



# Influence of bentonite in polymer membranes for effective treatment of car wash effluent to protect the ecosystem



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## ABSTRACT

In this study, modified polyethersulfone (PES) and cellulose acetate (CA) membranes were used in the treatment of car wash effluent using ultrafiltration. Hydrophilic sulfonated poly ether ether ketone (SPEEK) and bentonite as nanoclay were used as additives for the PES and CA membrane modification. Performances of modified membranes were compared with commercial PES membrane with 10 kDa molecular weight cut off (MWCO). The influencing parameters like stirrer speed (250–750 rpm) and transmembrane pressure (100–600 kPa) (TMP) were varied and their effects were studied as a function of flux. In the treatment of car wash effluent, a higher permeate flux of 52.3 L/m<sup>2</sup> h was obtained for modified CA membrane at TMP of 400 kPa and stirrer speed of 750 rpm. In comparison with modified PES membrane and commercial PES membrane, modified CA membranes showed better performance in terms of flux and flux recovery ratio. The highest COD removal (60%) was obtained for modified CA membrane and a lowest COD removal (47%) was observed for commercial PES membrane. The modified membranes were better at removing COD, turbidity and maintained more stable flux than commercial PES membrane, suggesting they will provide better economic performance in car wash effluent reclamation.

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## 1. Introduction

In recent years car washing has attained a great importance in human society in order to achieve better vehicle performance. Declining water resources across the globe is forcing the policy makers to impose stringent regulations on the usage of fresh water. A majority of countries have introduced a number of laws on waste water recycling associated with car washing (Dunn and Bush, 2001; Al-Odwan et al., 2007). In Netherlands and Scandinavian countries 60–70 L/car is the maximum allowable fresh water consumption (Boussu et al., 2007). A recycle of 80% car wash effluent is compulsory in Germany and Austria. The Australian commission has established a maximum limit of 100 L fresh water per car.

Car wash process constitutes the following steps which involves mainly (i) application of degreasing agent all over the surface of the automobile to desorb the dirt and grit accumulated on surface of the automobile. (ii) Addition of acid and alkaline cleaners to solubilize the dirt. (iii) Finally, a coating is provided to add

gloss to the surface and protect it against from any abrasion (Páxeus, 1996). Car wash discharge effluent has a varied source of pollutants which includes oil/grease, detergents/surfactants, degreasers, volatile organic and sulfur compounds, many phosphorous and nitrogen compounds, plasticizers, brake dust from rubber linings, various heavy metals (Flick, 1999). These pollutants are lethal to humans and aquatic organisms, its effects are clearly described in Table 1. Therefore, treatment of such effluent is essential to protect the ecosystem. Car washing requires a large amount of water for effectively removing pollutants. The depleting fresh water sources and increase in salinity of the ground water, strict regulations on the effluent discharge are major constraints for car washing in India (CPHEEO, 2012). However, in current scenario car wash industries do not have efficient treatment methods to reclaim car wash water.

Conventional treatment methods such as sand filtration, ozonation (Zaneti et al., 2011), electrochemical oxidation (Panizza and Cerisola, 2010) and biological treatments (Jefferson et al., (2004)) are widely used for the treatment of car wash effluent. Nowadays, biological treatment method was found to be very efficient in treatment of various effluents (municipal sewage, dairy waste) (Demirel et al., 2005) but it fails with car wash effluent due to the occurrence of mixed pollutants (Jefferson et al., 2004). Moreover ozonation leads to the formation of undesirable toxic products

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**Table 1**  
Toxic effects of car wash effluents.

Source of pollutants	Effects	Reference
Oil/Emulsions	<ul style="list-style-type: none"> <li>Adversely affect aesthetic merit, water transparency and Dissolved Oxygen (DO) content in the water.</li> </ul>	(Foo and Hameed, 2010)
Detergents/Surfactants	<ul style="list-style-type: none"> <li>A potential problem lies in the formation of suds and the probability of existence of nutrients such as phosphorous and nitrogen. Suds could persist in lakes and streams and the nutrients could create an algal bloom which may lead to eutrophication</li> <li>Surfactants create a bacterial population rise, transmitting through the food chain to protozoa, which are more sensitive to car wash toxins</li> <li>All detergents will destroy fish mucus membranes and gills to some degree. The gills may lose natural oils, interrupting oxygen transfer</li> </ul>	(Wang et al., 2009) (Verma et al., 2012) (Almeida et al., 2010)
Heavy metals (Lead, Cadmium and chromium)	<ul style="list-style-type: none"> <li>Lead has been shown to have effects on haemoglobin synthesis and anaemia has been observed in children at lead blood levels above 40 µg/dl. Cadmium interacts with the calcium metabolism of animals. In fish it causes lack of calcium (hypocalcaemia). Chromium can make fish more susceptible to infection; high concentrations can damage and/or accumulate in various fish tissues and in invertebrates such as snails and worms.</li> </ul>	(Karvelas et al., 2003; Malik, 2004)

such as aldehydes, ketones and carboxylic acids and require high investmental cost (Metcalf and Eddy, 2006). Lately, membrane technology has been considered as a promising technology in treatment of effluents from various industries such as paper (Saranya et al., 2014), textile (Srivastava et al., 2011), metal ion removal (Arthanareeswaran et al., 2007b; Arthanareeswaran and Thanikaivelan, 2012). The main advantage of membrane separation process is low cost, easy to scale up, low footprint and less energy consumption (Chelme-Ayala et al., 2009) though it suffers from limitations such as fouling and concentration polarization. Fouling is the phenomenon of adsorption and build up of solute particles on pores which cause concentration polarization on the membrane surface. Fouling in turn tends to shorten the life span of the membrane (Hilal et al., 2005).

Jönsson and Jönsson (1995) compared the UF and NF membrane as a function of flux and COD removal for the various car washing chemical solutions. Hamada et al. adopted hybrid methodology to effectively treat the car wash effluents. They observed that CA hollow fiber membrane flux performance rate was improved significantly with the pretreatment of feed solution using multiblended flocculating agent (Hamada and Miyazaki, 2004). Lau et al. (2013) compared the UF and NF membrane performance in the removal of COD, turbidity of the car wash effluent.

Optimization of process parameters and modification of pristine membranes are the general methods adopted to reduce the fouling in membrane separation processes. The process parameters such as transmembrane pressure (TMP), stirring speed and cross flow velocity has a significant role in improving the membrane performance. Mohammadi et al. (2003) studied the effects of transmembrane pressure on membrane fouling for the desalination of sea water. They inferred that fouling was increased with increase in TMP. Sondhi et al. (2000) investigated the effect of operating parameters on the treatment of chromium hydroxide suspension using porous alumina ceramic membranes. Azmi and Yunos (2014) found that permeate flux increased with increase in stirrer speed for treating palm oil using ultrafiltration membrane.

Studies on utilization of modified membrane for the treatment of car wash effluent is limited. In our earlier research, PES and CA membrane were fabricated using hydrophilic polymer sulfonated poly ether ether ketone (SPEEK) and inorganic nanoclay as bentonite to effectively treat dairy wastewater (Pagidi et al., in press). Further, above two modified membranes were compared with commercial PES 10 kDa membrane as a function of the removal

and flux performance of car wash effluent. Moreover, the influence of process parameters such as transmembrane pressure and stirrer speed on flux performance was also studied.

## 2. Materials and methods

### 2.1. Materials

Commercial grade polyethersulfone (PES) (Veradale 3000), Cellulose acetate (CA) were procured from M/s. Solvay Chemicals, Mumbai, India Limited and M/s. Mysore Acetate and Chemicals Company, India Limited. Synthesis of Sulfonated poly ether ether ketone (SPEEK) was followed as per earlier procedure adopted by Arthanareeswaran et al. (2004). N-methyl Pyrrolidone (NMP) and Sodium Lauryl sulfate (SLS) were purchased from M/s. Qualigens fine chemicals, India Limited. Nano-clay-Bentonite was purchased from M/s. Sigma-Aldrich limited. Commercial PES10kDa membrane was purchased from M/s. Orelis Environmental SAS, France. Double distilled (DD) water was used throughout the study.

### 2.2. Membrane preparation

PES and CA were used as base polymers and the membranes were fabricated using wet phase inversion technique. The protocol for the membrane fabrication was followed by Pagidi et al. (in press) and the characterization data for both SPEEK and bentonite was also provided in the earlier publication. The chosen additives are SPEEK and bentonite, NMP was used as a solvent. The detailed composition of the fabricated membranes along with their labeling is given in Table 3. Base polymer and nanoclay were dried in a hot air oven at the temperature of 60° C for 8 h. Initially 0.5 wt% of bentonite was dissolved in NMP for 2 h followed by ultrasonication. Thereafter SPEEK was added onto the casting dope solution and allowed for stirring until a clear homogeneous solution was attained. Next to that dried base polymer (PES/CA) was added to the casting dope and blended at 50° C for a period of 24 h. To attain homogeneity, casting dope solution was again ultrasonicated for 1 h. Then dope solution was casted on a smooth glass plate with the help of thin film applicator followed by evaporation for a period of 30 s. Afterwards, the glass plate was immersed in a nonsolvent water coagulation bath for 24 h at 10 °C. Later, synthesized membranes were stored in 0.1% formalin solution.

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