Preparation and characterization of low cost flat ceramic membranes from easily available potters' clay for dye separation

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Abstract. In the present day scenario, the crisis of safe drinking water is an extremely serious issue across many parts of the globe and needs efficient methods to overcome this problem. The effort made in this study is to develop a method to prepare a ceramic membrane with locally available cheap compositions such as potters' clay, stone dust and tea waste materials for efficient adsorptive dye removal from water. The preparation of ceramic membrane was carried out by a paste pressing method and sintered at an optimized temperature of 900°C to obtain flat ceramic membranes of 42 mm in diameter and 3 ± 0.5 mm thickness with good thermal and chemical stabilities with 52.51% porosity and average pore size of 0.49 μm . The membrane was capable of decolouring methylene blue and congo red from water with good efficiency and the used membrane was regenerated by calcining at 400°C for 30 min without much loss of its efficiency. Development of newer advanced products with the available local resources may be another way to sustain the small scale industry and livelihood of the people around.

Keywords. Potters' clay; ceramic membrane; characterization; decolourization; reusability.

1. Introduction

Ceramic filters and membranes have been extensively applied in a number of fields, such as food and beverage, biotechnology and pharmaceuticals, bulk and fine chemicals, waste recovery and recycling industries [1–4]. The ability of ceramic membranes to uniquely address the distinct need of frequent cleaning, high resistance to harsh operating environment and continuous flow conditions are some of their main advantages over other types of membranes or porous barriers [5]. In recent days, it is seen that tremendous attention is given towards membrane-based separation processes for application in different areas including water treatment, catalysis, industrial gas separation and many other biomedical applications [6–18]. Ceramic membranes can be regenerated for use over many cycles and can be applied to both aqueous and non-aqueous solution separations especially in petrochemical processing where organic membranes cannot be utilized [19].

Use of oxides of pure Al_2O_3 , TiO_2 , ZrO_2 , SiO_2 or their combinations for the preparation of ceramic membranes [5,10–26] with high chemical, mechanical and thermal stabilities are well established [27,28] and are common, but the use of high

cost inorganic precursors to obtain these oxides increases the cost as well as requires high sintering temperature ($> 1100^\circ\text{C}$) for fabrication. The use of cheaper precursors such as ball clay, kaolin, quartz, feldspar, CaCO_3 , clay, sand and pyrophyllite for preparation of microfiltration range ceramic membranes have been reported [29,30]. Out of these, quartz, feldspar and pyrophyllite are expensive raw materials in comparison with widely available materials such as kaolin, ball clay and CaCO_3 . Apart from these common minerals, use of some location-specific natural minor minerals, such as natural apatite, Tunisian silty marls, local clay, Moroccan perlite, Spanish clay mixture, industrial waste coal fly ash, starch as porogen, natural Moroccan pozzolan and Moroccan clay [31–41] are also reported for fabrication of ceramic membranes. On a close investigation of the reported works, it is seen that a number of methods are available for ceramic membrane fabrication, but many of them lag in terms of cost efficacy and easy synthesizability. Preparation of reusable economic adsorbent materials for use in rural areas requires cheaper raw materials available near the place where the rural community resides. In such a context, we have tried to gainfully utilize potters' clay (PC) from a well-known locality

in Assam, India which has been used from ancient times for earthenware pottery.

The rapid progress in the textile industry led to a high demand of dye molecules in the market [42,43], but the problem associated with it is the disposal of spent solutions [44,45] containing a high amount of residual dye molecules. Casual disposal of it to natural water bodies leads to pollution. Although governments bring out different regulations and acts to control such matters, the problem is becoming chronic and the shortage of safe water further aggravates the matter. Due to their complex structure and synthetic origin by design, dye molecules are resistant to breakdown with time or on exposure to sunlight, enzymes, chemical oxidizing agents and water. Hence, they cannot be easily removed by conventional wastewater treatment processes [46,47]. Most of these dyes are highly toxic and can cause mutagenic or carcinogenic effects on aquatic life and human beings even at low concentrations [48]. Methylene blue (MB) is known to cause eye burn, irritation to the gastrointestinal tract, nausea, vomiting and diarrhoea and the quantity exceeding 5 mg kg^{-1} may precipitate serious serotonin toxicity called serotonin syndrome [49].

Various adsorbents have been applied for dye removal from aqueous solution, including activated carbon [50,51], fly ash [52,53], red mud [54], mesoporous aluminium phosphate [55], free standing carbonaceous nanofibre membranes, magnetic powder like $\text{MnO}-\text{Fe}_2\text{O}_3$ [56] composites and porous CeO_2 [57]. Various nanomaterials with well-defined morphology, such as nanoparticles, nanowires, nanobelts, nanorods, nanoflowers and nanotubes [58–61] also have been applied to remove organic dyes.

The conventional methods for waste water treatment, such as ion exchange, chemical precipitation, electro dialysis, etc. are comparatively expensive and are less user friendly than membrane processes. There is a scope for further exploring the use of newer ceramic membranes for these applications using locally available low cost materials. The present study describes preparation of ceramic membranes from easily available materials such as local PC along with different other local materials like stone quarry dust (SQD) and tea factory waste dust. The PC from this region has been traditionally used by rural artisans for the last several hundred years to prepare storage pitchers for sugarcane molasses. With the invasion of modern food packaging practices, the art and the tradition of pottery is dwindling in the area. Therefore, development of newer advanced products with the available resources may be another way to sustain the small scale industry and livelihood of the people around.

2. Experimental

2.1 Chemicals and raw materials

Locally available PC was collected from the Dhekial region of Golaghat district, Assam, India (latitude $26^\circ 36.115 \text{ min}$

North, longitude $93^\circ 58.223 \text{ min}$ East, altitude 47 m above mean sea level) [62]. SQD was supplied by local suppliers who regularly crush stone boulders collected from Bihubor area of neighbouring Sibsagar district, Assam, India. Tea waste was collected from a local tea garden factory of Jorhat area. MB ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) and congo red (CR, $\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$) were purchased from RANKEM (India) and sodium hydroxide (NaOH) was purchased from HIME-DIA (India).

2.2 Collection and sizing of raw materials

All the samples were ground in a ball mill ($3 \times 4 \text{ HP}$, 415 V AC, fabricated by Mineral progress equipment Pvt. Ltd., Bombay, India) containing steel balls in a ball with a sample ratio of 5:1 kg per batch, mixed thoroughly by quartering and coning, sieved through 100 meshes ($149 \mu\text{m}$) and stored in sample packets in dried condition for further use.

2.3 Preparation of ceramic membranes

Microfiltration membranes were prepared by a paste pressing method. The stepwise preparation method is shown in figure 1. A paste of the homogeneous mixture of finely ground raw materials was prepared in a standardized ratio of the components (table 1) and cast into a disc shape using a hollow stainless steel cylinder and applying the pressure of 1 bar for 5 min using uniaxial hydraulic press to obtain a homogeneous flat green body.

Figure 1. Schematic illustration of ceramic membrane preparation.

Table 1. Composition of raw materials percentage of ceramic barrier.

Raw materials used	Composition (wt%)	
	Dry basis	wet basis
PC	25.0	19.23
SQD	41.67	32.06
TD	33.33	25.64
Water	0.00	23.07

The prepared raw support was then dried at 40°C for 24 h in a hot air oven and finally fired at three different temperatures i.e., 800, 900 and 1000°C for 6 h in a muffle furnace (IKON, made India model no. Ik-108, size 6" × 6" × 12", rating 4 kW). Ceramic sintered membranes were polished by an abrasive paper to smoothen the surface and ultrasonicated for 10 min to remove loose particles. The finally obtained membrane was dried and used for characterization and dye removal experiments.

2.4 Characterization of raw materials and ceramic membranes

The raw materials and the ceramic membrane before and after sintering were characterized by employing different analytical methods. Classical chemical analysis of the raw materials was carried out to investigate the chemical composition of local raw materials. Particle size of the raw materials was analysed using a Malvern 7 Mastersizer 2000 instrument from an aqueous dispersion of the material. Fourier transform infrared (FTIR) analysis of the samples were carried out using FTIR (model-IR Affinity-1) by using the KBr plate method in the range of 400–4000 cm⁻¹ at the spectral resolution of 4 cm⁻¹, 40 scans. Thermogravimetric analysis was carried out by using a TA instrument (SDT Q 600, Ms TA Instruments, USA) using alumina as a reference at a heating rate of 20°C per min under an argon atmosphere from 25 to 1000°C. X-ray diffractometry (XRD) analysis was carried out using a powder XRD instrument (model Rigaku-Ultima IV, Japan) using CuKα radiation at the scan rate of 2° per min. Field emission scanning electron micrographs (FESEM) were taken by using a FESEM apparatus from Carl Zeiss (Sigma VP). For measurement of zeta potential, a small portion of the ceramic barrier was ground in a planetary micro pulverizer (M/S Fritsch, Germany) at 600 rpm for 2 min using zirconium balls to obtain ceramic powder of particle size in the range of 1–200 μm. A dispersed 0.1% aqueous solution of the ceramic powder was prepared to measure the zeta potential (Zetasizer instrument, model Nano Zs, Malvern, UK).

Physical parameters like bulk density (ρ_b), apparent density (ρ_a), apparent porosity (ε (%)) and water absorption (w_a (%)) of the porous ceramic body were evaluated using Archimedes' method with water as the wetting liquid [63].

$$\rho_b = \frac{w_d}{w_{sat} - w_{sus}}, \quad (1)$$

$$\rho_a = \frac{w_d}{w_d - w_{sus}}, \quad (2)$$

$$\varepsilon (\%) = \frac{(w_{sat} - w_d)}{(w_{sat} - w_{sus})} \times 100, \quad (3)$$

$$w_a (\%) = \frac{(w_{sat} - w_d)}{w_d} \times 100, \quad (4)$$

where w_d , w_{sat} and w_{sus} are dry weight, saturated weight and suspended weight of a piece of the ceramic membrane, respectively. Ceramic membranes were dried at 110°C and kept in vacuum desiccators until it attained a constant weight and then the dry weight (w_d) of the specimens were noted down. Saturated weight (w_{sat}) of the nodules were determined by keeping the samples in boiling water for 2 h and cooled to room temperature and the weight was noted down. Suspended weight (w_{sus}) of the samples was determined by suspending the samples in water.

Chemical stability of the membrane towards harsh environmental conditions was evaluated by testing the stability of the membrane in acidic and basic conditions by subjecting it to concentrated HCl and NaOH solution for 20 consecutive days and results were analysed by calculating the mass losses in these conditions. The average pore diameter (d_s) of the membranes was calculated from the SEM images of the membranes of different selected areas using Image J software and average pore size was calculated using below equation considering cylindrical pores:

$$d_s = \left[\frac{\sum_{i=1}^n n_i d_i^2}{\sum_{i=1}^n n_i} \right]^{0.5}, \quad (5)$$

where n refers to the number of pores considered and d_i is the pore diameter (nm) of i th pore.

The pure water permeability of the membrane sintered at 900°C was measured using deionized water at room temperature (25 ± 2°C) conditions. The trans-membrane pressure was varied from 0 to 68.94 kPa. The permeate flux of the membrane is directly proportional to the pressure drop across the membrane in accordance with Darcy's law (equation 6):

$$J_W = L_P \Delta P, \quad (6)$$

where J_W is the flux, L_P the permeability and ΔP the pressure drop.

2.5 Decolourization experiments

A lab scale filtration unit was used for dead-end mode filtration for decolourization study as shown in figure 2. The filtration unit was made by fixing a membrane (height = 0.4 cm, diameter = 4.2 cm) in a polyethylene cylindrical

Figure 2. (a) Raw ceramic membrane, (b) ceramic membrane after sintered at 900°C, (c) home-made filtration unit by fabricating ceramic membrane in a polypropylene container (side view) and (d) top view of the filtration unit.

Table 2. Properties and structure of the dye molecules used.

Parameter	Value	
	MB	CR
Molecular formula	$C_{16}H_{18}ClN_3S$	$C_{32}H_{22}N_6Na_2O_6S_2$
Molecular weight (g^{-1})	319.85	696.665
Solubility in water ($g\ 100\ ml^{-1}$)	3.55	2.5 at 20°C
Absorption maxima (nm)	664	497.5
Molecular structure

container (height = 3.7 cm, diameter = 4.3 cm) as shown in figure 2c. CR and MB containing water was allowed to flow through the membrane simply by gravity with a flow rate of $1.6\ ml\ min^{-1}$. Permeate was analysed using a UV spectrophotometer. Percent rejection ($\%R$) was calculated by the following equation:

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100, \quad (7)$$

where C_0 and C_t are the initial concentrations of MB and CR at time t , respectively.

2.6 Analysis of concentrations of HB and CRI

We have used MB and CR as model dyes to evaluate the efficiency of the ceramic membrane. Residual concentrations of MB and CR solutions were analysed with the help of UV-visible spectrophotometer (MS-11-UV-1800 instrument) and a series of dye solutions with concentration between 0 and $10\ mg\ l^{-1}$ were used to obtain a calibration curve. The

Figure 3. UV-visible spectra of MB and CR showing absorbance maxima.

calibration curves were found to be linear in this concentration range and the maximum absorption occurs at 664 nm for MB and 497.5 nm for CR, respectively. The

Table 3. Chemical analysis of local materials.

Sample	wt (%)								Total
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	LOI*	
PC	55.48	20.78	7.6	0.45	0.65	1.01	1.01	12.63	99.61
SQD	73.21	3.67	8.24	7.22	1.6	0.82	1.08	3.2	99.04

*LOI, loss on ignition.

Figure 4. Characterization of raw materials: (a) particle size, (b) FTIR patterns, (c) PXRD pattern (Q, quartz; K, kaolinite; D, dolomite and A, muscovite) and (d) thermal analysis.

properties of the dye molecules and absorption maxima of 10 mg l⁻¹ dye solutions are shown in table 2 and figure 3, respectively.

3. Results and discussion

3.1 Characterization of raw materials and ceramic membranes

Oxidic chemical compositions of raw materials were calculated by classical chemical analysis of the PC and SQD as

presented in table 3. Silica and iron oxide content are higher in SQD. Local PC has a comparatively low content of silica, whereas it contains a higher percentage of alumina.

Average particle size of the raw materials of the ceramic membrane is found to be 10.54 μm for tea dust powder and 3.1 and 1.6 μm for stone dust and local PC, respectively (figure 4a). FTIR technique was used to identify surface functional groups present in PC, SQD, TD raw and sintered ceramic membranes. The band observed at around 3628 cm⁻¹ for local PC has been ascribed to OH stretching. The bands observed at around 3336 cm⁻¹ in PC and 3526 cm⁻¹ in SQD

Figure 5. Overlay (a) FTIR patterns and (b) PXRD pattern (Q, quartz; K, kaolinite; C, cristobalite and M, mullite) of ceramic membranes and (c) thermal analysis of raw membrane.

can be ascribed to H–O–H stretching, crystalline hydroxyl and chemically or physically absorbed water. The H–O–H bending of water is observed at 1620–1642 cm⁻¹. Peaks observed at around 1102 cm⁻¹ for PC and 1085 cm⁻¹ for SQD can be ascribed for Si–O stretching for quartz [24]. Peaks obtained at around 783–798 cm⁻¹ can be assigned to OH deformation linked to Al³⁺ and Mg²⁺. The peak observed at around 457–470 cm⁻¹ can be assigned to Si–O–Si bending. The peaks obtained from the XRD shows that the PC used is mainly composed of quartz, SiO₂ (ref. code: 00-046-1045) and kaolinite, Al₂Si₂O₅(OH)₄ (ref. code: 00-001-0527) along with small amounts of minerals like dolomite, CaMg(CO₃)₂ (ref. code: 01-071-1662) and muscovite, KAl₂(AlSi₃)O₁₀(OH, F)₂ (ref. code: 00-002-0467). In the SQD sample, quartz is the main composition along with a small amount of kaolinite.

The XRD analysis of the green membrane and the burnt ceramic membrane at 1000°C to investigate the phases formed during the firing process is shown in figure 5b. From the

XRD pattern, in the sintered barrier at 1000°C, quartz is the main mineral obtained along with new peaks assigned as mullite, 3Al₂O₃ · 2SiO₂ (ref. code: 00-002-0452) and cristobalite, SiO₂ (ref. code: 00-001-0424) in small proportions. It is seen that the intensity of the quartz peak with the (101) plane increases by the increase in firing temperature up to 900°C and slowly decreases at 1000°C due to the formation of other minerals like mullite and cristobalite at high temperature. Thermal analysis of individual components of ceramic membranes (figure 5c) was carried out to study the thermal stability and % weight loss. PC and SQD showed a weight loss of 8.47 and 3.52%, respectively. Individual components were found to be quite stable at 900°C, which is the sintering temperature of the ceramic membranes.

Thermal analysis shows that ceramic membranes are quite stable at high temperatures. In green composites, two main transitions were observed at around 40 and 360°C with a total weight loss of 30.7%. The higher weight loss obtained is due

Figure 6. FESEM and EDS analysis of ceramic membrane fired, (a, b, c) at 800°C, (d, e, f) at 900°C and (g, h, i) at 1000°C.

to the addition of tea dust materials as pore-forming agent. The clay used is a kaolinite type of clay. A collapse of kaolinite network is reported in the temperature range of 450–600°C. Removal of water transforms kaolinite to metakaolin in which the Si–O network remains unchanged and the Al–O network reconstructs itself as shown in equation (8). A further increase in the sintering temperature above 900°C results in the decomposition of the metakaolinite to mullite and cristobalite [64].

Electron microscopy analysis was carried out to analyse the possible surface defects and to confirm the pore generation in the membrane surface. FESEM monographs of sintered ceramic membranes (figure 6) shows that the surface

Table 4. Different physical properties of ceramic barriers with different compositions.

Parameters	Type of membrane		
	CM-800	CM-900	CM-1000
Firing temperature, °C	800	900	1000
Water absorption, %	57.86	47.43	21.62
Apparent density, g cm ⁻³	2.21	2.33	2.23
Bulk density, g cm ⁻³	0.97	1.11	1.5
Apparent porosity, %	56.1	52.51	32.58

is critically rough and highly porous with non-uniform pore distribution. On increasing the sintering temperature from 800 to 1000°C, the pores are observed to reduce as the grains are fused and minerals melt at higher temperature as seen in figure 6g and h, where the exposed surface of the membrane

Figure 7. Effect of sintering temperature on (a) porosity %, (b) chemical stability, (c) pore size distribution of the ceramic membrane and (d) pure water permeability of the ceramic membrane sintered at 900°C.

fired at 1000°C appears melted and pores were blocked. It is clear from table 4 that porosity decreases from 56.1 to 52.5% on increasing firing temperature from 800 to 900°C and decreased to 32.58% on further increasing the sintering temperature up to 1000°C which is explained that due to the melting of minerals at a higher temperature resulting in the pore blocking (figure 7a).

As water absorption is directly related to porosity %, the same trend was observed on increasing the firing temperature also. Figure 7d shows that the pure water permeability of the membrane sintered at 900°C, increases linearly with an increase in the applied pressure i.e., it follows the Darcy's law. The average pore size of membranes sintered at different temperatures are determined as 0.215, 0.49 and 0.211 μm for sintering temperatures of 800, 900 and 1000°C, respectively. Pore size distribution of the membranes corresponds to microfiltration range of ceramic membrane. Pore size distribution is observed to be closely related to the sintering temperature and found to increase initially on increasing the temperature from 800 to 900°C, but on further increase

Figure 8. Schematic representation of ceramic membrane formation mechanism.

to 1000°C, the pore size decreases, which is possibly due to the melting of minerals at higher temperatures causing reduction of the pore size and overall porosity of the membrane.

Figure 9. Dye removal of (a) MB, (b) CR by CM-900 and regenerated membrane, (c) simultaneous removal of CR and MB, (d) UV-Visible spectra showing variations in absorbance of CR and MB solutions with time after simultaneous removal by the barrier from 2 to 40 min, (e) comparison of MB and CR removal by the barrier and (f) amount of MB and CR removal by the barrier.

As density of the material is inversely related to the pore volume, bulk density and apparent density were observed to increase on increasing the firing temperature. Chemical

stability of the sintered membranes was checked in terms of weight loss in contact with acids or bases. A small part of the ceramic membrane was kept in acidic conditions in contact

Figure 10. Continuous mode decolorization set up (a) for MB, (b) for CR, absorbance spectra with time for the removal of (c) MB, (d) CR and colour change of the barrier (e) before and after (f) MB and (g) CR dye separation.

with HCl ($\text{pH} = 2$) and in alkali NaOH solution ($\text{pH} = 10$) individually for 20 consecutive days at room conditions and the net weight loss was calculated after drying.

The stability in terms of weight loss of the membrane as a function of firing temperature towards acidic and basic conditions followed the order of $800 < 900 < 1000^\circ\text{C}$. Stability towards acidic condition is found to be higher as compared to the basic condition (figure 7b). Stability of the membrane at high sintering temperature is due to the shrinking of grains at higher temperature and evaporation of acid and base leachable compounds at higher temperature.

The mechanism of growth of the ceramic membrane involves many stages in the sintering process (figure 8). The initial stage involves the burning of porogenic particles (tea dust) in the temperature range $200\text{--}500^\circ\text{C}$ resulting in the formation of pores and channels in the membrane. The second stage is shown as the formation of neck structures of clay particles at high temperature which is very common in ceramic sintering process and also observed in the FESEM

Figure 11. Regeneration of ceramic membrane by calcining at 400°C for 30 min.

images. This stage reduces the pores generated during the first stage. Finally, densification of the ceramic mass occurs at higher temperatures. For clay-based membranes, this step is achieved at a lower sintering temperature as compared to the metal oxide-based membranes. Further sintering decreases the pores due to melting and fusion of the mineral particles.

Table 5. Raw materials cost analysis study of ceramic membranes (in Indian rupees, Rs.).

Raw materials	Unit price (Rs. per kg)	Raw material used (g) per m ² of membrane	Raw material cost per m ² of membrane (Rs.)	Cost per m ² of membrane (Rs.)
PC	0.5	2166.157	1.083	42.46
SQD	0.79	3610.785	2.816	
Tea dust (TD)	10.00	2888.628	28.814	
Distilled water	5.00	1949.824	9.749	

3.2 Dye removal study

The efficacy of the adsorbent was studied in batch mode by using a home-made lab scale filtration unit in fixed bed condition. For this study, 10 mg l⁻¹ CR and MB aqueous solutions were prepared and the removal capacity of the barrier with respect to volume treated was analysed. Percentage removal (figure 9) was plotted with volume treated to compare the efficiency of fresh and regenerated membranes. The absorbance spectra of CR and MB with time are shown in figure 10 with the full setup of the decolourization experiments. It is clear that in the case of MB, removal efficiency is quite good when checked up to 100 min with a flow rate of 1.6 ml min⁻¹ and 98.53% was removed in 20 min. Then, it decreases slowly to 49.22% in 100 min. Figure 9f shows the removal of amount of dye with time. Dye removal is quite good in the initial stages and around 95% was removed up to 40 min which decreases on further treatment due to the occupation of the adsorption sites. In the case of MB, removal capacity decreased up to 50% after 100 min, whereas the removal capacity of the barrier for CR is poor in comparison with MB. Although it showed initially good removal efficiency, it became almost saturated in 100 min and the removal capacity decreased to 10%.

Regeneration of the used ceramic membrane is possible by calcining at low temperature [65]. The regeneration was carried out by calcining the exhausted membrane at 400°C for 30 min in air (figure 11) and used further for another cycle of dye separation. The regenerated barrier is also capable of separation of dye molecules from water with a good efficiency with >98% initial removal, but gets saturated gradually and the final removal capacity decreased to 39.3% in 100 min after treatment with 160 ml of 10 mg l⁻¹ MB solutions (figure 9a and b). However, in comparison with fresh barriers, regenerated barrier showed less efficiency towards dye adsorption. Initially, the separation capacity is almost similar, but after treatment of 40 ml MB solution, the removal capacity decreased by around 15% as compared to the fresh barrier and a continual decrease in removal efficiency is observed from the beginning in the case of CR removal by the regenerated barrier. The decrease in efficiency of removal between fresh and regenerated barriers remained constant and showed almost 15% decrease. This decrease in removal percentage on regeneration may be ascribed to localized heating

during burning of residual dye molecules present in the pores of the barriers.

Efficiency of the membrane for simultaneous removal of CR and MB was studied by preparing a mixed solution containing 3.96 mg l⁻¹ CR and 1.12 mg l⁻¹ MB. On mixing the two dyes, the maximum absorption peaks changed considerably in the case of CR from 497.5 to 473.5 nm due to the change in pH, whereas in the case of MB, no such major change is observed. It is observed that CR removal was quite good, but in the presence of CR, adsorption of MB is comparatively poor, which is only about 60% from 1.12 mg l⁻¹ solution (figure 9c), whereas on its own, it can remove around 99.99% in the absence of CR.

To understand whether removal is by adsorption or by microfiltration, a barrier was kept submerged in a 10 mg l⁻¹ CR and MB solution for 1 and 7 days. Only very small amount was adsorbed but on filtering through the barrier, 99.9% is removed immediately. From this study, it can be said that removal is a combination effort of both adsorption and microfiltration. This is also supported by the colour change of the barrier after dye separation (figure 10). From the zeta potential study of the ceramic barrier, the negative surface charge of -18.78 mV observed which is basically common for clay-based barrier and is responsible for the adsorption of the cationic dyes more easily as compared to the anionic dyes.

3.3 Cost analysis based on raw material

It is important to analyse the cost of any process to determine its practical feasibility. In this work, we have calculated the cost of raw materials used for the preparation of ceramic membranes. The cost of raw materials for preparing ceramic membrane was evaluated to be Rs. 42.46 per m² of membrane (US\$ 0.65 per m² of membrane; table 5). Hence, from the cost analysis, it can be concluded that the raw material cost of ceramic membranes is inexpensive and can easily be prepared and used for dye removal purposes.

4. Conclusions

Ceramic membranes have been successfully prepared and characterized from locally available PC, SQD and tea waste

materials that have negligible commercial value. The membrane obtained by the powder pressing method has a smooth surface, eventual generation of pores and showed very good thermal, chemical and mechanical stabilities. Sintering temperature was varied from 800 to 1000°C and it was observed that at 900°C a very good product with stability towards chemical corrosion, good mechanical strength and porosity is obtained. Thus, 900°C temperature was fixed as optimized sintering temperature. Decolourization experiments were carried out in continuous mode by a home-made fabricated filter unit which showed very good removal of CR and MB up to 99.92% reduction. Regeneration of the membrane with good efficiency is possible by calcining at 400°C for 30 min. However, from the reusability point of view, the membrane showed better performance for removal of MB than CR which can be explained as the clay-based membrane surface is generally negatively charged and adsorption of cationic dyes and molecules are more favoured. The raw material cost was found to be quite cheap, which is only about Rs. 42.46 per m² of membrane (US\$ 0.65 per m² of membrane). The membrane being very cheap could be highly promising for future wastewater treatment applications.

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