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Removal of BP-3 Endocrine Disrupting Chemical (EDC) using cellulose acetate and ZnOnano particles mixed matrix membranes

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Abstract. The effect of ZnO on cellulose acetate in the removal of benzophenone-3 (BP-3) was investigated. The benzophenone-3 (BP-3) which is an endocrine disrupting chemical (EDC) was completely removed (100%) from the drinking water using Cellulose Acetate (CA) and zinc oxide (ZnO) composite membranes. The membranes were prepared by DIPS method and the filtration experiments were conducted by dead end filtration unit. The macrostructure of the membrane were studied by ATR-IR and XRD Spectra's. Atomic force microscopy (AFM) and Scanning electron microscopy (SEM) were used to study the micro properties of the membranes. The laboratory experiments such as water uptake study and pure water flux performed to confirm the increasing hydrophilicity. The enhancing hydrophilicity was confirmed with respect to higher the concentration of nanoparticles. Evaluation of BP-3 removal was carried in different experimental conditions, such as, different Trans membrane pressure and different concentration of feed. The membrane with low pressure showed better performance by rejecting 100% of BP-3. However, 1 ppm, 3 ppm and 6 ppm of feed solution was used and among them 3 ppm of feed solution gives 100% rejection. The ZnO nanoparticales enhances the performance of CA membrane by showing maximum rejection.

Keywords: benzophenone-3; nanoparticales; endocrine disrupting chemical; composite membranes; increasing hydrophilicity

1. Introduction

Removal of emerging contaminants in drinking water is major challenges in present situation. Lot of chemicals came out from our daily usage to water. These products are very less in concentration ranging from ng/L to μg/L, but these are very dangerous by blocking hormone releasing glands in wildlife and humans (Bolong *et al.* 2009). Most of the ECs released to water by body care cosmetics. One of the major compounds is benzophenone-3 (BP-3), which is an endocrine disrupting chemical [EDC] (Bolong *et al.* 2009). BP-3 is widely used in sunscreen and cosmetics to protect from UV radiation. The BP-3 is photo stable, lipophilic (log K_{ow} = 4), potentially bio accumulative, strong anti estrogenic and anti androgenic as well as estrogenic

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activities (Rezaq *et al*. 2004, Rodil *et al*. 2009, Kunz *et al*. 2006, Schreurs *et al*. 2002). Recently, it was observed that BP-3 has direct interactions in vitro and are estrogenic in fish. (Rezaq *et al*. 2004) The UV screen benzophenone-3 (Bp-3) and its metabolite 2,4-dihydroxyben-zophenone have been detected in human urine from 4 hr after application of commercially available sunscreen products to the skin. Bp-3 has also been found to be readily absorbed from the gastrointestinal tract. Evidence for bioaccumulation in humans stems from analyses of human milk. In five out of six samples of human milk, Bp-3 and/or octylmethoxycinnamate were present in detectable amounts. Hence, removal of BP-3 is a major issue and its very serious, usually for EC's photocatalytic degradation is feasible process (Rezaq *et al*. 2004). But, BP-3 lacks functional groups that difficult to degrade in the fresh environmental water.

Membrane technology, already established a popular technology for water purification. The main advantage of membrane technology is that it is continues process, works without the addition of chemicals, relatively low energy and well arranged process conduction.Ultra filtration (UF), Nano filtration (NF) and Reverse osmosis (RO) are pressure driven filtration processes, are considered as new highly effective processes (Padaki *et al*. 2011a, 2012a, Adams *et al*. 2002, Strathmann 2001, Bruggen and Vandecasteele 2002, Ahmad *et al*. 2004, Qin *et al*. 2007, Walha *et al*. 2007, Nataraj *et al*. 2009, Hegde *et al*. 2013, Nazri *et al*. 2014, Ismail *et al*. 2015**)** inwater treatment toremoval of pollutants (Padaki *et al*. 2011a, 2012a) meets the high environmental standards.

However, more energy consumption in RO makes it less attractive than NF (Malaeb and Ayoub 2011). NF based membrane processes are offer able technique for removing huge loads of micro pollutants (Padaki *et al*. 2011a, b, c).The polymeric NF membranes are very attractive towards ECs removal (Padaki *et al*. 2010). The advanced material and treatment methods are required to produce novel polymeric membrane for removal of ECs. Several existing polymers already showed there efficiency in membrane technology (Padaki *et al*. 2010) Cellulose acetate is one of the better materials among them and it has their own impact in membrane technology (Padaki *et al*. 2015b). Cellulose acetate membranes were used for versatile applications such as, filtration of brackish water, desalination, heavy metal removal, oily waste water purification, separation of methanol/ethanol from water and removal of some Emerging contaminants (Aneela *et al*. 2015, Nataraj *et al*. 2007a, b, Padaki *et al*. 2011a, 2012a). The properties of Cellulose acetate such as, bio-compatibility, high potential flux, toughness, better desalting, relatively cheap and ease of availability, CA membranes havean outstanding hydrophilicity which is extremely important in minimizing membrane fouling with more productivity (Aneela *et al*. 2015).

Recent most the properties of the polymers enhanced by composing the metal oxides. TiO_2 Fe_2O_3, ZnO and many more metal oxides are improved the performance of the membranes by combining with polymers (Padaki *et al*. 2015a, Nataraj *et al*. 2011). Meanwhile, ZnO additive suppress the macro void formation in the membranes, which made the membrane mechanically stronger and membrane surface become denser (Sotto *et al*. 2014) Hence ZNO and cellulose acetate composite membrane was used for the removal of ECs.

To our knowledge limited studies were reported on mixed matrix membrane for EDC removal, hence, the present work was focused on removal of BP3 using CA/ZnO composite membrane. As for our literature knowledge, removal of BP3 using CA/ZnO was not yet reported. The membrane was prepared by phase inversion process with different concentration of ZnO nano particles. The prepared membrane was characterized by ATR-IR, XRD, SEM and AFM. Water uptake and water flux were also studied and results were correlate to the performance of the membrane. Industrial and artificial waste water was subjected to the membrane separation. The BP-3 compound was 100%

separated by the prepared membranes.

2. Experimental details

2.1 Materials

Cellulose acetate (CA, MW = 25,000 Da) was purchased from Aldrich. Zinc acetate dehydrate, Dimethyl formamide (DMF) and acetone were purchased from Merck (India) Ltd. ZnO was synthesized using double distilled water, generated from the double distil water plant in the lab.

2.2 Preparation of ZnO and CA/ ZnO composite membranes:

ZnO was prepared by combustion technique, the procedure followed from the literature (Ramasami *et al*. 2015). The membrane was prepared by phase inversion method (Mulder 2000). The different concentration of ZnO was used for membrane preparation. Table 1 shows the concentration of Nps in membranes. The NPs were sonicated in DMF for 1 Hr and stirred for 4 Hr to avoid the agglomeration. Further, CA was added and stirred for 24 Hr to get viscous solution. The different concentrations of ZnO and CA were listed in Table 1. The casting solution was also sonicated for 30 min and stand for 10 min before casting to remove the air bubbles. After degassing the solution was poured on glass plate and casted using smooth glass rod. The casted membrane was subjected to fuming hood for 15 seconds to evaporate the volatile solvent and forms dense layer on the surface. Further the glass plate was merged in coagulation bath containing cold water. The phase inversion takes place in the coagulation bath and membrane sheet precipitates out. The membrane was washed several times with distilled water and storedin distilled water for 24 hrs to improve its mechanical strength. The membrane with different concentration of nano particle ZnO was named as CAM, CAZ-1, CAZ-2 and CAZ-3.

2.4 Characterization of membranes

Before subjecting to characterization the membrane was dried in vacuum desiccators for complete dry. IR spectra were recorded using Bruker ATR-IR working in the range of 4000 – 400 cm^{-1}. X-Ray diffraction studies were analyzed with X-ray diffractometer (XRD- Shimadzu XD-D1) (Japan) using a Ni filtered CU K alpha X- ray radiation source with scanning rate of 20/min and a mono chromate CUK alpha (1.5406 Å) was used. Scanning electron microscopy (SEM) micrographs were recorded using Carl Zeiss field emission scanning electron microscope to study the surface and cross section morphology of the membranes. The cross sections were prepared by fracturing the membrane at the temperature of the liquid nitrogen. The gold sputtering was done to the sample before capturing. AFM images were taken by F 80 AFM with a nano scope SPM

Table 1 Membrane code and their composition

Membrane code	CA (g)	ZnO (g)	Acetone (ml)	DMF (ml)	Membrane descriptions
CAM	15.0	-----	60	25	Neat CA
CAZ-1	14.75	0.25	60	25	CA+ 0.25 wt% ZnO
CAZ -2	14.50	0.50	60	25	CA + 0.5 wt% ZnO
CAZ-3	14.75	0.75	60	25	CA + 0.75 wt% ZnO

controller and operated in tapping mode.

Hydrophilicity of membrane was determined by water uptake capacity, it was studied by the weight difference of the membrane before and after soaking in distilled water. The 1 cm^2area membrane was dried for 24 hr in vacuum desiccators. The dried membrane was soaked in distilled water for 24 hr. The weight of the wet membrane was recorded and once again same membrane was dried in vacuum desiccators. After drying the weight of the membrane was recorded. The samples with the % water uptake was calculated by using the weight difference between wet and dry membranes with the help of following equation (Padaki *et al*. 2012b, Adams *et al*. 2002, Mulder 2000). The effect of pH on water uptake was studied in various pH 4, 7 and 11. The pH solution was prepared by using HCl and NaOH solution.

$$\%\, water\ uptake = \left(\frac{W_w - W_d}{W_d}\right) \times 100$$

Where W_w and W_d are the sample weights before and after soaking in water. Swelling each specimen was tested for five times and its average value was reported.

2.5 Filtration experiments

2.5.1 Pure water flux study

Self constructeddead end filtration unit was used for all permeation experiments and carried out in room temperature. The procedure was followed as described in our recent publication (Padaki *et al*. 2012a, b). A 60 mm circular membrane was placed in the test cell with the top surface towards feed sample and membrane effective area is 5 mm. The water flux was measured by direct measurement of permeation and reported in liter per meter square per hour (L/m^2h) (Padaki *et al*. 2012a, b)

2.5.2 BP-3 removal

The removal of BP-3 experiment was carried in same filtration unit and followed by experimental procedure. The feed sample was prepared by dissolving BP-3 solution in distilled water. The different concentration 1, 3, and 6 ppm of BP-3 solution was prepared and rejection studies were conducted in different pressure, from 200 kPa to 1000 kPa with the difference of 200 kPa. The concentration of the BP-3 in feed and permeate was measured using UV spectroscopy by photometric method at the wavelength 298 nm. The percent of rejection was calculated using the following formula.

$$\%\, rejection = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

Where C_p is the concentration of permeate and C_f is the concentration of feed. The experiment was repeated 3 times and average value is reported. (Jyothi *et al*. 2016).

3. Results and discussion

3.1 ATR - IR analysis of membranes

ATR-IR of the membranes was done for the confirmation of the presence of functional groups in composition of the polymers. The interaction between ZnO and cellulose acetate were studied

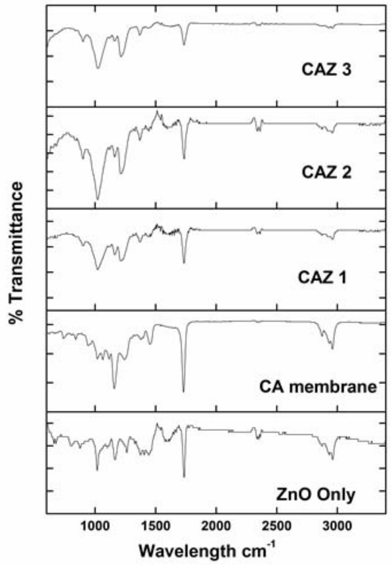


Fig. 1 IR spectrum of ZnO + CA composite membranes

and compared using ATR IR spectra. In Fig. 1 shows the ATR- IR spectra of pure CA and CA/ZnO composite membrane, respectively. The characteristic absorption peak at 3300 cm^{-1} can be attributed the presence of hydroxyl group and the peaks at 1743 cm^{-1}, 1270 cm^{-1} and 1050 cm^{-1} corresponding to the stretching of C = O group, ether group and –C–O– stretching of the –CH_2–OH group respectively, in cellulose acetate membrane (Kunz *et al*. 2006). In addition to the characteristics peaks of CA, a new peak around 477 cm^{-1} is assigned to the Zn–O vibration confirming the presence of ZnO. While, comparing the IR spectra of ZnO/CA composite membrane with that of pure CA membrane, the characteristics peak of –OH group was shifted to 3450 cm^{-1} from 3471 cm^{-1} as shown in Fig. 1. The band located near 600 cm^{-1} can be attributed to the Zn-O stretching mode. The band at 3200 to 3600 cm^{-1} corresponds to the stretching vibration of –OH bond and at 1680 cm^{-1} which appears at wavelength just half of 3200 to 3600 cm^{-1} has been assigned to the first overtone of fundamental stretching mode of –OH. These stretching vibrations correspond to the water molecule bound on the surface of sample.

3.2 XRD analysis

The XRD studies were conducted to find out the crystallinity of the prepared mixed matrix membranes. The XRD pattern of CA and ZnO embedded cellulose acetate are shown in Fig. 2. The CA fibers exhibit the diffuse characteristics pattern of an amorphous phase with the typical peak around 23°. The observed peaks in the range of 30° to 50° could be indexed as the wurtzite structure of ZnO which is well matched with standard diffraction data (JCPDS: 36-145). No additional peaks were detected, which indicates the presence of ZnO in the CA membranes (Wongsasulak *et al*. 2010).

3.3 SEM analysis of membrane

Transport properties of membrane are closely related to morphological properties such as surface porosity and variation in their pore structure of membrane SEM is a powerful tool to investigate the surface morphology study of the membrane. In the higher magnification the electron bombardment is more and it will damage the surface of the membrane. Hence, images are taken in

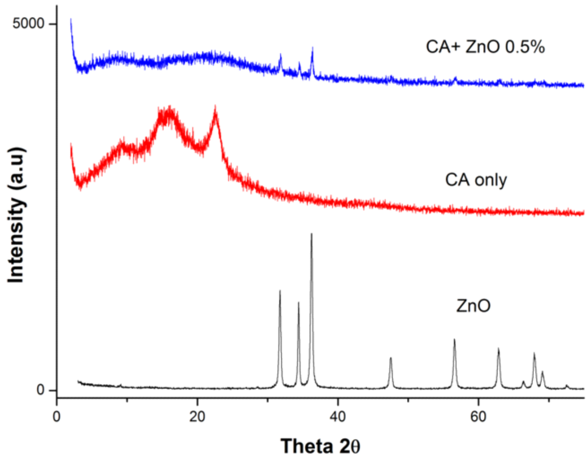


Fig. 2 X- Ray diffraction studies of ZnO and different CA+ ZnO composite membranes

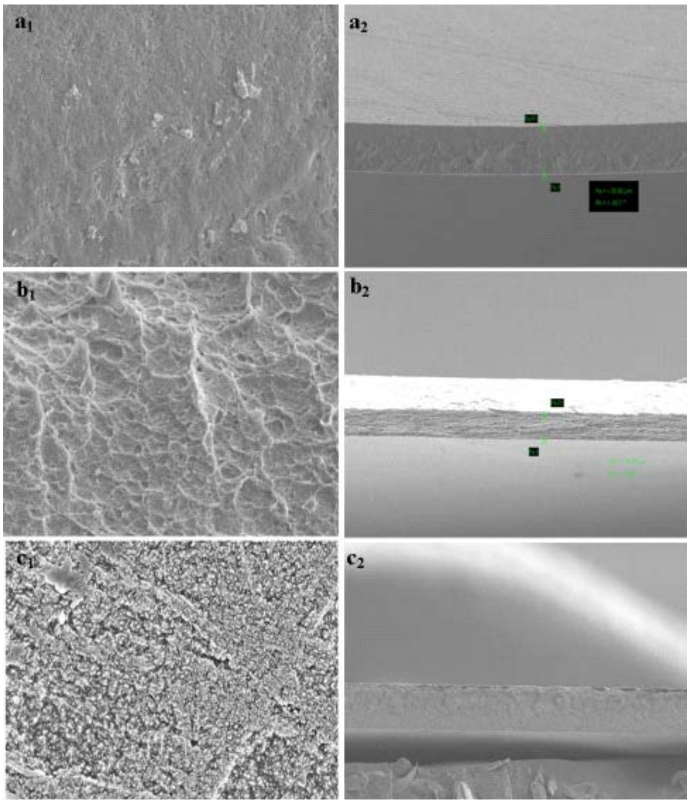
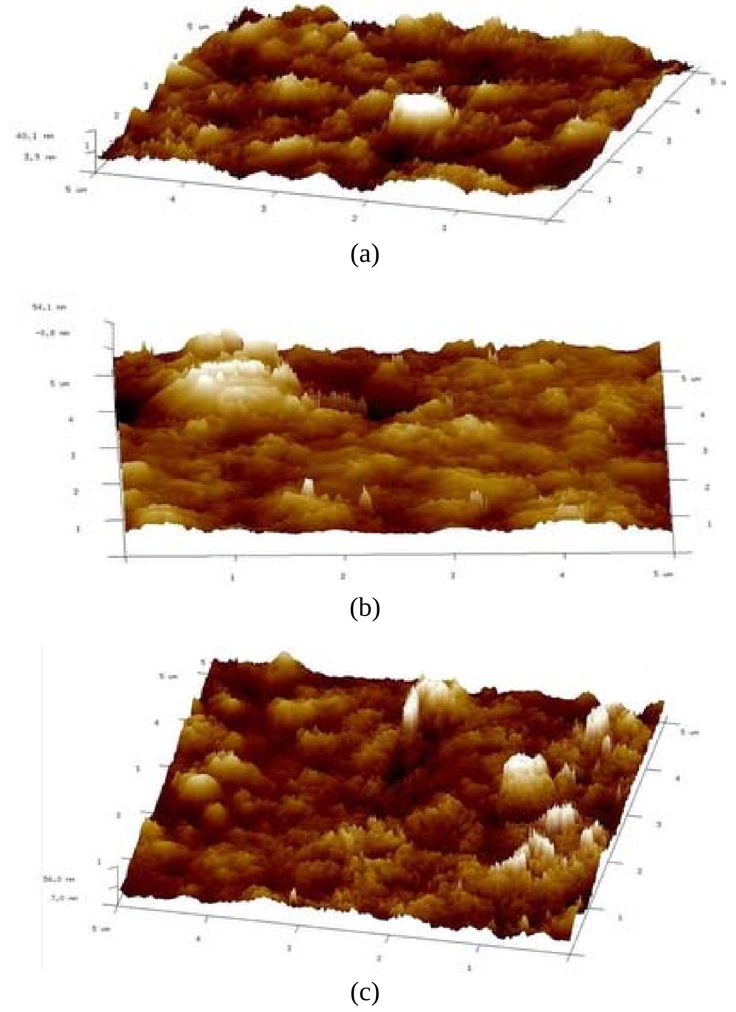


Fig. 3 SEM images of membranes with cross section (a) CA membrane (CA only); (b) CA+0.25% ZnO (CAZ -1); (c) CA + 0.50% ZnO(CAZ - 2)

lower magnification. The cross section of the membrane was prepared to study the inner morphology of the membrane. The images are clearly explain influence of ZnO particles on CA membrane. The morphology of pure CA and CA with ZnO membrane are as shown in Fig. 3(a). It indicates the smooth surface of pure CA membrane while addition of nanopillers increases the surface roughness. More protrusions on the surface of the composition membrane were observed which shows presence of ZnO (Fig. 3). Across section of the membrane showed a dense layer without differencing in the layers. The metal oxide leads to denser membrane evidenced by non spongy holes. In the cross section Figs. 3(a) and (b) the addition of metal oxide particles increases the viscosity of the casting solution which leads to denser membrane. Meanwhile, the viscosity of composite would increase the mass content of metal oxide which reduced the vaporization rate of acetone and DMF hence surface was more roughened as compare to plane membrane (Ziel *et al*. 2008). However cross-section images were no much differences.



(a)

(b)

(c)

Fig. 4 AFM mages of membranes with its 3D structure (a) CA only; (b) CA+ 0.25% ZnO(CAZ-1); and (c) CA+ 0.75% ZnO (CAZ-3)

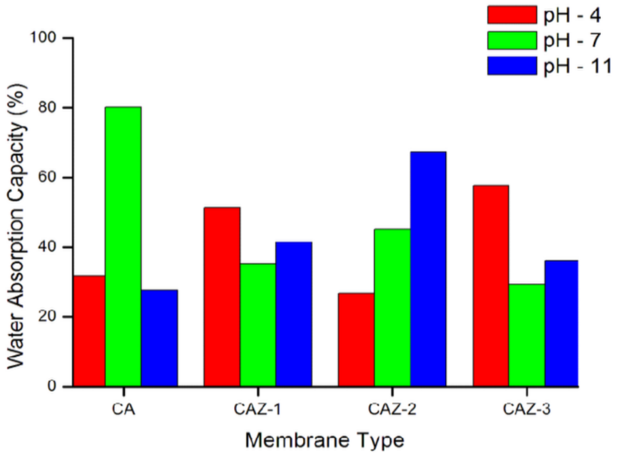


Fig. 5 Water absorption capacity of CA+ ZnO composite membranes

3.5 AFM analysis of membrane

Further surface roughness was measured using AFM analysis. The Fig. 4 was showed AFM images of the membranes. The comparison of Figs. 4(b) and (c) showed the deposition of ZnO on the membranes pores with comparison with plane CA membrane in Fig. 4(a). Fig. 4(c) shows the surface images of CA/ZnO mixed matrix membranes, with the increase of ZnO concentration. The deposition of nano particles increases, which has seen different sizes of flakes indicating agglomeration. The penetration of nano particles into the polymer sublayer was restricted because of higher concentration of nano particles, which leads to agglomeration of NPs. The presence of ZnO nano particle in the membrane matrix created some superficial disorders on the membrane surface causing the surface roughness (Ziel *et al*. 2008). That the roughness of membrane is inversely proportional to the concentration of ZnO nano particle.

3.6 Hydrophilicity of membrane (*Water uptake*)

Water absorption capacity is considered to be important characterization parameter; it is an indirect indication of hydrophilicity of membranes and also related to the porosity of the membrane (Mollahosseini and Rahim 2013). Water uptake test was performed in different pH the data presented in Fig. 5 indicated a slight increase in swelling ratio with increase of ZnO content in the CA blend and also acidic and basic pH membranes showed more water swelling as compared to neutral pH. The overall uptake ratio is due to the three factors one factor is due to the absorption of water into the polymer matrix and second factor is due to water retained by capillary in the pores, there is possibly opening of pore under different pH conditions (Arthanareshwaran *et al*. 2004, Hegde *et al*. 2011).The membrane CA only showed more water absorption and membrane CAZ 3 showed lesser membrane swelling at neutral pH compared to other membranes. Well known that, CA membrane is hydrophilic in nature while insertion of nanopills close the pores, which hinder water retained in capillary of the membrane. In neutral and basic medium the water uptake was mainly driven by solvent diffusion, but in acidic pH the chain relaxation effect due to the protonation. In addition the samples with higher porosity had higher extent of water uptake which seemed to preside over the diffusion of solvent in the matrix.

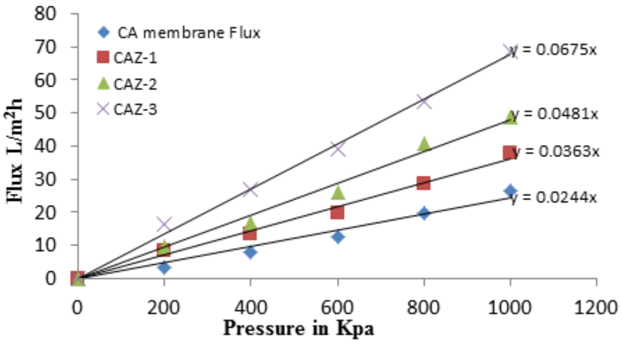


Fig. 6 Pure water flux versus pressure for CA+ ZnO composite membranes

3.7 Pure water flux of membranes

Pure water flux was studied using dead end filtration unit. The active surface area is 50 mm and top surface is facing towards feed water. The flux studied in the different pressure from 200 kpa to 1000kpa with the difference of 200 kpa. The Fig. 6 shows pure water flux of membrane. All the membranes showed same trend by processing increase in the flux with respect to pressure. However, the ZnO mixed membrane showed more flux as compared to CA membranes.

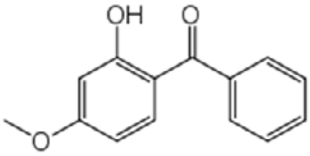
3.8 Filtration performances

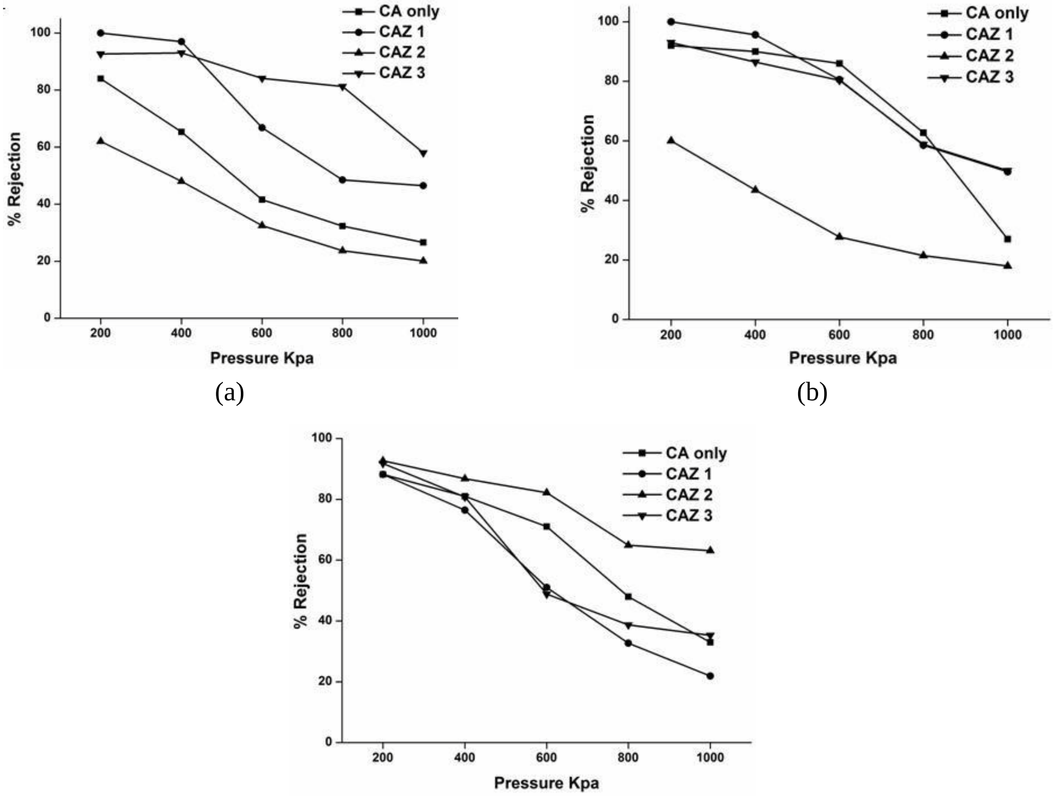
The rejection of BP 3 experiment was conducted as same as water flux study. The experiments were repeated three times and mean results were reported. The effect of pressure and feed concentration on performance were studied. The permeate of feed was also observed and mean value is reported, the Fig. 7 shows rejection and Fig. 8 shows permeate flux of the feed sample.

As compared to plane CA membrane, the ZnO mixed membrane showed more rejection. CAZ-2 which is having 50 mg of ZnO showed 100% of rejection of BP-3 at 200 kpa pressure. While increase in the concentration of ZnO decreases the rejection this is because of agglomeration. Moreover the rejection was decreased with respect increasing the pressure as well as concentration of feed. The membrane showed better reject at 200 kpa up to 3 ppm of feed concentration. The permeate of the feed sample clearly indicates more productivity in ZnO mixed membrane as compared to CA membrane. The permeate flux is higher with respect to increasing concentration of NPs. While increasing pressure the permeate flux increases. However the feed concentration was not so much effected on the productivity.

However, reported membrane has commercial intrest because it is showing better rejection than the commercial membrane. The commercial NF membrane (HL, GE Osmonics) could efficiently remove most of the ECs dissolved in ultrapure water or in municipal secondary effluent (Acero *et al*. 2010). Of the 11 ECs investigated, the rejection rates of five ECs, i.e., metoprolol, antipirine, flumequine, atrazine, hydroxybiphenyl and diclofenac were promising and remained in the range of 86.1–100%, 76.7–88.2%, 80.3–94.4%, 76.1–91.3%, 82.7–96.8% and 93.3–98%, respectively, depending on process conditions such as pressure, velocity, temperature and pH. High rejection against caffeine (85.8%), sulfamethoxazole (97.7%), ketorolac (95.8%) and isoproturon (83.7%) was also able to achieve when the NF membrane was operated under optimized process conditions. Furthermore, a study reporting the removal of EDC/PhACs of 52 compounds by NF membrane

Table 2 Physical Properties of BP3

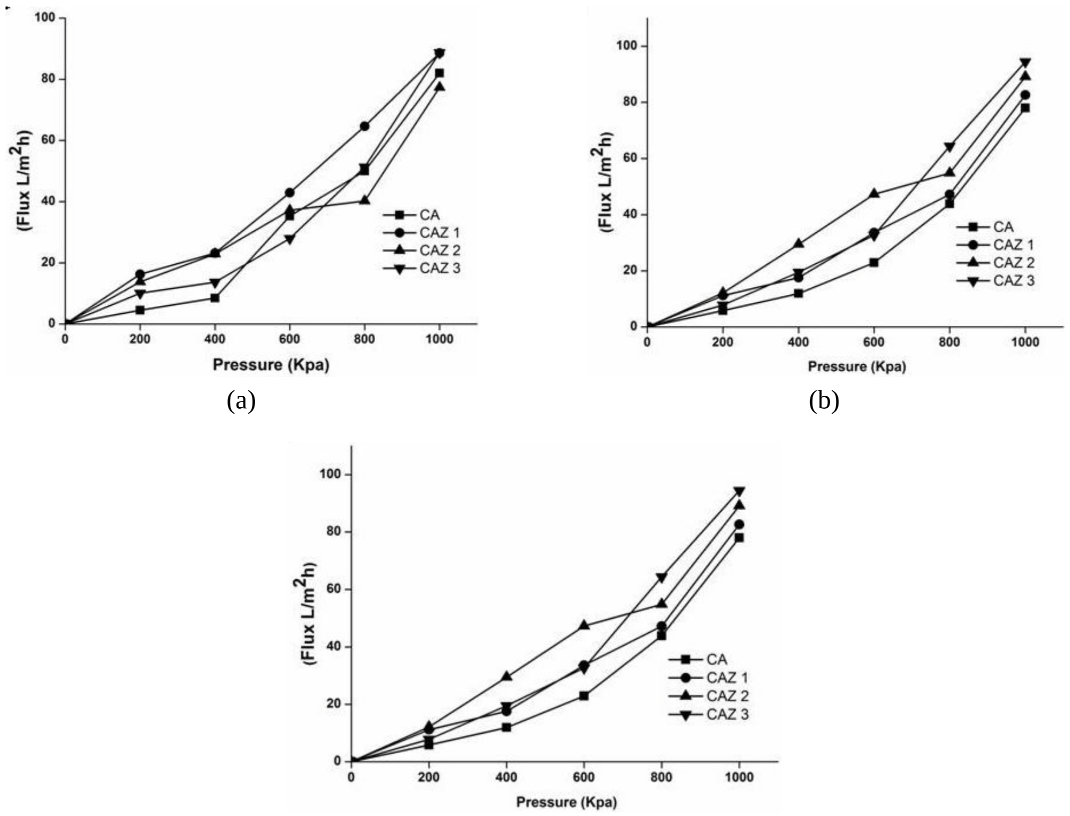
Properties	Benzophenone-3
Molecular weight	228.24
Molecular size (length and width)	This crystallizes in the non-centro symmetric orthorhombic space group. The lattice parameters are reported as *a* = 10.26 Å, *b* = 12.09 Å and *c* = 7.88 Å having four atoms per unit cell.
Acid dissociation constant (pKa)	7.6 (H2O)
Log K_{ow}	> 3.7 (n-octanol/water) 3.8, 3.8 (Roche 3)
Diffusion coefficient@ 23°C	4.27 , D exp $Cm^2/S \times 10^{-8}$
Structure $C_{14}H_{12}O_3$	



(a) (b)

(c)

Fig. 7 Rejection rates of BP-3 versus pressure for (a) 1 ppm of BP-3 solution; (b) 3 ppm of BP-3 solution; and (c) 6 ppm of BP-3 solution



(a)

(b)

(c)

Fig. 8 Permeate flux of BP-3 versus pressure for (a) 1 ppm of BP-3 solution; (b) 3 ppm of BP-3 solution; and (c) 6 ppm of BP-3 solution

(ESNA, Hydranautics) has revealed that ECs having less polar, more volatile and more hydrophobic (group II) e.g., chrysene, endrin, anthracene, fluorene, naphtalene, etc were greater retained by membrane than those of having more polar, less volatile and less hydrophobic (group I) e.g., triclosan, progesterone, oxybenzone, naproxen, etc. (Yoon *et al*. 2006). Reported membrane showed 100% rejection BP-3 which is equal to the commercial membrane. Hence, it has potential to be commercialized.

The rejection experiment was extended to the laboratory prepared feed water. The 3 ppm of BP 3 was used in the feed sample. Table 2 showed rejection results of the membrane. The results implied that the incorporation of ZnO showed more rejection as compared to plane. The rejection was increased with respect to higher concentration of NPs. The physical properties of the BP-3 such as molecular weight (MW) molecular size (length and width), pk_a, values, log k_{ow} and diffusion constant are key factors in rejection experiment however the membrane properties pore sizes charge on membrane surface, hydrophilicity and surface roughness are simultaneous considered for the filtration. Table 2 shows the physical properties of the BP-3.

It is a known factor that rejection increase with respect to log $k_{ow} > 2.8$ which indicates their hydrophobic nature. However BP-3 has log $k_{ow} > 3.8$.hence, it is showing rejection meanwhile nano particles increase the roughness of membrane surface which allows deposition of BP-3 on the membrane surface. AFM image was confirmed that CAZ membrane surface is more rough as compared CA membrane hence CAZ membranes showing more rejection with respect to pressure the rejection decreases in all the membranes. This is because of pore size increase in the higher pressure. Hence the permeate flux increase with respect to higher pressure, however the feed concentration plays dominant role in the separation experiment, the prepared all membrane have draw backs with respect to filtration of high concentrated feed samples.

4. Conclusions

The novel method for BP-3 removal was established. The ZnO and CA composite membrane were prepared by DIPS method. The filtration experiment was carried out for the removal of BP-3 from water. Addition of ZnO to CA membrane casting solution played an important role to suppress the macro void formation in the membrane. Meanwhile, membrane surface becomes less porous and more roughened. AFM results indicate that the surface area roughness also increases with the addition of ZnO. The membrane with 0.5 gm ZnO content (CAZ-2) shows the maximum BP-3 rejection of 100%, which was in good agreement with Log K_{ow} of feed and hydrophilicity of the membrane. The presence of ZnO nano particles in CA membrane enhances the hydrophilicity as well as productivity with selectivity by rejecting BP-3.

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