**RESPONSE TO REVIEWERS**

**Manuscript No:** 6794-35829-2-RV

**Title:** "Synthesis of Crosslinked PVA-Flyash Supported Composite Membrane for Phenol Removal from Aqueous Solution"

Authors would like to thank the reviewers and editors for evaluation of our manuscript and providing the valuable and useful comments to improve the quality of manuscript. Authors have revised the manuscript as per the reviewer’s comment. The changes made in the manuscript are highlighted with yellow mark. The detailed point wise response to each reviewer is given below and the same have been considered for revising the manuscript.

**Reviewer # A**

**Q1:** Line 36 inadequate 9 and 12, not membrane filtration processes. Look for: Desalination 245 (2009) 680–686, IPCBEE 83 (2015) DOI: 10.7763/IPCBEE.2015. V83. 31, Desalination 163 (2004) 287-296.

**Author’s response:** Following the reviewer’s suggestion, reference 9 and 12 is removed. In place of reference 9 and 12, the following reference is added and cited for membrane filtration processes in the revised manuscript (Page No: 02 & Line No: 36).

**Reference No 9:** A. Bodalo, E. Gomez, A.M. Hidalgo, M. Gomez, M.D. Murcia, I. Lopez, *Desalination.* 245 (2009) 680.

**Q2:** Line 59 reference 23 patent about tissue, there is more appropriate and newer reference, like Desalination 287 (2012) 35–40.

**Author’s Response**: Following the reviewer’s suggestion, reference 23 is removed. In place of reference 23, the following reference is added and cited in the revised manuscript (Page No: 02 & Line No: 59).

**Reference No 22:** A.L. Ahmad, N.M. Yusuf, B.S. Ooi, *Desalination*. **287** (2012) 35

**Q3:** Line 60 in the literature need references like: Progress in Polymer Science 34 (2009) 969–981, European Polymer Journal 44 (2008) 4098–4107.

**Author’s Response:** Following the reviewer’s suggestion, the following new references are added and cited in the revised manuscript (Page No: 02 & Line No: 60).

**Reference No 23:** B. Bolto, T. Tran, M. Hoang, Z. Xie, *Prog. Polym. Sci.* **34** (2009) 969

**Reference No 24:** A. Hasimi, A. Stavropoulou, K.G. Papadokostaki, M. Sanopoulou, *Eur. Polym. J.* **44** (2008) 4098

**Q4:** Line 61 references 24, 27 not crosslinking

**Author’s Response:** Following the reviewer’s suggestion, authors have checked the references of 24, 27 (Revised Reference: 25 & 28). It has been found that glutaraldehyde and maleic anhydride was used as crosslinking agents with PVA which is mentioned in their experimental section. Hence, authors have considered these references (Revised Reference: 25 & 28) in addition with one more suitable reference 29 in the revised manuscript which explains about formaldehyde crosslinking with PVA.

**Reference No 29:** G. Bourne, M.S. Buiser, T.V Casey, S. Keenan, J.L. Lanphere, J. Li, E.P. Mckenna, Z. Minasian, D. Rao, US 7,611,542 B2, (2009)

**Q5:** Line 64 references 3, 6, 30 not PVA membrane

**Author’s Response:** Following the reviewer’s suggestion, reference 3, 6 & 30 cited in the page no: 03 & line no: 64 (revised line No: 65) are removed from the revised manuscript.

**Q6:** Line 300 dead link replace with <https://archive.epa.gov/teach/web/pdf/benz_summary.pdf>

**Author’s Response:** Following the reviewer’s suggestion, <http://www.epa.gov/iris/toxreview/0276-tr.pdf> is replaced by <https://archive.epa.gov/teach/web/pdf/benz_summary.pdf> link in the revised manuscript (Page No: 15 & Line No: 310-311).

**Q7:** Line 327 delete -12

**Author’s Response:** Following the reviewer’s suggestion, 12 is deleted from reference and given as follows in the revised manuscript (Page No: 16 & Line No: 339).

**Reference No 25:** A. Higuchi, T.D. Lijima, [*Polymer*](http://www.sciencedirect.com/science/journal/00323861). **26** (1985) 1833

**Q8:** Line 339 change 81 to 87

**Author’s Response:** Following the reviewer’s suggestion, 81 is changed to 87 in the reference and given as follows in the revised manuscript (Page No: 16 & Line No: 351).

**Reference No 33:** K.J. Kim, A.G. Fanen, R. Ben-Aim, M.G. Liu, G. Jonsson, I.C.Tessaro, A.P. Broek, D. Bargeman, *J. Membr. Sci.* **87** (1994) 35

**Q9:** Line 102-103 Equation 1 is not in agreement with other authors or papers Look: Journal of Industrial and Engineering Chemistry 18 (2012) 1398–1405, International Journal of Hydrogen Energy 40 (2015) 1731-17322. Please supply reference for eq. in your paper and explain determination of Sw, or correct it.

**Author’s Response:** Authors are agreeing with the reviewer’s comment, usually the researchers follow the following standard equation for calculating the swelling degree which is also given in the Journal of Industrial and Engineering Chemistry 18 (2012) 1398–1405 and International Journal of Hydrogen Energy 40 (2015) 1731-17322.

where, Wd, Ww are the dry and wet weight of membrane.

However, in this study authors have considered only the swelling degree of polymeric active layer in terms of amount of crosslinking (Formaldehyde) added in the polymeric layer to increase the stability and mechanical strength of the active layer with support. Hence, swelling degree of composite membrane is subtracted by swelling of support (Sw) and the resulted expression is given as equation 1 in the revised manuscript.

Swelling degree of active layer (Sda) can be calculated as follow

where, Wcd and Wcw are the dry and wet weight of CM. Sw is the swelling degree of support in distilled water.

The swelling degree of support is calculated as per the following standard equation 17, 19, 27

(2)

Equation 2 is newly added in the revised manuscript for better understanding (Page No: 05 & Line No: 109).

**Reference 17:** S.Y. Hu, Y. Zhang, D. Lawless, X. Feng, *J. Membr. Sci.***417** (2012) 34

**Reference 19:** S.Y. Li, R. Srivastava, R.S. Parnas,*J. Membr. Sci.***363**(2010) 287

**Reference 27:** R. Rudra,V. Kumar, P.P. Kundu, *RSC Adv.***5** (2015) 83436

**Q10:** Line 233 is there any sorption or rejection from support? Did you made any experiment without PVA?

**Author’s Response:** Yes, we had tested the sorption capacity of support separately. But, it was found that the support has less than 20% sorption capacity of phenol.

**Q11:** Line 238 Sieving property is questionable since due to pore size prepared membranes are nanofiltration membranes, transport is due to diffusion and sorption not sieving. Thought on support of flyash and clay sieving is possible. Please explain!

**Author’s Response**: Authors agree with the reviewer’s comment about the sieving property of membranes. Generally, diffusion and sorption mechanism is reported for nanofiltration membranes by many researchers. Other than diffusion and sorption, some researchers have also reported the sieving mechanism of nanofiltration membrane.

For instance, Han et al., 2008 reported that there are two main reasons for sieving mechanism. First, the probability of the molecules finding the pore from the bulk solution would be affected by the sizes of both the molecule and pore. This is due to the ‘Steric Hindrance’ or due to some additional long-range interactions such as electrostatic repulsions between the charged molecule and charged wall (Debye layer repulsion) when both the pore wall and the molecule are charged.

Hence, authors have considered sieving mechanism which may also play a little role in addition with the sorption mechanism. The following reference is added to support the sieving mechanism in the revised manuscript (Page No: 11 & Line No: 250).

**Reference 35:** J. Han, J. Fu, R.B. Schoch, *Lab Chip.* **8** (2008) 23

**Q12:** Line 18 unusual value for pressure assumable because of conversion from psi

**Author’s Response:** Authors agree with the reviewer’s comment. During the experimentation psi values were considered for pressure measurement which was available in the pressure gauge. However, as per the journal format pressure values should be given in SI unit, hence the psi values are converted into kPa which shows unusual values. Reviewer’s suggestion will be carefully taken care in the future studies to provide the pressure data with proper scale.

**Q13:** Line 46 the object of concern change to object of interest or matter of interest

**Author’s Response:** Following the reviewer’s suggestion, the “object of concern” is changed to “matter of interest” and written as follows in the revised manuscript (Page No: 2 & Line No: 46).

*“The matter of interest in this study is the preparation of inexpensive polymeric TFCM and enhancement of its industrial applicability”.*

**Q14:** Line 51 instead of polymeric – different (polymer, ceramic, carbon tubes according to reference not only polymer)

**Author’s Response**: Following the reviewer’s suggestion, statement is corrected and rewritten as below in the revised manuscript (Page No: 2 & Line No: 50-52).

*“Some researchers have reported synthesis of CM using polyvinyl alcohol, cellulose acetate, polydimethylsiloxane, polysulfone etc. coated on different substrate (polymeric, ceramic, carbon nanotube etc.) with good separation efficiency”.*

**Q15:** Line 60-61 literature, among… Ionic crosslinker replace with aluminium acetylacetonate

**Author’s Response**: Following the reviewer’s suggestion, “ionic crosslinker” in the statement is replaced with “aluminium acetylacetonate” and rewritten as follows in revised manuscript (Page No: 3 & Line No: 61).

*“Among which, glutaraldehyde, maleic acid, aluminium acetylacetonate and formaldehyde are widely used”.*

**Q16:** Line 82 Table1. Table 1

**Author’s Response**: Following the reviewer’s suggestion, “Table1” is changed into Table 1. in the revised manuscript (Page No: 3 & Line No: 84).

**Q17:** Line 92 delete Fig 1, casting of polymer is not shown in picture. On picture number 19 is missing.

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Fig. 1. Schematic diagram of composite membrane synthesis and dead-end membrane filtration

**Author’s Response**: Following the reviewer’s suggestion, Fig. 1. is removed from the specified line and notation of 19 in Fig 1 is added and given in the revised manuscript (Page No: 4).

**Q18:** Line 114 Fig.1 (12-18)

**Author’s Response**: Following the reviewer’s suggestion, changes in the Figure citation is incorporated and given as follows in revised manuscript including number 19 of Fig. 1 for dead-end filtration setup (Page No: 5 & Line No: 120).

*“The schematic diagram of dead-end filtration setup is shown in the Fig.1 (12-19)”.*

**Q19:** Line 127 20kDa change to 20 kDa

**Author’s Response**: Following the reviewer’s suggestion, “20kDa” is changed into “20 kDa” in revised manuscript (Page No: 6 & Line No: 135).

**Q20:** Line 135 explanation for R, cf and cp is missing

**Author’s Response:** Following the reviewer’s suggestion, the terms R, Cf and Cp given in the equation 4 (revised equation 5) is explained and given as follows in revised manuscript (Page No: 6 & Line No: 139-141).

Percentage rejection (%R) was determined by following equation:



Where Cf and Cp are feed and permeate concentration, respectively.

**Q21:** Line 133 calculated instead of measured

**Author’s Response**: Following the reviewer’s suggestion, “measured” word in the statement is replaced by “calculated” and the line is rewritten as follows in revised manuscript (Page No: 6 & Line No: 142).

*“Average pore radius of membrane can be calculated by Guerout-Elford-Ferry relation given below”*

**Q22:** Line 155-156 equation 2 not 1

**Author’s Response**: Authors have crosschecked the equation 1 and 2. The equation 1 is for calculation of swelling degree in terms of water uptake whereas equation 2 (revised equation 3) denotes the flux through the membrane. Therefore, equation 1 mentioned in the suggested line for correction is given as it is without any changes in the revised manuscript (Page No: 7& Line No: 165-166).

**Q23:** Table 2 correct .0.8 and 0,06

**Author’s Response**: Following the reviewer’s suggestion, the given values of “.0.8 and 0,06” in Table 2 is corrected and rewritten as 0.8 and 0.06 in the revised manuscript (Page No: 7 & Table: 2).

**Q24:** Line 174, 253, 259 repetition: smaller pores became permeable!

**Author’s Response**: Following the reviewer’s suggestion, to avoid the repetitions of the specified line, line 174 and 259 is deleted in the revised manuscript.

**Q25:** Line 175 delete it

**Author’s Response**: Following the reviewer’s suggestion, Line 175 is deleted in revised manuscript.

**Q26:** Line 207 correct thathe

**Author’s Response**: Following the reviewer’s suggestion, the word “that the” in suggested line is corrected as “that the” in revised manuscript (Page No: 10 & Line No: 218) and given as follows:

*“It was found that the contact angle between water droplet and active layer of CMs increases in order of PF0<PF1<PF2< PF3<PF4<PF5”.*

**Q27:** Fig 5b and 6b unclear, put legend on side so bars could be higher.

**Author’s Response**: Following the reviewer’s suggestion, Fig. 5b and 6b is modified to clearly show the legend of Fig. 5b and 6b in the revised manuscript (Page No: 12 & 13).

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| --- |
| C:\Users\sys care info\Pictures\5b2.tif |
| Fig. 5b. Phenol rejection and flux profile for effect of feed phenol concentration with respect to time. |
| C:\Users\sys care info\Pictures\6b2.tif |
| Fig. 6b. Phenol rejection and flux profile for effect of pressure with respect to time. |

**Q28:** Line 247 delete

**Author’s Response**: Following the reviewer’s suggestion, line 247 is deleted in the revised manuscript.

**Q29:** Check the reference according to <https://www.shd-pub.org.rs/index.php/JSCS/announcement/view/11>

**Author’s Response**: Following the reviewer’s suggestion, formatting of all the references given in the manuscript is checked and corrected accordingly in the revised manuscript.

**Reviewer # B**

**Q1:** In Table 2 on page 7, pure water flux values were 202.37; 84.4; 47.99 and 5.56 Lm-2h-1. I would suggest instead 202.4 instead 202.37 and so on.

**Author’s Response**: Following the reviewer’s suggestion, decimal values of numerical are checked throughout the manuscript to avoid too many decimals. Also, decimal values in Table 2 are corrected in the revised manuscript (Page No: 7, Table 2).

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| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| TABLE 2. Physiochemical properties of composite membrane. | | | | | | | | |
| **Parameter** | | **Support** | **PF0** | **PF1** | **PF2** | **PF3** | **PF4** | **PF5** |
| Avg pore size (nm) | | 14 | 14 | 3.6 | 2.8 | 1.9 | **-** | **-** |
| Active layer thickness (mm) | | - | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| Pure water flux (Lm-2 h-1) | | 325 | 202.4 | 84.4 | 48 | 5.6 | 0 | 0 |
| Contact angle (°) | | - | 32.4 | 39.5 | 46.9 | 52 | 57.1 | 63.9 |
| Chemical stability (wt.loss%) | pH 2 | - | Not stable | 1.1 | 1.2 | 1.5 | 1.6 | 1.7 |
| pH 12 | - | Not stable | 0.18 | 0.11 | 0.35 | 0.06 | 0.06 |