Van der Waal's Interaction between Methylene Blue functional ($-SO_3^-$) and Zinc Oxide ($Zn(OH)^+$) in CTPP-ZnO Polyelectrolyte Membrane

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Abstract: ***In synthesis of zinc oxide impregnated-chitosan tripolyphosphate (CTPP) polyelectrolyte membrane, the concentration of tripolyphosphate (TPP) may varied, (0.5%, 1.0% & 1.5%) at pH 5.0, with chitosan to zinc oxide nanoparticle ratio is 8:1, 4:1 and 2:1, having specific wider pore radius of CTPP-ZnO membrane. The membrane performance test have applied by using of methylene blue solution with a 4ppm concentration is passed or diffused through the membrane under pressure controlled by valve in 10 bar. Where the addition of zinc oxide reported that the van der Waal's interaction between functional groups of methylene blue and ZnO nanoparticles mainly consider as the ionic bonding between the positively charged of zinc oxide ($Zn(OH)^+$) and negatively charged of methylene blue ($-SO_3^-$), which led to affect in hydrophilicity of polyelectrolyte membrane with high performance as to improve adsorbent or the antifouling performance in membrane surface.***

Keywords: Chitosan, tripolyphosphate, zinc oxide nanoparticles, membrane

1. Introduction

A membrane is a thin lining selective barrier which allow something to pass through but stop others. Such things may be molecules, ions or other small nanoparticles. Mostly, membrane are often used for purification, in process such as haemodialysis[1], biodiesel[2] and waste water purification[3], which on comparing with other waste- water treatment methods such as adsorption and coagulation, a membrane is effective because it saves time is continuous and to conserves energy, but some of antifouling in membrane based filtration process including bioreactor-membranes to microorganism's degraded contaminants aspect with minimize fouling in the filtration process as well as improving the efficiency of the membranes used[3]. Recent studies has been carried out the effort in to membrane synthesis from natural polymers, for example, the membranes made from polysaccharide such as cellulose[4] but ought chitosan based[5,6]. Chitosan is a one of the natural polymers which are prepared through deacetylation of chitin, usually sourced from shrimp or crab skin[7], and is often use to creat chitosan membranes crosslinked with tripolyphosphates to remove humic acid from water, resulting polyelectrolyte complex PEC-CTP membrane which can serve as a good adsorbent of metal compounds[8] and dye[9].

In current paper, we have been reported the chitosan crosslinked with tripolyphosphate as a complex polyelectrolyte membrane[10] made of CTP combined with zinc oxide nanoparticles, where a rapid developed ecofriendly ZnO inorganic nanoparticle, which are more reactive than at normal sized to potential for degrading pollutant by oxidizing-reducing based modified complex polyelectrolyte membrane with nanoparticles to reduced fouling effects in the membrane. The impregnation of nanoparticles into a membrane is expected to degrade pollutants trapped on the membrane surface with improved antifouling performance[11,12]. The pollutant use to test membrane performance in this study is methylene blue dye pigment[13]. It has high solubility in water, and so, in the fixation process a large amount of dye is lost with waste water. Another, one of the weakness of chitosan membrane is its instability in acid pH. To improve the stability of chitosan membrane, one possible method is to be crosslinking of chitosan with tripolyphosphates as a complex polyelectrolyte membranes for best performance. The structure of chitosan and tripolyphosphate in CTPP and predicted structure of there CTPP-ZnO membrane have shown in figure-1.

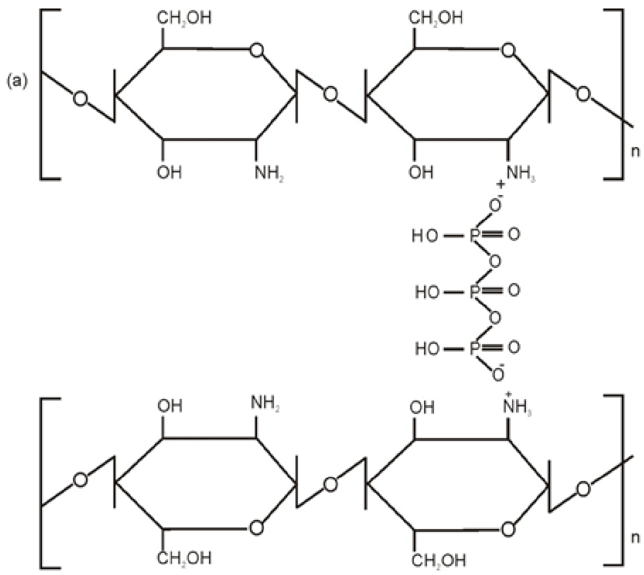

Fig. 1 (a) Chemical structure of cross - linking between chitosan and TPP in CTPP

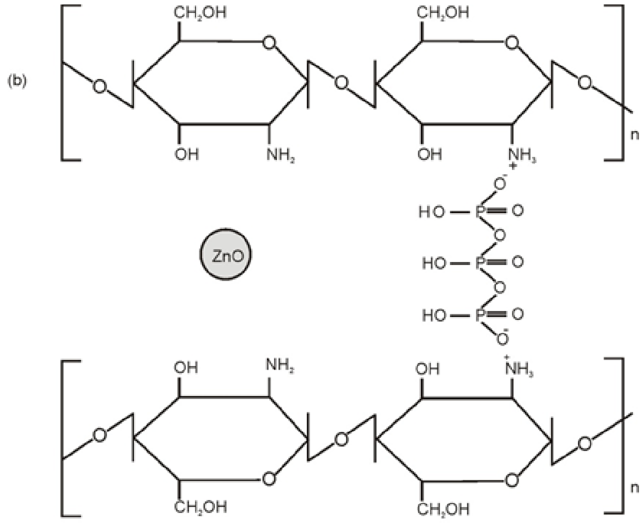

Fig. 1 (b) Prediction of structure of CTPP- Zinc oxide Molecules

2. Materials and Methods

In experimental procedures, the materials used in this study such as chitosan, sodium tripolyphosphate, acetic acid and ZnO nanoparticles (< 50nm in size) have industrial and laboratory grade. These experimental work which are adopted from the work described by Febriasari et al[14]. Firstly, chitosan (polysaccharide) is dissolved in about 2% CH_3COOH (acetic acid) with a ratio of 1:50, then stirred and heated at 60℃. After the chitosan solution is homogeneous, it is mixed with zinc oxide (ZnO) nanoparticles. The ratio of chitosan by weight to zinc oxide nanoparticles by weight are 2:1, 4:1 & 8:1, respectively, and solution is stirred at 1300rpm for 30 minutes. Once it is homogeneous, then sodium tripolyphosphate solution is added at 0.5%, 1% & 1.5% concentration variation (each at pH 4.5) until a clear suspension is formed. Then 50ml of the resulting solution have taken to be moulded in teflon moulds and oven-dried at 60℃, until a CTP-ZnO membrane film is formed.

The characterization and performance test of the CTPP and CTPP-ZnO membrane may performed by the instruments used in this study are a teflon membrane mould with 10cm diameter, a set of membrane performance test equipment as scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX), FTIR, surface pore size or particle size analysis by BET analyser (N_2 adsorption at 77.35K) equipment and water contact angle measurement as well as flux recovery ratio (FRR) for target compounds used as artificial waste in this study are methylene blue pigment which analysis by its performance on spectrophotometer UV-visible of wavelength.

3. Results and Discussion

In preparation of chitosan-TPP membrane the dominant polymer solution is chitosan and acetic acid which are added with sodium tripolyphosphate (TPP) with 0.5, 1.0 & 1.5% conc. variation at pH 5.0. Notable, in acedic pH, chitosan has in cation form, so it had an NH_3^+ group which could bind with anion TPP[15]. The figure-1 is an illustration of the bond between chitosan and TPP[16]. The chitosan membrane is cross linked to TPP which impregnated with zinc oxide nanoparticles. The mixing of chitosan-TPP with zinc oxide is performed at 1300 rpm until homogeneous. It is dried at 60℃ until a CTP-zinc oxide (ZnO) membrane film is formed.

The physco-chemical analysis measurement determines the comparison with wider average pore radius/volume and surface area of CTPP and CTPP membrane impregnated with zinc oxide nanoparticles in respect of flux recovery ratio (FRR) value (Table-1), based on membrane adsorption of nitrogen at 77.35K, where zinc oxide addition influence the pore radius (8:1, 4:1 and 2:1) of CTPP membranes. The water contact angle measurement is to evaluate the hydrophilicity of the membrane and performed by surface membrane during addition of tripolyphosphate and zinc oxide nanoparticles. The intermolecular bonding between membrane and water is conducted by van der Waal's forces. The presence of TPP and ZnO nanoparticles may inhibit the adsorption of water since they could obstruct the -OH (hydroxyl) and amine functional group of membrane.

Table 1: Physico-chemical data of chitosan-tripolyphosphate and chitosan-Tripolyphosphate membrane impregnated with zinc oxide nanoparticles

S.N.	Membrane (sample)	Average pore radius (10Å)	Total pore volume (10^{-2} cc/g)	BET surface area (m^2/g)	Water contact angle(°)	FRR value ($L.m^{-2}h^{-1}$)
1.	Chitosan	4.128	2.341	11.340	46	74.375 ± 0.04
2.	CTPP 0.5%	3.568	2.717	15.225	48	74.500 ± 0.02
3.	CTPP 1%	4.259	2.163	10.159	50	76.426 ± 0.03
4.	CTPP 1.5%	4.436	2.221	10.014	54	88.889 ± 0.02
5.	CTPP-ZnO (8:1)	4.671	1.956	08.375	64	89.333 ± 0.03
6.	CTPP-ZnO (4:1)	5.039	2.037	08.085	65	94.583 ± 0.02
7.	CTPP-ZnO (2:1)	4.683	2.347	10.021	66	95.769 ± 0.04

The membrane performance is demonstrated that, by using of methylene blue dye, where the methylene blue solution with a 4ppm concentration is passed through the membrane using membrane performance test equipments and transport membrane take place in reverse osmosis. Although, using of methylene blue dye may influence the pH on adsorption with their photocatalytic degradation activity also observed[17]. The feed solution are pumped through the membrane under controlled pressure by valve in 10 bar. The filtration is varied by measurement time. The water of methylene blue solution are diffused through the membrane since the CTP membranes are hydrophilic and methylene blue molecules are trapped in the membrane surface. The measured time (1, 2, 3, 4 and 5h) variable is chosen in order to evaluate the stability of flux permeate of the membrane transport. The flux decrease since the first minute of transport, this indicated that the fouling of methylene blue has appeared in the surface of membrane. The determination of antifouling performance test by calculating of flux recovery ratio (FRR) value[18], (Flux recovery ratio (%) = $J_{w2} \times 100/J_{w1}$)[19], where J_{w1} is flux value of the membrane when passed by the target compounds and J_{w2} is flux value after backwashing of the membrane by demineralized water. The zinc oxide nanoparticles may predicted to have capability degrading compound as methylene blue dye in membrane surface, where van der Waal's interaction mainly considered as the ionic bonding between negatively charged of methylene blue ($-SO_3^-$) and positively charged of zinc oxide as ($Zn(OH)^+$) form as well.

4. Conclusion

In conclusion, on the basis of finding results, we have been reported that the van der Waal's forces may interact between negatively charged methylene blue functional ($-SO_3^-$) as well as positively ZnO ($Zn(OH)^+$) in CTPP-ZnO polyelectrolyte membrane. In synthetic, the impregnated nanoparticles zinc oxide (ZnO) to chitosan are being crosslinked with tripolyphosphates (TPP) in CTPP-ZnO membrane which can influence the membrane surface where the pore radius increased by the addition of TPP with variation of particles percentage and ratio at about pH 5.0. The zinc oxide nanoparticles impregnation can affect membrane morphology, making the surface rougher, as well as it affect the hydrofilicity of the membrane surface, the more zinc oxide nanoparticles have the good performance test by using dye (methylene blue) pigment with a 4ppm concentration is diffused or passed through the membrane under pressure controlled by valve in 10 bar, which showed that the addition of zinc oxide nanoparticles in CTPP membrane is proven to improve antifouling performance in the membrane.

References

[1] W.I. Mortada, K.A. Nabieh, A.F. Donia, A.M. Ismail and I.M.M. Kenawy, *J.Trace Elem. Med. Biol.*, 36, 52,(2016)
[2] I.M. Atadashi, M.K. Aroua, A.R.A. Aziz and N.M.N. Sulaiman, *Appl. Energy*, 88, 4239,(2011)
[3] S. Judd, *Trends Biotechnol.*, 26, 109,(2008)
[4] F.M. Sukma and P.Z. Culfaz-Emecen, *J. Memb. Sci.*, 545, 329,(2017)
[5] A.A. Alshahrani, H. Al-Zoubi, L.D. Nghiem and M. Panhuis, *Desalination*,418,60,(2017)
[6] S.Tamburaci and F. Tihminlioglu, *Mater.Sci.Eng. C*, 80,222 (2017)
[7] H. Altaher, *J. Hazard. Mater*.,233-234, 97,(2012)
[8] M. Ahmad, K. Manzoor and S. Ikram, *Int. J. Biol. Macromol.*, 105,190(2017)
[9] C.C. dos Santos, R. Mouta, M.C.C. Junior and S.A.A. Santana, *Carbohydr.Polym.*,180,182(2018)
[10] Minkal .M. Ahuja and D.C. Bhatt, *Int. J. Biol. Macromol.*,106,1184(2017)
[11] L. Djerahov, P. Vasileva, I. Karadjova, R.M.Kurakalva and K.K. Aradhi, *Corbohyr. Polym.*,147,45(2016)
[12] R. Ma, Y.L. Ji,Y.S. Guo, Y.F. Mi, Q.F. An and C.J. Gao, *Desalination*,416,35(2017)
[13] J. Kalmar, G.Lente and I.Fabian, *Dyes Pigments*,127,170(2016)
[14] A. Febriasari, D.Siswanta, N.Riyanto, N.Hidayat Aprilita and F. Silvianti, *Asian J. Chem.*,30,2509(2018)
[15] C.P. Kiilll, H.S. Barud, S.H. Santagneli, S.J.L. Ribeiro, A.M. Silva, A. Tercjak, J. Gutierrez, A.M. Pironi and M.P.D. Gremiao, Carbohyr. Polym.,157,1695(2017)
[16] F. Razga, D.Vnukova, V. Nemethova, P. Mazancova and I.Lacik, *Carbohydr. Polym.*,151,488 (2016)
[17] A. F. Alkaim, A. M. Aljeboree, N. A. Alrazaq, S. J. Baqir, F. H. Hussein and A. J. Lilo, *Asian J. Chem.*,26,8445(2014)
[18] Y. Feng, K.Wang, C.Davies and H. Wang, *Nanomaterials*, 5,1366 (2015)
[19] Z. Xu, X. Li, K. Teng, B. Zhou, M. Ma, M. Shan, K. Jiao, X. Qian and J. Fan, *J. Membr. Sci.*, 535,94 (2017)