Adsorptive removal of phenolic compounds using cellulose acetate phthalate–alumina nanoparticle mixed matrix membrane

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**HIGHLIGHTS**

- Composite membrane of cellulose–acetate–phthalate and alumina nanoparticle is cast.
- Surface charge of the membrane changes with nanoparticle concentration and pH.
- Separation of phenolic compounds occurs due to adsorption.
- The removal efficiency is maximum for 20% nanoparticle with 91% removal of catechol.
- Transmembrane pressure drop has negligible effect on solute separation.

**ABSTRACT**

Mixed matrix membranes (MMMs) were prepared using alumina nanoparticles and cellulose acetate phthalate (CAP) by varying concentration of nanoparticles in the range of 10 to 25 wt%. The membranes were characterized by scanning electron micrograph, porosity, permeability, molecular weight cut off, contact angle, surface zeta potential, mechanical strength. Addition of nanoparticles increased the porosity, permeability of the membrane up to 20 wt% of alumina. pH at point of zero charge of the membrane was 5.4. Zeta potential of the membrane became more negative up to 20 wt% of nanoparticles. Adsorption of phenolic derivatives, catechol, paranitrophenol, phenol, orthochloro phenol, metanitrophenol, by MMMs were investigated. Variation of rejection and permeate flux profiles were studied for different solutes as a function of various operating conditions, namely, solution pH, solute concentration in feed and transmembrane pressure drop. Difference in rejection of phenolic derivatives is consequence of interplay of surface charge and adsorption by alumina. Adsorption isotherm was fitted for different solutes and effects of pH were investigated. Catechol showed the maximum rejection 91% at solution pH 9. Addition of electrolyte reduced the rejection of solutes. Transmembrane pressure drop has insignificant effects on solute rejection. Competitive adsorption reduced the rejection of individual solute.

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1. Introduction

Petrochemical and other chemical industries produce aromatic and semi-volatile phenol and phenolic derivatives which are extremely toxic [1] and carcinogenic [2]. This class of compounds is in the 11th position out of 126 chemicals, which are labeled as priority pollutants according to United States Environmental Protection Agency. Exposure to phenol leads to high irritation to eyes, skin and mucous, causes headache and dizziness. Long term exposure results in high blood pressure, liver and kidney damage. Existing technologies for removal of phenolic compounds are solvent extraction [3–6], adsorption [7], chemical oxidation [8,9], biological treatment [10] and distillation [11]. However, all these methods require high input of energy and/or additional chemicals and hence are cost intensive. Moreover, low separation efficiency and post processing of streams are important issues. Thus, there is a need to develop energy efficient and economical method for separation of phenolic compounds. Membrane based processes can offer attractive alternative in this regard. Reverse osmosis (RO) can be used to remove phenol [12]. But, low permeability and higher pressure limit the commercial applicability of RO membranes. Micellar enhanced ultrafiltration (MEUF) is another alternative for removal of phenol [13]. However, it involves surfactant that increases the operating cost and hence, recovery of surfactants from the

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**Abbreviation:** np, nanoparticle; CAP, cellulose acetate phthalate; CAPI-0, membrane with CAP and 0% alumina nanoparticle; CAPI-10, membrane with CAP and 10% alumina nanoparticle; CAPI-15, membrane with CAP and 15% alumina nanoparticle; CAPI-20, membrane with CAP and 20% alumina nanoparticle; CAPI-25, membrane with CAP and 25% alumina nanoparticle; CC, catechol; PNP, paranitrophenol; OCP, orthochloro phenol; Ph, phenol; MEUF, micellar enhanced ultrafiltration; MMM, mixed-matrix membrane; MNP, meta-nitrophenol.

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0304-3894/—see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2013.11.012
retentate is a critical issue in MEUF. Composite ultrafiltration membrane with high selectivity toward phenolic compounds can be proven as viable alternative owing to higher permeability and lower pressure requirement.

Choice of base polymer plays a crucial role in selection of membrane. Derivatives of cellulose acetate (CA) are popular polymers to cast organic membranes. Advantages of CA over other polymers are, good mechanical strength, biocompatibility, good desalting and high permeate flux. Hydrophilic nature of CA also enhances the anti-fouling property [14–17].

Nanoparticle doped mixed matrix membrane (MMM) has generated considerable interest among researchers recently [18–20]. This is primarily due to the fact that tailor made membranes can be fabricated targeting specific application [21,22]. Presence of charged nanoparticles in the membrane matrix has potential application in wastewater treatment by electrostatic interaction [23–25]. MMMs improve various properties, like mechanical [26], thermal [27], magnetic [28] and electrostatic. It can enhance solute diffusivity [24], antibacterial property [29] and reduce flux decline [30,31]. MMMs have widespread application in case of gas separation and pervaporation [32]. In case of treatment of liquid stream, some of its applications include separation of sulfur from gasoline [33], silver using functionalized silica [34], humic acid using TiO2 [35], metal ions using polyelectrolyte [36], lead by hydrous manganese dioxide [37], arsenic [38] from aqueous stream. MEUF for removal of methylene blue using titanium dioxide–polyvinylidene fluoride MMM is also reported [39]. Zeolite, modified silica and graphene impregnated composite membranes are also used for separation of salts in desalination applications [40–42].

Addition of alumina as an inorganic additive has been studied considerably in past. MMM of granular alumina and CA shows interesting properties like flux enhancement, good mechanical strength [43]. Alumina nanoparticles in PVDF membranes at low percentage improved membrane hydrophilicity, porosity and protein retention [44]. Most studies reported doping of nanoparticle in small quantities, typically less than 5 wt%. While added in large proportion, significant amount of nanoparticles are retained in the matrix even after leaching during phase inversion to impart desirable properties like porosity, permeability, etc. [45].

In the present work, MMM was prepared using cellulose acetate phthalate (CAP) as base polymer, di-methyl formamide (DMF) as solvent and alumina nanoparticle as dopant. The superiority of CAP compared with cellulose acetate is presence of numerous acidic and carbonyl functional groups on its structure. These groups, in addition to impregnation of nanoparticle in the membrane induce more surface charge. The morphology, wettability and porosity of the membrane are also modified. This is manifested through the removal efficiency and performance during filtration of polar phenolic compounds.

2. Materials and methods

2.1. Materials

Cellulose acetate phthalate (CAP) was purchased from GM Chemicals Company Limited, Mumbai, India. N,N-dimethyl formamide (DMF), polyethylene glycol (PEG) (Molecular weight 35, 20, 10, 6, 4 and 0.4 kDa), all phenolic derivatives, meta-nitrophenol (MNP), catechol (CC), para-nitrophenol (PNP), orthochlorophenol (OCP) and phenol were procured from Merck (India) Ltd., Mumbai, India. Dextran (molecular weight—70 kDa) was purchased from Sigma Aldrich Chemicals (USA). The alumina nanoparticle was provided by US Research Nanomaterials Inc. (Houston, USA). Bovine Serum Albumin was purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India.

2.2. Membrane preparation

MMM using CAP and alumina nanoparticle was prepared by phase inversion method. Initially, DMF was heated to 60 °C and alumina nanoparticles were mixed in various weight percentage (10%, 15%, 20% and 25%). The mixture was sonicated for 2 h to prevent agglomeration [45,46]. CAP being a nanoparticle-stabilizer itself was added (15 wt%) slowly to the suspension under continuous stirring. The mixture was again sonicated for 6 h with occasional stirring to prevent agglomeration [43]. Casting solution for membrane without alumina was prepared by mixing CAP (15 wt%) in DMF (75 wt%).

Non-woven polyester fabric (product number: TNW006013, supplied by Hollytex Inc., New York, USA) was attached to the glass slides and was fixed by tape. The cast solution was drawn manually with a speed of 20 mm/s using a doctor’s blade with gap 150 μm. The membranes were put in water bath at 27 °C for 16 h to complete the phase inversion and labeled as CAPAl-0, CAPAl-10, CAPAl-15, CAPAl-20, CAPAl-25 indicating weight percent of nanoparticles in casting solution as 0%, 10%, 15%, 20% and 25%, respectively.

2.3. Experimental set-up

Membrane compaction, rejection of protein and phenolic compounds were carried out in a 600 ml batch cell with 34 mm diameter and effective filtration area 36.3 cm². A nitrogen cylinder was used to pressurize the cell. Cumulative weight of permeate was collected on a digital balance, connected to a computer via data-logging device to monitor cumulative weight as a function of time. The schematic of the experimental set up is shown in Fig. 1.

2.4. Experimental procedure

The feed solution of each batch was prepared by mixing measured amounts of solutes in distilled water. The concentration of catechol, PNP, MNP, OCP and phenol, were 100, 100, 50, 100 and 100 ppm, respectively. In case of solution of mixed solutes (PNP,
CC and OCP, MNP) the concentration of each solute was 50 ppm. The operating transmembrane pressure drop for all experiments was 550 kPa. Cumulative weight of permeate, collected, from the bottom of the cell was measured by electronic balance. The cumulative weight was converted to cumulative volume. From the slope of cumulative volume versus time curve, the permeate flux was obtained as a function of time. After each experiment, the membrane was thoroughly washed with distilled water for 15 min at a pressure of 690 kPa until initial permeability of the membrane was restored. All the experiments were repeated 3 times. Feed and permeate concentration of organic solutes were measured by UV spectrophotometer (model: Lambda 35, supplied by Perkin Elmer, Connecticut, USA). The maximum wavelengths were 316, 277, 317, 260 and 280 nm for MNP, CC, PNP, OCP and Phenol, respectively. A standard method was used to calculate the concentrations of different solutes in the mixture [47].

2.5. Characterization

2.5.1. Particle size analysis

Size distribution of alumina particles was carried out by Zetasizer (model: Zetasizer nano ZS 90) supplied by M/s, Malvern instruments, Worcestershire, U.K.

2.5.2. Membrane morphology

The surface morphology and the cross section of the membranes were studied by scanning electron micrograph (model: ESM—5800, JEOL, Japan). For cross sectional images, membranes were fractured in liquid nitrogen for 1 min.

2.5.3. Elemental analysis

Presence of each element, their number and atomic percentage were analyzed by Energy-dispersive X-ray spectroscopy, EDX (model EVO 600, Zeiss, Germany).

2.5.4. Porosity

Porosity of the membranes was estimated gravimetrically [48], using Eq. (1).

\[ \varepsilon = \frac{w_0 - w_1}{\rho_w A t} \times 100\% \] (1)

where, \( \varepsilon \) is the membrane porosity, \( w_0 \) and \( w_1 \) are the weight of dry and wet membrane, \( \rho_w \) is water density, \( t \) is the membrane thickness, and \( A \) is the average area of the membrane samples. Porosity was calculated three times for each sample and the average value was reported.

2.5.5. Permeability

The membrane was thoroughly washed and cut into circular disc to be fitted in the batch cell. The cell was filled up by distilled water and the membrane was compacted at 827 kPa for 3 h. The permeate flux was measured at 276, 414, 552 and 690 kPa. The volumetric water flux was calculated using the following equation,

\[ J_w = \frac{Q}{\Delta t \times A} \] (2)

where \( J_w \) is the pure water flux and \( Q \) is the amount of permeate collected; \( \Delta t \) is the time interval of permeate collection and \( A \) is the membrane area (m²).

2.5.6. Molecular weight cut off (MWCO)

MWCO refers to the molecular weight of solute (in daltons) that is retained 90% by the membrane. To determine MWCO of the membranes, feed solutions were prepared using neutral solutes of various molecular weights, i.e., dextran (70 kDa), polyethylene glycol (PEG) (35, 20, 10, 6, 4 and 0.4 kDa). The experiments were conducted using concentration 20 kg/m³, transmembrane pressure drop 207 kPa and stirring speed 2000 rpm. The rejection of solutes was determined using the following equation,

\[ R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \] (3)

where \( R \) is the percentage rejection, \( C_p \) is the permeate concentration and \( C_f \) is the feed concentration. \( C_p \) and \( C_f \) was measured using a digital refractometer (Model no. 300034, manufacturer: SPER scientific, supplied by Cole-Parmer, Kolkata, India), against the calibration with known solute concentration. Thus, MWCO values are estimated from retention versus molecular weight curve corresponding to \( R = 0.9 \).

2.5.7. Contact angle

The contact angles of different membranes were measured by a Goniometer, manufactured by Rame-Hart instrument Co., New Jersey, USA (model number: 200-F4), supplied by Labline instrument, Mumbai, India.

2.5.8. Pore radius

Average pore radius of each membrane, was calculated using Guerout–Elford–Ferry equation, presented in Eq. (4) [49].

\[ r_m = 16.73 \times 10^{-10} M_w^{0.557} \] (4)

Here, \( r_m \) is the pore radius in centimeter, \( M_w \) is MWCO in Da. The pore radius of the membranes was also determined by Brunauer–Emmett–Teller (BET) analysis. The BET instrument was supplied by Quantachrome instruments, Florida, USA (model AUTOSORB–1).

2.5.9. Mechanical stability

Parameters representing mechanical stability of the membrane were considered as breaking stress and elongation at break. These were measured by Universal Testing Machine, procured from M/s, Tinius Olsen Ltd., Redhill, England of model no. H50KS.

2.5.10. Membrane zeta potential

Membrane zeta potential was measured by measuring streaming potential using cross flow ultrafiltration cell. The operating conditions were: transmembrane pressure (ΔP): 0 to 2 bar; solution pH: 4 to 10; NaCl concentration 1 mM; cross flow velocity: 0.12 m/s. The detailed procedure and instrumentation are available in literature [50,51].
2.5.11. Verification of membrane nanoparticle

To verify the charged behavior of the membranes, solutions of bovine serum albumin (BSA) at different pH values were filtered by the membrane. The solutions were prepared in phosphate buffer at 500 mg/l at pH 3, 4.7 and 9. pH of acidic solution was adjusted by acetate buffer and alkaline solution by phosphate buffer.

2.5.12. Adsorption isotherm

Solutions of all the phenolic compounds were prepared of concentrations 50, 100, 200, 300 and 700 ppm. One piece of membrane of size 2 x 2 cm was put in the solution. All the solutions were kept in shaker at 35 °C for one day. Then, the residual concentrations were analyzed. The amount of solutes (q_e) adsorbed was calculated from mass balance and plotted against equilibrium concentration to get the desired isotherm.

3. Result and discussion

3.1. Membrane characterization

3.1.1. Nanoparticle size distribution

The average diameter of the particle after mixing 20 wt% nanoparticle in solvent DMF and sonicating for 2 h was analyzed by Dynamic Light Scattering (DLS). The result is shown in Fig. 2. There is a sharp peak at 62 nm. The trailing tail of the peak indicates distribution of the nanoparticles in the dispersion. No further agglomeration is expected as the casting solution was further sonicated for 6 h.

3.1.2. Membrane morphology

SEM images of external surface and cross section of composite membranes are shown in Fig. 3. The top views of CAPAI-0, 10, 15, 20, 25 are presented in Fig. 3(a)–(e) and the cross-sectional images are presented in Fig. 3(f)–(j), respectively. Accumulation of alumina can be seen clearly in the top views. It can be noted that with increasing nanoparticle concentration, the density of particles on the surface increases till 20 wt%. Due to hydrophilicity of alumina, more particles come to the surface. Appearance of additive at the top surface, is also observed by Teow et al., for TiO_2/PVDF MMM [35]. However, at higher percentage, some agglomerated particles settle at the bottom, which is pointed out at Fig. 3(j).

From the cross-sectional images, it can be observed that membranes become more porous with concentration of alumina. Membrane thickness decreases with concentration of alumina nanoparticles. The thickness of CAPAI-0, 10, 15, 20 and 25 is 269, 220, 208, 158 and 136 μm, respectively. With increase in nanoparticles concentration, the solution becomes more viscous (as the solvent amount decreases at the same polymer content) that prevents swelling of the membrane and consequently, reduces its thickness. Alumina nanoparticles prevent polymer chains to come closer, therefore creating free volume [43]. Addition of nanoparticles increases thermodynamic instability of the membrane [52]. It leads to instantaneous demixing in the coagulation bath. Both of these phenomena result to more porous structure of the membrane. This fact is supported by SEM images. However, agglomeration of nanoparticles occurs at concentration beyond 20% and membrane pores are blocked resulting to a compact structure with reduced porosity.

3.1.3. Elemental analysis

One sample EDX image of CAPAI-20 is shown in Fig. 4, confirming presence of alumina in the membrane matrix. No other significant peak can be observed, except carbon and oxygen. This observation corroborates the fact that, contamination was successfully avoided in the process of membrane preparation. The weight and atomic percentages of each peak are presented in Table 1. Values in the table confirm that alumina is not washed away during phase inversion process.

3.1.4. Porosity and permeability

The porosity and permeability of each membrane was calculated using Eqs. (1) and (2), respectively. Variation of membrane porosity with alumina is presented in Fig. 5. It is observed from this figure that membrane porosity increases from 41% to 53% with concentration of nanoparticles and decreases thereafter for CAPAI-25. This trend is also verified from SEM images. Porosity values are reported to be in the same range, around 0.6, for modified silica/CA MMM by Ladhe et al. [34]. As discussed earlier, membrane porosity increases with alumina concentration upto 20 wt%. The agglomerated nanoparticles clog the pores, leading to decreased porosity for CAPAI-25.

Variation of permeability with concentration of nanoparticle is shown in Fig. 5. It is observed that, from 0 to 20%, permeability of the membrane increases, and at 25%, it decreases. Effect of silica loading on membrane permeability shows similar trend for functionalized silica/CA MMMs [34]. Membrane permeability increased from 1 x 10^-11 to 7 x 10^-11 m/Pa s with silica concentration from 10% to 40% [34]. This result is a direct consequence of variation of porosity with nanoparticle concentration. Since, porosity of the membrane increases upto 20 wt% and decreases thereafter, the same trend is observed for membrane permeability.

3.1.5. Molecular weight cut off (MWCO), contact angle and average pore radius

Variation of MWCO of each membrane is shown in Fig. 6(a). It can be observed that MWCO increases with concentration of alumina nanoparticles. MWCO increases to 104 kDa for CAPAI-10, from 82 of CAPAI-0, without nanoparticle. It is increased further to 122 kDa for CAPAI-20 that again decreases to 103 kDa for CAPAI-25. As shown in Fig. 5, porosity increases with increasing nanoparticle. With higher porosity, rejection of high molecular weight polymers are less, which is reflected in higher MWCO. As the porosity of CAPAI-25 is less than CAPAI-20, it has lower MWCO.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Weight and atomic percentages of elements, present in CAPAI-20 by EDX analysis.</th>
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</thead>
<tbody>
<tr>
<td>Element</td>
<td>Weight%</td>
</tr>
<tr>
<td>C</td>
<td>18.0 ± 5.0</td>
</tr>
<tr>
<td>O</td>
<td>61.0 ± 4.0</td>
</tr>
<tr>
<td>Al</td>
<td>21.0 ± 2.0</td>
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</tbody>
</table>
Fig. 3. SEM images of top view of (a) CAPAl-0, (b) CAPAl-10, (c) CAPAl-15, (d) CAPAl-20, (e) CAPAl-25; Cross-sectional image of (f) CAPAl-0, (g) CAPAl-10, (h) CAPAl-15, (i) CAPAl-20, (j) CAPAl-25.
more hydrophilic. This observation also indicates that nanoparticles are mainly present at membrane surface. Similar trend has been observed by Teow et al. [35] in case of TiO₂/PVDF MMM. However, the reported values of contact angle (67°–73°) are larger than the values obtained in this work.

Average pore radius of each membrane is calculated using Eq. (4) and also by BET method. The values of pore radii of different membranes are shown in Table 2. It is seen that with addition of nanoparticle, average pore radius increases to 104 Å for CAPAl-10 from 91 Å of CAPAl-0. It subsequently increases to 114 Å for CAPAl-20, then it comes down to 103 Å for CAPAl-25. Values of the pore radii, obtained by BET, differ slightly from the calculated results. However, the trend is similar, altering only in case of CAPAl-0. Probable reason is presence of a few large pores, which is confirmed by pore size histogram plot shown in Appendices A and B, Fig. S1. This finding about the nature of variation of pore radii is the direct consequence of variation of MWCO with percentage of alumina nanoparticle. One sample BET pore size distribution of CAPAl-20 is shown in Fig. 6(b). It is observed that the distribution is bimodal in nature. The highest number of pores had a size around 50 Å. However, because of presence of larger pores in considerable percentage, the average pore radii is calculated to be around 85 Å. This finding indicates that pore radius calculated from Eq. (4) gives quick estimation of average pore radii.

### 3.1.6. Mechanical strength

Breaking stress and elongation percentage are represented in Fig. 7. It can be observed that both the mechanical strength parameters increase with increasing concentration of alumina nanoparticles. However, percentage elongation was almost invariant for CAPAl-15, 20 and 25. It has also been shown by Lin et al. [33] that mechanical strength is enhanced for nanoparticle doping unto 20 wt% due to good inter-mixing of polymer and inorganic. Nanoparticles act as a binder among various polymer molecules and do not create much non-uniformity. Consequently, mechanical strength of doped membranes is enhanced. It was also previously
reported by Yan et al. [44], that doping nanoparticle with base polymer, results in enhanced mechanical strength. The enhancement of mechanical stability also corroborates that the casting solution was homogeneous.

3.1.7. Zeta potential

Variation of membrane zeta potential with nanoparticle concentration is shown in Fig. 8(a). It is observed that the sign of zeta potential of all the membranes, at pH 7, is negative. The zeta potential of the non doped membrane, CAPAI-0 was found to be −12 mV. It decreases from −18 mV for CAPAI-10 to −27 mV for CAPAI-20, then increases to −18 mV for CAPAI-25. The zeta potential values were smaller (−8 to −10 mV) for MMM of TiO2/PVDF system, but follows similar trend with nanoparticles concentration [35]. Negative surface charge of the membranes results negative zeta potential. Negative surface charge arises from the deprotonation of acetate group of CAP in aqueous solution and also from the negative surface charge of alumina nanoparticles. γ-alumina nanoparticles possess negative surface charge in aqueous solution due to accumulation of hydroxyl (OH−) ions on alumina surface [54,55]. However, for CAPAI-25 membrane, presence of lesser alumina on the surface reduces the surface charge.

Variation of zeta potential of CAPAI-20 with solution pH is shown in Fig. 8(b). It is observed that the membrane has positive charge at low pH, and negative charge at higher pH. The isoelectric point (i.e.p.) of CAPAI-20 is found 5.4. The change of sign of the membrane charge is due to accumulation of different charges on alumina at membrane surface. At lower pH, H+ ions are accumulated and at higher pH, OH− ions are accumulated on alumina surface [56]. The i.e.p. of alumina is reported around 7.5 [57]. Two opposing phenomena occur at lower pH: negative charge due to de-protonation of the acetate group of CAP, and accumulation of positively charged H+ ions. At very low pH (pH < 5.4), accumulation of H+ ions are higher, making the concentration of H+ ions more than −COO−. The balance between the proton and acetate charge is achieved at pH 5.4, where the membrane is neutral. In the intermediate pH range (5.4 < pH < i.e.p.Ai), the positive charge due to accumulation of H+ cannot overcome negative charge due to −COO−. At higher pH (pH > i.e.p.Ai), OH− ions are accumulated on the membrane surface. This phenomenon, with addition to deprotonation of acetate groups, leads to negative surface charge of membranes.

3.1.8. Verification of charged behavior

Variation of permeate flux and rejection of BSA solutions through CAPAI-20 for different pH of feed solutions is shown in
than 4.7, adsorption capacity is less because membrane and BSA molecules both possess same surface charge. Hence, electrostatic repulsion hinders adsorption, lowering the rejection value. However, at pH > 4.7, rejection increases due to more adsorption. With increased rejection, higher flux decline is observed at a slower rate due to enhanced adsorption resistance.

3.1.9. Adsorption study

Variation in adsorption of different phenolic solutes is presented in Fig. 10(a). Effect of pH on the adsorption of catechol on membrane surface is presented in Fig. 10(b). From Fig. 10(a), it is observed that the extent of adsorption varies in the order CC > PNP > OCP > phenol > MNP. Catechol adsorption increases with solution pH due to enhanced adsorption (Fig. 10b).

Langmuir isotherms are fitted with regression coefficient $R^2 > 0.97$. The Langmuir isotherm is represented by Eq. (7)

$$q_e = \frac{k q_m C_s}{1 + k q_m C_s}$$

The isotherm constants for various solutes are shown in Table 3. It can be observed that the value of $q_m$ and $k$ decrease as one goes down in the table, from CC to MNP. This finding indicates that both the adsorption capacity and the energy of adsorption are in descending order for CC, PNP, OCP, phenol and MNP. It has been reported earlier that with increasing additive concentration, maximum adsorption capacity goes up; it increased more than two times as hydrous manganese oxide (HMO) content increased from 0.5% to 2% for HMO/PES MMM [37].

Maximum adsorption capacity on the MMM, at solution pH and pKa value of different solutes is presented in Table 4. It is already mentioned that pHzpc of the membrane CAPAI-20 is 5.4. In case of CC, it is mostly non-ionized, hence, neutral, in nature at its solution pH (8.2) and the membrane has predominantly negative charge on the surface. This induces opposite polarity of the solute (CC) and membrane surface facilitating transport of CC toward membrane leading to its maximum adsorption capacity (66 mg/g). In case of PNP, solution pH is 6.5. At this pH, the membrane is negatively charged and the solute has less negative charge. Again, this leads to more adsorption of solute on the membrane surface. However, this pH gradient is less in case of PNP compared to CC. Thus, adsorption of PNP is quite high (62 mg/g) but less than that of CC. For OCP, as solution pH is 6.6, the membrane is negatively charged. However, due to vicinity of Cl− and OCP is hydroxyl ion, hydrogen bonding builds up between H + and Cl−. This results into lowering in residual surface charge of OCP. This makes the adsorption of OCP less compared to PNP onto membrane surface. In case of phenol, at solution pH 5.9, the solute has more acidic characteristics. Since the membrane is also almost neutral, at this pH, there is negligible charge–charge interaction and solute adsorption is less (55 mg/g). Similar phenomenon happens to MNP. But, MNP having a bulkier nitro group, its adsorption on the membrane surface is less than that of phenol. It can be also noticed that, despite of being isotope by structure, MNP is adsorbed lesser than PNP. The possible reason is in meta position, nitro group has higher degree of delocalization of electron from oxygen, compared to para position. Lesser electron negativity of oxygen in PNP molecule, leads to lower adsorption. The values of maximum adsorption capacity of As(III) are in the comparable range (20–80 mg/g) for PES/Fe–Mn binary oxide membrane [38].

Table 3

<table>
<thead>
<tr>
<th>Solutes</th>
<th>Constants</th>
<th>$q_m$ (mg/g)</th>
<th>$k$ (l/mg)</th>
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<tr>
<td>CC</td>
<td></td>
<td>74.0</td>
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<td>PNP</td>
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Table 4

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<th>Compound</th>
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<th>Solution pH</th>
<th>$q_e$ (mg/g)</th>
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<td>CC</td>
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</tr>
<tr>
<td>OCP</td>
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<td>6.6</td>
<td>57</td>
</tr>
<tr>
<td>Phenol</td>
<td>10.0</td>
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<td>MNP</td>
<td>9.3</td>
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3.2. Rejection and permeate flux decline

The permeate flux decline profiles of different membranes, for different solutions, constituting Catechol, OCP, PNP, MNP and Phenol are shown in Fig. 11(a)–(e), respectively. In all the cases, initial permeate flux is high (around 42 l/m² h), which subsequently decreases sharply up to 15 min. Later on, the flux decreases at a slow rate. The final order of flux for different membranes is the same as that of the membrane permeability as shown in Fig. 5.
The rejection of each solute, at solution pH, by each membrane is measured using Eq. (6) and is presented in Table 5. It is inferred from Table 5, that the solute rejection is almost negligible for undoped membrane. Rejection increases with nanoparticle concentration till 20 wt% and decreases beyond that. Therefore, CAPAl-20 has optimum removal efficiency. It is seen from Table 5, that the maximum rejection is obtained for catechol among all the solutes. The order of percentage rejection of different solutes are CC > PNP > OCP > phenol > MNP. As observed from Fig. 8(a), zeta potential, hence the surface charge of all the membranes are in decreasing order for 20, 15, 0 wt% of alumina. Therefore, the charge–charge interaction is also less in the same order leading to lowering in adsorption on these membranes. Thus, the rejection of these solutes also follows the same trend as one goes up in any column of Table 5 from fourth row (corresponding to CAPAl-20). For CAPAl-25, the zeta potential is also less than that of CAPAl-20 as explained earlier. Therefore, adsorption of the solutes on the membrane is less leading to lowering in rejection. The radius of each molecule has been calculated considering water as solvent, using the volarea code [59] which is used as a plugin to molecular graphics software Visual Molecular Dynamics (VMD) [60]. The calculated values (CC: 4.74, OCP: 4.9, PNP: 5.06, MNP: 4.98, phenol: 4.61 Å) are much smaller than the pore size of the membranes (10–20 nm). Hence, probability of sieving action for rejection of phenolic solutes is negligible.

**Table 5**

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Compounds</th>
<th>CC</th>
<th>PNP</th>
<th>OCP</th>
<th>Phenol</th>
<th>MNP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAPAI-0</td>
<td>2.0</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>2.0</td>
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<tr>
<td>CAPAI-10</td>
<td>23.0</td>
<td>56.0</td>
<td>11.0</td>
<td>23.0</td>
<td>9.0</td>
<td></td>
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<tr>
<td>CAPAI-15</td>
<td>43.0</td>
<td>32.0</td>
<td>34.0</td>
<td>35.0</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td>CAPAI-20</td>
<td>87.0</td>
<td>80.0</td>
<td>47.0</td>
<td>51.0</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>CAPAI-25</td>
<td>17.0</td>
<td>28.0</td>
<td>7.0</td>
<td>17.0</td>
<td>15.0</td>
<td></td>
</tr>
</tbody>
</table>

The rejection of each solute, at solution pH, by each membrane is measured using Eq. (6) and is presented in Table 5. It is inferred from Table 5, that the solute rejection is almost negligible for undoped membrane. Rejection increases with nanoparticle concentration till 20 wt% and decreases beyond that. Therefore, CAPAl-20 has optimum removal efficiency. It is seen from Table 5, that the maximum rejection is obtained for catechol among all the solutes. The order of percentage rejection of different solutes are CC > PNP > OCP > phenol > MNP. As observed from Fig. 8(a), zeta potential, hence the surface charge of all the membranes are in decreasing order for 20, 15, 0 wt% of alumina. Therefore, the charge–charge interaction is also less in the same order leading to lowering in adsorption on these membranes. Thus, the rejection of these solutes also follows the same trend as one goes up in any column of Table 5 from fourth row (corresponding to CAPAl-20). For CAPAl-25, the zeta potential is also less than that of CAPAl-20 as explained earlier. Therefore, adsorption of the solutes on the membrane is less leading to lowering in rejection. The radius of each molecule has been calculated considering water as solvent, using the volarea code [59] which is used as a plugin to molecular graphics software Visual Molecular Dynamics (VMD) [60]. The calculated values (CC: 4.74, OCP: 4.9, PNP: 5.06, MNP: 4.98, phenol: 4.61 Å) are much smaller than the pore size of the membranes (10–20 nm). Hence, probability of sieving action for rejection of phenolic solutes is negligible.
As electrostatic attraction between solute molecule and membrane surface becomes stronger, rejection becomes higher. The order of strength of the opposite charge attraction for different solutes, are as following: CC, PNP, OCP, phenol and MNP. With stronger attraction, solute rejection goes up from right to left (from MNP to CC) in Table 5. This observation holds good for all the membranes. Rejection is highest in case of CAPAI-20 and for catechol solute. This particular membrane and solute are considered as sample case for parametric study.

### 3.2.1. Effect of pH

Effects of pH on permeate flux and rejection of CC are shown in Fig. 12. It is observed from the figure in inset that rejection of CC increases with solution pH. Similar effect of pH has been reported for PES/HMO ultrafiltration MMM, which increased upto 100% at pH 8 from 30% at pH 2 [37]. This observation is due to enhanced adsorption of CC with solution pH. This effect is reflected in the profiles of permeate flux at different pH. As adsorption of CC increases with pH, the membrane resistance also increases due to solute adsorption. Therefore, permeate flux is maximum for pH 5 and minimum for pH 10. For a particular pH, the permeate flux decreases with time and finally reaches its saturation value at this pH and thereafter flux reaches to a pseudo steady-state.

### 3.2.2. Effect of transmembrane pressure drop

Effects of transmembrane pressure drop on the permeate flux and rejection of CC are presented in Fig. 13. Since solute adsorption is independent of transmembrane pressure drop, there is no change of solute rejection as shown in the figure, in the inset of Fig. 13. The profiles of permeate flux exhibit expected trend. Permeate flux is more at higher transmembrane pressure drop due to higher driving force. At a fixed pressure drop, the gradual decline of permeate flux is due to gradual adsorption of solutes on membrane surface. It has been reported by Ciobanu et al., that even after operating pressure increased from 1 to 4 bar, rejection remained constant at around 60% and 80% for zeolite loading of 25% and 60%, in case of zeolite/polyurethane MMM [40].

### 3.2.3. Effect of electrolyte concentration

Effects of electrolyte concentration on the permeate flux and solute rejection are shown in Fig. 14. The zeta potential of the membrane decreases with the concentration of electrolyte [49]. Therefore, the electrostatic interaction of the solute and the membrane surface becomes weaker leading to less adsorption of solute on the surface. Hence, more solutes permeate through the membrane; declining rejection.

The permeate flux profiles indicate that the maximum flux is obtained with no electrolyte. Permeate flux decreases with electrolyte concentration. The profiles almost superpose on each other for 0.01 (M), 0.1 (M) and 1 (M) electrolyte concentration. As porosity lies in ultrafiltration range, the rejection of salt is extremely low. Thus, the concentration difference of salt across membrane remains almost same, leading to invariant osmotic pressure difference. Thus, the permeate flux decreases with respect to “no electrolyte” case and they are identical for different electrolyte concentrations.

### 3.2.4. Multi-component effect

The permeate flux profile, through CAPAI-20, with two phenolic compounds, is presented in Fig. 15. Two sets of experiments are conducted, comprising OCP–MNP and CC–PNP. In case of mixture of catechol and PNP, the rejection was 73% for catechol and 66% for PNP. In other case, the rejection was 42% for OCP and 21% for MNP. However, flux decline was higher in set 2 compared to set 1. It can be noted from adsorption isotherm that PNP and CC are adsorbed on alumina in higher amount, than OCP and MNP. Adsorption of
solutions blocks the pores of the membrane and also reduces surface charge. There exists competitive force between two different solutions. Presence of competing solution reduces the effect of electrostatic force acting between each solute and the membrane, leading to lowering of rejection of each solute compared to pure component. For example, in single component system, rejection of CC was 87% and that for PNP was 80% (refer Table 5). Thus, the adsorption isotherm for multicomponent system is not expected to match with the single component system and can be expressed in the form of extended Langmuir isotherm [61–63].

4. Conclusion

Alumina and CAP MMMs were characterized and their suitability in application of separation of phenolic compounds was investigated in this study. Membrane porosity, permeability, MWCO and hydrophilicity increased up to 20 wt% of alumina. These values were 53%, 1.9 x 10−11 m2/Pa·s, 122 kDa and 59%. Beyond, 20 wt%, coagulation of nanoparticles occurred resulting to deterioration of these properties. Average pore diameter measured as 85 Å for 20 wt% alumina doped membrane. This membrane showed maximum zeta potential −28 mV with a pHpzc of 5.4. Among the phenolic compounds, adsorption and hence the rejection by MMM was in the order of CC > PNP > OCP > phenol > MNP. The adsorption capacity of CC was maximum at pH 9.0 and its value was 65 mg/g. The rejection of CC at this pH was 91% for feed solution of 100 ppm. Effect of pressure on the permeate flux was significant but that on the rejection is negligible, confirming no sieving effect. Presence of electrolyte reduced the rejection of CC due to shielding effect. For mixture of CC and PNP, the flux decline is more with a reduced rejection due to competitive adsorption.

Acknowledgment

This work is partially supported by a grant from Department of Science and Technology, New Delhi, Government of India, under the scheme DST/TMC/2K11/339 dated 23-05-2012. Any opinions, findings and conclusions expressed in this paper are those of the authors and do not necessarily reflect the views of DST.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2013.11.012.

References


