Enhanced fouling resistance of organosilane-grafted ceramic microfiltration membranes for water treatment

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A facile surface modification technique for imposing antifouling properties on ceramic microfiltration (MF) membranes was developed based on the chemical conjugation of organosilane molecules on ceramics. The ceramic MF membranes (pore size: approximately 0.1 μm) were fabricated using conventional dip coating in an alumina slurry with nano-sized particles. The membranes were subsequently subjected to organosilane grafting with different molar concentrations (25, 50, and 100 mM). The physicochemical analysis of the organosilane-grafted membranes revealed a small decrease in pore size/roughness, which resulted from the new formation of organosilane multilayers (i.e., pore-filling effect). The pure water permeability was also diminished to some extent while exhibiting minimal influence on the permeation flux. Because of the electrostatic repulsion force between the surface-modified MF membranes and the model foulants, serious foulant adsorption followed by flux decline was significantly alleviated. In particular, the lowest organosilane concentration (25 mM) showed the greatest flux performance. This was mostly attributed to the reduced effect of pore-size restriction and electrostatic repulsion forces. We therefore achieved the optimum organosilane-grafting conditions for ceramic MF membranes, which not only minimized the alteration of surface morphology/pore size and hydraulic permeability but also remarkably improved the antifouling properties.

Key-words : Ceramic membrane, Microfiltration, Water treatment, Antifouling, Surface modification

1. Introduction

Ceramic microfiltration (MF)/ultrafiltration (UF) membranes are extensively utilized for physical removal of particles, 0.01 to 10 μm in size, by sieving.¹ These ceramic membranes typically comprise multiple layers with different pore sizes: a support layer, an intermediate layer, and a thin separation layer. Nanosized ceramic particles are deposited on the support layer using conventional membrane-coating techniques (i.e., the dip-coating method) and sintered to form a stable membrane skin. The pore size of membranes can be controlled not only by the size of the deposited ceramic particles but also by the sintering conditions.²

This ceramic membrane technology has been extensively used in water/wastewater treatment and in pretreatment during the nanofiltration/reverse osmosis process.³ Regarding the membrane materials, many studies have focused on new types of inorganic membranes using alumina (Al₂O₃),⁴ zirconia (ZrO₂),⁵ titania (TiO₂),⁶ and silica (SiO₂),⁷ as well as carbon⁸ and zeolite.⁹ Cost-effective raw materials have also been developed to offset the use of expensive raw materials and high-temperature sintering processes (>1300°C).⁴,¹⁰ Although ceramic membranes are usually more costly than commercial polymeric membranes, their usage is required in fields demanding greater chemical or thermal resistance. For example, they have been successfully implemented in the chemical, metal, textile, and food/beverage industries.¹¹ In particular, the unique advantages of ceramic membranes over polymeric membranes are mostly because of the intrinsic properties of ceramics: (1) excellent mechanical/chemical/thermal stability, (2) a controlled pore-size distribution and higher porosity, and (3) good hydrophilicity.¹²,¹³

Membrane fouling is regarded as a serious and poorly resolved obstacle that interferes with the stable separation/purification process for water treatment. This mainly arises from specific physicochemical interactions between the membrane surface and impurities in the raw water. The mechanism of membrane fouling is usually recognized as having three key elements: (1) pore adsorption, (2) pore plugging, and (3) cake formation. Solutes smaller than the pore diameter adsorb on the pore walls, restricting the pore diameters and causing flux decline. Solutes similar in size to the pore diameter block pores completely, and solutes larger than the pore diameter form a cake layer on the membrane surface.¹⁴ Consequently, membrane fouling would lead to a decrease in permeate flux and water quality and an increase in the transmembrane pressure (TMP) and operational costs.¹⁵ To achieve reliable membrane performance, the fouled membranes should be periodically recovered using hydraulic back-washing (for reversible fouling) or chemical cleaning (for irreversible fouling).¹⁶ Even though other methods (such as pretreatment of the feed and optimization of the operating conditions) are available for membrane maintenance, they do not provide satisfactory results because of the increased operation cost and decreased membrane lifetime.¹⁷ Thus, surface modification is becoming a critical technique for the development of novel ceramic membranes with excellent fouling resistance.

In our previous work, we extensively studied the effect of surface charges on membrane fouling resistance using humic acid (HA) as a model foulant.¹⁸ Three organosilanes presenting neutral, positive, and negative charges, respectively, were grafted onto alumina support membranes through a simple silanization process. During this chemical reaction, organosilane molecules usually undergo hydrolysis/condensation, thus forming a stable chemical bond with the alumina support membranes. Because of
the electrostatic repulsion force between the organosilane-grafted membranes and the similarly charged HA, very high flux patterns were found with the negatively charged membranes but not with the pristine alumina and positively/neutraly charged membranes. This meant that these negatively charged membranes would have the greatest impact on flux behavior, such as the lowest flux decline, the highest flux recovery, and the lowest membrane fouling. Thus, the highest efficacy of antifouling properties could be successfully accomplished using negatively charged alumina membranes prepared via a simple chemical reaction.

In this work, we applied an organosilane-grafting technique to ceramic MF membranes (instead of to macroporous support membranes) to facilitate the development of antifouling properties. The ceramic MF membranes were prepared by conventional dip coating using an alumina slurry with nano-sized particles to achieve an average pore size of approximately 0.10 μm. The physicochemical properties of the organosilane-grafted membranes were evaluated in terms of surface morphology, pore-size distribution, and root mean square (RMS) roughness. Noticeable fouling resistance against model foulants was further demonstrated according to the time-dependent flux data obtained during the membrane filtration procedures.

2. Experimental procedure

2.1 Preparation of alumina MF membranes

To prepare an alumina support layer, an α-alumina powder with a mean particle size of 4.8 μm was purchased (AM-210, Sumitomo Chemical Co. Ltd., Japan) and used without further treatment. Using polyethylene glycol (Sigma-Aldrich, USA) as a binder, the powder was molded into circular shapes and dry pressed under a pressure of 15–20 MPa. The samples were sintered in a furnace at 1600°C for 1 h using a heating rate of 5°C/min. The final dimensions of the sintered alumina membranes were measured to be 34 mm in diameter and 2.7 mm high.

A conventional coating procedure was used to fabricate alumina-coated MF membranes using the aforementioned alumina support layers. Briefly, a table-top dip coater (E-flex, Republic of Korea) was used to form an alumina separation layer onto an alumina support layer. The coating slurry consisted of 10 wt% α-alumina with a mean particle size of 0.27 μm (AKP-30, Sumitomo Chemical Co. Ltd., Japan), 2-propanol, ethyl alcohol, glycerol (Sigma-Aldrich, USA), polyvinyl alcohol (Junsei Chemical, Japan), and deionized (DI) water. This alumina slurry was uniformly mixed and immediately utilized. The alumina support samples were dip coated for 10 s and subsequently withdrawn at a speed of 1 mm/s. The coated samples were dried under ambient conditions for 1 d and then heat treated in a furnace at 1300°C for 1 h using a heating rate of 2°C/min.

2.2 Surface modification of alumina MF membranes

For surface modification of the alumina MF membranes, organosilane was selected to introduce a negative surface charge on the alumina membranes. This is based on our previous research work, which revealed that organosilane had improved fouling resistance against negatively charged hydrophobic HA (IEP 4.7).19

In this work, 3-(trihydroxysilyl)-1-propanesulfonic acid (ABCR GmbH, Germany), which contains sulfonic (-SO3) groups in its chemical structure, was grafted to provide negative charges. Prior to the chemical reaction, the alumina membranes were placed in a petri dish and cleaned using ethanol. Organosilane solutions were prepared with different molar concentrations (25, 50, and 100 mM) using anhydrous ethanol and added to the alumina MF membranes. The chemical reaction occurred over 5 h at 25°C with gentle shaking. Upon completion of the reaction, the organosilane solution was discarded and replaced with fresh ethanol to thoroughly rinse the alumina MF membranes. The surface-modified membranes were then dried at 50°C for 12 h. The alumina MF membranes were thus chemically grafted with organosilane that possessed sulfonic groups on its surface. These membranes were denoted as 25, 50, and 100 mM S–SO3 according to the molar concentration.

2.3 Characterization of surface-modified alumina MF membranes

The alumina MF membranes that underwent the surface modification and membrane fouling tests were characterized to investigate their physicochemical properties. For surface morphology analysis, the alumina MF membranes were observed using a field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL, Japan) at magnifications from 1000× to 50,000×.

The pore-size distributions of the membranes were characterized via mercury intrusion porosimetry (Autopore IV 9510, Micromeritics, USA).

Atomic force microscopy (AFM, XE-100, Park Systems, Republic of Korea) was employed to characterize the surface topography of the unmodified and surface-modified alumina MF membranes. The AFM images were acquired in non-contact mode with a scan area of 5.0 × 5.0 μm. The RMS method was used to evaluate the surface roughness of the alumina MF membranes.

2.4 Filtration set-up of surface-modified alumina MF membranes and fouling procedure

The membrane permeation tests of the unmodified and surface-modified MF membranes were performed using a cross-flow microfiltration system (Lab-MPT, SepraTec Membrane System, Republic of Korea).19 The temperature of the feed solution was maintained at 25°C using a circulating bath (JEIO TECH, Republic of Korea). The filtration tests were then operated at a TMP of 2.0 bar with a fluid velocity of 2.5 L/min. Flux data were calculated based on the weight of the permeate, which was measured using an electronic mass balance (CAS, Republic of Korea).

The membrane fouling procedures consisted of four steps. In step 1, the membranes were filtered using DI water for 30 min until a stable baseline flux was reached (J0). In step 2, two model foulants [HA and bovine serum albumin (BSA)] were introduced to develop membrane fouling for 1 h (J1). The two foulant solutions were prepared at concentrations of 10 mg/L for HA (pH 6.5) and 0.5 g/L for BSA (pH 7.4). In step 3, the fouled membranes were subjected to back-washing for 10 min using a 10 mM sodium dodecyl sulfate solution (Sigma-Aldrich, USA) at pH 11. In step 4, DI water was supplied again for 30 min to reach a stable flux (Jf). These fouling processes were performed at least in triplicate using three separate membranes, and their mean values were used for analysis. Based on the flux data obtained, antifouling properties such as flux decline ratio (%) and flux recovery ratio (%) were calculated using the following equations:

\[
\text{Flux decline ratio (\%)} = \left(1 - \frac{J_f}{J_0}\right) \times 100 \quad \text{(1)}
\]

\[
\text{Flux recovery ratio (\%)} = \left(\frac{J_f}{J_0}\right) \times 100, \quad \text{(2)}
\]
where $J_0$ is the DI water flux in step 1, $J_p$ is the flux of the foulant solutions in step 2, and $J_1$ is the DI water flux in step 4.

For quantitative analysis of antifouling features against HA and BSA, the membrane filtration was done in circulation mode. This means that only 1 L of HA or BSA solution was supplied to the feed tank in step 2, and the permeate was sent back to the feed tank. Ten milliliters of the permeate in the feed tank was subsequently collected every 10 min. The concentrations of the foulants could be then be detected at 254 or 280 nm by ultraviolet–visible (UV–vis) spectroscopy (Cary 5000, Agilent Technologies, USA). The membrane fouling ratio (%) was calculated using the following equation:

\[
\text{Membrane fouling ratio (\%)} = \left(1 - \frac{C_p}{C_0}\right) \times 100, \quad (3)
\]

where $C_0$ is the initial concentration of the foulants, and $C_p$ is the concentration of the permeates in step 2.

3. Results and discussion

3.1 Characterization of organosilane-grafted alumina MF membranes

In our previous research, the preparation and characterization of alumina-coated MF membranes were extensively investigated. Flat, tube-type ceramic support layers consisting of alumina or natural materials were dip coated in an alumina slurry. The resultant ceramic MF membranes were analyzed in terms of pore-size distribution and pure water permeability. In brief, the average pore sizes of the separation layers ranged from 0.10 to 0.18 µm, depending on the sintering temperature and support material. The pure water permeability of the natural material-based MF membranes was identical to that of the alumina-based MF membrane, at approximately 200 L/m²·h.

In this work, the disc-type porous alumina support layers were dip coated using a 10 wt% alumina slurry and heat treated at 1300°C for 1 h to obtain pristine alumina MF membranes. The SEM morphological images of alumina-coated MF membranes are presented in Fig. 1 at low (1000×) and high (20,000×) magnifications. In the cross-sectional image [Fig. 1(A)], two different pore structures were successfully generated to build an anisotropic membrane, which played an important role in the ceramic MF membranes. This unique membrane structure comprised a porous support layer (formed by the coarse alumina particles) and a separation layer (formed by the fine alumina particles). In particular, the separation layer was stably retained on the top surface throughout the membrane filtration procedures. The coating thickness of the separation layer was determined to be approximately 27 ± 1 µm. The top surface morphologies of the unmodified and surface-modified MF membranes were observed under a high magnification of 20,000× [Fig. 1(B)]. The pristine alumina MF membrane seemed to have relatively larger pore volumes between the alumina particles than the organosilane-grafted MF membranes (25, 50, and 100 mM S–SO₃). This was mostly ascribed to the newly formed organosilane multilayers (or aggregates), which are thought to have covered the surfaces and valleys of the alumina particles. Nevertheless, no distinct alteration of membrane morphology was found for the organosilane-grafted membranes with a minimal effect of organosilane grafting.

The pore-size distributions of the MF membranes were analyzed using mercury intrusion porosimetry so as to investigate the influence of the organosilane-grafting process (Fig. 2). The figure shows two representative peaks for each layer and similar pore-size distribution profiles. The average pore sizes of the pristine MF membrane were 0.86 µm for the support layer and 0.12 µm for the separation layer. Because of the organosilane conjugation on the membrane surface, the pore sizes of surface-modified membranes decreased to some extent. The average pore sizes of the organosilane-grafted membranes decreased slightly to 0.75–0.77 µm for the support layer and 0.10 µm for the separation layer. However, the pore size remained almost constant, regardless of the organosilane concentration. In our previous research,
the thickness of the newly formed organosilane layers led to a small reduction in the pore sizes in the ceramic membranes via chemical conjugation.\(^{19}\)

In addition to the SEM morphological analysis (Fig. 1), AFM topological analysis was also conducted to reveal the three-dimensional AFM images [Fig. 3(A)] and RMS roughness [Fig. 3(B)]. As compared to the pristine alumina MF membranes, the organosilane-grafted membranes were more susceptible to morphological variations because of the chemical conjugation. Although it was difficult to precisely distinguish them on the AFM images, the corresponding RMS roughness was provided based on a 5.0 × 5.0 μm scan area. The RMS roughness of the pristine alumina MF membranes was shown to be 71 nm, and it gradually decreased from 63 to 48 nm with increasing organosilane concentration from 25 to 100 mM S-SO\(_3\). These results imply that the new formation of organosilane multilayers filled the surface pores between alumina grains and smoothed the surface, thereby lessening the roughness of the membrane surface.

When comparing the pore-size distribution (Fig. 2) with the RMS roughness (Fig. 3), it was found that the average pore-size reduction of the organosilane-grafted membranes was not in good agreement with the surface roughness. This could be ascribed to (1) the high pressure (33,000 psi) used with mercury intrusion porosimetry and (2) the flexibility of the organosilane molecules. These two factors could result in minor differences in the average pore sizes between the organosilane-grafted membranes (support layer: 0.75–0.77 μm, separation layer: 0.10 μm).

The hydraulic permeability of surface-modified membranes has been considered a key parameter for evaluating membrane productivity and efficiency. Thus, the pure water permeability of the organosilane-grafted MF membranes was characterized and the results are shown in Fig. 4. Because of the effect of organosilane conjugation, the permeation flux gradually decreased with increasing organosilane concentration from 25 to 100 mM S-SO\(_3\). Nevertheless, there was a small reduction of hydraulic permeability from 473 ± 21 L/m\(^2\)·h·bar for the pristine MF membrane to 415 ± 21 L/m\(^2\)·h·bar for the 100 mM S-SO\(_3\) membrane. These results indicate that the minimal influence of organosilane grafting was involved in the pure water permeability.

The effects of surface modification (i.e., grafting or coating) with polymers or monomers on the surface morphology, roughness, and pore size have been extensively discussed in many publications.\(^{21–23}\) In addition, the alteration of membrane pore sizes after surface modification is associated with the membrane permeation properties. It is generally recognized that an increase in the degree of surface grafting would decrease the pore size, surface roughness, and hydraulic permeability. Despite the many advantages of surface modification, it usually causes a decline in the flux because of the "pore-filling" effect.\(^{21}\) One possible explanation may be that the surface-grafted polymer chains stretch out toward the solution, leading to a noticeable shrinkage of pore diameter.

In this work, organosilane grafting on alumina MF membranes did not seriously affect either the physical properties of the membrane or the hydraulic permeability. Furthermore, some membrane properties, such as pore-size distribution, surface roughness, and hydraulic permeability, could be controlled by regulating the organosilane concentration. We thus aimed to discover the optimum conditions for organosilane grafting, which would not only minimize changes to the surface morphology/pore size and hydraulic permeability but also facilitate the development of antifouling properties against model foulants.

### 3.2 Antifouling features of surface-modified alumina MF membranes

A schematic illustration of organosilane-grafted alumina MF membranes and feasible interactions with model foulants (HA and BSA) is presented in Fig. 5. As described in section 2.1, the pristine alumina MF membranes were subjected to chemical conjugation using organosilane molecules, which contain sulfonic (–SO\(_3\)) groups in their chemical structure. Thus, strong negative charges were created throughout the organosilane-grafted alumina MF membranes. According to our previous research, the isoelectric point (IEP) of this negatively charged membrane was 3.2. In contrast, the IEP of the pristine alumina membrane was analyzed to be 8.8.\(^{19}\)
In this work, hydrophobic HA (IEP: 4.7) and hydrophilic BSA (IEP: 4.7) were selected as model foulants to simulate soluble humic substances and proteins that are ubiquitous in secondary, treated effluents. The membrane fouling behavior would likely differ between the model foulants, depending on the physicochemical properties of the foulant. Because of the electrostatic repulsion between the sulfonated MF membranes and the negatively charged foulants (HA and BSA), it is expected that the membranes would mitigate significant foulant adsorption on the membrane surface and the subsequent flux decline.

Following each operation step (step 1: DI water, step 2: foulant solutions, step 3: back-washing, and step 4: DI water), the normalized time-dependent flux behavior of the organosilane-grafted membranes is exhibited in Fig. 6. The membrane fouling experiments were carried out at least three times for each MF membrane to obtain reliable results. All the MF membranes maintained stable flux behavior at step 1. When the HA solution was supplied in step 2 [Fig. 6(A)], a very sharp flux decline took place for each MF membrane, followed by a more gradual decrease with increasing time. The flux level descended in the order of 25 mM S–SO₃ > pristine MF membrane > 50 mM S–SO₃ > 100 mM S–SO₃. On the other hand, the flux decline ratio (%) ascended in the order of 25 mM S–SO₃ < pristine MF membrane < 50 mM S–SO₃ < 100 mM S–SO₃ (Table 1). In this case, the 50 and 100 mM S–SO₃ membranes had lower flux values (or higher flux decline ratios) than the pristine MF membranes, whereas the 25 mM–SO₃ membrane manifested the greatest flux capability. As explained in section 3.1, the hydraulic permeability is deeply associated with the membrane pore size. Despite no serious grafting effect on flux permeation (Fig. 4), the surface modification decreased the pore sizes to within a small range, allowing the pores to be easily plugged by low-molecular-weight foulants and consequently dropping the flux levels. This is the main reason why the 50 and 100 mM S–SO₃ organosilane-grafted membranes exhibited inferior flux patterns as compared to the pristine MF membranes. Accordingly, the 25 mM S–SO₃ membrane containing the lowest organosilane concentration would have the highest fouling resistance because of the reduced effect of pore-size restriction and electrostatic repulsion forces. When DI water was fed again after back-washing for 10 min (step 4), all of the MF membranes featured excellent flux recovery ratios (96–100%), irrespective of surface modification (Table 1). This meant that the dominant cause of the membrane fouling was reversible fouling rather than irreversible fouling.

The membrane fouling experiments were also carried out using a BSA solution [Fig. 6(B)]. The descending tendency of the flux level at step 2 was identical to the case of the HA solution: 25 mM S–SO₃ > pristine MF membrane > 50 mM S–SO₃ > 100 mM S–SO₃. However, the normalized flux (J/J₀) for the BSA solutions decreased gradually with increasing filtration time, and they retained relatively higher values than the HA solutions. As
a result, the flux decline rates (%) were found to be smaller (Table 1). The flux recovery ratios (%) were approximately 97–100%.

For another criterion to determine antifouling properties, the membrane fouling ratios (%) of the organosilane-grafted membranes were analyzed and the results are shown in Fig. 7. It was found that all MF membranes were seriously fouled by HA solution at the early stage of filtration before reaching steady values [Fig. 7(A)]. The pristine MF membranes demonstrated the largest membrane fouling ratio (96.6%), and the others followed in the order of 25, 50, and 100 mM S−SO3 with slight differences. The more negatively charged the membrane surface, the smaller the membrane fouling ratio (%). On the other hand, the MF membranes subjected to BSA solutions presented much lower membrane fouling ratios (less than approximately 20%), but the pattern was the same as that for the HA solutions [Fig. 7(B)].

Depending on the characteristics of the two foulants (HA and BSA), the corresponding features of fouling resistance can be described in terms of a membrane permeation profile (Fig. 6) and membrane fouling ratio (Fig. 7). The effects of natural organic matter on membrane fouling have been reported in detail.24)–26) Basically, it is important to notice the apparent molecular weight distributions for HA and BSA so that they can be compared with membrane pore sizes. The membrane fractionation method revealed that the HA solution contained a wide molecular weight distribution (approximately 10 kDa to 0.45 μm).24) In particular, the fraction of high-molecular-weight components exceeding a size of 0.1 μm was approximately 8%. These large-molecular-weight components, whose sizes were close to or larger than the membrane pore sizes, caused pore plugging and cake layer formation.26) This in turn led to the rapid flux decline during the early stage and the subsequent more gradual decrease [Fig. 6(A)]. Much higher membrane fouling ratios (%) were found for the HA-fouled membranes, regardless of surface modification [Fig. 7(A)]. In contrast, the BSA solution exhibited a narrow molecular weight distribution of 67 kDa and possessed no components with molecular weights above 100 kDa.24),27) Thus, the BSA solution, whose particles were smaller than the membrane pore sizes, would either pass through the MF membranes or get adsorbed on the pore surface, resulting in a gradual flux decline [Fig. 6(B)]. Accordingly, the membrane fouling ratios (%) remained constant, below 20% in the case of BSA [Fig. 7(B)].

The SEM morphological images of the fouled and back-washed MF membranes are shown in Fig. 8. Generally, the initial MF membranes were severely fouled, but they largely recovered after back-washing. For the membrane fouling using HA solution [Fig. 7(A)], the gross images are provided as well in order to distinguish the effective antifouling features of the negatively charged MF membranes. The pristine MF membrane turned dark brown in step 2, which was mostly caused by the excessive HA fouling. On the other hand, the fouling patterns of the surface-modified membranes varied in color depending on the organosilane concentrations. The largest organosilane-grafted MF membranes (100 mM S−SO3) displayed the least fouling, followed by the descending organosilane concentrations, 50 and 25 mM S−SO3. Nonetheless, the 25 mM S−SO3 membrane manifested much greater fouling resistance than the pristine MF membrane. The great consistency with the corresponding SEM images is also evidenced. Ironically, the lower flux behaviors happened with the larger organosilane concentrations [Fig. 6(A)], even though the
higher fouling resistance was evidenced in Fig. 8(A). This could be explained by the pore-size restriction after surface modification. Overall, there are optimum organosilane concentrations that can not only preserve the unique porous structures but also contribute to the antifouling properties. The gross images for the BSA solution are not given because this solution was transparent [Fig. 8(B)]. In spite of that, the fouling resistance seemed identical to the results of the HA solution in terms of the fouling/back-washing processes.

4. Conclusions

In this work, the remarkable effectiveness of sulfonated ceramic MF membranes against negatively charged foulants (HA and BSA) was established with respect to antifouling properties. This investigation originated from our previous research, in which we carried out surface modification on alumina support membranes (pore size: about 0.9 μm) with enhanced fouling resistance. In this work, we endeavored to extend our surface-grafting technique to ceramic MF membranes (pore size: approximately 0.1 μm). A larger flux decline resulted from the narrowed pore sizes because of denser organosilane grafting (50 and 100 mM S–SO₃). However, the efficacy of surface modification was successfully confirmed at an organosilane concentration of 25 mM S–SO₃, which demonstrated the highest flux levels (or the lowest flux decline) during the membrane fouling process (step 2).

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References