Optimisation of additives on the performance of loess/fly ash-based ceramic membrane supports

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Abstract

Inorganic ceramic membranes have received a lot of attention due to their resistance to acid and alkali corrosion and ease of cleaning and utilisation, however, their high cost has limited their widespread use. To obtain lower-cost ceramic membranes with better performance, in this paper, single-channel tubular ceramic membrane supports were prepared using natural loess and solid waste ash material. This paper firstly investigated the effects of various additives (including carboxymethyl cellulose (CMC), graphite, calcium carbonate, copper oxide, magnesium oxide, and manganese dioxide,) on the pore size distribution, pure water flux, and flexural strength of the supports to select the appropriate additives; secondly, the response surface methodology was used to determine the amount of each parameter to be added. The results showed that CMC was more viscous and malleable compared to graphite and CaCO₃, thus increasing the density and pure water flow of the supports. MnO₂ improved both the pure water flow and flexural strength of the supports compared to CuO and MgO. The best sample was obtained when the contents of CMC, MnO₂, and kaolinite were 9.85 wt%, 10.62 wt%, and 4.8 wt%, respectively, the best sample obtained exhibited a pure water flux of 4985.52 L·m⁻²·h⁻¹·MPa⁻¹ and a flexural strength of 45.4 MPa. The support obtained meets the conditions for the application of porous ceramic carriers and provides a viable pathway for the wide application of low-cost ceramic membrane carriers.

1. Introduction

The continuous advances in science and technology have led to the rapid development of membrane separation technology, which finds applications in many industries, such as the chemical, pharmaceutical, metallurgical, and food industries [1–3]. With the increasing national water quality requirements to improve discharge standards and people’s concern about drinking water quality, membrane technology has become an important alternative to traditional water treatment and clarification processes. Separation membranes are indispensable in the fields of energy and water resource management, and their use can affect the environment [4, 5].

Most membranes currently in use can be classified as organic and ceramic membranes. Compared to organic membranes, ceramic membranes are more commonly utilised in water treatment [6] owing to their higher strength, superior stability, longevity, ease of cleaning, and regeneration. Ceramic membranes are composed of three layers: a support layer, an intermediate layer, and a membrane layer, with the pore size decreasing layer by layer. The support layer, which accounts for more than 95% of the membrane volume, provides ceramic membranes with strong support. In addition, the utilisation of high-performance support is an important condition for membrane water permeability. A uniform pore size distribution of the support facilitates the deposition of the intermediate and membrane layers. By contrast, asymmetric membranes can effectively reduce mass transfer resistance. Therefore, a support layer is essential for high-performance ceramic membranes.
High-performance ceramic membrane supports are typically manufactured from high-purity powders, such as alumina and silicon oxide powders, at sintering temperatures above 1600 °C [7]. However, their large-scale applications are limited because of their expensive raw materials and high production energy consumption.

Fly ash is a solid waste from coal combustion in power plants and is generally used in the cement industry [8]. It mainly contains metal oxides such as Al₂O₃ and SiO₂. The use of fly ash as a scaffold raw material minimises the cost of ceramics membrane preparation while maximising its value. Fang et al. constructed tubular ceramic membrane carriers using fly ash with varied particle size distributions [9]. Li et al. [10] prepared mullite-phase ceramic supports with a flexural strength of 59.1 MPa and a porosity of 26.8% using fly ash as the raw material and adding Al₂O₃ at a temperature of 1200 °C. The surface of the fly ash supports prepared in our previous study [11] was relatively dense, without any pore structures; specifically, the fly ash supports were prepared at the sintering temperature of approximately 1200 °C, which was obtained from the thermogravimetric curve, and the melting point of the fly ash particles was approximately 1200 °C. These results confirmed that fly ash can reduce the sintering temperature and energy consumption of ceramic supports, which is consistent with D. Zou’s findings [12].

Loess is a low-cost natural resource with high viscosity, while fly ash is a barren material. Thus, the addition of loess facilitates the dense bonding of the fly ash matrix and eliminates the need for organic binders (e.g., polyvinylpyrrolidone, hydroxypropyl methylcellulose, etc.). The porosity of loess is 40%–50%, and the particle combination is relatively loose. Spherical fly ash particles can form suitable gradations with loess particles. Kaolin is employed as a ceramic material owing to its good mineralogical composition. The film structure has good refractory and plastic characteristics because of its crystal order and thermal properties [13]. We chose kaolin as an additive because it can be sintered at temperatures lower than those required to sinter alumina. The alkaline metal components, such as Na₂O and Fe₂O₃, in kaolin and fly ash provide supporting functions in the sintering process [14]. However, natural minerals and industrial wastes contain large amounts of impurities.

The supports prepared from these substances have a high shrinkage rate, and it is difficult to ensure high porosity and high strength properties at the same time. Therefore, adding ceramic additives is one of the current research directions to improve the performance of new material carriers [15].

In this study, natural loess and fly ash, which is an industrial waste, were used as the raw materials to prepare ceramic membrane supports. In addition, the number of additives was optimised from different aspects: (1) the types of pore-forming agents and sintering aids, (2) the contents of pore-forming agents, sintering agents, and other additives, and (3) the response surface methodology (RSM). This study aims to investigate the effects of various additives on the pure water flux, flexural strength, pore size distribution, and microscopic morphology of ceramic membrane supports in order to a high-performance support material at a low cost.

2. Materials and methods

2.1. Materials

Loess was taken from the Luochuan National Geological Park in Shaanxi Province, China. The fly ash is taken from the Xijiao Thermal Power Plant in Xi’an, Shaanxi Province, China. Carboxymethyl cellulose and kaolin were purchased from Tianjin Fuchen Chemical Reagent Factory, China. Graphite was purchased from Chenglin Graphite Products Factory, Panshui, China. Calcium carbonate was purchased from Xi’an Chemical Reagent Factory, China. The copper oxide was purchased from Chengdu Kolon Chemical Reagent Factory, China. Magnesium oxide was purchased from Tianjin Beilian Fine Chemical Development Co. Manganese dioxide was purchased from Tianjin Fuchuan Chemical Reagent Factory, China.

Fly ash is barren, while loess is clayey and the addition of loess also facilitates embryo formation. They can be utilized as pore-forming agents because carboxymethyl cellulose, graphite, and calcium carbonate can all disintegrate at temperatures between 200 °C and 900 °C to release CO₂ or other chemicals, and the gas escapes to create pore structures.

CuO can react at low temperatures to produce a liquid phase, reducing the sintering temperature of the support. MgO is an alkaline metal oxide with cubic dense stacking and a crystal structure like that of NaCl. When an impurity phase is generated during the sintering process, the relative area of the grain boundary decreases, lowering the melting temperature at the grain boundary. When the sintering process reaches a low eutectic point, the impurity phase transitions into a liquid phase, promoting sintering and increasing material density. MnO₂ efficiently enters the Al₂O₃ lattice when sintered with it, forming a doped solid solution with it.

With the crystalline formula 2SiO₂·Al₂O₃·2H₂O, kaolin is a layered silicate that is flexible, can take on many different shapes without breaking, and doesn’t alter over time. Additionally, kaolin helps the sintering process produce mullite (3Al₂O₃·2SiO₂), which can significantly increase the material’s strength.
2.2. Preparation of the loess/fly ash supports
Loess, fly ash, pore-forming agents, sintering aids, and kaolin were mixed in certain proportions (as shown in table S1, available online at stacks.iop.org/MRX/9/095201/mmedia), with a loess to fly ash mass ratio of 54:36 with an appropriate amount of water. The mixture was then stirred for 30 min at about 25 °C and for another 1 h at 90 °C in a water bath to evaporate the excess water and obtain mud with a water content of approximately 15%. The mud was then wrapped in a plastic wrap and aged in an incubator with constant temperature and humidity (25 °C, 30 RH%) for 48 h. The aged mud was extruded using a ceramic tube extrusion machine at 10 MPa to obtain a wet blank of the support (15 mm outer diameter and 3 mm thickness) followed by drying at about 25 °C. The support was then fired at 1100 °C in a muffle furnace according to a certain sintering regime. The preparation process for the support is shown in figure 1.

2.3. Characterisation of the loess/fly ash supports
The supports were thermally analysed using a thermogravimetric analyser (TGA/SDTA851e, Mettler-Toledo, Switzerland). The particle size distributions of loess and fly ash were analysed using a laser particle size metre (S3500, Microtrac, America). The average pore size of the support was measured using the Mercury intrusion method (AutoPore IV9500, Micromeritics Instrument, USA). By exploiting its property of not infiltrating solid surfaces, mercury was forced into the pores of the porous body at high pressure to overcome the capillary resistance. Scanning electron microscopy (SEM, JCM-6000, Carl Zeiss, Germany) was used to characterise the surface morphology of the support. The physical phases of the support were analysed using x-ray diffraction (BD68000156-01 from Rigaku, Japan) over the 2θ range of 1–90° at a radius greater than or equal to 150 mm and a scanning speed of 5°/min.

Equation (1) was used to calculate the pure water flux:

\[
J_w = \frac{V}{A \cdot t}
\]

where \(J_w\) is the pure water flux in L m\(^{-2}\) h MPa, \(V\) is the amount of liquid permeation in L, respectively, \(A\) is the effective permeation area of the sample in m\(^2\), and \(t\) is the permeation time in h.

The flexural strength of the support (sample size: 3.0 mm × 4.0 mm × 40 mm) was measured by a three-point bending method in a universal Material Testing Machine (CMT3105, Shenzhen New Sansi Materials Testing Co., China). Each sample was tested four times.

The apparent porosity of the support was determined using the Archimedes method with water as the immersion medium. The opening ratio was calculated using equation (2) [17].

\[
\text{Apparent porosity(%) = } \frac{W_w - W_d}{V \times \rho} \times 100
\]

where \(W_w\) and \(W_d\) are the weights of the wet and dry supports, respectively, \(V\) is the total volume of the support, and \(\rho\) is the density of water.

The corrosion resistance of the supports was assessed using harsh acidic and alkaline solutions. The supports were soaked in H\(_2\)SO\(_4\) (pH = 1) and NaOH (pH = 13) solutions at different times, ultrasonically cleaned, and dried at a temperature of 100 °C. The difference between the dry weights of the untreated and treated supports
The chemical composition of loess and fly ash (wt%).

| Raw materials | SiO₂ | Al₂O₃ | CaO | Fe₂O₃ | K₂O | Na₂O | MgO | TiO₂ | other |
|---------------|------|-------|-----|-------|-----|------|-----|------|-------|
| Loess         | 56.7 | 15.6  | 12.2| 6.86  | 3.54| 1.19 | 2.37| 0.92 | 0.62  |
| Fly ash       | 47.36| 30.85 | 6.82| 10.80 | 0.66| 0.48 | 0.91| 0.38 | 0.26  |

was used to calculate the corrosion resistance of the supports using equation (3):

\[ \text{Mass loss(\%)} = \frac{W_i - W_f}{W_i} \times 100\% \]  

where \( W_i \) and \( W_f \) correspond to the dry weights of the support before and after corrosion, respectively.

### 2.4. Optimization of pure water flux and flexural strength

The trials were carried out in two stages to optimize the pure water flux and flexural strength of the supports. In the first phase, single factor experiments (SFE) were used to assess the effects of CMC (0–20 wt%), MnO₂ (0–20 wt%), and kaolin (0–10 wt%) on the pure water flux and flexural strength of the supports. Through the response surface methodology (RSM) of the central composite test, the second stage focuses on the interplay of numerous parameters on the pure water flux and flexural strength of the support (CCD). CMC addition (A), MnO₂ addition (B), and kaolin addition (C) were chosen as independent variables, while pure water flux and flexural strength were chosen as response values. Equations (4) and (5) [18] were used to fit the experimental data.

\[ Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j \]  

\[ Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 \]

where \( Y \) is the predicted response (pure water flux and flexural strength), \( \beta_i, \beta_{ii}, \beta_{ij} \) are the constant, linear, quadratic and interaction coefficients respectively; \( X_i \) and \( X_j \) are the dependent variables.

The CCD included 20 sets of trials, and the experimental ranges for the independent variables were selected using the results of the first phase of the investigation, as shown in table S2.

### 2.5. Data analysis

Data were analyzed with Design Expert Version 8.0.6, and experimental models for equations (4) and (5), as well as 3D plots and contour plots of the models, were obtained. The appropriateness of the model was assessed using analysis of variance (ANOVA) and diagnostics nodes.

### 3. Discussion

#### 3.1. Characterization of raw materials

The chemical composition of loess and fly ash, which primarily consists of SiO₂ and Al₂O₃, are displayed in table 1. K₂O, Na₂O, and other metal oxides, for example, can act as melting agents and lower the sintering temperature[19]. Figure 2(a) displays their size distribution, with \( D_{50} \) values of 14.35 \( \mu m \) and 4.25 \( \mu m \), respectively. Quartz and sodium hydrogen make up the majority of the two substances’ crystalline phases.

#### 3.2. Thermal analysis

For thermal effects analysis, a part of the dried support (mass ratio loess: fly ash: CMC = 54:36:6) was taken, milled into a powder, and heated to 1300 °C at a rate of 10 °C min \(^{-1}\), as indicated in figure 3. Evaporation of water and decomposition of organic matter[20] may be the main causes of weight loss of the support from room temperature to 500 °C. The decomposition of substantial organic content in the raw material to create gas causes a significant weight loss (about 5.5%) at 500 °C–00 °C. When the temperature is between 800 °C and 1100 °C, there is a 0.13% weight loss. The weight loss rate increased somewhat from 1100 °C to 1300 °C, but the DTG curve remained unchanged, therefore the sintering temperature was fixed at roughly 1100 °C. The sintering regime is as follows: at the rate of 1 °C min \(^{-1}\), 2 °C min \(^{-1}\), 1 °C min \(^{-1}\), 1 °C min \(^{-1}\) from room temperature to 300 °C, 500 °C, 800 °C, 1100 °C, and kept for two hours respectively, and finally cool to room temperature in the furnace.
3.3. Effect of the pore-forming agent

3.3.1. Effect of the types of the pore-forming agent

As shown in figure 4, the performance of the pore-forming agent CMC was relatively good. At this point, the pure water flux of the support reached 2843 L·m\(^{-2}\)·h\(^{-1}\)·MPa\(^{-1}\), and the flexural strength was 33.52 MPa. CMC, as a long-chain polymer, relies on hydrogen bonding and van der Waals forces within its molecules to form a net-like structure in the support clay [21], which serves as both a bonding, pore-forming and stabilizing structure during the firing process.

3.3.2. Effect of CMC addition

The surface morphology of the support was employed to quickly screen the unsuitable preparation conditions visually. When 20 wt% CMC was added, the support surface was extremely loose, with an overall foamed, and the pure water flux and flexural strength were not measurable. As shown in figure 5(a), with an increase in the CMC content, the pure water flux of the support increased. By contrast, the flexural strength first increased slowly and then decreased sharply. It reached the maximum value of 44.19 MPa when 10 wt% CMC was added. This is because CMC is a long-chain polymer that relies on hydrogen bonds and van der Waals forces to form a network structure in the support mud so that the support powder coagulates and the flexural strength of the support is improved [22]. With an increase in the CMC content, the continuous distribution of CMC leads to a decrease in the probability of interparticle contact [23], and the base material remaining after the burning of CMC is not sufficient to fill the pores between fine particles, forming voids and hindering sintering. When 10 wt% CMC was added, the apparent porosity of the support was 37.26% (From figure 5(b)).

Figure 2. (a) Particle size distributions of loess and fly ash; (b) XRD patterns of loess and fly ash with a mass ratio of 6:4.

Figure 3. TG-DTG curve of the support.

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As shown in figure 6, as the CMC content increases, the quartz gradually decreases and the plagioclase content increases. When the CMC content reaches 15 wt%, plagioclase becomes the main crystalline phase. Silica-oxygen tetrahedra that extend into three spaces and are joined at their top corners make up the framework of quartz. It is challenging for other particles to enter the mesh because of how densely coupled they are and how their covalent bonds hold them together. Additionally, quartz has a strong acid resistance, which somewhat improves the acid resistance of the support. The plagioclase feldspar, which is a member of the trigonal crystal system, has a specific gravity of 2.6–2.76 and a Mohs hardness of 6–6.5. It has a porous construction that expands the support’s internal pore space and increases the flux of pure water while diminishing flexural strength (figure 5).

Without the addition of CMC, the particles stacked inside the support had different sizes and were unevenly distributed. When the addition was 5 wt%, the surface of the support tended to be smooth, and the grains began to grow at this time. As a long-chain polymer, CMC exhibits both bonding and pore formation during firing, thus stabilising the structure. Figure 7(c) shows that the surface of the support was smooth, the grains grew significantly, the particles were aggregated, and a large number of neck connections could be observed. Furthermore, the cross-section had an abundant pore structure, which indicates that CMC effectively improved the ratio of the particles inside the support (surface area), resulting in uniform grain distribution. The surface of the support became increasingly dense, as the amount of CMC added increased. In conjunction with figure 6, this can be attributed to the presence of the dense pearl mica phase.

In addition, the pore structure of the support with 10 wt% CMC was investigated. The average pore size of the support was 0.023 μm, and the maximum pore frequency was 34% at 6.3 μm, as shown in figure 8(a). Over the pore-throat-radius range of 1.0–10.0 μm, the primary peak pore volume exceeded 90% of the overall pore volume, showing a consistent pore size.
3.4. Effect of the sintering aid

3.4.1. Effect of the types of the sintering aid

From figure 9, it can be observed that the sintering aid MnO_2 exhibited relatively good performance (high levels of pure water flux and flexural strength). The addition of the sintering aid MnO_2 caused the formation of a solid melt with raw material sintering \[16\], thus reducing the sintering temperature and contributing to the densification of the support simultaneously. The water flux of the support reached 2078 L·m^{-2}·h^{-1}·MPa^{-1}, and flexural strength of 34.67 MPa could be achieved.

Figure 6. Effect of CMC addition on the XRD patterns of the supports with different CMC contents (C1, C2, C3, and C4 are the supports with 0 wt%, 5 wt%, 10 wt%, and 15 wt% CMC, respectively).

Figure 7. Sectional SEM images of the supports with different CMC contents.
3.4.2. Effect of MnO2 addition

Figure 10(a) shows that the physical properties of the support first improved and then deteriorated with an increase in the MnO2 content. The water flux of the support reached a maximum value of 2593.24 L·m\(^{-2}\)·h\(^{-1}\)·MPa\(^{-1}\) when 10 wt% MnO2 was added. The flexural strength of the support reached a maximum of 38.45 MPa when 15 wt% MnO2 was added. This is because, with an increase in the sintering aid content, the internal pore space decreases as the support densifies after the development of the excess liquid phase [24]. As the amount of MnO2 added increases, MnO2 reacts with the element Si to reduce the quartz phase, as a result, flexural strength is reduced. When the addition of MnO2 was 10 wt%, the apparent porosity of the support was 39.64%. The average pore-throat radius of the support was 2.019 μm (figure 8(b)).
The surface morphology of the support at different MnO₂ additions are shown in figure 11. In the absence of MnO₂, the cross-sectional structure of the support was loose, the internal pores were mostly composed of accumulated grains, and the grain size was relatively uneven. The surface of the support became smooth with the addition of MnO₂. The grains grew gradually, a pore size distribution emerged, and the phenomenon of grain wrapping appeared. The internal grains were exposed and fully matured when the addition quantity was increased to 10 wt%, and the structure was stable and rich in pores, indicating that the addition of 10 wt% MnO₂ successfully promoted sintering [25]. When the addition was 15 wt%, the particle distribution in the section was not uniform, and the number of pores decreased as the particles shaded each other, creating local densification. Based on these results and those shown in figure 10(a), it can be stated that the addition of 10 wt% MnO₂ improved the performance of the support.
3.5. Other additives

The flexural strength of the support first increased and then decreased with an increase in the kaolin content, as shown in figure 12. With the addition of kaolin, the combination of Al₂O₃ and SiO₂ in the raw material is promoted to form 3 Al₂O₃·2SiO₂, which is the only compound that exists stably in the Al₂O₃-SiO₂ binary system under normal pressure, and can improve the flexural strength of the support. When the addition of kaolin exceeds 5 wt%, the liquid phase increases, the support shrinks and cracks, and the flexural strength and pure water flux decrease. In conclusion, adding the optimal amount (5 wt%) of kaolin can improve the physical properties of the support.

As can be observed from figure 8(c), the average pore size of the support after the addition of 5 wt% kaolin was 0.97 μm, with a pore size distribution of 100% within the 0.1–2.5 μm radius range, probably because kaolin doping can effectively reconfigure the internal interparticle mesh structure and homogenise the pore size [26], thus keeping the pore size within a certain range.

3.6. Optimisation experiments

3.6.1. Response surface methodology (RSM)

Based on the range of parameters obtained in Phase 1, the optimization results regarding the observed values of pure water flux and flexural strength of the support, as shown in table S3. Equations (6) and (7) demonstrate the regression models for second-order polynomials derived using the experimental results.

\[
Y_1 = 4928.99 + 134.35A + 210.23B - 16.93C
+ 152.59AB - 302.68AC - 94.03BC
- 436.40A^2 - 292.99B^2 - 321.43C^2
\]

\[
Y_2 = 44.54 - 3.49A + 2.22B - 1.31C
- 0.15AB - 0.76AC - 0.90BC
- 2.93A^2 - 3.63B^2 - 2.36C^2
\]

(6) (7)

Where \( Y_1 \) = pure water flux, \( Y_2 \) = flexural strength, \( A \) = CMC, \( B \) = MnO₂, \( C \) = kaolin.

3.6.2. ANOVA results

The adequacy of equations (6) and (7) was assessed using ANOVA and the results were displayed in table 2 and table 3. The p-values calculated by ANOVA were all <0.0001, indicating that the chosen model fitted the experimental data well. The p-values for the lack of fit were 0.1047 and 0.1396 indicating that the error was not related to the pure error [27]. The predicted R-Squared were 0.9695 and 0.7948, respectively, and the adjusted R-Squared were 0.9908 and 0.9351 indicating that the experimental values were highly correlated with the predicted values [28].

Figures 13(a) and 14(a) show that the normal probability plots of the model residuals are fairly close to the diagonals of the pure water flux and flexural strength of the support. This indicates that the residuals are normally distributed and the model satisfies the normality assumption [29]. The phylograms of residuals versus predicted values (figure 13(b), figure 14(b)) show that the distributions of all residuals are scattered, indicating that equations (6) and (7) fit the experiment well data. The plots of residuals versus a number of runs are shown...
As shown in Figure 13(c), 14(c), where the residuals are plotted in a randomly dispersed manner. This indicates that the hypothetical conditions are independent under the developed experimental conditions. Figures 13(d) and 14(d) are diagnostic graphs of the predicted and actual values of the pure water flux and flexural strength of the support. The actual value of the flexural strength of the support in Model 20 agrees with the predicted value, which indicates that the model used is significant and sufficient [30]. Therefore, this regression model is suitable for optimization of independent variables within the range of variables.

### 3.6.3. Three-dimensional (3D) response surface analysis

As shown in figure 15, the response surface had obvious salience, and the influence of each factor was relatively significant. As shown in figure 15(a), CMC and MnO₂ have a synergistic effect on the pure water flux of the support, that is, when the addition amount is more than 10 wt%, the pure water flux increases. As shown in figure 15(b), the degree of the beneficial influence of CMC gradually diminished. This is because CMC (pore-forming agent) deteriorated the flexural properties of the support. This is consistent with the results obtained in our previous study. Figures 15(c) and (d) highlight the range of values for the factors corresponding to highly pure water flux and flexural strength, indicating that factors A and C had a significant impact on the support. As shown in figures 15(e) and (f), to achieve a high pure water flux and flexural strength, a MnO₂ content of more than 10 wt% was required. Adding more than 5 wt% kaolin harmed the properties of the support. This was due

**Table 2.** Analysis of Variance (ANOVA) for response surface for the prediction of Pure water flux.

| Source      | Sum of squares | df | Mean square | F value | p-value | Prob > F |
|-------------|----------------|----|-------------|---------|---------|----------|
| Model       | 6.45E + 006    | 9  | 7.171E + 005| 657.79  | < 0.0001| significant |
| A-CMC       | 2.46E + 005    | 1  | 2.46E + 005 | 22.11   | < 0.0001|          |
| B-MnO₂      | 6.03E + 005    | 1  | 6.03E + 005 | 764.45  | < 0.0001|          |
| C-Kaolin    | 3916.36        | 1  | 3916.36     | 24.04   | 0.0295  |          |
| AB          | 1.86E + 005    | 1  | 1.86E + 005 | 322.21  | < 0.0001|          |
| AC          | 7.32E + 005    | 1  | 7.32E + 005 | 423.12  | < 0.0001|          |
| BC          | 70738.77       | 1  | 70738.77    | 139.70  | 0.5008  |          |
| A²          | 2.745E + 006   | 1  | 2.74E + 006 | 2959.98 | < 0.0001|          |
| B²          | 1.237E + 006   | 1  | 1.237E + 006| 587.18  | < 0.0001|          |
| C²          | 1.489E + 006   | 1  | 1.489E + 006| 1364.47 | < 0.0001|          |
| Residual    | 31439.89       | 10 | 3143.99     |         |         |          |
| Lack of Fit | 24230.17       | 5  | 4846.03     | 3.36    | 0.1047  | not significant |
| Pure Error  | 7209.72        | 5  | 1411.94     |         |         |          |

**Table 3.** Analysis of Variance (ANOVA) for response surface for the prediction of Flexural strength.

| Source      | Sum of squares | df | Mean square | F value | p-value | Prob > F |
|-------------|----------------|----|-------------|---------|---------|----------|
| Model       | 600.32         | 9  | 66.70       | 31.40   | < 0.0001| significant |
| A-CMC       | 166.73         | 1  | 166.73      | 78.50   | < 0.0001|          |
| B-MnO₂      | 67.43          | 1  | 67.43       | 31.75   | 0.0002  |          |
| C-Kaolin    | 25.55          | 1  | 40.84       | 11.09   | 0.0076  |          |
| AB          | 0.17           | 1  | 0.17        | 0.081   | 0.7823  |          |
| AC          | 4.58           | 1  | 4.58        | 2.15    | 0.1729  |          |
| BC          | 6.43           | 1  | 6.43        | 3.03    | 0.1126  |          |
| A²          | 123.44         | 1  | 123.44      | 58.12   | < 0.0001|          |
| B²          | 189.74         | 1  | 189.74      | 89.33   | < 0.0001|          |
| C²          | 80.21          | 1  | 80.21       | 37.76   | 0.0001  |          |
| Residual    | 21.24          | 10 | 2.12        |         |         |          |
| Lack of Fit | 15.69          | 5  | 3.14        | 2.82    | 0.1396  | not significant |
| Pure Error  | 5.56           | 5  | 1.11        |         |         |          |
| Cor Total   | 621.56         | 19 |             |         |         |          |

**Mean**

| Standard deviation | R-Squared | p-value |
|--------------------|-----------|---------|
| 56.07              | 0.9952    |         |

**Adjusted R-Squared**

| Mean                | Adjusted R-Squared |
|---------------------|--------------------|
| 4211.45             | 0.9908             |

**Coefficient of Variation %**

| Coefficient of Variation % | Predicted R-Squared | Adequate Prediction |
|---------------------------|--------------------|--------------------|
| 3.79                      | 0.7948             | 15.203             |

**Standard deviation**

| Standard deviation | R-Squared | p-value |
|--------------------|-----------|---------|
| 1.46               | 0.97658   |         |

**Mean**

| Mean                |
|---------------------|
| 38.45               |

**Coefficient of Variation %**

| Coefficient of Variation % | Predicted R-Squared | Adequate Prediction |
|---------------------------|--------------------|--------------------|
| 3.79                      | 0.7948             | 15.193             |

**Press**

| Press |
|-------|
| 127.56 |

in figures 13(c), 14(c), where the residuals are plotted in a randomly dispersed manner. This indicates that the hypothetical conditions are independent under the developed experimental conditions. Figures 13(d) and 14(d) are diagnostic graphs of the predicted and actual values of the pure water flux and flexural strength of the support. The actual value of the flexural strength of the support in Model 20 agrees with the predicted value, which indicates that the model used is significant and sufficient [30]. Therefore, this regression model is suitable for optimization of independent variables within the range of variables.
to the excessive amount of kaolin resulting in too much liquid phase, less void space, shrinkage and cracking of the support and therefore a reduction in both pure water flux and flexural strength. The optimal conditions of CMC, MnO₂, and kaolin determined according to the optimization process, as well as the predicted and obtained pure water flux and flexural strength of the support were shown in Table 4. The results show that the errors of pure water flux and flexural strength between the predicted and actual values were 1.13% and 1.88%.
3.7. Optimal sample characterisation

The average pore size of the support was 1.25 $\mu$m, as shown in figure 8(d). The supports were prepared with the analysed ratios (the addition amounts of CMC, MnO$_2$, and kaolin were 9.85 wt%, 10.62 wt%, and 4.8 wt%, respectively). The microstructures of the supports were analysed using SEM, and their crystal morphologies were examined.

![Figure 15. Response surface analysis of different factors.](image)

**Table 4.** Predicted and actual values of pure water flux and flexural strength under optimal conditions.

| CMC (wt%) | MnO$_2$ (wt%) | Kaolin (wt%) | Pure water flux L/(m$^{-2}$·h$^{-1}$·MPa$^{-1}$) | Flexural strength (MPa) |
|-----------|---------------|--------------|---------------------------------------------|------------------------|
| 9.85      | 10.2          | 4.8          | Predicted 4928.99                          | Observed 4985.52       |

3.7. Optimal sample characterisation

The average pore size of the support was 1.25 $\mu$m, as shown in figure 8(d). The supports were prepared with the analysed ratios (the addition amounts of CMC, MnO$_2$, and kaolin were 9.85 wt%, 10.62 wt%, and 4.8 wt%, respectively). The microstructures of the supports were analysed using SEM, and their crystal morphologies were examined.
Figure 16. Sectional SEM images of the support at different magnifications (a) 1000, (b) 10000, and (c) 23000.

Figure 17. EDS analysis of the best sample support.

Table 5. Element content of the best sample.

| Element | O   | Na  | Mg  | Al  | Si  | K   | Ca  | Ti  | Cr  | Mn  | Fe  | Ba  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| wt%     | 53.79 | 7.4 | 0.45 | 11.09 | 19.87 | 1.22 | 0.6 | 0.34 | 0.25 | 0.25 | 4.26 | 0.47 |
| wt% Sigma | 0.07 | 0.02 | 0.01 | 0.03 | 0.04 | 0.01 | 0.02 | 0.02 | 0.02 | 0.04 | 0.04 |    |

Figure 16 (a) shows that the specimen had a smooth section and tight structure. As shown in figure 16(b), the bridging between the grains formed a network structure. The grains were evenly distributed and placed in a reasonable order in the section, with a uniform pore structure. Under 23000x magnification (figure 16(c)), the pore distribution, interjunction bonding, and grain growth pattern of the specimens could be well observed. The physical properties of the support were optimal under these conditions. This indicates that under optimised process conditions, the sintering of solid particles can effectively realise grain rearrangement.

From figure 17(b), it can be seen that the elemental points were densely distributed, and there was no agglomeration. The elemental composition shown in figure 17(c) is listed in table 5. The supports consisted mainly of O, Si, and Al, which accounted for 53.79, 19.87, and 11.09 wt%, respectively, along with small amounts of K, Na, Fe, and Mg.

The chemical stability of the support is also one of the criteria for evaluating its performance. Figure 18 showed the acid-base loss rate of the support. Acid and alkali losses increase with the delay in corrosion time, the mass loss of the support after 24 h was 4.296% and 0.928% respectively. The support exhibited alkali but not acid resistance, probably due to the alkali metal content of the components.

Table 6 summarises the features of the supports developed in this study as well as the values reported in the literature. The supports developed in this study outperformed the previously reported supports[11, 31]. The flexural strength of the supports with comparable pure water fluxes in [10] was also lower than that of the supports prepared in this work.

4. Conclusions

(1) Fly ash and loess are excellent sources of SiO2 and Al2O3 and can be used to make the raw materials for ceramic membrane supports. A suitable amount of CMC increased the plasticity of the embryos while
increasing the apparent porosity of the supports, and MnO2 and kaolin promoted sintering while avoiding the negative impact of the pore-forming effect of CMC on the flexural strength.

(2) Three parameters (CMC, MnO2, and kaolin) were examined for their influence on the pure water flux and flexural strength of loess/fly ash-based ceramic membrane supports. Utilizing the RSM of CCD, the additions of the three components (CMC, MnO2, and kaolin) were optimized. When the additions of CMC, MnO2 and kaolin were 9.85 wt%, 10.62 wt% and 4.8 wt% respectively, the pure water flux and flexural strength of the supports were 4985.52 L·m⁻²·h⁻¹·MPa⁻¹ and 45.4 MPa, with an average pore size of 1.25 μm, which satisfied the conditions for porous ceramic applications.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Conflicts of interest

The authors declare no conflict of interest.
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