

# Coating Carboxylic and Sulfate Functional Groups on ZrO<sub>2</sub> Nanoparticles: Antifouling Enhancement of Nanocomposite Membranes during Wwater Treatment

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## Abstract

This research proposes a novel method for intensifying the presence of nanoparticles in the top layer of blended nanocomposite membranes. To this end, carboxylic acid and sulfate functional groups were coated on the surface of zirconia nanoparticles. The functionalized nanoparticles were embedded in the matrix of PAN and PSf membranes, and six nanocomposite membrane models were synthesized including  $m\text{ZrO}_2@n\text{PAN}$ ,  $m\text{CZrO}_2@n\text{PAN}$ ,  $m\text{SZrO}_2@n\text{PAN}$ ,  $m\text{ZrO}_2@n\text{PSf}$ ,  $m\text{CZrO}_2@n\text{PSf}$ , and  $m\text{SZrO}_2@n\text{PSf}$ . The aim was to exploit proper arrangement of nanoparticles in the membrane matrix to strengthen the antifouling properties of the membrane. Overall, the change in the superficial and structural properties of the membrane in response to presence of functional groups caused the internal pore blocking in  $^{2.68}\text{CZrO}_2@^{13}\text{PAN}$  and  $^{2.68}\text{SZrO}_2@^{13}\text{PAN}$  to be 50.9 and 41.8% less than that of the raw membrane, respectively. On the other hand, for the membrane lacking the functional group  $^{2.68}\text{ZrO}_2@^{13}\text{PAN}$ , this improvement was calculated to be only 30.9%. In terms of total fouling ratio,  $^{2.68}\text{CZrO}_2@^{11}\text{PAN}$ ,  $^{2.68}\text{CZrO}_2@^{13}\text{PAN}$ , and  $^{2.68}\text{CZrO}_2@^{15}\text{PAN}$  membranes had 42.8, 39.3, and 35.6% less total filtration resistance respectively compared to the raw membrane. In term of Considering PWF,  $^{2.68}\text{SZrO}_2@^{13}\text{PAN}$  and  $^{2.68}\text{SZrO}_2@^{13}\text{PSf}$  had 46.2% and 52.1% more PWF than bare  $^{13}\text{PAN}$  and bare  $^{13}\text{PSf}$  membrane. Regarding the role of functional groups in improving the membrane separation properties,  $m\text{CZrO}_2@^{13}\text{PSf}$  membranes improved dye separation percentage by 20%, compared to the raw membrane. On the other hand,  $^{2.68}\text{SZrO}_2@^{11}\text{PSf}$  membranes managed to separate 100% of Red BRLS dye due to the role of sulfate functional group in reducing the size of the membrane pores.

**Keywords:** Carboxylic Functional Group; Sulfate Functional Group; ZrO<sub>2</sub> Nanoparticles; Nanocomposite Membrane; Antifouling

## 1. Introduction

Superficial and structural modification of membranes with the aim of improving their antifouling properties has been of great interest in recent years [1-4]. Among the most practical modifiers which can modify the surface and structure of the membranes are nanostructures including carbon nanotubes [5], graphene planes [6, 7], metal organic frameworks [8, 9], zeolites [10], and metal as well as metal oxide nanoparticles [11, 12]. Presence of these nanostructures in the surface and structure of membrane leads to development of nanocomposite membranes, whose application has been suggested as one of the most powerful tools for mitigating membrane fouling, according to different researchers [13]. Among the mentioned nano-structured modifiers, metal oxide nanoparticles have attracted high attention in recent years, because of