

Preparation of activated carbon incorporated polysulfone membranes for dye separation

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Abstract. Immediate use of activated carbon incorporated polysulfone membrane application for dye separation was reported in this work. Dimethylformamide (DMF) was used as the solvent for the membrane preparation. The membrane thus prepared were characterized in terms of surface morphology, ATR-FTIR, AFM, experimental results as membrane performance. The resultant nanofiltration (NF) membranes were tested with Congo red dye concentration 200 mg/L. The water permeability was found to be considerably higher than that reported in literature. Experimental results show that the real rejection of the Congo red is 99.57% over the transmembrane pressure 100 psi using 30% activated carbon incorporated membrane. Prepared NF membranes shows the corresponding permeates fluxes were 40 Lm⁻²h⁻¹ to 82 Lm⁻²h⁻¹ with different activated carbon percentage incorporated in polysulfone membrane. The present study demonstrated that dye rejection enhanced NF may be a feasible method for the dye wastewater treatment. The overall observations thus indicated that toxic residual dyes can be appreciably separated from the membrane technology, provided that the accompanying polymeric membrane, activated carbon as binding agents and the process parameter levels are astutely selected.

Keywords: polysulfone membrane; powdered activated carbon; congo red; membrane separation; dye rejection

1. Introduction

Nowadays membrane technology is steadily growing in various industries due to competitive energy prices and environmental concerns. Although a number of pressure driven solvent separations processes had been explored till date, and among all membrane technologies nanofiltration (NF) is relatively a younger technology for the separation of industrial effluent. As

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we know one of the major sources of water pollution is colored wastewater, coming out from pigment, textile and dye industries. The population raise is the key factor for the constraint of millions of tons of dyes; those are being consumed mainly by various textile industries (Ahmed 2016). These textile industries dyes are not easily biodegradable due to their complex structures. Moreover, the degraded intermediates are also toxic. It was reported that even ~ 1 ppm dye makes the effluents colored very dark and perilous (Mohan *et al.* 2002). The colored waste water is a real threat to the enhanced microtoxicity to aquatic life, and reduced light penetration and retardation of photosynthetic activity (Malik *et al.* 2007) Thus, it is essential to remove the dyes from effluent, without disturbing the quality of water and make it reusable for various industrial and agricultural purposes. Among the various chemical, physical, and biological treatment processes, membrane separation is a simple and effective method. The use of polysulfone (PSf) as a material for the synthesis of NF membrane and ultrafiltration (UF) is well-known because of its good chemical, thermal, and mechanical stability (Ingole *et al.* 2012). Phase inversion technique is most versatile, economically reasonable, easy to scale up and reproducible mechanisms for the fabrication of polymeric asymmetric membranes (Ingole *et al.* 2014a, b). These membranes possess a skin-layer at the top followed by a porous sub layer. Reasonably priced approach for the bulk modification is the incorporation of hydrophilic additives in polymer solution itself. Additives affect the structure and state of the casting solution, altering the physical, morphological and permeation characteristics of asymmetric membranes. The use of different organic additives, like, polyethylene glycol (PEG) (Kim and Lee 1998, Panda and De 2013), poly (vinylidene fluoride-hexafluoropropylene) composite, polyvinylpyrrolidone (PVP) (Reinholdt *et al.* 2011, Ahmad *et al.* 2015, Han and Nam 2002), has been reported. Nanofiltration membranes recently have gained their importance in the field of drinking water, industrial water and waste water treatment, dye adsorption/separation, energy generation and chiral molecule separation (Hagmeyer and Gimbel 1999, Xu and Lebrun 1999, Bhatt *et al.* 2015, Georgin *et al.* 2016, Choi *et al.* 2015, Ingole and Ingole 2014, Sharma and Purkait 2016).

Powdered activated carbon is the powder form of activated carbon with superior porosity than charcoal and prepared using different activation methods and carbon precursors. Activated carbon and their modified forms provide the effective removal of dyes contamination for aqueous solution (Demirbas 2009, Rivera-Utrilla *et al.* 2011). The great enhancement in the adsorption capacity can be easily achieved by the tailoring of carbon surface with different function groups according to the nature of the adsorbent (acidic or basic) (Demirbas 2009). Although the commercially available activated carbon provided the better adsorption capacity for dyes and pigments, their higher cost makes the major obstacle between their effective uses. Hence numbers of researchers have taken hard work to synthesize the activated carbon starting straightforwardly available/waste, stumpy cost and renewable predecessors with amendment in separation techniques (Dias *et al.* 2007).

The preparation parameters including carbon precursor, activating agent, preparation condition plays a crucial role in its textural characteristics. Due to large demand by the various industries including air purifier, water purifier, chemical, food and metal industries etc. along with household applications, it has been extensively prepared using widely available carbon sources such as agriculture residues like coconut shells, palm shells, husk and saw dust. The coal or petroleum coke is also one of the extensively used carbon precursor due to high surface area. Various carbon precursors including agriculture residue (Johns *et al.* 1999), petroleum coke (Rambabu *et al.* 2013), coal (El Qada *et al.* 2007), polymers (Esfandiari *et al.* 2012, Sawant *et al.* 2013a, b), tyres (Mui *et al.* 2010), Oil Palm Biomass (Rafatullah *et al.* 2013), pumice and walnut (Heibati *et al.* 2014) etc.

have been utilized for the preparation of carbon materials. By using chemical activation method, we prepared activated carbon membrane for dye separation for our experimental study.

Escalating, wide ecological and environmental concerns generate numerous research efforts on the efficient disposal of dye effluents. Conventional dye removal technologies could be categorized into chemical, physical, and biological methods. Compared with chemical and biological technologies, such as photo-catalysis oxidation, chemical coagulation and oxidation, biological oxidation etc. (Lee *et al.* 2006, Zheng *et al.* 2009, Pandit and Basu 2004, Banat and Al-Bastaki 2004), membrane filtration typically including pressure-driven nanofiltration (NF) and ultrafiltration (UF), emerges as a promising physical treatment method for separating, concentrating and purifying dye solution. Because of the membrane separations have the distinct advantages such as facile and green operation, high efficiency and low cost.

Congo red (CR) dye is a colored essence used in many industries. This CR is an anionic diazo dye with a coupling of tetrazotised benzidine including two naphthionic acid molecules. Wastewater containing CR is typically difficult to biodegrade because of its complex aromatic structure. So water is heavily contaminated and far above the ground in both color and organic content (Purkait *et al.* 2007, Jain and Sikarwar 2008, Kondru *et al.* 2009). This study aims to examine the performance of a carbon based NF membrane for the removal of hazardous CR dye with special attention paid to the percentage dye removal, fouling flux behavior and mechanism of the membrane fouling. The membranes studied were characterized in terms of permeability, morphological study, and ATR-FTIR. Performance of activated carbon incorporated NF membrane was tested in terms of rejection of cango red dye. Thus, the novelty of this work is that it is the first attempt to use activated carbon in PSF/DMF system to get NF membrane.

2. Experimental

2.1 Materials

Polysulfone (PSf, Ultrason E6020P, BASF, Germany), used as the base polymer, was purchased from General Electric Company. N-methyl-2-pyrrolidion (NMP) with purity more than 99.5%, KOH, HCl, were purchased from Merck and was used as solvent without further purification. Lithium chloride (LiCl, Sigma Aldrich) was used as pore former in dope solution. Congo red, MW: 696.65, was supplied by Sigma Aldrich. Distilled water was used as the non-solvent in the coagulation bath. All chemicals were of analytical grade and used without further purification. The structure of polysulfone and Congo red are shown in Fig. 1.

2.2 Preparation of activated carbon

Petroleum cokes are used as carbon precursor. Synthesis of activated carbon was carried out by mixing the finely powdered petroleum coke (5 g) with KOH (20 g) and water (10 mL) in SS316 vessel and heated up to 800°C for 3 h under nitrogen atmosphere in tubular furnace with heating rate of 20°C/minute. The reaction mass was removed after natural cooling and washed with water for several time to remove the alkali followed by 5% v/v of HCl wash till its pH reaches ~7. The sample was dried overnight at 120°C. Chemical activation set-up for activated carbon preparation is shown in Fig. 2.

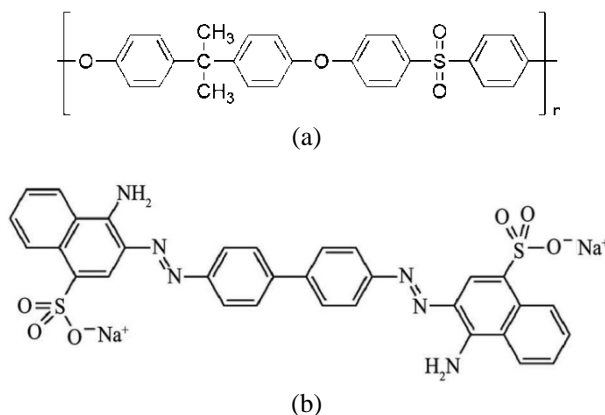


Fig. 1 Chemical structure of (a) Polysulfone; and (b) Congo red dye molecule

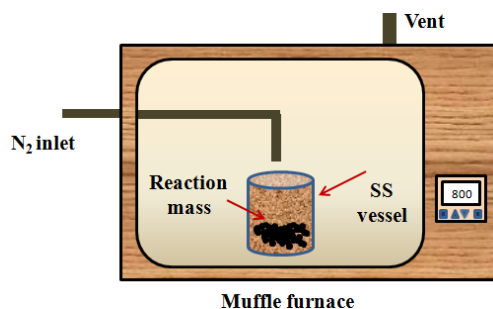


Fig. 2 Chemical activation set-up for activated carbon preparation

2.3 Membrane preparation

Different types of flat sheet PSf membranes were prepared by phase inversion method and the steps involved in the membrane fabrication were as follows. Variable amount of activated carbon (10%, 20%, 30%) were added to a premixed 18% PSf (weight of carbon in correspondence to PSf weight) in DMF dissolved at 70°C. The solution was magnetically stirred for at least 15 h to make sure complete dissolution of the polymer. During the whole process of stirring, the lid of the container was kept closed to prevent the loss of solvent due to evaporation. The prepared solutions were kept for at least whole night without stirring at room temperature to remove air bubbles. In the first step of casting of membranes, non-woven polyester fabric of thickness $120 \pm 20 \mu\text{m}$ (product number TNW006013, supplied by M/s, Hollytex Inc., New York, USA) was attached to a clean glass plate using adhesive tape. The casting solution was drawn down the fabric using a doctor's blade with an adjustable thickness fixed at $180 \mu\text{m}$ and was immediately immersed in a precipitation bath containing distilled water at room temperature to initiate the non-solvent induced phase separation. The membrane was kept in the precipitation bath for 10 min and then, it was transferred to another container having fresh distilled water for 24 h to remove the excess solvent. After that, the membrane was ready to be tested by using membrane testing unit as shown in Fig. 3.

2.4 Experimental details

As shown in Fig. 3 type of membrane testing unit was used to separate the dye solution. A nanofiltration activated carbon incorporated polysulfone membrane with an effective area of $195 \times 10^{-3} \text{ cm}^2$ was loaded in the permeation cell of a lab-scale cross-flow NF unit, which is schematically shown in Fig. 3. The membranes were pre-compacted by filtration of de-ionized water at 100 psi and $27 \pm 1^\circ\text{C}$ for 1 h to achieve a steady flux. Initial experiments using the activated carbon incorporated polysulfone membranes were performed with the dye solution at constant pressure and variable concentrations activated carbon incorporated polysulfone membranes. The filtration performances of the activated carbon incorporated polysulfone membranes with 200 mg/L dye solution were then conducted. Samples of the feed solution and permeate were taken throughout the dye separation process. All of the permeation experiments were carried out at $27 \pm 1^\circ\text{C}$. Finally the concentration of solute in permeates was measured by UV-vis spectrophotometer (Shimadzu UV-2550).

2.5 Theoretical interpretation of performance parameters

The performance of membrane process is primarily judged by two most important parameters namely permeability and selectivity. The permeability is an indicative of productivity and selectivity indicates the efficiency of the process.

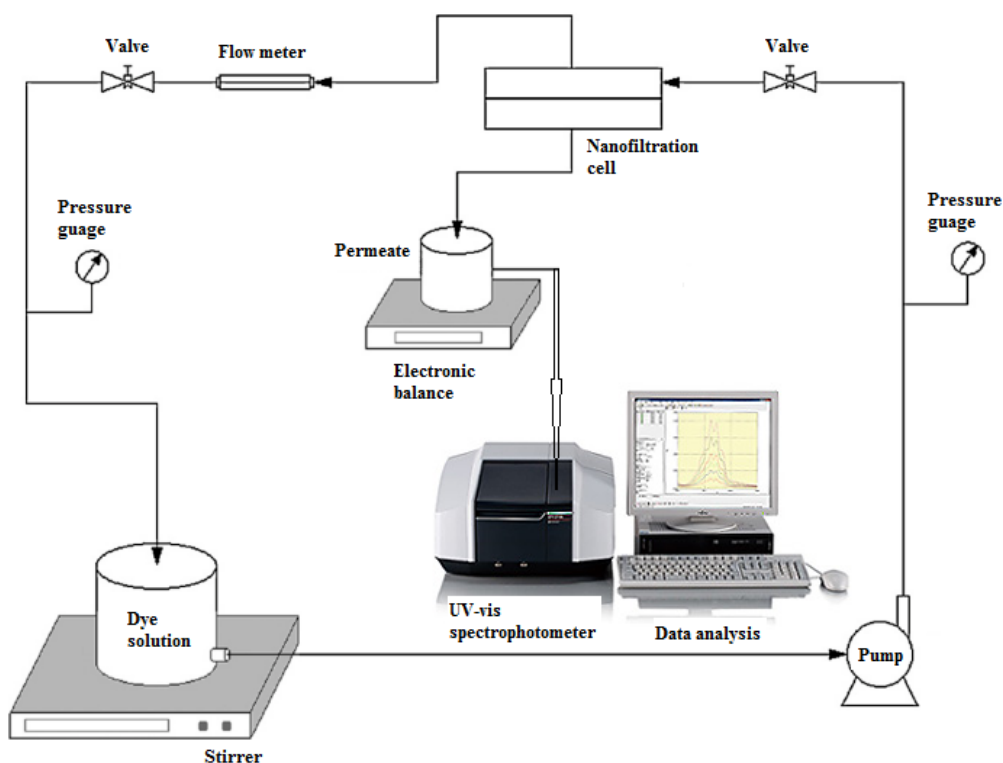


Fig. 3 Schematic diagram of nanofiltration unit for dye separation

The solvent as well as solute permeates through the membrane therefore it is more appropriate to explain liquid permeability and solute permeability of membrane separately.

Liquid permeability describes how easily a fluid can flow through the material. The Darcy's Law describes the kinetics of fluid flow through porous media in terms of driving force (pressure) and permeability of the medium therefore can be used to calculate permeability of a liquid through porous materials under pressure. The Darcy's law is given by following equation

$$Q_f = \frac{PA\Delta p}{\eta\Delta L} \quad (1)$$

Here, Q_f is flow rate of liquid (M^3/s), P is permeability coefficient (m^2), A is area of sample (M^2), Δp is Pressure difference across the medium (kPa), L is thickness (mm) and η = fluid viscosity (Pas).

The liquid permeability of membrane is termed as "volumetric flux (J_v)" and reported as the volume of liquid permeated through per unit area of membrane per unit time ($Lm^{-2}h^{-1}$).

The selectivity of porous membranes is described by its rejection of solute from the liquid stream. The porous membranes selectively permit solute molecules to pass through according to the size of the pores in the membrane. The solute molecules of molecular size smaller than the pores sizes in the membrane permeate while bigger size molecules are retained by the membrane. Thus selectivity of membrane is expressed in terms of percentage rejection (% R) given by following equation

$$\%R = \frac{(C_f - C_p)}{C_f} \times 100 \quad (2)$$

Here, C_p and C_f are concentrations of solute in permeate and feed respectively.

3. Results and discussions

3.1 Surface area analysis

The obtained powdered activated carbon was characterized using nitrogen sorption at 77 K for textural properties and listed in Table 1. Powdered activated carbon prepared and utilized in this study showed the very high specific BET surface area, 3081 m^2/g with micro-porous textural property. Nitrogen sorption isotherm of powdered activated carbon (Fig. 4) depict major

Table 1 Textural properties of powdered activated carbon derived from petroleum coke using chemical activation method

Entry	Surface area (m^2/g)				Pore Volume (cm^3/g)		Pore width (nm)	
	BET	Lang ^a	Micro ^b	Ext ^c	Total ^d	Micro ^e	BET ^f	BJH ^g
Powdered activated carbon	3081	4238	2796	285	1.50	1.26	2.0	2.3

^a Langmuir surface area; ^b t-plot micropore area; ^c t-plot external surface area;

^d Single point adsorption total pore volume; ^e t-plot micropore volume;

^f Adsorption average pore width ($4V/A$ by BET); ^g BJH adsorption average pore width ($4V/A$)

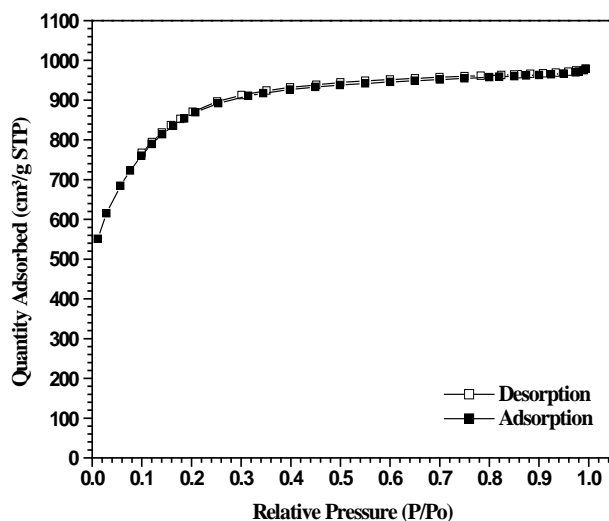


Fig. 4 Nitrogen sorption isotherm of powdered activated carbon at 77 K

adsorption below 0.2 p/p_o regions with sharp increase at lower pressure and no hysteresis in desorption indicating the presence of micro-porous characteristics.

3.2 Raman spectroscopy analysis

Raman spectroscopy is a very useful characterization tool for carbon materials. Mainly two Raman modes are observed at 1582 cm^{-1} (G-band) and 1342 cm^{-1} (D-band) (the shear mode of two adjacent sheets) for a single crystal of graphite (Tuinstra and Koenig 1970, Sawant *et al.* 2014). A typical Raman spectrum (Fig. 5) of the prepared sample shows the presence of the D- and G-bands, located at 1347 and 1598 cm^{-1} , respectively. The Raman spectrum of obtained activated carbon is slightly different than that of CNTs which may be due to the disordered structure of activated carbon and the presence of amorphous carbon (Shao *et al.* 2004, Sawant *et al.* 2015).

3.3 Fourier Transform Infrared Spectroscopy (FTIR) analysis

The ATR-FTIR Spectra of polysulfone support membrane and activated carbon incorporated composite membranes are given in Fig. 6. The absorption bands in the region of 1151 cm^{-1} , 1244 cm^{-1} , and 1585 cm^{-1} are characteristics of sulfone groups, bands in the range of 1000 cm^{-1} – 675 cm^{-1} and above 3000 cm^{-1} are for C-H stretching of aromatic rings in polysulfone polymer (more details, 3000 cm^{-1} C-H stretching mode, 2308 cm^{-1} O = C = O stretching, 1765 cm^{-1} Phenyl ring, 1596 cm^{-1} phenyl ring, 1239 cm^{-1} C–O–C asymmetric stretch, 1166 cm^{-1} C–O–C symmetric stretch, 1073 cm^{-1} SO₂ asymmetric stretch, 744 cm^{-1} SO₂ symmetric stretch, 635 cm^{-1} C–S–C asymmetric mode) (Ingole *et al.* 2013a, b, 2014, Yun *et al.* 2015). In details, characteristic bands for hydrogen bonded –OH at 3435 cm^{-1} (availability of surface hydroxyl groups (transmission band at 3435 cm^{-1} stretching) on activated carbon) and at 1382 cm^{-1} (bending) were observed (Li *et al.* 2005). The transmission band at 1602 cm^{-1} corresponds to the presence of sp^2 hybridized aromatic C = C groups in activated carbon. The very weak transmission band at about 2856 – 2960 cm^{-1} can be attributed to the stretching mode of –C–H bond (Yue *et al.* 2004).

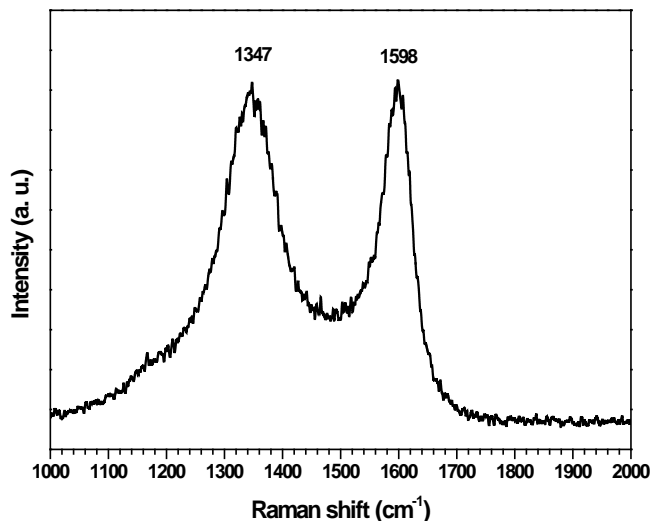


Fig. 5 Raman spectrum of powdered activated carbon

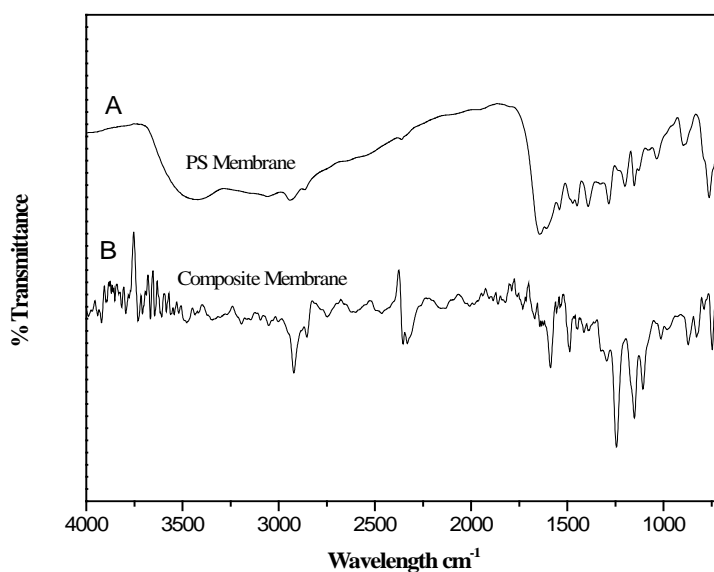


Fig. 6 ATR-FTIR spectra of polysulfone support membrane before coating (A) and after 30% activated carbon incorporated polysulfone membranes (B)

3.4 Scanning Electron Micrograph (SEM)

SEM images were analyzed using a scanning electron microscope (SEM, S-4700, Hitachi). First, the membrane was carefully removed from the substrate. It was then cut into small pieces, dried using a filter paper, dipped in liquid nitrogen for 1 min and then fractured cryogenically. The fractured samples were dried under vacuum. The samples were gold sputtered and then mounted on the sample pad. The observations were carried out at the top surface and on the cross-sections

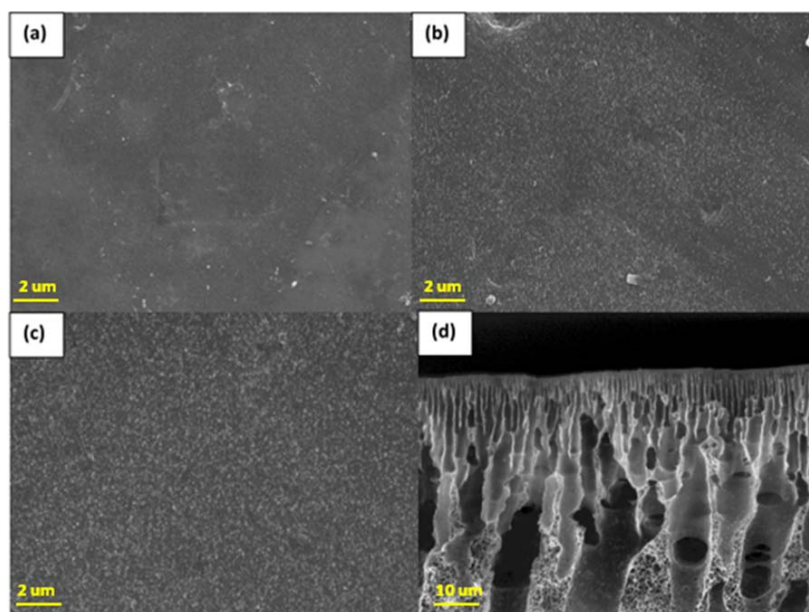


Fig. 7 SEM images of (a) 10% activated carbon; (b) 20% activated carbon; (c) 30% activated carbon; and (d) cross section of 30% activated carbon incorporated polysulfone membranes

to evaluate the membrane thickness and morphology. Fig. 7 shows the surface (Figs. 7(a)-(c)) and cross section (Fig. 7(d)) images of activated carbon incorporated membranes. The surface morphology of membrane changes according to the carbon incorporation and performance also affected.

3.5 Atomic force microscopy (AFM)

The image obtained by AFM has different pore shapes and their sizes. As can be seen in Fig. 8, the bright regions correspond to the highest points and the dark regions are the pores. This may be due to the disordered structure of activated carbon and the presence of amorphous carbon. The sizes of pores were obtained by the visually inspecting the line profiles of different pores on the AFM images of the different areas of the same membrane.

3.6 Contact angle measurement

Water contact angle of the activated carbon incorporated composite membranes was measured at room temperature using sessile drop technique on water contact angle analyzer (Phoenix 300 Plus, SEO Co., Ltd.) utilizing Milli-Q deionized water as the probe liquid. Surfaces of the membranes were wetted with 3 µL of distilled water via thin needle to form a tiny droplet. Contact angle with water is a common measurement to check the hydrophilicity/hydrophobicity of a membrane surface. In order to investigate the wetting properties of the modified polysulfone membranes, water contact angle was measured by sessile drop technique. In case of porous membranes, contact angle is not an efficient way to estimate the hydrophilicity because the surface porosity of substrate readily affects the contact angle by capillary action (Yip *et al.* 2010). Contact

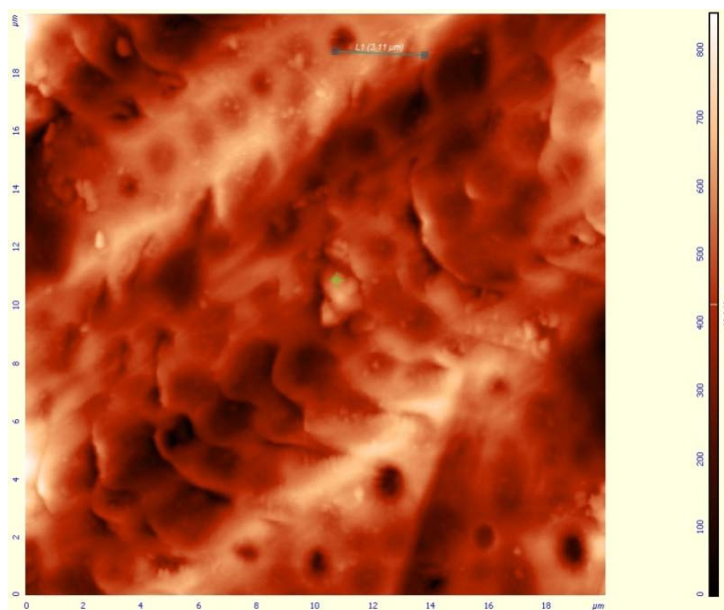


Fig. 8 AFM image of the 30% activated carbon incorporated polysulfone membranes, where the darker regions represent the pores

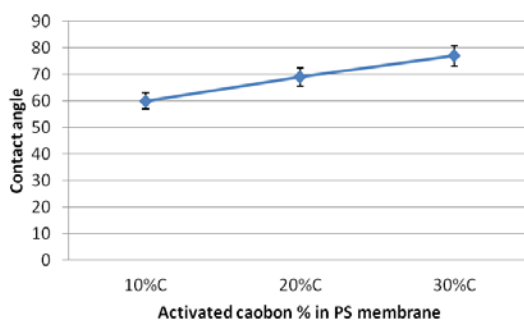


Fig. 9 Contact angle of 10% activated carbon, 20% activated carbon and 30% activated carbon incorporated polysulfone membranes

angle measurement with water was found to be in the range of 60° to 77° to showing that the surfaces of the all membranes are hydrophobic as expected due to activated carbon material in the polysulfone membranes. The contact angle measurements for all membranes are shown in Fig. 9.

3.7 Effect of activated carbon adding amount on volumetric flux (J_v)

The volume of liquid from 200 mg/L concentrated solutions of Congo red at 100 psi (689.42 kPa) permeated through the membranes (volumetric flux, J_v) as a function of permeation time up to 6 h depicted in Fig. 10 indicated higher flux of 10% incorporated activated carbon compare with 30% activated carbon. The J_v decreases up to 6 h thereafter remains stable for all membranes. The reduction in J_v with time is due to the common phenomenon “concentration polarization and

fouling” of membranes. The concentration polarization is an ordinary upshot of the selectivity of a membrane which leads to accretion of particles or solutes in a mass transfer boundary layer adjacent to the membrane surface. The basic of concentration polarization was described by Blatt et al., in 1970 stated that when solute is rejected by the membranes its concentration builds up at membrane surface thus actual concentration of the solute near the membrane surface is higher than the bulk concentration resulting in the reduction of flux as well as rejection (Blatt and David 1970). The solute molecules accrued at the membrane surface due to concentration polarization condense the solvent activity thus trim down the solvent flow through the membrane. The fouling cause blockage of membrane pores thus restricts the liquid flow. The fouling occurs due to membrane-solute interactions, membrane morphology, and solute-solute interactions. The membrane-solute interactions if specific may result in adsorption of solute molecules and other particles available in the feed solution to the membrane surface as a result flow is obstructed. The membranes prepared from 10% activated carbon indicated higher J_v comparative to the membranes prepared from 20 and 30% activated carbon. The all calculation data regarding UV absorbance for rejection calculation and flux calculation data are shown in Table 2.

Table 2 Calculation data by using UV absorbance for rejection and permeanc data for volumetric flux
(1) 10% Activated carbon incorporated polysulfone membranes

Exp. time (h)	Abs.	% rejection	Flux = $\text{Lm}^{-2}\text{h}^{-1}$
1	0.309393	95.13	82.1
2	0.233115	96.33	75.9
3	0.22083	96.53	67.7
4	0.212835	96.65	61.5
5	0.210008	96.70	57.4
6	0.203215	96.80	51.3

(2) 20% Activated carbon incorporated polysulfone membranes

Ext. time (h)	Abs.	% rejection	Flux = $\text{Lm}^{-2}\text{h}^{-1}$
1	0.048275	99.06	55.4
2	0.035775	99.30	52.3
3	0.034562	99.41	49.0
4	0.02605	99.49	46.2
5	0.023275	99.55	41.5
6	0.0219	99.57	40.0

(3) 30% Activated carbon incorporated polysulfone membranes

Ext. time (h)	Abs.	% rejection	Flux = $\text{Lm}^{-2}\text{h}^{-1}$
1	0.048275	99.06	55.4
2	0.035775	99.30	52.3
3	0.034562	99.41	49.0
4	0.02605	99.49	46.2
5	0.023275	99.55	41.5
6	0.0219	99.57	40.0

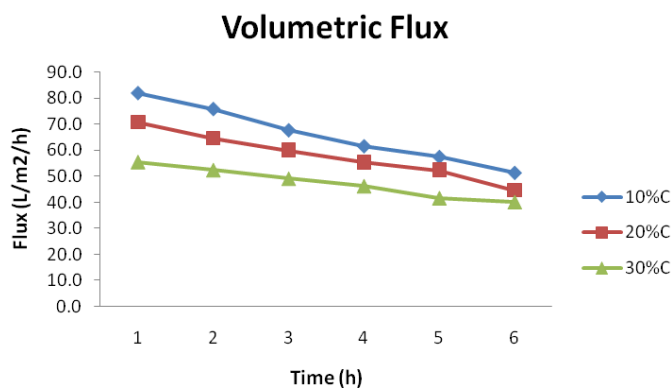


Fig. 10 Volumetric fluxes through 10% activated carbon, 20% activated carbon and 30% activated carbon incorporated polysulfone membranes

As shown in Fig. 10, under a constant operation pressure of 100 psi, the NF permeation flux is gradually decreased from $82 \text{ Lm}^{-2}\text{h}^{-1}$ to a pseudo-constant value of about $40 \text{ Lm}^{-2}\text{h}^{-1}$ as the activated carbon adding amount is increased from 10% to 30%. It is proposed that activated carbon in the feed would deposit or adsorb on the membrane surface, forming a activated carbon filter cake layer and consequently causing a drop of the permeation flux (Tomaszewska and Mozia 2002).

3.8 Effect of activated carbon adding amount on rejection

The rejection of 200 mg/L concentrated solutions of Congo red at 100 psi (689.42 kPa) as a function of permeation time depicted in Fig. 11 indicated higher rejection of Congo red (99.57%) through 30% activated carbon incorporated membrane. The rejection of solute by nanofiltration membranes is well described by solute-diffusion model primarily governed by the interaction of solute with the membrane material (Vito and Punzi 1990). The organic solutes rejection is depends on physicochemical characteristics of the solutes together with solute-membrane contacts as steric hindrance, electrostatic relations, hydrophobic-hydrophobic/adsorptive connections etc., and operating circumstances as trans-membrane pressure, feed concentration, time, recovery ratio etc. (Mulder 1997). On the basis of solute diffusion model of membrane transport, higher contact involving membrane material and solute at the membrane surface facilitates the diffusion of the solute throughout membrane while in synchronization to pore flow model the higher interaction stuck between membrane and solute hinders the solute transport (Higuchi *et al.* 1994). The 30% activated carbon incorporated membrane exhibited maximum solute rejection and 10% activated carbon incorporated membrane minimum. The primary factors influences the rejection performance of composite membrane are membrane chemistry and morphology and composite conditions. The composition of selective layer (membrane chemistry) solely depends on the concentration of activated carbon and an appropriate composition yield optimum selectivity and flux. The defect free selective layer exhibits high solute rejection is well known and hence because of 30% activated carbon incorporation this membrane shows good effect. Minimum rejection by 10% activated carbon incorporated membrane indicates defective layer might be due to inappropriate concentration of carbon and resultant selective layer exhibited inferior rejection and flux properties.

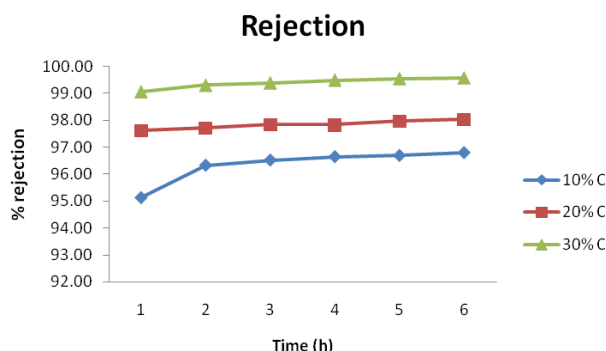


Fig. 11 Rejection (%) of Congo red dye through 10% activated carbon, 20% activated carbon and 30% activated carbon incorporated polysulfone membranes

Table 3 Dye removal through membrane process

Membrane	Dyes	Removal (%)	Condition	Reference (s)
NF 200, NF270	Everzol Black, Everzol Blue, Everzol Red	> 90	Initial dye concentration: 600 mg L ⁻¹ , pressure: 3-12 bar	(Aouni <i>et al.</i> 2012)
PMIA	Eriochrome Black T	> 99	Initial dye concentration: 1 g L ⁻¹ , pressure: 0.4 MPa, 1 g L ⁻¹ NaCl	(Huang and Zhang 2011)
Acrylic grafted polysulfone	9 textile dyes	86–99	Initial dye concentration: 50 mg L ⁻¹	(Amini <i>et al.</i> 2011)
CMCNa/PP thin film composite (700 Da)	Sunset Yellow Methyl blue Congo Red	82.2 99.7 99.9	Initial dye concentration: 100 mg L ⁻¹ , pH: 6.8, pressure: 0.8 bar, flux: 40-55.4 L m ⁻² h ⁻¹	(Yu <i>et al.</i> 2012)
Polysulfone–polyamide thin film	Reactive Black 5	60-97	Initial dye concentration: 0.4-2 g L ⁻¹ pressure: 5-25 psi	(Maurya <i>et al.</i> 2012)
UV grafting on sPPSU (1627 1674 Da)	Safranin O, Orange II	99.9 86.76	Initial dye concentration: 50 mg L ⁻¹ , 30 min, pressure: 5 bar	(Zhong <i>et al.</i> 2012)
30% Activated carbon incorporated polysulfone membrane	Congo red	99.57	Initial dye concentration: 200 mg L ⁻¹ , 6 h, pressure: 100 psi, flux: 40-55.4 L m ⁻² h ⁻¹	This study

The rejection data through different membranes were obtained and shown in Fig. 11. The experiments were conducted using the concentration of 10, 20, and 30% of activated carbon incorporated polysulfone membranes. The real rejection remained always greater than 95% for the entire membranes. As the activated carbon percentage increased, the osmotic pressure would in turn decrease which would increase the driving force for the rejection. As a result of this, the observed rejection increased with increase in concentration of activated carbon while the real rejection increased up to 99.57 % for 200 mg/L conge red dye.

Comparative data for the dye removal through polymeric membrane process in this study and in the literature are listed in Table 3. While taking into consideration the data shown in Table 2 the former data and present work results its clearly found that the activated carbon incorporated polysulfone membranes prepared after addition of 30% activated carbon shows very high removal (%) of Congo red and have good water flux, 99.57% and 40-55.4 Lm⁻² h⁻¹ respectively.

4. Conclusions

Activated carbon incorporated polysulfone membrane application for dye separation was reported in this work. Membrane modification using activated carbon was successfully carried out to make them more effectual and less prone to agglomeration. All the prepared membranes were comprehensively characterized to quantify the intrinsic properties. It was found out that addition of 30% activated carbon enhanced the rejection performance of the membrane. Water permeation performance of the composite membranes was tested on the lab scale unit to study the effect of percentage loading of activated carbon on the water flux and dye rejection of the membranes. It was found that the addition of 30% activated carbon in membrane matrix decreases the water flux and increases CR rejection. Maximum water flux 82 Lm⁻²h⁻¹ and a rejection 99.57 were obtained in this present study. To better understand the impact of this work, water flux and dye rejection obtained here is compared with various types of membranes and the results are summarized in Table 3. Accumulated data from literature (Table 3) indicates that incorporation of activated carbon in the PSf NF membrane results in superlative water flux and dye rejection. As a result more that 99% Congo red dye rejection was found by using 30% activated carbon incorporated polysulfone composite membrane.

References

- Ahmed, M.J. (2016), "Application of agricultural based activated carbons by microwave and conventional activations for basic dye adsorption: Review", *J. Environ. Chem. Eng.*, **4**(1), 89-99.
- Ahmad, A., Mohd-Setapar, S.H., Chuong, C.S., Khatoon, A., Wani, W.A., Kumar, R. and Rafatullah, M. (2015), "Recent advances in new generation dye removal technologies: Novel search for approaches to reprocess wastewater", *RSC Adv.*, **5**(39), 30801-30818.
- Amini, M., Arami, M., Mahmoodi, N.M. and Akbari, A. (2011), "Dye removal from colored textile wastewater using acrylic grafted nanomembrane", *Desalination*, **267**(1), 107-113.
- Aouni, A., Fersi, C., Cuartas-Urbe, B., Bes-Pa, A., Alcaina-Miranda, M.I. and Dhabbi, M. (2012), "Reactive dyes rejection and textile effluent treatment study using ultrafiltration and nanofiltration processes", *Desalination*, **297**, 87-96.
- Banat, F. and Al-Bastaki, N. (2004), "Treating dye wastewater by an integrated process of adsorption using activated carbon and ultrafiltration", *Desalination*, **170**(1), 69-75.
- Bhatt, D.R., Maheria, K.C. and Parikh, J. (2015), "Enhanced separation of toxic Blue BG dye by cloud point extraction with IL as an additive: Effect of parameters, solubilization isotherm and evaluation of thermodynamics and design parameters", *J. Environ. Chem. Eng.*, **3**(2), 1365-1371.
- Blatt, W.F. and David, A. (1970), *Membrane Science & Technology*, (J.E. Flynn Ed.), New York, NY, USA, pp. 47-97.
- Choi, W., Bae, H., Ingole, P.G., Lee, H.K., Kwak, S.J., Jeong, N.J., Park, S.C., Kim, J.H., Lee, J. and Park, C.H. (2015), "Solid-salt pressure-retarded osmosis with exothermic dissolution energy for sustainable electricity production", *Membr. Water Treat., Int. J.*, **6**(2), 113-126.
- Demirbas, A. (2009), "Agricultural based activated carbons for the removal of dyes from aqueous solutions:

- A review”, *J. Hazard. Mater.*, **167**(1-3), 1-9.
- Dias, J.M., Alvim-Ferraz, M.C.M., Almeida, M.F., Rivera-Utrilla, J. and Sánchez-Polo, M. (2007), “Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review”, *J. Environ. Managem.*, **85**(4), 833-846.
- El Qada, E.N., Allen, S.J. and Walker, G.M. (2007), “Kinetic modeling of the adsorption of basic dyes onto steam-activated bituminous coal”, *Ind. Eng. Chem. Res.*, **46**(14), 4764-4771.
- Esfandiari, A., Kaghazchi, T. and Soleimani, M. (2012), “Preparation and evaluation of activated carbons obtained by physical activation of polyethyleneterephthalate (PET) wastes”, *J. Taiwan Inst. Chem. Eng.*, **43**(4), 631-637.
- Georgin, J., Dotto, G.L., Mazutti, M.A. and Foletto, E.L. (2016), “Preparation of activated carbon from peanut shell by conventional pyrolysis and microwave irradiation-pyrolysis to remove organic dyes from aqueous solutions”, *J. Environ. Chem. Eng.*, **4**(1), 266-275.
- Hagmeyer, G. and Gimbel, R. (1999), “Modelling the rejection of nanofiltration membranes using zeta potential measurements”, *Sep. Purif. Technol.*, **15**(1), 19-30.
- Han, M.J. and Nam, S.T. (2002), “Thermodynamic and rheological variation in polysulfone solution by PVP and its effect in the preparation of phase inversion membrane”, *J. Membr. Sci.*, **202**(1-2), 55-61.
- Heibati, B., Rodriguez-Couto, S., Amrane, A., Rafatullah, M., Hawari, A. and Al-Ghouti, M.A. (2014), “Uptake of Reactive Black 5 by pumice and walnut activated carbon: Chemistry and adsorption mechanisms”, *J. Ind. Eng. Chem.*, **20**(5), 2939-2947.
- Higuchi, A., Hara, M., Horiuchi, T. and Nakagawa, T. (1994), “Optical resolution of amino acids by ultrafiltration membranes containing serum albumin”, *J. Membr. Sci.*, **93**(2), 157-164.
- Huang, J. and Zhang, K. (2011), “The high flux poly (m-phenylene isophthalamide) nanofiltration membrane for dye purification and desalination”, *Desalination*, **282**, 19-26.
- Ingole, P.G. and Ingole, N.P. (2014), “Methods for separation of organic and pharmaceutical compounds by different polymer materials”, *Korean J. Chem. Eng.*, **31**(12), 2109-2123.
- Ingole, P.G., Bajaj, H.C. and Singh, K. (2012), “Optical resolution of racemic lysine monohydrochloride by novel enantioselective thin film composite membrane”, *Desalination*, **305**, 54-63.
- Ingole, P.G., Bajaj, H.C. and Singh, K. (2013a), “Preparation and performance evaluation of enantioselective polymer composite materials”, *RSC Advances*, **3**(11), 3667-3676.
- Ingole, P.G., Bajaj, H.C. and Singh, K. (2013b), “Synthesis of solid enantioselective macromer of trimesic acid for the enantiomeric separation of chiral alcohols”, *Adv. Mater. Res.*, **2**(1), 51-64.
- Ingole, P.G., Bajaj, H.C. and Singh, K. (2014a), “Membrane separation processes: Optical resolution of lysine and asparagine amino acids”, *Desalination*, **343**, 75-81.
- Ingole, P.G., Choi, W., Kim, K.H., Park, C.H., Choi, W.K. and Lee, H.K. (2014b), “Synthesis, characterization and surface modification of PES hollow fiber membrane support with polydopamine and thin film composite for energy generation”, *Chem. Eng. J.*, **243**, 137-146.
- Jain, R. and Sikarwar, S. (2008), “Removal of hazardous dye Congo red from waste material”, *J. Hazard. Mater.*, **152**(3), 942-948.
- Johns, M.M., Marshall, W.E. and Toles, C.A. (1999), “The effect of activation method on the properties of pecan shell-activated carbons”, *J. Chem. Technol. Biotechnol.*, **74**(11), 1037-1044.
- Kim, J.H. and Lee, K.H. (1998), “Effect of PEG additive on membrane formation by phase inversion”, *J. Membr. Sci.*, **138**(2), 153-163.
- Kondru, A.K., Kumar, P. and Chand, S. (2009), “Catalytic wet peroxide oxidation of azo dye (Congo red) using modified Y zeolite as catalyst”, *J. Hazard. Mater.*, **166**(1), 342-347.
- Lee, J.W., Choi, S.P., Thiruvenkatachari, R., Shim, W.G. and Moon, H. (2006), “Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes”, *Dyes Pigm.*, **69**(3), 196-203.
- Li, J., Vergne, M.J., Mowles, E.D., Zhong, W.H., Hercules, D.M. and Lukehart, C.M. (2005), “Surface functionalization and characterization of graphitic carbon nanofibers (GCNFs)”, *Carbon.*, **43**(14), 2883-2893.
- Liu, Y., Koops, G.H. and Strathmann, H. (2003), “Characterization of morphology controlled

- polyethersulfone hollow fiber membranes by the addition of polyethylene glycol to the solution and bore liquid solution”, *J. Membr. Sci.*, **223**(1-2), 187-199.
- Malik, R., Ramteke, D.S. and Wate, S.R. (2007), “Adsorption of malachite green on groundnut shell waste based powdered activated carbon”, *Waste Manage.*, **27**(9), 1129-1138.
- Maurya, S.K., Parashuram, K., Singh, P.S., Ray, P. and Reddy, A.V.R. (2012), “Preparation of polysulfone–polyamide thin film composite hollow fiber nanofiltration membranes and their performance in the treatment of aqueous dye solutions”, *Desalination*, **304**, 11-19.
- Mohan, D., Singh, K.P., Singh, G. and Kumar, K. (2002), “Removal of dyes from wastewater using fly ash, a low-cost adsorbent”, *Ind. Eng. Chem. Res.*, **41**(15), 3688-3695.
- Mui, E.L.K., Cheung, W.H., Valix, M. and McKay, G. (2010), “Mesoporous activated carbon from waste tyre rubber for dye removal from effluents”, *Micro. Meso. Mater.*, **130**(1-3), 287-294.
- Mulder, M. (1997), *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, pp. 123-129.
- Panda, S.R. and De, S. (2013), “Role of polyethylene glycol with different solvents for tailor-made polysulfone membranes”, *J. Polym. Res.*, **20**(7), 179-195.
- Pandit, P. and Basu, S. (2004), “Dye and solvent recovery in solvent extraction using reverse micelles for the removal of ionic dyes”, *Ind. Eng. Chem. Res.*, **43**(24), 7861-7864.
- Purkait, M.K., Maiti, A., DasGupta, S. and De, S. (2007), “Removal of Congo red using activated carbon and its regeneration”, *J. Hazard. Mater.* **145**(1-2), 287-295.
- Rafatullah, M., Ahmad, T., Ghazali, A., Sulaiman, O., Danish, M. and Hashim, R. (2013), “Oil Palm Biomass as a Precursor of Activated Carbons: A Review”, *Critical Rev. Environ. Sci. Technol.*, **43**(11), 1117-1161.
- Rambabu, N., Azargohar, R., Dalai, A.K. and Adjaye, J. (2013), “Evaluation and comparison of enrichment efficiency of physical/chemical activations and functionalized activated carbons derived from fluid petroleum coke for environmental applications”, *Fuel Process. Technol.*, **106**, 501-510.
- Reinholdt, M.X., Kaliaguine, S. and Che, R. (2011), “Silicalite-1/SPEEK composite membranes: influence of the zeolite particles loading or size on proton conductivity and water uptake”, *New J. Chem.*, **35**(11), 2573-2583.
- Rivera-Utrilla, J., Sánchez-Polo, M., Gómez-Serrano, V., Álvarez, P.M., Alvim-Ferraz, M.C.M. and Dias, J.M. (2011), “Activated carbon modifications to enhance its water treatment applications. An overview”, *J. Hazard. Mater.*, **187**(1-3), 1-23.
- Sawant, S.Y., Somani, R.S., Panda, A.B. and Bajaj, H.C. (2013a), “Formation and characterization of onions shaped carbon soot from plastic wastes”, *Mat. Let.*, **94**, 132-135.
- Sawant, S.Y., Somani, R.S., Panda, A.B. and Bajaj, H.C. (2013b), “Utilization of plastic wastes for synthesis of carbon microspheres and their use as a template for nanocrystalline copper(ii) oxide hollow spheres”, *ACS Sustainable Chem. Eng.*, **1**(11), 1390-1397.
- Sawant, S.Y., Somani, R.S., Sharma, S.S. and Bajaj, H.C. (2014), “Solid-state dechlorination pathway for the synthesis of few layered functionalized carbon nanosheets and their greenhouse gas adsorptivity over CO and N₂”, *Carbon*, **68**, 210-220.
- Sawant, S.Y., Somani, R.S., Cho, M.H. and Bajaj, H.C. (2015), “A low temperature bottom-up approach for the synthesis of few layered graphene nanosheets via C–C bond formation using a modified Ullmann reaction”, *RSC Adv.*, **5**(58), 46589-46597.
- Sharma, N. and Purkait, M.K. (2016), “Racemic and enantiomeric effect of tartaric acid on the hydrophilicity of polysulfone membrane”, *Membr. Water Treat., Int. J.*, **7**(3), 257-275.
- Shao, M.W., Wang, D.B., Yu, G.H., Hu, B., Yu, W.C. and Qian, Y.T. (2004), “The synthesis of carbon nanotubes at low temperature via carbon suboxide disproportionation”, *Carbon*, **42**(1), 183-185.
- Tomaszewska, M. and Mozia, S. (2002), “Removal of organic matter from water by PAC/UF system”, *Water Res.*, **36**(16), 4137-4143.
- Tuinstra, F. and Koenig, J.L. (1970), “Raman spectrum of graphite”, *J. Chem. Phys.*, **53**, 1126-1130.
- Vito, L. and Punzi, V.L. (1990), “A comparison of solute rejection models in RO membrane”, *Ind. Eng. Chem. Res.*, **29**, 259-263.
- Xu, Y. and Lebrun, R.E. (1999), “Comparison of nanofiltration properties of two membranes using

- electrolyte and non-electrolyte solutes”, *Desalination*, **122**(1), 95-106.
- Yip, N.Y., Tiraferri, A., Phillip, W.A., Schiffman, J.D. and Elimelech, M. (2010), “High performance thin-film composite forward osmosis membrane”, *Environ. Sci. Technol.*, **44**(10), 3812-3818.
- Yu, S., Chen, Z., Cheng, Q., Lu, Z., Liu, M. and Gao, C. (2012), “Application of thin-film composite hollow fiber membrane to submerged nanofiltration of anionic dye aqueous solutions”, *Sep. Purif. Technol.*, **88**, 121-129.
- Yue, Z.R., Mangun, C.L. and Economy, J. (2004), “Characterization of surface chemistry and pore structure of H₃PO₄-activated poly(vinyl alcohol) coated fiberglass”, *Carbon*, **42**(10), 1973-1982.
- Yun, S.H., Ingole, P.G., Choi, W.K., Kim, J.H. and Lee, H.K. (2015), “Synthesis of cross-linked amides and esters as thin film composite membrane materials yields permeable and selective material for water vapor/gas separation”, *J. Mat. Chem. A*, **3**(15), 7888-7899
- Zheng, L.L., Su, Y.L., Wang, L.J. and Jiang, Z.Y. (2009), “Adsorption and recovery of methylene blue from aqueous solution through ultrafiltration technique”, *Sep. Purif. Technol.*, **68**(2), 244-249.
- Zhong, P.S., Widjojo, N., Chung, T.S., Weber, M. and Maletzko, C. (2012), “Positively charged nanofiltration (NF) membranes via UV grafting on sulfonated polyphenylenesulfone (sPPSU) for effective removal of textile dyes from wastewater”, *J. Membr. Sci.*, **417-418**, 52-60.

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