

## Ceramic membrane overview and applications in textile industry: a review

Meltem Ağtaş<sup>a,b</sup>, Mehmet Dilaver<sup>c</sup> and İsmail Koyuncu<sup>IWA a,b,\*</sup>

<sup>a</sup> Department of Environmental Engineering, Istanbul Technical University, Istanbul 34467, Turkey

<sup>b</sup> National Research Center on Membrane Technologies, Istanbul Technical University, Maslak, Istanbul 34469, Turkey

<sup>c</sup> TUBITAK Marmara Research Center, Environment and Cleaner Production Institute, Kocaeli 41470, Turkey

\*Corresponding author. E-mail: koyuncu@itu.edu.tr

### ABSTRACT

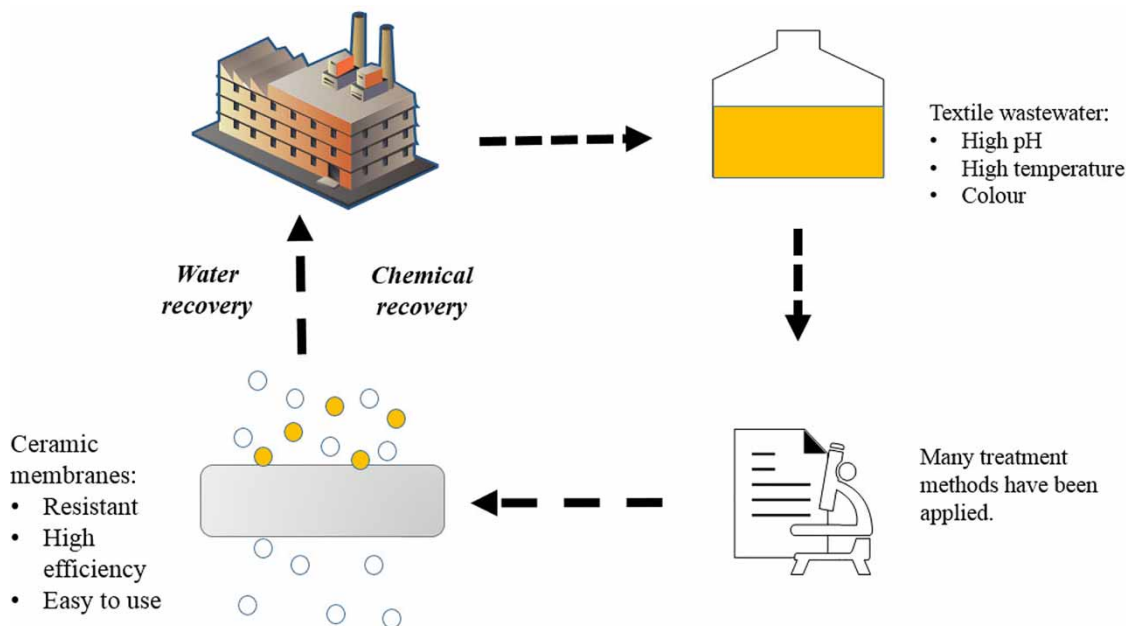
The importance of water recovery and reuse is increasing day by day. Therefore, the use of advanced technologies is applied for the treatment and recovery of textile wastewater. The fact that ceramic membranes are resistant to the challenging characteristics of textile wastewater makes the use of ceramic membranes useful. Within the scope of this review, general information about the textile industry and treatment techniques are mentioned, as well as the properties of ceramic membranes and textile wastewater treatment. In the literature review made in this study, recent studies on the production of ceramic membranes and laboratory applications have been compiled. However, it has been observed that although the real-scale studies are relatively higher in industries such as the food and petrochemical industry, it is rather limited in the textile industry.

**Key words:** ceramic membrane filtration, membrane technologies, recovery, textile effluent treatment, textile industry

### HIGHLIGHTS

- General information about the textile industry and treatment techniques are mentioned.
- The properties of ceramic membranes and usage in textile wastewater treatment are analysed.
- Recent studies on the production of ceramic membranes and laboratory applications have been compiled.
- It was aimed to highlight the importance of ceramic membranes in the treatment and recovery of textile wastewater.

### GRAPHICAL ABSTRACT



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## 1. INTRODUCTION

Increasing population, impetuous urbanization, improper use of water resources and climate change are increasing the need for safe water. It is very difficult to lead a healthy life as approximately 15% of 7 billion people in the world do not have access to clean water (Sheikh *et al.* 2020).

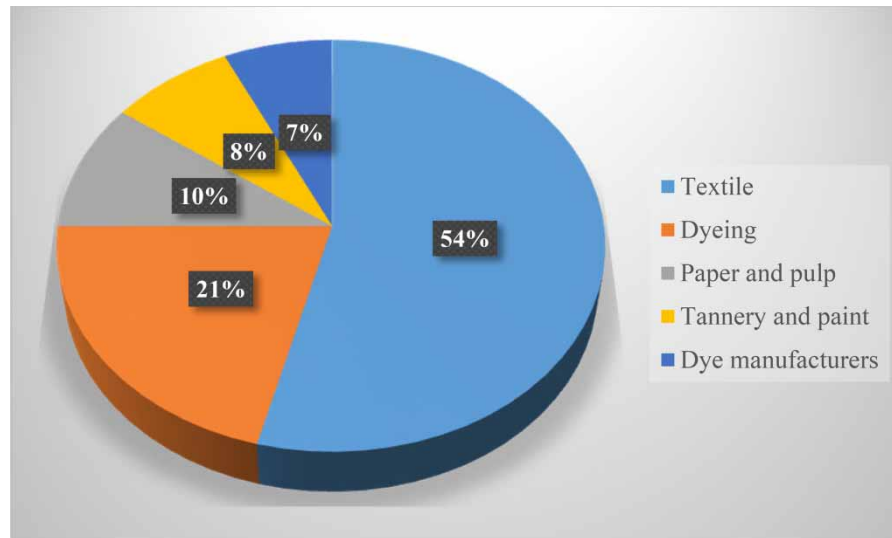
The world has a lot of critical environmental problems and industrial wastewater which has dangerous and detrimental contaminants in it is one and an important part of these problems. The main ones from these industries are the textile, mining, pharmaceutical, pulp and paper and petrochemical industries. All of these industries have detrimental effects on soil, air and water ecosystems because of their wastewater (Samaei *et al.* 2018). When the textile industry is evaluated with a global approach, the demand for textile products is increasing with a constant rate and it is expected that it will continue to increase given the economic developments and population growth (Sandin & Peters 2018).

In the textile sector, China is a leading country in fabrication and export. In the global textile exporter list regarding 2016, China was in the first place with nearly 106 billion US dollars export and Turkey was in fifth place after European Union, India and the USA (Rovira & Domingo 2019). In the Turkish manufacturing sector, the textile industry employs 27% of all workers. The textile industry in Turkey consists of small-and large-scale establishments and a lot of complicated processes. Because of the regulations and strict discharge standards, efficient water and chemical usage became more important in the Turkish textile sector and cleaner production procedures are started to implement based on Turkish BREF and IPPC-IED directive. Most action is carried out to modify processes and equipment to decrease water and chemical usage (Ozturk *et al.* 2016a). Within this context, using water recovery and reuse applications in the food, textile, metal, paper and chemical industries where water consumption is intense will contribute significantly to the reduction of raw water consumption, wastewater discharge to the receiving water bodies and the amount of pollutants contained in the wastewater (Dilaver *et al.* 2018).

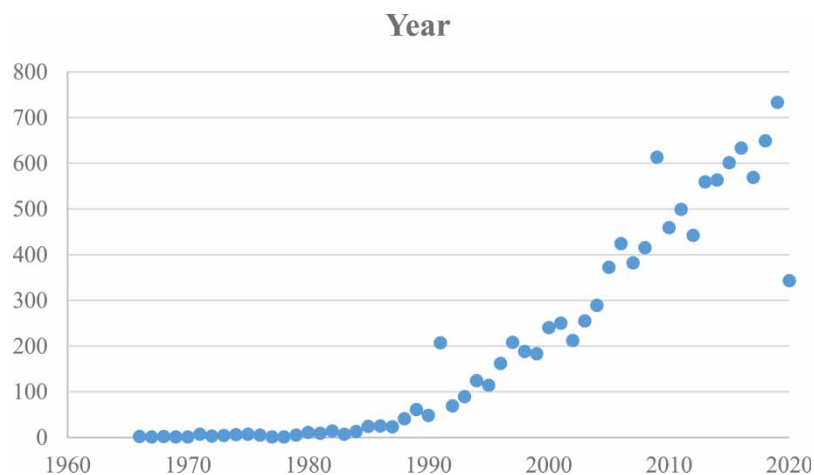
In finishing and dyeing processes in a conventional textile factory, an average of 150 m<sup>3</sup> of water has to be used for manufacturing every tone of the fabric product. Besides the use of water, in different textile mill processes such as bleaching, finishing, dyeing and printing, 3600 different types of dyes and 8000 types of various chemicals are put to use and therewith human health and aquatic ecosystem can be affected by these compounds because of the pollution of soil and water (Hussain & Wahab 2018). Industries responsible for the presence of dye effluent in the environment are given in Figure 1. US Environmental Protection Agency made a classification for wastes from textile and divided into groups. These groups were named as hard to treat, hazardous and toxic, high volume and dispersible. Textile industry wastewater generally contains high amounts of colour, salt, turbidity, chemical oxygen demand (COD), total dissolved solids (TSS) and complex chemicals. In addition, the temperature and pH of this wastewater can be in extreme conditions (Dasgupta *et al.* 2015). For the treatment of textile industry effluent, generally physicochemical and biological treatment methods were applied. Nevertheless, these methods are not sufficient enough to remove surfactants, salts, some kinds of dyes and so on. To obtain high quality water after treatment, advanced technologies are required to be used (Cinperi *et al.* 2019). Membrane technology can be identified as a suitable choice for the textile wastewater treatment since most of textile effluents have high temperature and high basic nature. For commercial applications, polymeric membranes are quite popular but ceramic membranes are more resistant to temperature and have high mechanical and chemical stability compared with polymeric membranes (Zebić Avdičević *et al.* 2019). For instance, more effective chemicals can be used for the membrane cleaning procedure without the risk of damaging the membrane (Lee *et al.* 2013). Another advantage of ceramic membranes is having longer service life than polymeric membranes. But the cost of ceramic membranes can be shown as a drawback although in recent years the cost of ceramic membranes has been decreasing (Zebić Avdičević *et al.* 2017).

The data obtained in the search made in the literature using the keyword 'ceramic membrane' (demonstrates the results of 'Scopus' search) are given in Figures 2–4, between 1966 and 2020. When Figure 2 is analysed, it is seen that there has been a rapid increase in studies involving ceramic membranes since 1990. When we look at the countries where the studies are carried out, it is seen that China is in the first place and USA comes after. When we look at the kinds of studies, it is seen that the studies are most widely published as articles and then the conference papers and reviews come (data obtained from Scopus, 7 June 2020).

In this review, studies on characterization and treatment of textile industry wastewater have been studied and the properties and applications of ceramic membranes have been emphasized. In addition, it was aimed to highlight the importance of ceramic membranes in the treatment and recovery of textile wastewater. For this reason, important studies in recent years have been gathered together to the best of our knowledge.



**Figure 1** | Industries responsible for the presence of dye effluent in the environment (Katheresan *et al.* 2018). Please refer to the online version of this paper to see this figure in colour: <http://dx.doi.org/10.2166/wst.2021.290>.

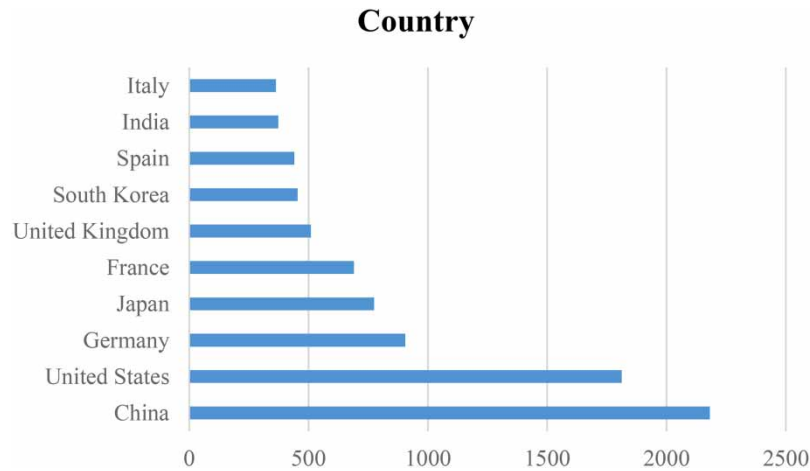


**Figure 2** | Number of publications on ceramic membranes per year using the keyword 'ceramic membrane'. The data are based on the citation database Scopus in June 2020.

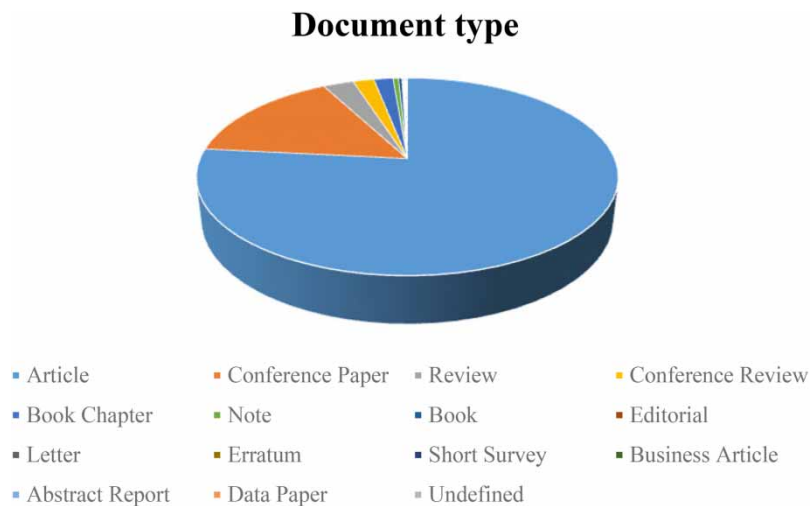
## 2. GENERAL INFORMATION ABOUT TEXTILE PROCESSES

Textile industry is an industry that consumes large amounts of water and therefore limits global water resources. Especially in wet processes, due to high water usage, the textile industry produces high amount of wastewater with high pollution (Hussain & Wahab 2018). For instance, in dyeing process, approximately 100–150 L of water per 1 kg fibre can be used. Not only water but also different types of dyes and chemicals are required for this process and consequently process wastewater contains unused dyes, salts and surfactants (Zheng *et al.* 2016). The processes in textile industry start with treatment of raw materials. For fabrication of woven and knitted products, to give products aesthetic and physical properties, printing, dyeing, bleaching, coating, impregnating and similar processes can be applied (Bullon *et al.* 2017).

In Figure 5, flow chart of an exemplary factory is given. Alkaya and Demirer included this factory in their work. This company is located in Bursa with 10,000 m<sup>2</sup> factory area and produces woven products. They use cotton, polyester and lycra based materials for fabrication. The average fabric production of 2009, 2010 and 2011 is approximately 2226 tons/year (Alkaya & Demirer 2014).



**Figure 3** | Number of publications on ceramic membranes based on country using the keyword 'ceramic membrane'. The data are based on the citation database Scopus in June 2020.



**Figure 4** | Number of publications on ceramic membranes based on document type using the keyword 'ceramic membrane'. The data are based on the citation database Scopus in June 2020. Please refer to the online version of this paper to see this figure in colour: <http://dx.doi.org/10.2166/wst.2021.290>.

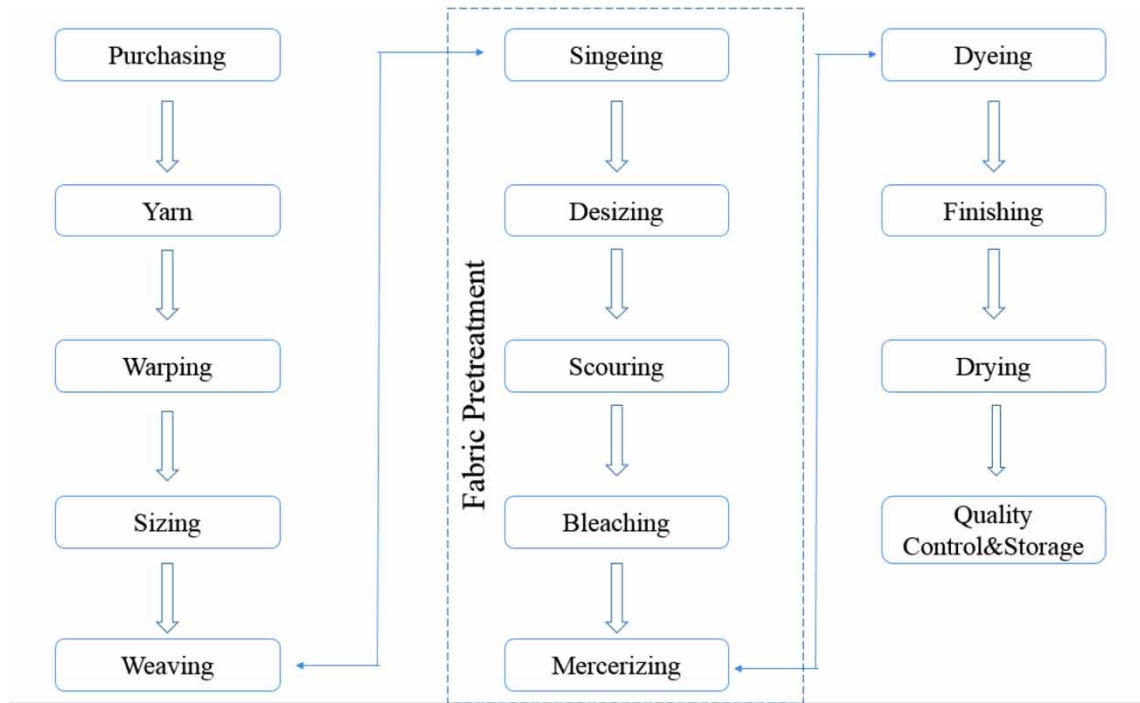
The processes that are considered important in the flow chart of the textile industry are mentioned below.

Before weaving or spinning process, the sizing process is applied to yarns to make yarns more durable and prevent fibre breakdown. Wastewater generated from sizing process has a high level of pollution parameters such as biochemical oxygen demand (BOD), COD and suspended solids (SS), although only a low amount of wastewater is generated (Bisschops & Spanjers 2003).

Scouring and bleaching processes are generally applied consecutively. The purpose of the scouring process is to remove substances such as oil, wax and fat from the product to increase the absorbency level using an alkaline chemical (Harane & Adivarekar 2017).

In the mercerization process, alkali solutions are used for enhancing the tension of fibre, improving fibre's surface gleam and ameliorate the affinity of dye. Accordingly, the wastewater generated as a result of the mercerization process has a high base content and is mixed with wastewater from other processes to be treated (Zhang *et al.* 2014).

Dyeing operation is a process that is used to colour the product, using many types of dyes, different equipment and methods and can be done at different points of production (Varol 2008).



**Figure 5** | Example of a textile mill flow diagram (Bursa, Turkey) (adapted from Alkaya & Demirer 2014).

For making the fabric more favourable for final use, the fabric goes through some processes to alter its look or performance. Finishing operations are important in many aspects. For instance, it is able to change the texture of the product, make products appropriate for a specific use, and advance the appearance of the product (Bullon *et al.* 2017).

### 2.1. Textile wastewater characterization

Textile industry wastewater contains different biological and physicochemical parameters such as salinity, pH, temperature, COD, BOD, total nitrogen, TSS, total phosphorus, non-biodegradable organic compounds, heavy metals (Cr, Cu, Zn, Ar, etc.) and wide range of types of dyes (Berradi *et al.* 2019). The dyes used in the textile industry are based on various chemical structures, for instance sulphur, azoics, triphenyl methane and others. Depending on the technological developments, chemicals used in colouring processes have also been developed. In particular, different chemicals are used to provide properties such as softness, flame retardancy and wrinkle-free effect to the end product. Approximately 90% of the chemicals used in this last stage remain on the fabric and the rest passes into the wastewater through washing processes (Nimkar 2018).

There are a lot of studies including textile effluent characterization in literature. In this study, the most general and current ones are tried to be mentioned. In a recent study involving real wastewater from the hot discharges mixing point of disperse printing and reactive printing washing baths, average values for COD, total hardness and total organic carbon (TOC) were 580 mg/L, 49 mg CaCO<sub>3</sub>/L and 161 mg/L respectively (Ağtaş *et al.* 2020). Tomei and colleagues studied analysing performance of real textile wastewater (dyeing bath of a textile factory) bio-decolourization. According to experiments they have performed, COD, BOD<sub>5</sub>, TSS and TOC values were 1017 mg/L, 9.8 mg/L, 535 mg/L and 158 mg/L respectively. pH was reported as approximately 9 (Tomei *et al.* 2016). Bilińska *et al.* investigated treatment of textile wastewater with electrocoagulation and ozone processes. Studied wastewater's pH was 11.82 and conductivity was 57.56 mS/cm. They also measured NaCl as 53.66 g/L, COD as 1315 ± 5 and TOC as 264 ± 20 mgO<sub>2</sub>/L. Since high pH and high salinity values are common properties for textile wastewater, their results are expectable (Bilińska *et al.* 2019). When these results are examined, it can be said that even for similar processes, wastewater characterization can vary in a wide range. In Yaseen *et al.*'s paper, this variation was attributed to textile wastewater consisting of different effluents which are outlet streams of particular processes or passed through specific stages. For instance, in textile manufacturing steps, different dyes and additives are used and these are the reason for metal presence in this process wastewater (Yaseen & Scholz 2019). Wastewater characterization (average values) in literature is given in Table 1.

**Table 1** | Wastewater characterization (average values) in literature

Parameter	Literature values
COD (mg/L)	580 <sup>a</sup> , 1017 <sup>b</sup> , 1315 <sup>c</sup> , 281 <sup>d</sup> , 1581 <sup>d</sup> , 1560 <sup>e</sup> , 185.6 <sup>f</sup> , 329.4 <sup>g</sup>
Hardness (mg CaCO <sub>3</sub> /L)	49 <sup>a</sup> , 500 <sup>e</sup>
Colour	0.33 <sup>a*</sup> , 137 <sup>d**</sup> , 713 <sup>d**</sup> , 2.98 <sup>f*</sup>
Conductivity (µs/cm)	57.56 <sup>c</sup> , 27,700 <sup>d</sup> , 92,200 <sup>d</sup> , 568 <sup>f</sup> , 8620 <sup>g</sup>
TOC (mg/L)	161 <sup>a</sup> , 158 <sup>b</sup> , 264 <sup>c</sup> , 390 <sup>e</sup> , 49.05 <sup>f</sup>
BOD <sub>5</sub> (mg/L)	9.8 <sup>b</sup>
TSS (mg/L)	535 <sup>b</sup> , 34 <sup>d</sup> , 196 <sup>d</sup>
pH	9 <sup>b</sup> , 11.82 <sup>c</sup> , 10.5 <sup>d</sup> , 10.7 <sup>d</sup>
NaCl (g/L)	53.66 <sup>c</sup>

\*value for 525 nm.

\*\*unit as Pt-Co.

<sup>a</sup>Ağtaş *et al.* (2020).<sup>b</sup>Tomei *et al.* (2016).<sup>c</sup>Bilińska *et al.* (2019).<sup>d</sup>Ozturk *et al.* (2016b).<sup>e</sup>Blanco *et al.* (2014).<sup>f</sup>Güyer *et al.* (2016).<sup>g</sup>Fersi & Dhahbi (2008).

## 2.2. Textile wastewater treatment methods

As mentioned in the previous section, textile wastewater has a characteristic that includes a wide variety of parameters such as COD, colour, hardness, conductivity, TSS, BOD and so on.

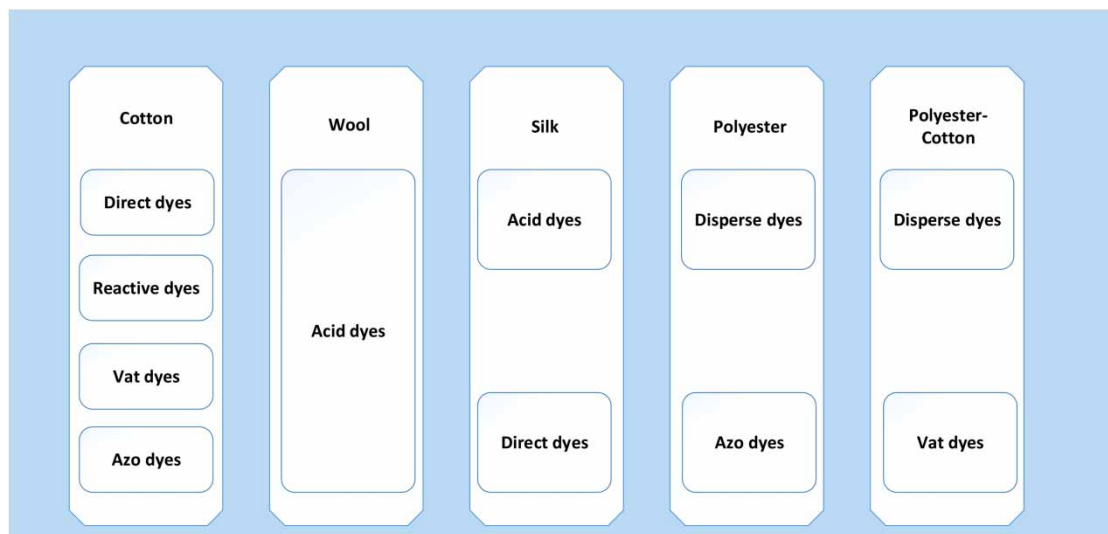
For treatment of this kind of wastewater, various treatment technologies have been studied and applied up until now. To select a proper method for treatment, there are several factors which have to be considered. Textile factory's process chart, types of chemicals and dyes which are used in these processes local standards of discharge and cost of treatment options are important. If wastewater is aimed to be recovered or reused, it may be necessary to change the perspective for treatment options and in this case wastewater streams may need to be separated and managed separately (Jegatheesan *et al.* 2016).

Many treatment techniques have been applied for textile wastewater treatment. Physical methods such as coagulation–flocculation, adsorption, advanced and chemical oxidation, biological methods and membrane processes are available in the literature (Holkar *et al.* 2016; Yukseler *et al.* 2017). Considering all the various pollutants which are found in textile wastewater, dyes are thought to be the most persistent source of pollution (Lafi *et al.* 2018). Also, the types of dyes vary depending on the material. Different dyes used for different materials are given in Figure 6 (Holkar *et al.* 2016).

For dye-containing wastewater, the coagulation process has been used as a pretreatment or main treatment option for many years. Its low investment cost also allowed it to be used frequently. But there is a major drawback for this process which is sludge generation. Besides, the coagulation process cannot be effective for removal of some kinds of soluble dyes (Verma *et al.* 2012).

Adsorption, which is another method frequently used in dye removal, is preferred due to its ease of use and high removal efficiency. Carbon nanotubes, zeolite, graphene, activated carbon obtained from some different materials are commonly used for adsorption process (Abd-Elhamid *et al.* 2019). Activated carbon is an efficient, common adsorbent but there are some limitations because of the cost of providing and regeneration of adsorbent (Streit *et al.* 2019). Since the regeneration of the adsorbent is expensive and there is a loss of material while regenerating, there are restrictions in the application of the process (Khandegar & Saroha 2013).

In the past years, advanced oxidation techniques have also been an extensively studied method for dye removal. These techniques are mainly based on the degradation of impurities by chemical methods and oxidation of pollutants until they are mineralized by using reactive oxidants e.g. hydroxyl radical. Radicals for oxidation are produced *in situ* and they degrade the organic matters with fast chemical reaction rates (Nidheesh *et al.* 2018). Ozone has advantages such as not forming sludge and eliminating colour and organic matter in one step. In a study using the oxidation process with ozone, the degradation of three types of azo dyes was modelled and the results were supported by experiments. Correlation coefficients which



**Figure 6** | Types of dyes for different materials (adapted from Holkar *et al.* 2016).

indicated compatibility between model and the experiments were found approximately as 0.97. High degradation rates were also obtained (Muniyasamy *et al.* 2020). Although the ozone process has its advantages, high costs as well as the formation of by-products that may be toxic or carcinogenic as a result of the process are the main disadvantages (de Souza *et al.* 2010).

Biological treatment methods have been categorized as an effective and environmentally-conscious process for treating textile wastewater when compared with other methods since they are more expensive and may have by-products after treatment. In literature there are lots of studies about biological methods for textile industry effluents because of the biological degradation of dyes under aerobic/anaerobic circumstances. For further and more efficient treatment of these effluents, membranes and biological activated sludge can be used together which is called membrane bioreactors (MBRs). Besides, MBR technology has lots of advantages which are high water quality, lower sludge requirement and lower maintenance need (Khouini *et al.* 2020).

Although all the processes mentioned above have obvious advantages and disadvantages, in most processes, dyes and salt, which are valuable chemicals, cannot be recovered or reused. When approached from a holistic point of view, water resources will be protected by both the process being sustainable and the efficient treatment of textile wastewater and its recovery, and the amount of water used by the industry will decrease. In this context, the use of membrane technologies instead of traditional methods is more suitable in terms of having high treatment efficiency of membranes and being more environmentally friendly (Lu *et al.* 2020; Yang *et al.* 2020a, 2020b). There are many studies in the literature using membrane processes. In a very recent study, ultrafiltration (UF) membranes were fabricated by using polyimide polymer and according to filtration results, approximately 98% of dye was retained on the membrane while monovalent and divalent salts passed into the permeate stream. It was stated that the fabricated membrane can be used for separating dye/salt mixtures (Yang *et al.* 2020b).

As it is known, textile wastewater can contain high salt and acidic compounds. Production of membranes resistant to these conditions is also studied in the literature. For example, with a doped polymeric nanofiltration (NF) membrane produced for this purpose, high dye removal was achieved in saline and acidic dye solution (Lu *et al.* 2020).

In Table 2 discharge limits for the textile industry in different countries is given. As can be seen from the table, although some values are the same or similar for all countries in the table, some values are quite different. It can be seen that the same parameters are not evaluated especially in each country.

In addition to legal discharge limits, there is an approach regarding hazardous chemicals that companies should not use while manufacturing. This approach was named Zero Discharge of Hazardous Chemicals (ZDHC) and designated the Manufacturing Restricted Substances List (MRSL). Companies that adopt this concept by not using these dangerous and prohibited chemicals manage to produce cleaner ([https://mrsl.roadmaptozero.com/MRSL2\\_0](https://mrsl.roadmaptozero.com/MRSL2_0)). Since the same organizations will adopt the zero discharge concept after 2020, it is thought by the authors of this article that the use of membranes will be very useful in this regard.

**Table 2** | Discharge limits for the textile industry in different countries

Parameter	China <sup>a</sup>		Germany <sup>a</sup>	USA <sup>a</sup>	India <sup>a</sup>	Turkey <sup>b</sup>		
	Direct discharge	Indirect discharge	Point of discharge			Open fibre, yarn production and finishing	Woven fabric finishing and similar processes	Cotton textiles and similar processes
pH	6–9	6–9	–	6–9	6–8.5	6–9	6–9	6–9
Chemical oxygen demand (mg/L)	80	200	200	80	250	350	400	250
Biochemical oxygen demand (mg/L)	20	50	20	50	30	–	–	–
Total suspended solids (mg/L)	50	100	–	30	100	–	140	160
Total dissolved solids (mg/L)	–	–	–	2000	5034	–	–	–
Colour	50	80	–	–	20	280 (Pt-Co)	280 (Pt-Co)	280 (Pt-Co)
Ammonia nitrogen (mg/L)	10	20	10	0.0002	–	5	5	5
Chlorine dioxide (mg/L)	0.5	0.5	–	–	–	–	–	–
Free chlorine (mg/L)	–	–	–	1	1 (residual)	0.3	0.3	0.3
Sulphide (mg/L)	0.5	0.5	–	0.2	100	1	1	1
N total (mg/L)	15	30	20	–	–	–	–	–
P total (mg/L)	0.5	1.5	3	0.005	–	–	–	–
Nitrite (mg/L)	–	–	1	–	–	–	–	–
Nitrate (mg/L)	–	–	–	20	–	–	–	–
Iron/manganese (mg/L)	–	–	–	–	0.25	–	–	–
Total chromium(mg/L)	–	–	–	–	–	2	2	2
Fish bioassay (ZSF)	–	–	–	–	–	4	4	4
Oil and grease (mg/L)	–	–	–	–	–	10	–	10
Phenol (mg/L)	–	–	–	–	–	–	1	–

<sup>a</sup>Adapted from Senthil Kumar & Saravanan (2017).

<sup>b</sup>Adapted from Resmi Gazete 2004. All values are for 2-hour composite samples.

### 2.3. Textile wastewater recovery and reuse approaches

The textile industry has a lot of different production processes that consume energy, water and raw materials and as a result of these processes, a high amount of wastewater is formed containing many different chemicals. To dispose of these effluents in the environment poses a risk for both human health and the ecosystem. Also, considering the amount and characteristics of textile wastewater, it is considered to be a more polluting industry than other industries (Alkaya & Demirer 2014). Recycling and reuse of wastewater are getting more important because of decreasing water supplies, discharge regulations and treatment and supply costs (Güyer *et al.* 2016). Water reuse reference values for the textile industry are given in Table 3. There are some studies in the literature for water and chemical recovery from textile industry wastewater.

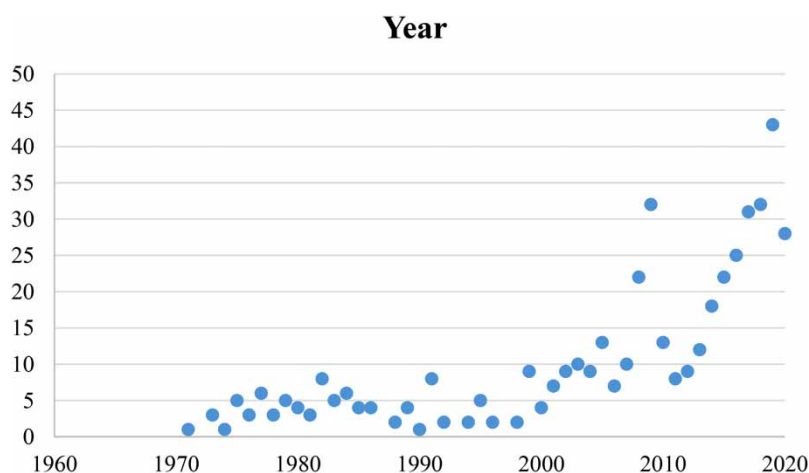
The data obtained in the search made in the literature using the keyword ‘textile wastewater recovery’ (demonstrates the results of ‘Scopus’ search) are given in Figures 7–9 between 1971 and 2020. When Figure 7 is analysed, it is seen that there has been a rapid increase in studies involving ceramic membranes since 2010. When we look at the countries where the studies are carried out, it is seen that India is in the first place, China comes after and Turkey is in the third place. Since these three countries have a large market in the textile industry, these figures are expected. When we look at the kinds of studies, it is seen that the publication is the most widely published as article and then the conference paper and reviews come (data obtained from Scopus, 19 July 2020).

For recycling or reusing wastewater of cotton fabric processes, advanced oxidation technology was used. Ozone oxidation, ultraviolet (UV) and H<sub>2</sub>O<sub>2</sub> oxidation were applied to wastewater in different combinations. Resulting effluent was tested in



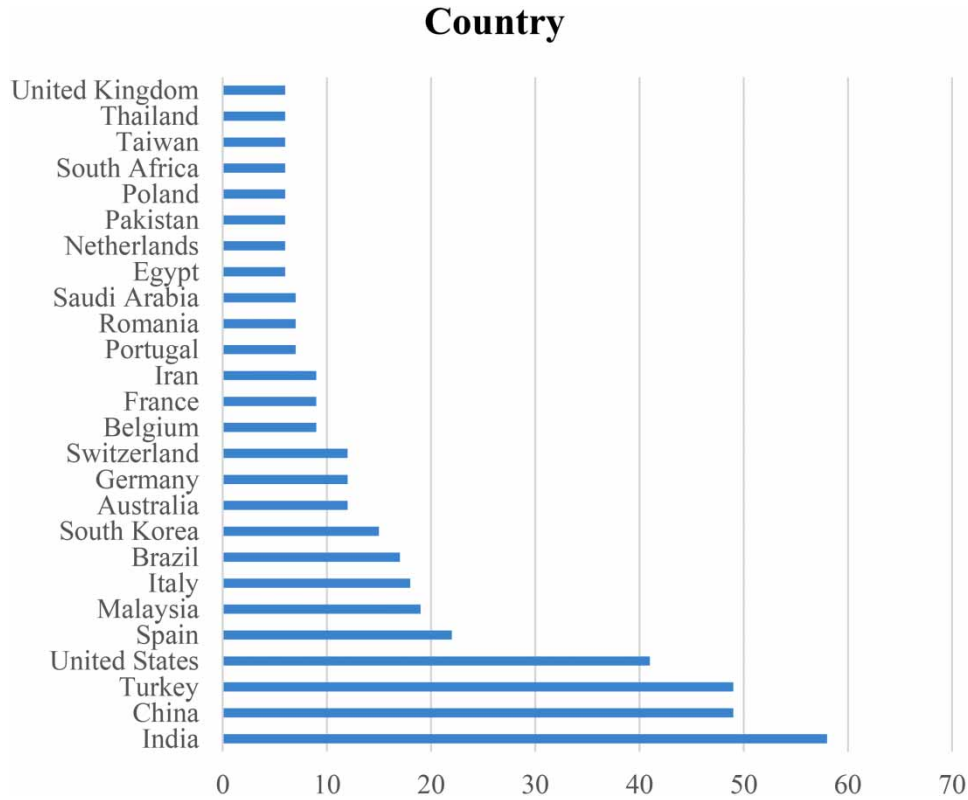
**Table 3** | Water reuse reference values for textile industry (adapted from Lafi *et al.* 2018)

Parameter	Criteria
COD (mg/L)	60–80
Conductivity ( $\mu\text{S}/\text{cm}$ )	1000
pH	6–8
Turbidity (NTU)	1
Colour	None
Suspended solids (mg/L)	5
Dissolved solids (mg/L)	500
Total hardness (mg $\text{CaCO}_3/\text{L}$ )	25–50

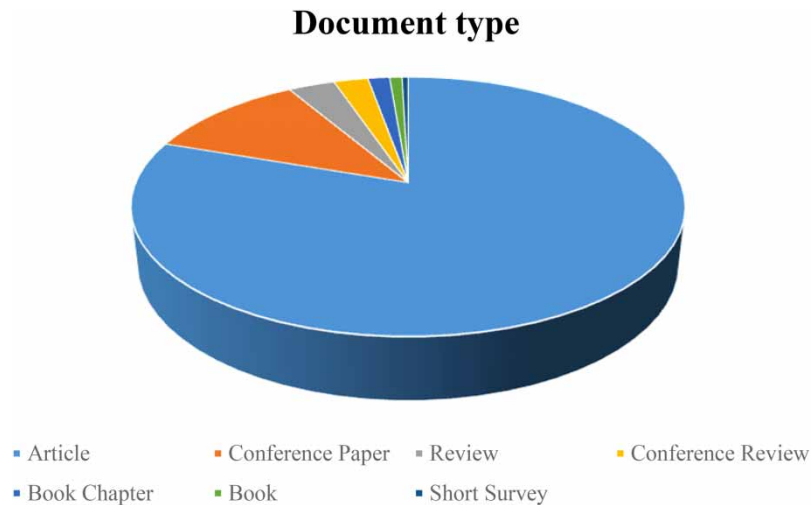
**Figure 7** | Number of publications on ceramic membranes per year using the keyword 'textile wastewater recovery'. The data are based on the citation database Scopus in July 2020.

dyeing experiments to investigate if it is reusable or not in the fabrication processes again. It was found out that no adverse effects have been observed on product quality (Güyer *et al.* 2016). In the study conducted in a textile factory to recycle wastewater and reuse it in various processes at the facility, studies were carried out with composite wastewater and separate wastewater streams from three different processes. For this purpose, MBR, reverse osmosis (RO) and NF processes which were all pilot scale were used in different combinations. Disinfection with ultraviolet light was also applied to the treated water. After dyeing experiments with treated water, it was reported that MBR-RO-UV and MBR-NF-UV combinations did not have a negative effect on the quality of the product (Cinperi *et al.* 2019). In another study where pilot-scale MBR + NF processes were used together, the studies were carried out on-site and the concentrate of the NF process was recirculated back to MBR to gain a large amount of water recovery. It was indicated that NF concentrate has a noteworthy effect on the removal of pollutants in the MBR. Besides, the payback period was calculated for this process and found to be 3.11 years (Li *et al.* 2020b). In Balcık-Canbolat *et al.*'s study, the RO process was evaluated for the recovery of water by using real dye effluent which was treated biologically before RO process. They also investigated the effect of the NF process as a pretreatment before RO. According to results, it can be said that RO was very effective to obtain an adequate level of treated water quality (Balcık-Canbolat *et al.* 2017).

Since zero liquid discharge or near zero liquid discharge concept has been drawing more attention in the industrial sector to maintain water conservation to prevent high water consumption and meet discharge regulations, different processes are being used together for water recovery. To remove ions which cause scaling from textile wastewater concentrate of RO process, pellet reactor and UF process were used. The filtrate from these processes was reintroduced to the RO membrane to increase water recovery. It was also reported that near zero liquid discharge was achieved (Sahinkaya *et al.* 2018).



**Figure 8** | Number of publications on ceramic membranes based on country using the keyword 'textile wastewater recovery'. The data are based on the citation database Scopus in July 2020.



**Figure 9** | Number of publications on ceramic membranes based on document type using the keyword 'textile wastewater recovery'. The data are based on the citation database Scopus in July 2020.

Sierra-Solache and colleagues used the UF membrane process and biological method which includes encapsulated fungal cells in an aerobic bioreactor to recover two kinds of dyes contained wastewater. As a result of this study, they stated that the quality of treated water has the potential to use in the textile industry (Sierra-Solache *et al.* 2020).

Textile wastewater can also show high alkaline properties and recovering caustic by membrane processes have been applied in a wide variety of industries. In a study conducted for caustic recovery from mercerizing process wastewater,

polymeric microfiltration (MF), UF and NF membranes were used and the resulting caustic filtrate was intended to be used again. It was underlined that obtained permeate can be reused in mercerization process after concentration step (Varol *et al.* 2015).

### 3. CERAMIC MEMBRANE PROCESSES

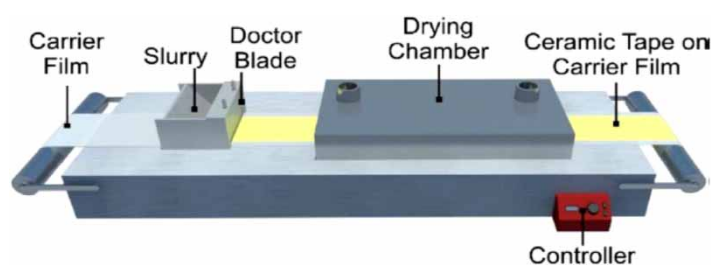
In the past 20 years, it has become a remarkable option for industrial wastewater treatment. Ceramic membranes have many advantages over polymeric membranes/counterparts. Some of these are being easy to clean, high chemical, thermal and physical resistance and ease of backwash (Samaei *et al.* 2018). Because of the resistance of ceramic membranes to high temperatures and highly acidic and basic solutions, it has been successfully used in applications involving difficult conditions. Ceramic membranes commonly are fabricated by using alumina, titania, zirconia and silica materials (Lee *et al.* 2015). According to chemical stability, ceramic membrane materials are listed from the highest strength to the lowest as follows; titania > zirconia > alumina > silica (Hofs *et al.* 2011). It should also be noted that commercial NF or tight UF production is very limited. The reasons for this situation can be listed as follows. Since the membrane thickness does not exceed 50 nm, in addition, high quality support layer and intermediate layers are required for the NF membrane, making it difficult to manufacture defect-free membranes. The need for the use of organic solvents and the need for special technical measures for this can be counted as one of these reasons (Voigt *et al.* 2019).

#### 3.1. Ceramic membrane fabrication

As mentioned above, the main materials of ceramic membranes are usually silica, alumina, zirconia and other oxide mixtures (Li *et al.* 2020a). The pore size of the ceramic membranes is divided into three groups. (1) lower than 2 nm – microporous, (2) between 2 and 50 nm – mesoporous and (3) greater than 50 nm – macroporous (Nishihora *et al.* 2018). In general, every ceramic membrane production procedure involves sintering these materials at high temperatures and obtain a nonsymmetric membrane (Li *et al.* 2020a). First of all, ceramic membrane production starts with the preparation of adequate powder. By using wet or dry forming methods and with the help of organic additives, the membrane begins to take its final shape. Subsequently, the heat treatment step is applied. If the main purpose is to detract organic additives from membrane texture, low temperatures would be enough and this process is called calcination. To obtain membranes with a dense or porous structure, multilayer conformation which includes a support layer for physical strength and active layer for separation is required (Buekenhoudt *et al.* 2010). By multi layered fabrication, pore size and thickness of layers changes gradually (Das & Maiti 2009). There are different techniques for ceramic membrane fabrication. The most used methods are as follows: tape casting, extrusion, slip casting, pressing and sol-gel (Nishihora *et al.* 2018; Issaoui & Limousy 2019).

##### 3.1.1. Tape casting

Tape casting method is used for the fabrication of flat-type ceramic membranes and the thickness of the membrane can be adjusted between 1 mm and 10  $\mu\text{m}$ . After preparation a powder-liquid suspension which is called slip or slurry, the tape is cast as a wet-shaping process (Nishihora *et al.* 2018). Permanence and rheological structure of the slurry can be controlled by dispersant and to alter durability and flexibility of produced tapes, plasticizers and binders are important. Subsequently, produced tapes are dried to remove the solvent by evaporation. As a final step, the desired shape is given by cutting the tapes, pressed for lamination and sintering process is applied. Tape casting method is also generally preferred for large-scale fabrications (Bernardo *et al.* 2020). In Figure 10, a typical ceramic membrane type-casting manufacturing device is given.



**Figure 10** | A typical ceramic membrane type-casting manufacturing device (Nishihora *et al.* 2018).

### 3.1.2. Slip casting

In slip-casting method, which is defined as an easy and flexible technology of moulding, slurries have to be mobile to be able to pour out and have high solid content. After pouring the slurry into casting mould, because of the capillary force solvent is taken away from the slurry and a solid layer with certain strength and thickness is formed. This solid layer is demoulded for the sintering process. The properties of the final product depend on the content of binder, particle size in slurry, duration and temperature of firing (Fan *et al.* 2016). In Figure 11, a schematic drawing of slip-casting method is given.

### 3.1.3. Extrusion

After preparing ceramic membrane mixture with suitable additives and dispersant, kneading should be applied to obtain high degree of viscosity. For shaping step, obtained viscous paste is processed in an auger type extruder with vacuum pressure to remove air in the paste. The main logic in extrusion is to put the mixture with a very high viscosity into a mould and form the membrane by applying repulsive force. Final configuration of the membrane is determined by the geometry of the mould, e.g. multichannel tubular, flat, etc. The applied pressure in extrusion and the process rate of extrusion are the most important parameters for controlling the process. Besides, particle size, dispersant content and material's character are the significant parameters which also affect the process (Mestre *et al.* 2019). In Figure 12, simple flow chart of production of ceramic membranes using extrusion or pressing method is given.

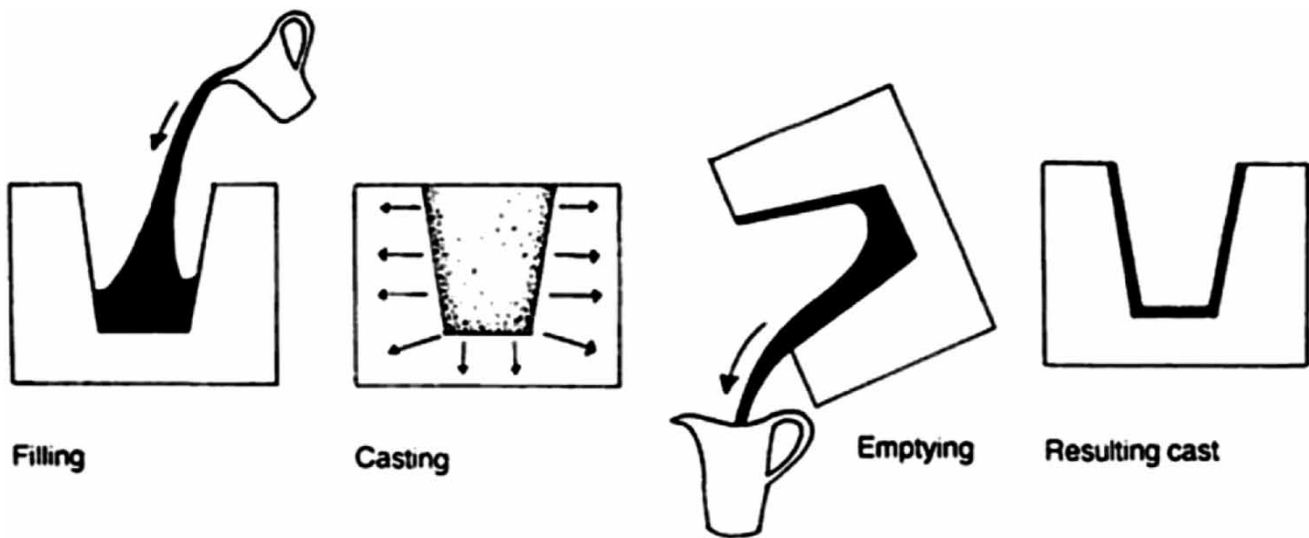


Figure 11 | Schematic drawing of slip-casting method (Hubadillah *et al.* 2018).

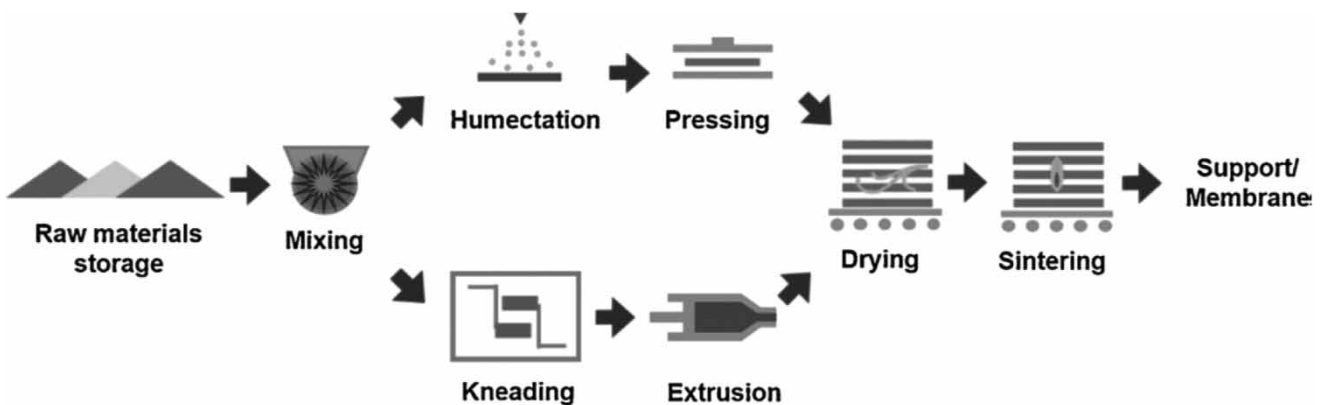


Figure 12 | Simple flow chart of production of ceramic membranes using pressing or extrusion method (Mestre *et al.* 2019).

### 3.1.4. Pressing

The pressing method can be classified as the most basic and well-recognized fabrication technique. In this method, powders can be used directly since slurry is not required. First, appropriate powders are weighed according to calculations and placed on the equipment (tungsten carbide or non-flexible steel) to be pressed and preferred pressure is applied (Hubadillah *et al.* 2018).

### 3.1.5. Sol-gel

For preparing inorganic membranes, the sol-gel method is defined as the most useful one when considering other preparation methods. This method has many advantages such as providing uniform pore distribution and products with high purity in spite of low temperature requirement. But the occurrence of cracks during drying can be identified as a disadvantage. In order to provide a solution to this situation and to prevent cracks during drying, organic binders are added to the solution and these substances are removed from the membrane during heating (Ahmad *et al.* 2005).

## 4. CERAMIC MEMBRANE APPLICATIONS IN TEXTILE INDUSTRY

For membrane processes, two materials are commonly used which are ceramics and polymers. Although polymeric membranes are used more frequently in treatment technologies today, their low stability, easy clogging and short lifetimes limit their use. At this point, ceramic membranes are starting to get attention from both laboratory and real applications (He *et al.* 2019). Especially properties like high chemical, thermal and mechanical endurance of ceramic membranes make them an alternative for polymeric membranes (López *et al.* 2020). When wastewater with very high temperatures, harsh chemicals and highly contaminated characterization needs to be treated, ceramic membranes must be used instead of conventional polymeric membranes. In fact, with the start of the production of low-cost ceramic membranes, the use of them on a larger scale has paved the way for application (Goh & Ismail 2018). If a comparison is made in terms of flux, it is stated in the literature that ceramic membranes have higher flux than polymeric membranes (Barredo-Damas *et al.* 2010). Especially when used in hot wastewater treatment in the textile industry, ceramic membrane flux values will increase further, depending on the viscosity decreasing with increasing temperature (Dilaver *et al.* 2018). In addition, because of the high pH and chemical resistance of the ceramic membranes, the membrane performance can be recovered more efficiently, as the membranes can withstand a more aggressive cleaning process (Cromey *et al.* 2015). Considering the characteristics of the textile wastewater and the properties of ceramic membranes together, the use of these membranes in textile wastewater treatment is also recommended in the literature (Barredo-Damas *et al.* 2012).

Despite the increase in ceramic membrane applications in water and wastewater treatment, its real-scale use is very low. The main reason for this is the high initial investment cost of ceramic membranes. This problem is tried to overcome by using lower cost materials such as kaolin and pyrophyllite in membrane production. In addition, aggressive cleaning methods (high concentration of sodium hydroxide or sodium hypochlorite or ozone, etc.), which cannot be used in polymeric membranes, are very effective in ceramic membranes in order to eliminate the clogging problem in membranes. However, since these experiments are generally done on laboratory scale, their effectiveness should be tested in full-scale studies. Hence, the fate of the waste that will come out as a result of this cleaning should be considered (Asif & Zhang 2021).

In this section, the lab-scale and pilot-scale studies found in the literature are compiled.

### 4.1. Laboratory-scale studies

Although there are more articles for ceramic membrane production in literature, many studies have been carried out in recent years on a laboratory scale for textile wastewater treatment using ceramic membranes. Within this review, the most recent ones will be compiled.

With the development of the ceramic membrane industry, it has become more accessible in commercial NF membranes. Especially in some studies, treatment of water containing dye and salt was carried out using NF and UF membranes. For instance, Chen *et al.* used ceramic NF (tubular MWCO of 900 Da) membrane for treatment of feed water which contains salts (NaCl and Na<sub>2</sub>SO<sub>4</sub>) and six different dyes with different charges (Evercion red H-E7B, Eriochrome black T, Reactive brilliant blue, Basic green 4, Methylene blue and Reactive black 5) and compared this ceramic membrane with commercial organic NF membranes. They also investigated effect of salt content on desalination. Ceramic NF membrane showed a better rejection performance (average 70% retention) for anionic dyes and Chen *et al.* attributed this to size exclusion and charge

effects which are the major separation way for ceramic membranes instead of solution-diffusion mechanism (Chen *et al.* 2017).

In a study conducted by the authors of this article, it was aimed to recover hot water using commercial membranes with different MWCO values (3, 15, 50 and 300 kDa) and real wastewater. Fouling mechanism of membranes and economic aspects of hot water recovery were also investigated. According to the findings of this research, it can be concluded that treatment of industrial wastewater with ceramic membranes has remarkable potential for recovery and reuse (Dilaver *et al.* 2018).

In another study, commercial tight ceramic UF membrane (MWCO = 2410 Da) was tested to separate reactive dyes from dye/salt mixture by Jiang *et al.* They reported dye rejection as on average 98.12% in which seven blue dyes (varying between 626.6 and 1205.4 Da) were used for experiments. They concluded that accumulation of dyes can be the reason for high rejection rates and they also mentioned that ceramic membrane's surface was negatively charged (Jiang *et al.* 2018). Alventosa-deLara *et al.* also used commercial UF ceramic membrane for treatment of reactive dye/salt solution, which is called simulation of textile wastewater in this article. Also, in this study, membrane fouling, which is an important issue for membrane processes, was mentioned in terms of various aspects. As stated in many other studies, they found that increasing salt concentration had a negative effect on dye removal (Alventosa-deLara *et al.* 2014). In their previous study, they investigated transmembrane pressure (TMP), cross-flow velocity (CFV) and dye concentration's impact on flux and rejection of Reactive black 5 by using commercial tubular ceramic membrane. They found that lower CFV and higher TMP leads to more significant flux decline (Alventosa-deLara *et al.* 2012). In addition to studies with commercial membranes, there are many studies in the literature that are conducted after ceramic membrane production.

For fabrication of commercial ceramic membranes, there are common metal oxides which are generally used such as zirconia, titania, silica and alumina. Especially with the increase in ceramic membrane studies, the most used raw material was alumina. However, there have been remarkable developments in the production of ceramic membranes in lab-scale studies that have both low cost and high stability, high mechanical strength and selectivity. Examples of the raw materials of these low cost ceramic membranes are starch, clay, sand and apatite, which are used for both UF and MF studies. In a recent study, Oun and colleagues fabricated tubular ceramic membrane by using alumina powder and natural kaolin clay and coated with TiO<sub>2</sub> nanoparticles to remove a specific dye. As a result of this work, they obtained approximately 99% colour removal (Oun *et al.* 2017). Because of its high chemical resistance and resistance to corrosion,  $\alpha$ -alumina membranes are drawing attention recently. In Zou's study, alumina nanoparticles were used in boehmite sol to obtain small pores on  $\alpha$ -alumina membranes. They reported pore sizes as below 5 nm and indicated that membranes have high rejection rates of different dyes such as Titan yellow and Direct red (DR) (Zou *et al.* 2019). When clay and common metal oxides such as silica, titania, alumina and zirconia are compared, it is known that clay is more resistant and in terms of firing temperature, lower temperatures are sufficient for clay. In a study where ceramic support was produced by mixing clay and banana peel, which is used to obtain porosity, MF membrane obtained by covering the support's surface with clay again succeeded in the treatment of textile wastewater. In addition to using clay for low cost fabrication, an ecologically friendly approach has been demonstrated by using banana peel (Mouiya *et al.* 2019). In another clay related study, natural clays were purified before membrane fabrication to obtain richer content of kaolinite and similar materials. After UF membrane production by using purified clay as the coating material, removal performance tests with DR80 dye solution were conducted and approximately 97% removal efficiencies were reported. They also remarked that better antifouling results were achieved (Ouaddari *et al.* 2019). A similar study was carried out by Saja *et al.* in 2020 by using bentonite clay to ameliorate the membrane's selectivity. The UF membrane produced with clay coating on the perlite support layer has been tested with two different dye solutions, anionic (DR80) and cationic (rhodamine B, RB). According to results, 97% and 80.1% rejection efficiencies were obtained for DR80 and RB, respectively (Saja *et al.* 2020). In addition to being used as a perlite support layer, it can also be used without coating. MF ceramic membrane was also fabricated by Saja *et al.* and performance tests were conducted by two kinds of industrial effluents. High turbidity removal rates were obtained (Saja *et al.* 2018). In another study showing that DR80 dye can be removed with UF membrane, MF membrane, which was obtained by pressing method, used as support layer is produced from natural bentonite and phosphate and coated with TiO<sub>2</sub>. The pore diameter of the membrane obtained was reported as 72 nm (Bouazizi *et al.* 2017).

In another very interesting study, ceramic hollow fibre membrane was produced using waste cow bone, which can be obtained hydroxyapatite due to its high calcium content. According to efficiency values which are reported as 99.9%, 80.1% and 30.1% for colour, COD and conductivity respectively, it can be understood that it has a potential for treatment of textile wastewater (Hubadillah *et al.* 2020). Geomaterials, which are another option for low cost raw material for ceramic

membrane production, have been getting attention in last 10 years. Manni and colleagues selected Moroccan natural magnesite for fabrication of membrane. One of the magnesite properties is that magnesite decomposes thermally during fabrication because of high temperatures in sintering process and it forms the porosity of the membrane. Thus, there is no need to add an additional pore former during production. After rejection experiments with real textile water, COD and turbidity removal efficiencies were reported as 69.7% and 99.9%, respectively (Manni *et al.* 2020).

Ceramic and polymeric materials were also used for the production of NF membranes. Especially ceramic tubular and hollow fibre membranes as a more comprehensive support option for thin film composite applications were studied to take advantage of the durability of the ceramic membrane. Chong and Wang synthesized polyamide thin films on MF ceramic membranes and obtained NF level of separation level. Removal of divalent salts and organic dyes was also achieved (Chong & Wang 2019).

Nanoparticles are also used frequently in membrane production to increase the performance of membranes in wastewater treatment. For example, it is aimed to improve the permeability and permeate quality of membranes produced using metal oxide nanoparticles. In a study where silica nanoparticles obtained from rice husk were used, it was aimed to increase the adsorptive properties of the membrane with silica added to the ceramic membrane. The main material of the membrane is calcium phosphate and ammonium acetate is used to form pores on the ceramic membrane. In the experiments performed with the dye solution, good removal efficiencies have been obtained. It is also stated in the study that the dye adsorbed on the membrane can be removed by calcination and the membrane can be reused (Tolba *et al.* 2016).

#### 4.2. Pilot-scale applications

There are pilot-scale studies related to seawater desalination (Cui *et al.* 2011), oily wastewater treatment (Abadi *et al.* 2011) and wastewater treatment (Lehman & Liu 2020). Although laboratory-scale studies are relatively various in the literature, the treatment of textile wastewater treatment on a pilot scale using ceramic membranes is quite limited. This section includes some pilot studies that we were able to investigate in the literature, which was very limited.

In 2001, Voigt *et al.* used titanium NF membranes with 0.9 nm pore size in a pilot-scale ceramic membrane system to remove colour from textile finishing wastewater. They also aimed to recover hot water and reuse as process water in the facility. For this purpose, 30 different wastewaters with different colour were used for experiments during six weeks to evaluate to obtain high rates of flux and low operation costs (Voigt *et al.* 2001).

In Barredo-Damas *et al.*'s study, pilot-scale ceramic UF system was tested for a pre treatment purpose for real textile wastewater from a textile manufacturing plant. UF ceramic membranes were tubular with titania support and zirconia active layer, and molecular weight cut-off values were 150, 50 and 30 kDa. Besides, different CFV values were applied to investigate the effect on membrane performance. Approximately 99% of turbidity removal was obtained and colour removal was 98% as the highest removal rate. COD removal values were also considerable. It was reported that ceramic UF membranes can be accepted as a viable option for pre treatment (Barredo-Damas *et al.* 2010).

In the study conducted to remove Reactive black 5 dye with a pilot-scale UF membrane system, the effects of TMP and CFV parameters as well as initial dye concentration on membrane performance were evaluated. Following the studies, flux reduction was more clearly observed in the combination of high TMP, low CFV and high dye concentration (Alventosa-deLara *et al.* 2012).

In a study conducted by the authors of this review and colleagues, pilot-scale UF and NF ceramic membrane systems were used to recover and reuse real textile hot wastewater *in situ*. The wastewater was taken from disperse and reactive printing washing baths which were mixing in hot discharge point. UF and NF membrane systems were tested both separately and together in a batch mode. Removal efficiencies for COD, TOC, colour and total hardness (for UF + NF cycles overall average removal efficiencies were 89, 83.5, 86.4 and 68% for COD, colour, TOC and hardness, respectively, for only nanofiltration cycles, overall average removal efficiencies were 90.1, 82.2, 76.8 and 82% for COD, colour, TOC and total hardness, respectively) for both operations were quite significant. In addition, fabric dyeing experiments with treated water were also successful for two dyes. According to the results, water recovery and energy saving were achieved due to hot water recovery (Ağtaş *et al.* 2020).

## 5. CONCLUSION AND SUGGESTIONS FOR FUTURE STUDIES

Gradually decreasing water resources making access to clean water difficult is perhaps the most important problem facing our world. It becomes mandatory to protect water resources and use them within the framework of logic. In this context, some

limitations and solutions are required for industries with high levels of water use. In particular, the high amount of water used in every stage of the textile industry, as well as the water pollution caused by the chemicals and dyes used, make water resources difficult. Therefore, wastewater treatment, water recovery and reuse have become important in the textile industry. Although many traditional methods have been used for textile wastewater over the past years, sufficient efficiency has not been achieved. In this case, membrane processes can be a solution. Ceramic membranes, which can withstand the difficult characteristics of textile wastewater, have become quite prominent in recent years. Cost, which is an important disadvantage of ceramic membranes, has started to decrease as the studies increase.

Based on the literature investigation made within the scope of this review, it is concluded that ceramic membrane production and application studies are given more importance in the laboratory rather than the pilot and real applications. Although laboratory studies are the starting point of many studies and are very valuable, pilot studies are thought to be necessary for real applications. As a result of this study, it can be given as advice for future studies, increasing the studies towards real applications.

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## COMPETING INTERESTS

The authors declare that they have no competing interests.

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## AUTHORS' CONTRIBUTIONS

MA did all the research, wrote the manuscript and evaluated the results. MD contributed to the corrections of the manuscript. İK provided consultancy throughout the entire study and contributed to corrections of the manuscript. All authors read and approved the final manuscript.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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