استخدام الرمل السوري في إنتاج أنسجة خزف غير عضوية جديدة

عبدالرزاق همال

قسم الكيمياء- كلية العلوم – جامعة حلب- سوريا

المستخلص: في هذا البحث حضرت أنسجة خزفية من الرمل السوري. تضمنت عملية التحضير مراحل عديدة، بدأت تنقية الرمل من الشوائب بالأحماض لإزالة معظم الشوائب وتصنيفها حسب الحجم. تحضر أنسجة الخزف بخلط الرمل بكميات مختلفة من سيليكات الصوديوم السائلة كغلاف ومن ثم دراسة تأثير نسبة الغلاف والضغط المتكون ودرجة حرارة المعالجة وحجم حبيبات الرمل على بعض خواص الأنسجة المحضرة. اختبرت فعالية الأنسجة المحضرة في معالجة مياه الصرف الصحي للغسالات وأن المعالجة تركز على التسوية ومن ثم الترشيح عبر الأنسجة المحضرة وأن الفعالية العالية للأنسجة المحضرة تنتج من تقليل الاحتياج للأوكسجين بنسبة ٧٢,٨٩% والأوكسجين الحيوي بنسبة ٨٢,٦٤% والعكر بنسبة ٩٩,٣٠% واللون بنسبة ٩٨,٩٠% والمواد المعلقة بنسبة ٩٩,٣٥%.

الكلمات المفتاحية: أنسجة، الرمل السوري، الخزف، الترشيح، النفاذية

References

- De Falco, M.; Di Paola, L.; Marrelli, L., Nardella, P. 2007. **Simulation of large-scale membrane reformers by a two-dimensional model.** Chemical Engineering Journal, Vol. 128, No. 2-3, pp. 115-125, ISSN 1385-8947.
- Judd, S., Judd, C., 2011. **The MBR Book: Principles and Applications of Membrane Bioreactors in Water and Wastewater Treatment**, Second edition. Elsevier
- Kang, Li., 2007. **Ceramic Membranes for Separation and Reaction**, John Wiley & Sons, Inc., England.
- Kumar, D., 2013. **Preparation of Ceramic Membranes for effluent treatment.** Thesis
- bachelor of Technology in Chemical Engineering, National Institute Of Technology Rourkela, India.
- Masturi, S., Mahardika P. A., EuisSustini, K., Mikrajuddin A., 2012. **Permeability, Strength and Filtration Performance for Uncoated and Titania-Coated Clay Wastewater Filters.** Am. J. Environ. Sci., 8 (2): 79-94.
- Takhttravanchi, M., Kaghazchi, T., Kargari, A., 2009. **Application of Membrane Separation Processes in Petrochemical Industry, Desalination** (235) 199-244
- Xia, Y.; Lu, Y.; Kamata, K.; Gates, B., Yin, Y., 2003. **Macroporous materials containing three-dimensionally periodic structures.** Chemistry of Nanostructured Materials, World Scientific 69-100.

Table 11: Chemical stability

Membrane	loss in weight(%)	
	after base treatment	after acid treatment
A3	0.021	0.011
M3	0.049	0.015
C3	0.051	0.016
D3	0.059	0.021

prepared membranes have emerged through decrease of chemical oxygen demand COD by 72.89%, biological oxygen demand BOD by 82.64%, turbidity by 99.30%, color by 98.90%, and suspended solids SS by 99.35% as shown in **Table 12, Fig 10**.

4. Practical application

The effectiveness of the prepared membranes was tested in wastewater treatment for one of the laundries in the city of Aleppo. Treatment was performed by settling then filtration through prepared membranes, the high effectiveness of the

Table 12. Specification of wastewater before and after filtration.

		Syrian standard /2580/	Before treatment	After treatment	removal ratio %
Chemical oxygen demand	COD	1600 mg/l	٨٤٥	229	٧٢,٩٠
Biological oxygen demand	BOD	800 mg/l	٦٥٧	114	٨٢,٦٥
Suspended solids	S.S	10 mg/l	1395	9	٩٩,٣٥
Turbidity	Turb	90 NTU	282	1.96	٩٩,٣٠
Total dissolved solids	TDS	2000 mg/l	2780	1360	٥١,٠٨
Color	TCU	100 mg/l	6780	74	٩٨,٩١

Fig 10: effectiveness of the prepared membranes in treatment laundry wastewater

5. Conclusion

Results showed that apparent porosity, water absorption, were decreasing, while the bulk density and apparent specific gravity were increasing in the cases of:

- increasing bender.
- decreasing treatment temperature.
- decreasing formation pressure.
- increasing grain size of sand

Volumetric flow, and permeability were increasing in the cases of:

- decreasing bender.
- increasing treatment temperature.
- decreasing formation pressure.
- increasing grain size of sand

Prepared membranes were high effected through decrease of chemical oxygen demand **COD** by 72.89%, biological oxygen demand **BOD** by 82.64%, **turbidity** by 99.30%, **color** by 98.90%, and suspended solids **SS** by 99.35%

Results in **Table 8** showed that apparent porosity, water absorption, volumetric flow, and permeability were decreasing with increasing formation pressure, while the bulk density and bulk density and apparent specific gravity were increasing with increasing formation pressure, because the pressure is causing agglutination of grains, consequently decreasing voids ratio. Also it cannot determine the optimum formation pressure because it depends on the requirements field of employment.

Table 8: Effect of formation pressure on the membranes properties

properties	Membrane				
	M3P2	M3P3	M3P4	M3P5	M3P6
Pressure (kg/cm ²)	200	300	400	500	600
Water absorption (%)	24.12	23.23	21.75	19.29	18.01
Apparent porosity (%)	36.74	34.22	32.93	31.96	29.14
Bulk density (g/cm ³)	1.43	1.54	1.63	1.73	1.79
Apparent specific gravity	2.30	2.34	2.39	2.67	2.71
Volumetric flow Q (m ³ /sec)	15.70 x10 ⁻⁶	8.051 x10 ⁻⁶	5.413 x10 ⁻⁶	4.491 x10 ⁻⁶	2.616 x10 ⁻⁶
Permeability P (darcy)	0.0347	0.0178	0.0119	0.0099	0.0057

3.2.6. Effect of grain size of sand on the membranes properties

Membranes were prepared according to the conditions described in **Table 9**.

Table 9: conditions of studying the effect grain size of sand

Membrane	Particle size of sand (μ)	Binder ratio (%)	Temperature (°C)	Pressure (kg/cm ²)
A3	63 >	15	1100	500
M3	63-100	15	1100	500
C3	100-160	15	1100	500
D3	160-250	15	1100	500

Results in **Table 10** showed that apparent porosity, water absorption, volumetric flow, and permeability were increasing with increasing grain size of sand, while the bulk density and bulk density and apparent specific gravity were decreasing with increasing grain size of sand, because the spaces between the fine grains less than the spaces between the larger grains. Also it cannot determine the optimum formation pressure because it depends on the requirements field of employment.

Table 10: Effect of grain size of sand on the membranes properties

properties	Membrane			
	A3	M3	C3	D3
Particle size of sand (μ)	63 >	63-100	100-160	160-250
Water absorption (%)	16.05	19.29	19.67	21.22
Apparent porosity (%)	26.68	31.96	34.41	35.26
Bulk density (g/cm ³)	1.74	1.73	1.71	1.69
Apparent specific gravity	2.71	2.67	2.61	2.60
Volumetric flow Q (m ³ /sec)	1.48 x10 ⁻⁶	4.49 x10 ⁻⁶	14.27 x10 ⁻⁶	52.33 x10 ⁻⁶
Permeability P (darcy)	0.0032	0.0099	0.0315	0.1157

4. Chemical stability

Membranes were treated with acid and base, results in **Table 11** showed that prepared membranes were more stable in acid than in base. Membranes properties didn't change after this test

well as the permeability decreased from

Preparing M3 was the easiest, due to mix binder with sand was easy and mixing time was short compared with the required time for M1 and M2, prepare M4 was the hardest because of the mixture was moist to a large degree, so need to dry

Membranes were prepared according to the conditions described in **Table 5**.

Table 5: conditions of studying the effect of treatment temperature

Membrane	Temperature (°C)	Binder (%)	Pressure (kg/cm ²)	Particle size of sand (μ)
M3T90	900	15	500	63-100
M3T10	1000	15	500	63-100
M3T11	1100	15	500	63-100
M3T12	1200	15	500	63-100
M3T13	1300	15	500	63-100

Results in **Table 6** showed that apparent porosity, water absorption, volumetric flow, and permeability were increasing with increasing treatment temperature, while the bulk density and apparent specific gravity were decreasing with increasing treatment temperature. These

0.0184 darcy in M1 to 0.0076 darcy in M4. before formation into the mold. So it can be said that under the applied conditions in these experiments the best percentage of binder was 15%.

3.2.4. Effect of treatment temperature on the membranes properties

due to a change in the crystal structure, because of formation of larger ratios of β -cristobalite when treatment at a higher temperature. Density of β -cristobalite is less than density of α -quartz, this explains the volumetric expansion of the membrane when treatment at a higher temperature.

α -Quartz 2.65 g/cm ³	$\xrightarrow{573^{\circ}\text{C}}$	β -Quartz 2.53 g/cm ³	$\xrightarrow{1050^{\circ}\text{C}}$	β -Cristobalite 2.20 g/cm ³
--	-------------------------------------	---	--------------------------------------	---

Also it cannot determine the optimum treatment temperature because it depends on the requirements field of employment.

Table 6 Effect of treatment temperature on the membranes properties

properties	Membrane				
	M3T90	M3T10	M3T11	M3T12	M3T13
Temperature (°C)	900	1000	1100	1200	1300
Water absorption (%)	16.17	17.54	19.29	23.49	27.08
Apparent porosity(%)	28.48	29.10	31.96	33.61	37.35
Bulk density (g/cm ³)	1.76	1.75	1.73	1.43	1.38
Apparent specific gravity	2.72	2.70	2.67	2.26	2.16
Volumetric flow Q (m ³ /sec)	4.878 x10 ⁻⁶	5.128 x10 ⁻⁶	5.479 x10 ⁻⁶	7.843 x10 ⁻⁶	10.256 x10 ⁻⁶
Permeability P (darcy)	0.0107	0.01134	0.0121	0.0173	0.0226

3.2.5. Effect of formation pressure on the membranes properties

Membranes were prepared according to the conditions described in **Table 7**.

Table 7: conditions of studying the effect of formation pressure

Membrane	Pressure (kg/cm ²)	Binder (%)	Temperature (°C)	Particle size of (sand μ)
M3P2	200	15	1100	63-100
M3P3	300	15	1100	63-100
M3P4	400	15	1100	63-100
M3P5	500	15	1100	63-100
M3P6	600	15	1100	63-100

Fig 9: SEM of membrane

3.2.3. Effect of binder on the membranes properties

Membranes were prepared according to the conditions described in **Table 3**.

Table 3: conditions of studying the effect of binder

Membrane	Binder (%)	Temperature ^o (C)	Pressure (kg/cm ²)	Particle size of sand (μ)
M1	5	1100	500	63-100
M2	10	1100	500	63-100
M3	15	1100	500	63-100
M4	20	1100	500	63-100

Results showed that apparent porosity, water absorption, volumetric flow, and permeability were decreasing with increasing the binder, while the bulk density and apparent specific gravity were increasing with increasing the binder, because the increasing of binder causing conglomerate of sand particles, thereby decreasing the voids ratio.

Table 4 showed that apparent porosity decreased from 37.25% in M1 to 29.18% in M4, and water absorption decreased from 20.97% in M1 to 17.94% in M4. Bulk density increased from 1.72 g/cm³ in M1 to 1.74 g/cm³ in M4, and apparent specific gravity increased from 2.27 in M1 to 2.77 in M4.

Table 4: Effect of binder on the membranes properties

properties	Membrane			
	M1	M2	M3	M4
Binder (%)	5	10	15	20
Water absorption (%)	20.97	19.76	19.29	17.94
Apparent porosity (%)	37.25	32.94	31.96	29.18
Bulk density (g/cm ³)	1.72	1.72	1.73	1.74
Apparent specific gravity	2.27	2.58	2.67	2.77
Volumetric flow Q (m ³ /sec)	8.33x10 ⁻⁶	5.48x10 ⁻⁶	4.49x10 ⁻⁶	3.47x10 ⁻⁶
Permeability P (darcy)	0.0184	0.0121	0.0099	0.0076

Volumetric flow decreased from 8.33 10⁻⁶ m³/sec in M1 to 3.47 10⁻⁶ m³/sec in M4, as

Fig 6: XRD spectrum of purified sand

Fig 7: SEM images of purified sand

3.2. Characteristics of prepared membranes

3.2.1. Crystal Phases

Spectrum of X-ray diffraction (Fig 8) showed that membrane contains two phases, the first one is α -quartz, and the

second phase is β -cristobalite, crystal system cubic, space group Fd_{3m} , the calculated unit cell parameters are: $a = 5.4334 \text{ \AA}$, $b = 5.4319 \text{ \AA}$, $c = 5.4309 \text{ \AA}$, $V = 160.1832 \text{ \AA}^3$, calculated density 2.33 g/cm^3 .

Fig 8: XRD spectrum of membrane

3.2.2. SEM analysis

Scanning electron microscope SEM (Fig 9) shows the distribution of sodium

silicate on the surface of sand particles, this means the correlation occurred on the surface level of sand grains only.

DTA analysis

Differential thermal curve of raw sand (Fig 4) showed presence two peaks:

First peak refers to endothermic reaction at 573°C as a result of transformation of α -quartz to β -quartz.

Second peak refers to exothermic reaction at 668°C as a result of decomposition organic matter and carbonates which

associated with raw sand, while differential thermal curve of treatment sand (Fig 5) showed presence of one peak refers to endothermic reaction at 573°C as a result of transformation of α - quartz to β - quartz, and disappeared the peak which refers to decomposition organic matter and carbonates, that appears the efficiency of the purification process.

Fig 4: Differential thermal curve of raw sand

Fig 5: Differential thermal curve of treatment sand

analysis

Spectrum of X-ray diffraction (Fig 6) showed that purified sand mainly contains α -quartz, crystal system trigonal, space group $P3_221$, the calculated unit cell parameters are: $a=4.9134 \text{ \AA}$, $b=4.9134 \text{ \AA}$, $c=5.4052 \text{ \AA}$, and $v = 113.0132 \text{ \AA}^3$, calculated density 2.66 g/cm^3 . In addition

XRD

the presence small peaks indicate the presence of small proportions of other secondary compounds such as hematite (iron oxide) and calcite (calcium carbonate); this corresponds to the result of chemical analysis. Quartz crystals were showed by SEM images (Fig 7).

2.3. Membranes characterization

Apparent porosity, water absorption, apparent specific gravity, and bulk density were determined by (ASTM C20–00).

Permeability was measured using the apparatus illustrated in Fig3. Darcy's law

states that $k = \frac{Q \cdot \mu \cdot \Delta L}{A \cdot \Delta p}$, where Q is the volumetric flow rate, k is the filter permeability, A is the filter surface area, Δp is the pressure difference between the two filter surfaces, μ is the dynamic viscosity of the fluid and ΔL is the membrane thickness (Masturi, S., 2012).

Fig3: Permeability test schematic

Membranes were investigated by XRD, SEM, DTA, and IR to study the phase changes. Chemical stability of the membranes was checked by immersing the membranes in a solution of NaOH (pH=13.5) and HCl (pH=1.0) separately for 24 h, then determine the loss of weight.

3. Results and discussion

3.1. Sand specifications

Tables (2) and (3) show effectiveness of the purification process, SiO₂% increased from 92.62% to 98.10%, all of associated impurities decreased, increased sand density and acid resistance, and change its color from orange yellowish to white. These results indicate an improvement in the properties of the sand and the acquisition of greater stability, which has positively effects of properties of the membrane to be prepared

Table 1: XRF data of sand before and after treatment

	before treatment %	after treatment %
SiO ₂	92.62	98.10
Al ₂ O ₃	1.29	0.78
Fe ₂ O ₃	1.26	0.03
CaO	2.77	0.51
MgO	0.43	0.27
SO ₃	0.01	0.00
K ₂ O	0.21	0.07
Na ₂ O	0.06	0.01
LOI	0.94	0.24

Table 2: Basic properties of sand

	before treatment %	after treatment %
Density (g/cm ³)	2.41	2.53
Associated clay material%	0.952	0.012
Acid resistant%	1.19	0.084
Color	orange yellowish	white

Fig2: Methods of preparation of ceramic membranes.

2. Materials and methods

2.1. Raw material

2.1.1. Sand

Sand was collected from the area of **Nabek- Syria**, then treated with the acidic way using hydrochloric acid extended by (1:1) to remove most of the impurities. Then it washed with distilled water, dry, grinded by laboratory mill, and classified according to grain size.

2.1.2. Chemicals

Liquid sodium silicate (Loba Chemie Pvt. Ltd) was used as a binder, hydrochloric acid 37% (Merck).

2.2. Membranes preparation

Membranes were prepared by pressing method by mixing the treated sand with liquid sodium silicate as a binder, then pressed the mixture into a cylindrical mold to form desks with

The chemical analysis was done by **XRF** (Philips, PW 2440 MagiXPRO), **DTA** analysis (Linseis), **XRD** analysis by (Bruker AXS D8 with CuK α radiation, operated at 40kV, 250mA), **SEM** by (LEO 1530-2 FESEM/EDS, operated at 3kv). Basic properties of the sand like density, associated clay material, acid resistant, were determined by standard procedures (ASTM C-33).

diameter 5cm and thickness 2-2.5 mm, then thermally treated the desks. The studied parameters were:

- binder (5, 10, 15, 20) %
- temperature of treatment (900, 1000, 1100, 1200, 1300) $^{\circ}\text{C}$
- formation press (200, 300, 400, 500, 600) kg/cm^2
- grain size of sand (63>, 63-100, 100-160) μm

Sand

Cylindrical mold

Pressing

Electric furnace

Membranes

Polymeric membranes operate between 100-300°C, inorganic membranes above 200 °C. Surely, for industrial

chemical process, the inorganic membranes are the most interesting (Xia, Y et al., 2003; De Falco, M et al., 2007).

Fig1: Scheme of a general classification of the membranes

2. Packing of the particles in the suspensions or mixture into a membrane precursor with a certain shape such as flat sheet, monolith or tube.
3. Consolidation of the membrane precursor by a heat treatment at high temperatures.

Fig2 shows the methods of preparation of symmetric and composite membrane ceramic membranes. Where various methods listed such as slip casting, tape casting, extrusion and pressing are the shaping techniques which turn the particle suspension (slurry or paste) into a membrane precursor. Figure 2 further illustrates that no matter which process is selected in preparation of the ceramic membranes, the final membrane product or membrane support can only be obtained through a firing step. Indeed, composite membranes (multi-layer membranes) can be further produced on a membrane support through a coating step using dip-coating, sol-gel, CVD or EVD process, followed by a repeated firing step (Kang, Li., 2007).

Ceramic membranes refer mainly to those prepared with porous ceramics like alumina, silica, clay or substrates like Titania and zirconia. These membranes find applications predominantly in the fields of solid-liquid separation and solid-gas separation. However, gas based separations also do exist with ceramic membranes. The structure of these membranes are unique with largest pore size at bottom as support and pore size decreases gradually towards the surface where the actual separation takes place. However these structures are highly amenable to modifications depending upon the selection of synthesis routes: from inner structures to top surface of membranes. The membrane is also available in different configurations like tubular, multi-channel monolith membrane etc. As indicated earlier, manufacturing methods have an impact on membrane configuration and structural properties and some of methods are described (Kumar, D., 2013).

In general, preparation of ceramic membranes involves several steps:

1. Formation of particle suspensions or mixture.

Using of Syrian Sand to Produce New Inorganic Ceramic Membranes

Dr.Abdulrazzaq Hammal

Department of Chemistry, Faculty of Science, University of Aleppo, Syria

E-mail: hammal1986@gmail.com

ABSTRACT::In this paper, ceramic membranes were prepared from Syrian sand. Preparation process included several stages began with purification of studied sand, by acidic way using hydrochloric acid extended by (1:1) to remove most of impurities associated, sorting according to the size granular, prepared ceramic membranes by mixing the sand with different portions of liquid sodium silicates as a binder, then study the effect of: ratio of binder, pressure formation, treatment temperature, and sand grains size on some properties of prepared membranes. Effectiveness of the prepared membranes were tested in treatment of laundries wastewater, treatment was performed by settling then filtration through prepared membranes, high effectiveness of the prepared membranes have emerged through decrease of chemical oxygen demand COD by 72.89%, biological oxygen demand BOD by 82.64%, turbidity by 99.30%, color by 98.90%, and suspended solids SS by 99.35%.

Key words: Membranes, Syrian sand, Ceramics, Filtration, Permeability.

1. Introduction:

Membrane is a semi permeable barrier, which separates two phases and restricts transport of various chemical in a selective manner. Membranes structure can be homogenous or heterogeneous, symmetric or asymmetric, solid or liquid; can carry a positive or negative charge or be neutral or bipolar. Membranes thickness may vary from as small as 10 μm to few hundred micrometers (Takhtravanchi, M et al., 2009).

The main driving force in most of the membrane processes is pressure difference or concentration gradient across the membrane depending upon the type of process and membrane used. Parameters such as pressure, concentration and even temperature may be considered as one of parameters. If an electric potential is applied for any membrane separation, the

electric potential difference also influences the transport of charged particles (Judd, S et al., 2011).

Fig1 shows a general classification of membranes, based on their nature, separation and geometry. The classification according to nature membranes distinguishes them into biological and synthetic, differing completely for functionality and structure. Biological membranes are easy to be fabricated but they present many drawbacks such as limited operating temperature (below 100°C) and pH range, problems related to the clean-up and susceptibility to microbial attack due to their natural origin. Synthetic membranes can be subdivided into organic (polymeric) and inorganic (ceramic, metallic).