechanical durability and excellent elasticity [18]. For example, Lefebvre et al. used polydopamine-coated polyurethane open cell foam for loading carbon media for dye adsorption [19]. Zhang et al. reported that super-hydrophobic graphene-coated polyurethane sponge showed excellent performance for oil-water separation [20]. Besides, polyurethane foams were also employed in desalination [21] and catalysis [22] as the support materials. Due to its easy accessibility and unique physical and mechanical properties, polyurethane foams have become potential supporting substrate materials for the development of membrane filtration in wastewater treatment. In our previous work, we investigated the removal of organic dyes including positively charged methylene blue (MB), neutrally charged rhodamine B (RB), and negatively charged methyl orange (MO) by PUF membrane stuffed with humic acid-chitosan crosslinked gels [23]. We found that the PUF membrane exhibited the ability of selectively separating MB from binary solutions including RB/MB and MO/MB mixed solution when the PUF membrane was only filled with chitosan gels. Noticeably, PUF membrane could simultaneously remove MB and RB from MB/RB binary solution when the membrane was filled with humic acid-chitosan crosslinked gels. However, the removal of mixed dye solutions including positively charged dye, neutrally charged dye, and negatively charged dye by PUF-based membrane needs further investigation. In addition, most of reported documents focused on the removal of cationic dyes or anionic dyes alone from wastewater by membrane filtration [24–26]. However, actual wastewater usually contains dyes with different charges. Thus it is necessary and significant to search for more suitable membrane materials to treat the complicated wastewater.

Metal organic frameworks (MOFs), also known as porous materials, are composed of inorganic metal ions (or clusters) and organic ligands by coordinate bonds. They have received considerable attention in recent years due to their adjustable pore size, numerous metal active sites, and large surface area [27,28]. These unique features make them very popular in various applications, such as the separation, adsorption and storage, smart sensors, and heterogeneous catalysis [29,30]. But most of metal organic frameworks still are subjected to insufficient hydrothermal stability, which hinders the applications of MOFs in processes involving water. Nevertheless, a series of zirconium-carboxylate MOFs (Zr-MOFs) have been emerged and synthesized with different topologies and various functional groups, mainly including —$NH_2$, —Br, —$NO_2$ [31–33]. The zirconium has a high attraction towards Lewis acid and oxygen ligands characteristic. It was reported that the zirconium-based MOFs can be synthesized from nanocrystal to single-crystal structures by adjusting the category and amount of modulators [34]. The Zr-MOFs exhibit remarkable thermal and chemical abilities via strong coordinate bonds between the zirconium atoms and carboxylate oxygens [31,35,36]. Moreover, zirconium cations can target specific adsorption behavior as open metal sites in the secondary building unit because of its high valence [37]. Benefiting from these outstanding qualities, Zr-MOFs family has acquired more and more attention in the area of wastewater treatment, especially in the adsorption of dyes [37,38], capture of toxic heavy metals [39], and removal of persistent organic pollutants [40]. However, because of its powdery or gelatinous nature, it is inconvenient to separate from solutions. And due to the relatively poor mechanical stability of MOFs [41], there is a growing demand for structured supporting materials.

In this work, zirconium-carboxylate MOFs combined PUF was designed and fabricated as a novel hybrid membrane (Zr-MOFs-PUF membrane) for removing differently charged organic dyes from wastewater. Rhodamine B (RB, neutral dye), Methylene blue (MB, cationic dye), and Congo red (CR, anionic dye) were used as model pollutants. The static adsorption experiments of Zr-MOFs-PUF membrane, as well as the effects of flow rate, initial concentration of dyes, pH, coexisting NaCl on single dye removal were investigated. Particularly, the filtration experiments for RB, MB, and CR removal from binary (RB/MB, RB/CR, and MB/CR) and ternary system (RB/MB/CR) by the Zr-MOFs-PUF membrane were also performed.

## 2. Materials and methods

### 2.1. Materials

Zirconium chloride ($ZrCl_4$, AR, 98%) and 1,2,4,5-Benzenetetracarboxylic acid ($H_4BTEC$, AR, 98%) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Flexible PUF of industrial grade (0.035 g/$cm^3$) was obtained from Lianda Technology Industrial Co., Ltd. (Shenzhen, China). Potassium dichromate ($K_2Cr_2O_7$, AR, 99.8%), MB (AR, 95%), RB (AR, 99%) and CR (AR, 99%) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China) and their chemical structures were shown in Fig. 1. Hydrochloric acid (HCl, GR, 37%), sulfuric acid ($H_2SO_4$, GR, 98%), sodium hydroxide (NaOH, AR, 96%), sodium chloride (NaCl, AR, 99.5%), acetone (AR, 99.7%) and ethanol (AR, 99.7%) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of chemical reagents were used as received without further purification.