SYNTHESIS AND INVESTIGATION OF A NOVEL NANOCOMPOSITE FOR IMPROVING SOLAR RADIATION ABSORBANCE OF MD MEMBRANES

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Abstract. Membrane distillation (MD) has emerged as a promising technology for seawater desalination to provide drinking water. The most notable advantage of MD is the ability to couple with solar energy to reduce its water production cost. However, limited thermal efficiency is one of the key challenges to the commercialization of solar-driven MD seawater desalination. Due to low thermal efficiency, most solar-driven MD systems require large arrays of solar thermal collectors, leading to discernibly high investment costs of the MD systems. Recently, MD membranes coated with solar radiation absorbing materials have been proposed for the solar-driven MD process to obviate the need for large solar thermal collectors. In this study, we synthesized a novel black spinel-carbon nanocomposite for MD membrane coating to improve the solar radiation absorbance of the membrane. The preliminary experimental results demonstrated that the Fe³⁺/Cr³⁺ ratio in the black spinel greatly affected its crystal sizes and light absorbance. The black spinel absorbed much more light in the visible (i.e. wavelength of 300–600 nm) than in the visible-near infrared range (> 600 nm). Combining black spinel with carbon black into the black spinel-carbon nanocomposite widened the high light absorbance range spanning from visible to far-red. Therefore, the combined black spinel-carbon nanocomposite exhibited increased solar radiation absorbance and hence water heating capacity compared with single materials.

Keywords: membrane distillation, black spinel nanocomposite, thermal efficiency, energy consumption, seawater desalination.

Classification numbers: 3.4.1, 3.4.2, 2.5.3.

1. INTRODUCTION

Membrane distillation (MD) has emerged as a promising hybrid process for seawater desalination to provide drinking water in many water-stressed areas around the world [1, 2]. The most notable advantage of MD compared with other seawater desalination processes is the ability to combine with solar energy to reduce the water production cost [3, 4]. Therefore, solar powered seawater MD desalination has been explored for drinking water supply in many remote areas and on islands worldwide [3, 5 - 7]. For example, Chafidz et al. [3] developed a portable solar-driven MD seawater desalination system to provide drinking water in arid remote areas of
Saudi Arabia. The system consisted of MD membrane modules connected with evacuated tube solar thermal collectors for heating supply and photovoltaic panels for electricity [3]. Andres-Manas et al. [5] built a pilot solar assisted MD seawater desalination system for drinking water supply at the University of Almeria (Spain). Solar thermal energy was collected using static collectors to provide the thermal energy to the MD system, while the electricity demand for running water circulation pumps was from the grid [5].

For solar powered MD seawater desalination, research to improve the process thermal efficiency is of vital importance. Most of solar powered MD systems use separate solar thermal collectors to convert solar radiation into heat supplied to the MD membrane module. Due to the limited light-to-heat conversion of solar thermal collectors and the heat loss on the tubing, these solar powered MD systems exhibit limited efficiency in the use of solar radiation. Recently, Summers and Lienhard V [8] proposed an innovative idea to improve the thermal efficiency of the solar powered MD process. In their solar-driven integrated MD system, the MD membrane was used directly as the radiation absorber (i.e. without the separate solar thermal collectors) to mitigate the heat loss on tubing to the environment [8]. The MD membrane in this system was coated with polycarbonate to increase its solar radiation absorbance. The experimental results demonstrated that the thermal efficiency of the MD process with the integrated membrane solar thermal collector was increased due to less heat loss to the environment [8].

In this study, we propose a novel MD membrane coating material to improve the membrane’s solar radiation absorbance and hence enhance the MD process thermal efficiency. The proposed novel coating material is black spinel-carbon nanocomposite having selectively high solar radiation absorbance [9]. Black spinel is a group of spinel oxides with the molecular formula of $\text{AB}_2\text{O}_4$, in which A is divalent ions (e.g. $\text{Cu}^{2+}$, $\text{Ni}^{2+}$, $\text{Mn}^{2+}$, $\text{Fe}^{2+}$, and $\text{Co}^{2+}$) and B is trivalent ions (e.g. $\text{Fe}^{3+}$ and $\text{Cr}^{3+}$) [10]. These spinel oxides can absorb nearly all visible light, giving them black appearance. The radiation-absorbing selectivity of the spinel oxides can be tailored by adjusting the atomic composition ratio of A ($\text{Cu}^{2+}/\text{Mn}^{2+}$) or B ($\text{Fe}^{3+}/\text{Cr}^{3+}$) [11, 12]. However, black spinel exhibits limited absorbance for the wavelengths in infrared radiation (IR), leading to considerable infrared emission loss. To reduce this infrared emission loss, black spinel needs to be combined with other materials that have high absorbance of the radiations with wavelength in and toward the IR range (i.e. $< 2 \, \mu\text{m}$). Carbon black exhibits high radiation absorbance at a significantly wider wavelength range than that of black spinel [13]. Thus, carbon black can be combined with black spinel to form a material that can absorb more radiation at wider wavelength from solar radiation.

In this preliminary study, black spinel-carbon nanocomposite was synthesized and investigated for improved solar radiation absorbance aimed for the solar-driven integrated MD seawater desalination process. The black spinel-carbon nanocomposites were based on black spinel $\text{CuCr}_2\text{O}_4$ doped with various $\text{Fe}^{3+}$ content. The black spinel-carbon nanocomposite was synthesized using the hydrothermal method and was characterized with respects to structural morphology and radiation absorbance properties. The water-heating capacity of the synthesized black spinel-carbon nanocomposite was examined under real solar radiation conditions in Ha Noi, Viet Nam.

### 2. MATERIALS AND METHODS

#### 2.1. Materials
Chemicals used to synthesize the black spinel-carbon nanocomposite in this study included copper nitrate (Cu(NO$_3$)$_2$·3H$_2$O), ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O), chromium chloride (CrCl$_3$·6H$_2$O), sodium hydroxide (NaOH), and carbon black (i.e. Super P® Conductive). All chemicals were of laboratory-grade and provided by Alfa Aesar.

2.2. Synthesis of black spinel-carbon nanocomposites

A two-step route was used to synthesize black spinel-carbon nanocomposites. In the first step, black spinel CuFe$_{x}$Cr$_{2-x}$O$_4$ nanoparticles were synthesized using the hydrothermal method. Then, the black spinel-carbon nanoparticles were prepared by mixing black spinel CuFe$_{x}$Cr$_{2-x}$O$_4$ and carbon black in resin using an ultrasonic bath.

The black spinel CuFe$_{x}$Cr$_{2-x}$O$_4$ nanoparticles were synthesized in an autoclave using the hydrothermal method. The mixtures of Cu(NO$_3$)$_2$ 0.01 M, Cr(NO$_3$)$_3$ 0.01 M, and Fe(NO$_3$)$_3$ 0.01 M with the Cu$^{2+}$/Cr$^{3+}$/Fe$^{3+}$ molar ratio of 1/x/2-x (i.e. with x = 0, 0.4, 0.8, 1.2, 1.6, and 2) were dissolved in 100 ml deionized (DI) water and then stirred for 30 minutes to form a homogeneous solution. Then, NaOH 0.15 M was dropped into the mixed solution under agitation until reaching the pH of 10 to facilitate the precipitation of hydroxides. The suspension was vigorously stirred for another 30 minutes before being transferred into a 200 ml Teflon-lined autoclave. The sealed autoclave was heated at 190 °C for 5 hours and cooled down to room temperature. The black spinel CuFe$_{x}$Cr$_{2-x}$O$_4$ was obtained from the mixture using filter paper after being washed with DI water until the filtrate water had neutral pH of 7. After washing, the black spinel was dried at 50 °C for 24 hours. Finally, CuFe$_{x}$Cr$_{2-x}$O$_4$ powder was calcinated at 800 °C for 2 hours.

Black spinel-carbon nanoparticles were prepared by mixing black spinel CuFe$_{x}$Cr$_{2-x}$O$_4$ and carbon black in acrylic resin using an ultrasonic bath. Briefly, 100 ml of dilute acrylic resin in water was homogenized in the ultrasonic bath for 2 hours. Then, a mixture of 0.5 g CuFe$_{x}$Cr$_{2-x}$O$_4$ and 0.5 g carbon black powder were added to the resin, following by 24 hours of continuous sonication in the ultrasonic bath. The obtained black slurry was sprayed layered-by-layer on the surface of square stainless-steel coupons (i.e. 5.0x5.0 cm) using a spraying gun under a constant pressure of 4 bar. The coated stainless-steel coupons were then naturally dried at room temperature. The use of acrylic resin in this step was to ensure the durability of the coating black spinel-carbon nanocomposite layers even under wetting condition.

2.3. Characterization of black spinel and black spinel-carbon nanocomposites

The structure and morphology of the black spinel CuFe$_{x}$Cr$_{2-x}$O$_4$ nanocomposites were examined using X-Ray diffraction (XRD) and scanning electron microscope (SEM) at Vietnam Academy of Science and Technology (VAST). The XRD analyses were conducted using the SIEMENS D-500 Bruker (i.e. from Germany) with the Cu-Kα diffraction source with the wavelength (λ) of 1.54058 Å, while the SM-6510LV (i.e. from Japan) was used for the SEM analyses.

The optical properties of the synthesized nanocomposites were analyzed using the differential reflectance spectroscopy (DRS) technique by the Jasco V-750 with the wavelength in the range of 250 - 900 nm. This testing was conducted at Hanoi University of Science and Technology.

The thermal efficiency of solar absorbing materials (e.g. black spinel and black spinel-carbon) was assessed using Figure of Merit (FOM) value. FOM value was calculated as below:
where $R$ was the calculated reflectance spectrum; $I$ was total solar irradiance (i.e., reported in ASTM G173); $C$ was the concentration factor (i.e., which is the ratio of absorber area to mirror collection area, and can be assumed to be 1 for the solar-powered MD process); $B$ was Planckian black body emission; $T$ was the temperature of coating layer (K); and $\lambda$ was the wavelength (nm).

The actual solar radiation absorbance capacity of the synthesized black spinel-carbon nanocomposites was evaluated by measuring the water heating capacity of stainless-steel coupons. For each test, the coated stainless-steel coupon was submerged in 100 mL water in a top-open beaker. The testing time was on the 26th May 2020 between 11:30 and 12:00 am under clear and sunny weather conditions. For comparison, a blank test using the non-coated stainless-steel coupon was conducted under the same testing conditions. The temperature of water after every 10 minutes heating under direct sunlight was recorded. The difference in absorbed heat per square meter of the non-coated stainless-steel coupon and that coated with the synthesized black spinel-carbon nanocomposites was calculated as:

$$\Delta Q = (T_c - T_{nc}) \times C_p \times m_{H_2O} \times \frac{1}{S_c}$$ (2)

where $\Delta Q$ was the difference in absorbed heat per square meter (kJ/m²); $T_c$ and $T_{nc}$ were the water temperature (°C) in the beaker with the nanocomposite coated and non-coated stainless-steel coupon, respectively; $C_p$ was the liquid water specific heat capacity (kJ/g); $m_{H_2O}$ was the mass of water in the beaker (g); and $S_c$ was the area of the stainless-steel coupon (m²).

3. RESULTS AND DISCUSSIONS

3.1. Structure and morphology of the synthesized black spinel nanocomposites

![XRD spectra](Figure 1. XRD spectra of the synthesized black spinel nanocomposites CuFe$_{x}$Cr$_{2-x}$O$_4$, with the Fe$^{3+}$ content ($x$) in the range from 0 to 2.0.)
The XRD analyses confirmed that the synthesized black spinel nanocomposites had clear crystal structures and the presence of Fe\textsuperscript{3+} in the black spinel nanocomposites affected their crystal structures (Fig. 1). Amongst the synthesized black spinel nanocomposites, \( \text{CuCr}_2\text{O}_4 \) (i.e. \( x = 0 \)) exhibited the tetragonal crystal structure, confirmed by the diffraction peaks for the Miller planes of (200), (112), (211), (202), (220), (321), (400) and (411), corresponding to the 2\( \theta \) value of 29.92°, 31.37°, 35.52°, 37.91°, 42.53°, 56.18°, 61.45°, and 64.72°, respectively (ICDD-PDF 01-085-2313). The XRD spectra of \( \text{CuCr}_2\text{O}_4 \) crystals pointed out the tetragonal symmetry (space group \( I4/amd \)). The lattice constant values of this sample were \( a = 6.0305 \) Å and \( c = 7.7823 \) Å.

When doping Fe\textsuperscript{3+} to replace Cr\textsuperscript{3+} (i.e. \( x = 0.4 \)– 2), the tetragonal symmetry structure tended to change to a more symmetrical structure: cubic crystalline with space group \( Fd3m \). The number of diffraction peaks reduced as seen in Fig. 1, but all samples had a peak at a 2\( \theta \) angle of \( \sim 35° \), which is the main peak for spinel oxide. The XRD spectra allowed for the calculation of the crystallite diameter using the Scherrer equation as below:

\[
d = \frac{0.9\lambda}{B \cos \theta}
\]

where \( d \) was the average crystallite size; \( \lambda \) was the X-ray wavelength (i.e. 0.15406 nm); and \( B \) was the full width at half-maximum (FWHM) (i.e. radian). The crystal size of all samples was calculated at the 2\( \theta \) position of (200) plane with \( \text{CuCr}_2\text{O}_4 \) and of (211) plane with other samples.

The calculation results revealed that the Fe\textsuperscript{3+}/Cr\textsuperscript{3+} ratio in the synthesized black spinel also affected the size of the crystals obtained. Increasing Fe\textsuperscript{3+} content of the black spinel resulted in the decrease in the 2\( \theta \) value and the crystal diameter (d) (Fig. 2). This was also confirmed by SEM analyses. The SEM images demonstrated that the black spinel nanocomposites had clear crystal structure with relatively uniform crystal sizes (Fig. 3). Moreover, \( \text{CuCr}_2\text{O}_4 \) (\( x = 0 \)) crystals were several times bigger than \( \text{CuFe}_2\text{O}_4 \) crystals (\( x = 2 \)) (Fig. 3). It is noteworthy that black spinel nanoparticles with various crystal sizes can be applied in tandem-structured solar
absorbing layers with the porous particles on the top and dense one on the bottom. This tandem structure exhibits a remarkably high solar-to-thermal conversion efficiency (i.e. termed as figure of merit (FOM)) [14]. This will be discussed more detailed in the next section.

**Figure 3.** The SEM images of the black spinel nanocomposites CuCr$_2$O$_4$ ($x = 0$) and CuFe$_2$O$_4$ ($x = 2$).

### 3.2. The optical properties of the synthesized black spinel and black spinel-carbon nanocomposites

The optical properties of the synthesized black spinel and black spinel-carbon nanocomposites were evaluated using the DRS spectra. It is noteworthy that all black spinel absorbed light in the visible range with wavelength from 300 to 600 nm, and their absorbance noticeably decreased when the light moved to the violet range (Fig. 4a).

**Figure 4.** DRS spectra of a) black spinel (CuFe$_x$Cr$_{1-x}$O$_4$) and b) carbon black at different wavelength ($\lambda$).

Moreover, the absorbance of the black spinel nanoparticles with different Fe$^{3+}$ content (i.e. $x$) maximized at different wavelength, moving toward the lower end of the visible range. The higher absorbance range of wavelength shifted from orange-red light to violet-blue light with the increased Fe$^{3+}$ content in black spinel. Therefore, Fe$^{3+}$ doping in CuCr$_2$O$_4$ could strengthen the red intensity and weaken the blue intensity of black spinel. On the other hand, the light absorbance of carbon black was lower than all black spinel in the visible range, but it gradually increased as the wavelength shifted to higher end of the visible-near IR spectra (Fig. 4b). Therefore, when black spinel and carbon black are combined in a composite coating layer, the
solar-to-thermal conversion efficiency of the composite might increase because of its high absorbance at almost visible-near IR wavelength.

As envisaged, combining black spinel (CuFe\textsubscript{x}Cr\textsubscript{2-x}O\textsubscript{4}) with carbon black into black spinel-carbon nanocomposite flattened their light absorbance curves and prevented their declined absorbance when the light shifted toward the violet range (Fig. 5a). The light absorbance of six black spinel-carbon nanocomposites gradually increased with the wavelength below 400 nm, and levelled-off in the higher range of wavelength (400 - 600 nm). The flattened light absorbance in the wider wavelength range allows the black spinel-carbon nanocomposites to absorb more solar radiation from the sunlight because the sunlight is composed of lights at various wavelength. The high solar radiation absorbance of the black spinel-carbon nanocomposites was also manifested by their DRS reflection spectra (Fig. 5b). All black spinel-carbon nanocomposite samples had low reflection (i.e. 3 - 7 %) in almost visible and far-red range. The low reflection in the visible and far-red wavelength rendered the synthesized black spinel-carbon nanocomposites ideal coating materials for solar absorber. Therefore, they can be coated on MD membrane to enhance its solar radiation absorbance in the solar-driven MD seawater desalination application.

![Figure 5. DRS absorbance a) and reflection b) spectra of the synthesized black spinel CuFe\textsubscript{x}Cr\textsubscript{2-x}O\textsubscript{4}-carbon nanocomposites with different Fe\textsuperscript{3+} content (x).](image)

![Figure 6. The calculated FOM value of the synthesized black spinel CuFe\textsubscript{x}Cr\textsubscript{2-x}O\textsubscript{4}-carbon nanocomposites with different Fe\textsuperscript{3+} content (x).](image)
The Figure of Merit (FOM) value calculated using the equation (1) demonstrated the thermal efficiency of the solar absorbing materials. The wavelength was in the range from 250 nm to 900 nm corresponding to the reflection data measured from the DRS spectra. It is noteworthy that all black spinel-carbon nanocomposites had FOM values above 95% (Fig. 6), indicating their adequate light-to-heat conversion capacity. Particularly, amongst the synthesized black spinel-carbon nanocomposite samples, CuFe₁.₆Cr₀.₄O₄-carbon exhibited the highest FOM value (i.e. 96.7%). The highest FOM value of the CuFe₁.₆Cr₀.₄O₄-carbon is consistent with its highest DRS absorbance and lowest DRS reflection demonstrated in Fig. 5a&b.

3.3. The solar radiation absorbance capacity of the synthesized black spinel-carbon

Given its best optical properties, CuFe₁.₆Cr₀.₄O₄-carbon nanocomposite was selected for the solar radiation absorbance test with actual solar light. The experimental results confirmed the solar radiation absorbance capacity of the CuFe₁.₆Cr₀.₄O₄-carbon nanocomposite. Compared with the blank test, the water temperature in the test with CuFe₁.₆Cr₀.₄O₄-carbon coated stainless-steel coupon was always of several degrees higher (Table 1). The small increase in the water temperature between the test with the CuFe₁.₆Cr₀.₄O₄-carbon coated and non-coated stainless-steel coupon was due to the small size of the coupon used (5.0×5.0 cm). However, when comparing the specific absorbed heat (i.e. heat per square meter of the coupon), the CuFe₁.₆Cr₀.₄O₄-carbon coated stainless-steel exhibited a considerably higher solar radiation absorbance capacity. The specific absorbed heat of the CuFe₁.₆Cr₀.₄O₄-carbon coated stainless-steel coupon was about 285 - 352 kJ/m² higher than that of the non-coated one after every 10 minutes under direct sun light (Table 1).

<table>
<thead>
<tr>
<th>Heating time (minutes)</th>
<th>Temperature of water in the beaker (°C)</th>
<th>ΔQ (kJ/m²)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Non-coating, $T_{nc}$</td>
<td>CuFe₁.₆Cr₀.₄O₄-carbon coating, $T_c$</td>
</tr>
<tr>
<td>0</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>42.8</td>
<td>44.5</td>
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<tr>
<td>20</td>
<td>61.3</td>
<td>62.6</td>
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<tr>
<td>30</td>
<td>73.2</td>
<td>75.3</td>
</tr>
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</table>

The preliminary experimental results reported here revealed great potential of the black spinel-carbon nanocomposites for coating the MD membranes to enhance its solar radiation absorbance capacity. The black spinel-carbon nanocomposite itself demonstrated adequate solar radiation absorbance. Further studies should focus on the integrity of this coating material with the MD membrane polymers to ensure the thermophysical and chemical stability of the coated membrane.

4. CONCLUSIONS

In this study, we synthesized black spinel and black spinel-carbon nanocomposites and investigated their morphological structure, optical properties, and actual solar radiation absorbance. The experimental results demonstrated that doping Fe³⁺ in black spinel CuFe₂.₃Cr₀.₄O₄ nanocomposites affected not only their crystal sizes but also their light absorbance. Thus, the sizes and light absorbance of the black spinel nanocomposites could be tailored by adjusting the
Fe$^{3+}$/Cr$^{3+}$ ratio. The black spinel with a higher Fe$^{3+}$/Cr$^{3+}$ ratio had smaller crystals and absorbed more light in the visible range than in the violet range. Given the carbon black’s high light absorbance in the visible-near IR, the combined black spinel-carbon nanocomposites had flattened and widened light absorbance curves, thus exhibiting high solar radiation absorbance capacity.

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**REFERENCES**


