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A β-(1-4) linked polysaccharide (Chitosan) in tripolyphosphate-zinc oxide (CTPP-ZnO) eco-conductive membrane

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Abstract
In article, we have reported a β-(1-4) linked polysaccharide as chitosan is crosslinking to tripolyphosphate (TPP) which on impregnated with zinc oxide (ZnO) nanoparticles, formed an ecofreindly chitosan tripolyphosphate - zinc oxide (CTPP-ZnO) membrane film. These CTPP-ZnO membrane act as conductive behavior and serve as a good adsorbent or to improve the antifouling performance in membrane surface. In synthesis of CTPP-ZnO membrane, the concentrations of TPP is being 0.5%, 1.0% and 1.5% about at pH 5.0 with chitosan. Then CTPP is dried over to ZnO at 60 °C until a CTPP-zinc oxide (ZnO) thin film is formed. The membrane performance test have been checked by using of methylene blue pigment dye when 4 ppm concentration is passed through the membrane. The addition of ZnO reported that the interaction of methylene blue and ZnO nanoparticles mainly consider as the ionic bonding between the positively charged of ZnO and negatively charged of methylene blue ($-SO_3^-$), which led to affect in hydrophilicity of polyelectrolyte membrane with high performance to reverse transport in osmosis during performance test.

Keywords: Polysaccharide, chitosan, tripolyphosphate, zinc oxide nanoparticles, membrane

1. Introduction

Knowing, a membrane is a thin living materials which can selectively transport the mass of a component as a result of thrust force and the physico-chemical properties between the membrane and permeated compound. Membrane are often used for purification, in process such as haemodialysis [1] and biodiesel [2], and waste water purification [3], 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 micro-organisms degraded contaminants aspect with minimize fouling in the filtration process as well as improving the efficiency of the membranes used [3, 4]. Although, in ʿprotein-polysaccharide worldʾ there are several kinds of protein (gelatin) as well as polysaccharides such as cellulose, chitosan, dextran, heparin, inulin and chondroitin sulphate etc. have been potential importancy in hydrogel mediated biomedical-engineering application [4], due to their practical performance such as delivery of bioactive-selective components, regeneration of tissue cell as well as encapsulation of nanoparticles [5]. 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 [6, 7], but ought chitosan based [8, 9]. Here the chitosan is a one of the natural polymers which are prepared through deacetylation of chitin, usually sourced from shrimp or crab skin [10], and is often use to create chitosan membranes cross-linked with tripolyphosphates to remove humic acid from water, resulting polyelectrolyte complex (PEC-CTP) membrane which can serve as a good adsorbent of metal compounds [11], dye [12].

In this paper, we have been reported the ecofriendly chitosan cross-linked tripolyphosphate-zinc oxide (CTPP-ZnO) electro-conductive membrane which are more active than others modified polyelectrolyte membrane with nanoparticles [13, 14], as to reduced fouling effects in the membrane. Indeed, the zinc oxide (ZnO) is a nontoxic solid substance and having n-type conducting property and others [15-17]. The impregnation of ZnO into a membrane is expected to degrade the pollutants as trapped on the membrane surface with improved antifouling performance [18].

The pollutant use to test membrane performance in this study is methylene blue dye pigment [19]. It has high solubility in water, and so, in the fixation process a large amount of dye is lost with waste water. Although, one of the weakness of chitosan membrane is its instability in acid pH. Thus, to improve the stability of chitosan membrane an one possible method is to be crosslinking of chitosan with tripolyphosphates (CTPP) as a complex electro-conductive membranes for best performance. Here, figure 1 has shown the hexagonal crystal structure of zinc oxide nanoparticles which can be considered as to composed of two interpenetrating hexagonal closed packed (hcp) sublattices of cation-anion (Zn^{++} and O^{2-}).

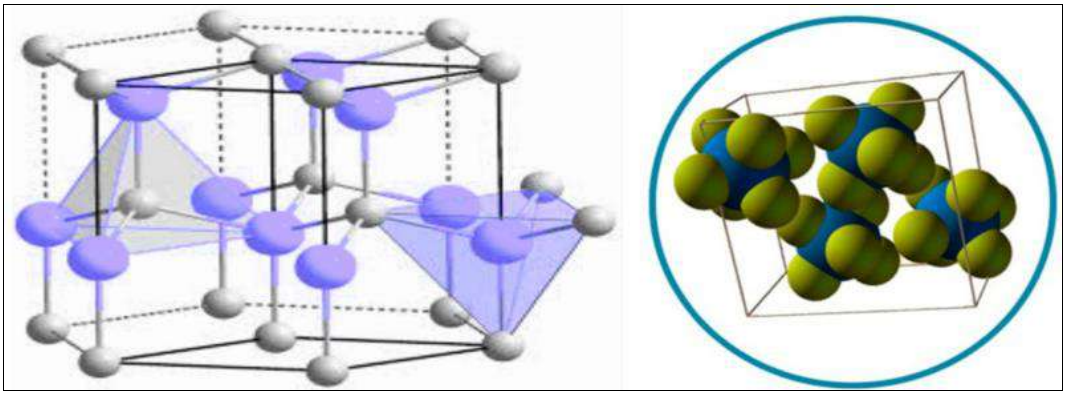

Fig 1: The hexagonal crystal structure model of zinc oxide (ZnO) nanoparticles

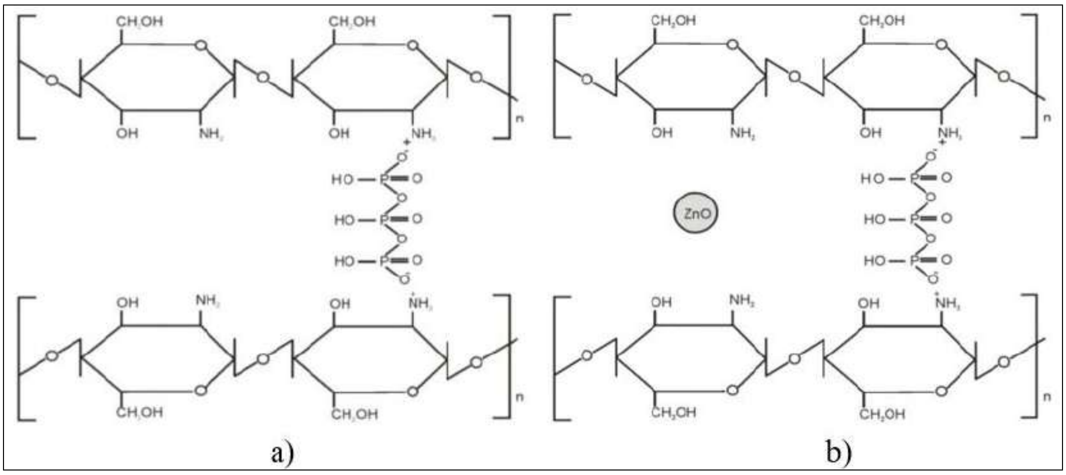

Fig 2: The chemical structure of- (a)- a cross-linking in between CTPP, and, (b)- in CTPP-ZnO molecule

2. Experimental

In experimental procedures, the materials used in this study such as chitosan, sodium tripolyphosphate, acetic acid and zinc oxide (ZnO) nanoparticles (< 50nm in size) have been as laboratory graded. These experimental work which are adopted and followed the work as well described [20]. Firstly, chitosan (polysaccharide) is dissolved in about 2% CH_3COOH (acetic acid) with a ratio of 1:50, then stirred and heated at 60 °C. After the chitosan solution is homogeneous, it is mixed with zinc oxide. The ratio of chitosan by weight to zinc oxide nanoparticles by weight are 2:1, 4:1 and 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% and 1.5% concentration variation (each at pH 4.5) until a clear suspension is formed. Then 50 ml of the resulting solution have taken to be molded in teflon moulds and oven-dried at 60 °C, until a CTPP-ZnO membrane film is formed. The characterization and performance test of the CTPP and CTPP-ZnO membrane was 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 77.35 K) 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

Indeed, in zinc oxide (ZnO) nanoparticles the presence of structural interstitials point defect or oxygen vacancies in their lattice which gives as n-type of conductivity in it, and is may responsible for active electrolytic or electro-conducting properties in chitosan based tripolyphosphate-zinc oxide (CTPP-ZnO) membrane. The preparation of chitosan-TPP membrane is performed by the mixing and evaporation method. The dominant polymer solution which is chitosan in acetic acid is added with sodium tripolyphosphate (TPP) with 0.5, 1.0 and 1.5% concentrations 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 [21]. The figure 2 is an illustration of the bond between chitosan and TPP [22]. The chitosan membrane is crosslinked 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 °C until a CTP-zinc oxide (ZnO) membrane film is formed. The physco-chemical analysis measurement determines the comparison with wider average pore radius or volume and surface area of CTPP and CTPP membrane impregnated with zinc oxide nanoparticles (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 CTPP and ZnO nanoparticle based CTPP-ZnO membrane

S.N.	Membranes	Average pore Radius (10Å)	Total pore volume (in 10^{-2} cc/g)	BET surface area (in m^2/g)	Water contact angle (°)
1.	Chitosan	4.128	2.341	11.340	46
2.	CTPP 0.5%	3.568	2.717	15.225	48
3.	CTPP 1%	4.259	2.163	10.159	50
4.	CTPP 1.5%	4.436	2.221	10.014	54
5.	CTPP-ZnO (8:1)	4.671	1.956	08.375	64
6.	CTPP-ZnO (4:1)	5.039	2.037	08.085	65
7.	CTPP-ZnO (2:1)	4.683	2.347	10.021	66

The membrane performance is demonstrated that, by using of methylene blue dye, where the methylene blue solution with a 4 ppm 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 [23]. 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 time measured (1 to 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 [24], (Flux recovery ratio (%) = $J_{w2} \times 100/J_{w1}$) [25], 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 hexagonally nanoparticles may predicted to have capability degrading compound as methylene blue dye in membrane surface, where interaction of methylene blue and zinc oxide nanoparticle mainly considered as the ionic bonding between positively charged of ZnO ($Zn(OH)^+$) and negatively charged of methylene blue ($-SO_3^-$) [26].

4. Conclusion

In conclusion, we have been reported the study of the zinc oxide (ZnO) nanoparticles impregnation with β-(1-4) linked linear polysaccharide as to chitosan, which are crosslinked with tripolyphosphate (TPP) in ecofriendly chitosan tripolyphosphate-zinc oxide (CTPP-ZnO) membrane. These CTPP-ZnO can influence the membrane surface where the pore radius increased by the addition of tripolyphosphate (TPP). The impregnation of zinc oxide nanoparticles can affect membrane morphology and making the surface rougher as well as it affect the hydrofilicity of the membrane surface. Although, the zinc oxide nanoparticles have the good performance test using dye (methylene blue) pigment which showed that the addition of zinc oxide nanoparticles in CTPP membrane is proven to improve antifouling performance in the membrane.

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