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Application of composite membrane from chitosan-cellulose diacetate-TiO_2 for waste detergent treatment

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GRAPHICAL ABSTRACT

ABSTRACT

The synthesis of composite membrane from chitosan, cellulose diacetate and TiO_2 as well as its application for waste detergent treatment were described here. Chitosan was synthesized from small crab shell using a chemical process involving deproteination, demineralization, depigmentation and deacetylation steps. Cellulose diacetate was synthesized from banana kepok using pulping, bleaching and acetylating steps. The production of composite membrane using inversion phase method by varying the concentration of cellulose diacetate 2%, 4%, 6%, 8% and 10%. The optimum mechanical properties of composite membranes were carried out with concentration variation of TiO_2 0.1% 0.15%, 0.20%, 0.25% and 0.30%. The produced composite membranes of chitosan - cellulose diacetate - TiO_2 were characterized by its thickness, performance, mechanical, morphology and were applied to waste detergent treatment. The results showed that the increasing of the concentration of cellulose diacetate made the composite membrane were more porous so the flux increases and the greater concentration of TiO_2, the greater mechanical properties of the composite membranes. The optimum composite membrane was obtained with the concentration of chitosan 3%, cellulose diacetate 4% and TiO_2 0.3%, thickness of 0.01 mm, flux of 1099.95 L/m^2.day, rejection of 97.70%, stress at 0.0225 kN/mm^2, strain at 0.3906, Modulus Young of 0.0576 kN/mm^2 and can be applied to waste detergent treatment process with flux 832.93 L/m^2.day and rejection of 95.39%.

Keywords: chitosan, cellulose diacetate, composite membrane, TiO_2, detergent

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1. INTRODUCTION

Increasing population indirectly leads technology development. This situation not only provides benefits for life but also causes damages to environment such as water pollution. Detergent (NaLS) is the most water pollution which is produced from domestic waste. General detergent has active ingredients such as LAS (Linear alkylbenzenesulfonate) surfactant [1]. In the following use, LAS discharges into waste water ecosystems and if it accumulates into the environment in large amounts, it may cause damages to the aquatic biota.

Some of waste detergent treatment processes have been done by using anaerobic degradation with the degradation percentage of 79% but it takes a very long time [2]. Waste detergent treatment has been degraded by using TiO_2 photocatalyst with the degradation percentage of 60% but its hard to separate the catalyst from the waste. Degradation of waste detergent using Camomonas testoteroni aerobic bacterial showed a percentage of degradation of 87.5%, but also took a very long time [4]. Waste detergent degradation using activated carbon was capable of degrading detergent with degradation percentage of 80%, but takes a long time, difficult to control pH and need appropriate temperature control [5]. Detergent treatments using composite membrane have been developed since the chitosan composite membrane can degrade detergent up to 86.43% [6], the higher concentration of chitosan, the higher mechanical properties of composite membrane, but the flux decreases. Furthermore, detergent degradation using cellulose acetate composite membrane showed the percentage degradation of 93.09%, the higher concentration of cellulose diacetate, the higher flux composite membrane but low mechanical properties.

A synthesis of composite membrane from chitosan - cellulose diacetate - TiO_2 for waste detergent treatment is reported here. The main objective of this research is to synthesize composite membrane with high flux and mechanical properties so it can be optimal in waste detergent treatment. High flux of composite membrane give high permeat, if the volume of permeat is high the process of detergent treatment be more effective. High mechnical properties of composite membrane give strong membrane to hold driving force during process of detergent tretment [14].

The composite membrane of chitosan - cellulose diacetate - TiO_2 was characterized by measuring the composite membrane thickness and performance, mechanical properties, SEM analysis and the degradation ability by UV-Vis spectrophotometer.

2. EXPERIMENTAL

2.1 Materials, instruments and methods

The sample materials used in this research were shell crab (Portunus pelagicus) and kepok banana stem (Musa paradisiaca fa typica). The chemicals used in this research have pro-analysis purity: sulfuric acid (H_2SO_4), titanium dioxide (TiO_2), Sodium Lauryl Sulfate (NaLS), glacial acetic acid (CH_3COOH), acetic anhydride, methanol, phenolphthalein indicator, chloroform, sodium dihidrogen phospate ($NaH_2PO_4.2H_2O$), acetone, sodium hypochlorite (NaOCl) 12%, hydrochloric acid (HCl), technical calcium hydroxide ($Ca(OH)_2$), technical sodium hydroxide (NaOH), methylene blue, potassium bromide (KBr), indicator pH and distilled water. The instruments of research were thermometer, magnetic stirrer, analytical scales, heating (hot plate), oven, Petri dish, shaker, desiccator, Autograph AG-10 TE Shimadzu, Oswald viscometer, Scanning Electron Microscope (SEM), Ultraviolate-visible (UV-vis) spectrophotometer 6100PCS Mapada, dead-end filtration cell devices, photocatalytic reactor and Bruker Tensor 27 Fourier Transform InfraRed (FT-IR) spectrophotometer.

2.2 Synthesis of chitosan

The synthesis of chitosan was done by isolating the shell chitin from crab waste through deproteination step using 3.5% NaOH solution with ratio of 1:10 (w/v) by heating at 65 °C for 120 minutes, demineralization step using 2 N HCl solution with ratio of 1:15 (w/v), depigmentation step using acetone and deacetylation step using 50% NaOH in the chitin with ratio 1:10 (w/v) and was heated for 120 minutes at temperature 95 °C. The characterization of chitin was done by analyzing the solubility and the deacetylation degree while the characterization of chitosan was done by analyzing the solubility, the deacetylation degree and molecular weight determination.

2.2.1 Synthesis of cellulosa diacetate

Cellulose diacetate was synthesized through the pulping step using 2.5% $Ca(OH)_2$ and 17.5% NaOH. In bleaching step, it used 2% NaOH solution and 5% NaOCl solution. In acetylation step, glacial acetic acid and acetic anhydride was hydrolyzed for 15 hours to form cellulose diacetate. Cellulose diacetate was characterized by using FT-IR to analyze its vibration of functional group and determine its molecular weight [8-10].

2.4 Preparation of Composite membrane Chitosan-Cellulose Diacetate-TiO_2

The composite membrane was made by varying the concentration of cellulose diacetate 2%, 4%, 6%, 8% and 10% while chitosan concentration constant 3% to obtain composite membrane with high mechanical properties. The composite membranes were prepared by dissolving 3% chitosan in 2% acetic acid and dissolving cellulose diacetate in acetone. The result was added with 8% formamide and then stirred to form a homogeneous solution which is free of bubbles and used to create composite membrane using inversion phase method. Phase inversion is a process whereby a polymer is transformed in a controlled manner from liquid to a solid state [14]. First, dope solution was poured on Petri dish, then shaken and rotated until form a thin layer of composite membrane to shape and smooth the composite membrane surface. Composite membrane that had been printed then dried in oven at 80 °C and left for 3 hours [9]. After that, membrane on Petri dish was added 4% NaOH as coagulation liquid and then washed with distilled water and dried. The optimum membrane from variying concentration of cellulose diacetate was added TiO_2 0.10%, 0.15%, 0.20%, 0.25% and 0.30% to made the composite membrane chitosan-cellulose diacetate-TiO_2. The composite membrane performance, mechanical properties and morphology were characterized using SEM analysis.

2.5 Composite membrane performance based on flux and rejection properties

Flux and rejection were determined by an instrument called dead-end filtration cell. First, a piece of filter paper and the composite membrane was placed in cell filtration and add about 150 mL of distilled water then pressured at 2 atm. The composite membrane was compacted for 30-45 minutes, then the distilled water was replaced by the detergent solution. The flux of composite membrane was determined by measuring the volume of permeat detergent in cell filtration for three minutes. The rejection of composite membrane was determined by measuring the concentration of detergent before and after passed through the composite membrane using UV-vis spectrophotometer [10].

The morphology of composite membrane was determined by using SEM. The mechanical properties such as stress, strain and Young's modulus were determined by using tensile test. The functional group of composite membrane was determined by using FT-IR spectrophotometer.

2.6 Application of composite membrane from chitosan-cellulose diacetate-TiO_2 for waste detergent treatment

Composite membrane was applied to waste detergent treatment. Samples of waste detergent before and

after filtered with composite membranes were analyzed by using UV-vis spectrophotometer.

3. RESULTS & DISCUSSION

3.1 Synthesis of chitosan

Chitosan was obtained through deproteination, demineralization, depigmentation and deacetylation steps. These processes obtained bright colored powder with 77.32% yield chitin weight. Chitosan was characterized by solubility test using 1% acetic acid. The solubility chitosan caused by the formation of hydrogen bonds between the N of the amine group on chitosan with H^+ from acetic acid. The molecular weight of chitosan has been synthesized was 553495.22 g/mol which was measured using Ostwald viscometer. Ostwald viscometer is measurements of solution viscosity which is usually made by comparing the effluxe time solut and solvent to flow through a capillary tube [15]. The transformation of chitin into chitosan was analyzed by using FT-IR to determine its functional group. The presence of chitosan was indicated from decreasing intensity of vibration band of –OH group at 3448.72 cm^{-1} than on chitin and vibration band of –NH group at 1658.78 cm^{-1} that is not owned by chitin. From the result DD (Deacetylation Degree) of chitin was 43.54% and chitosan was 84.42%. The chitin was indicated from vibration bands of C=O, –NH secondary, –CN and C–O groups at 1627.92 1550.77, 1072.42 and 1026.13 cm^{-1}, respectively which is not owned by chitosan due to the disconnection of acetyl group [11].

3.2 Synthesis of cellulosa diacetate

Cellulose diacetate was obtained through the pulping, bleaching, acetylating and hydrolysis steps. Cellulose diacetate obtained was 32.16 gram (109.57% yield). The synthesized cellulose diacetate was soluble in acetone while cellulose was insoluble in acetone. Molecular weight derived from synthesized cellulose diacetate was 49742.03 g/mol. The presence of cellulose diacetate was indicated from vibration band of –OH group at 3502.73 cm^{-1} with a lower intensity than that of cellulose, vibration band of C–H) group at 2954.95 cm^{-1}, C=O at 1751.36 cm^{-1}, –COO– at 1658.78 cm^{-1}, –CH at 1373.32 cm^{-1}, CO at 1049.29 cm^{-1}, and the absorption band groups (-COC-) which is a glycoside bond between monosaccharide appeared at 1234.44 cm^{-1} (**Figure 1**).

3.3 Characterization of composite membrane of chitosan-cellulose diacetate-TiO_2

The mechanical properties of composite membrane with concentration constant of chitosan 3% and variation concentrations of cellulose diacetate were analyzed using an autograph. This test was obtained the style and the length of the composite membrane when the composite membrane is broken. The relationship beetwen variation concentration of cellulose diacetate with stress is described in **Figure 2**.

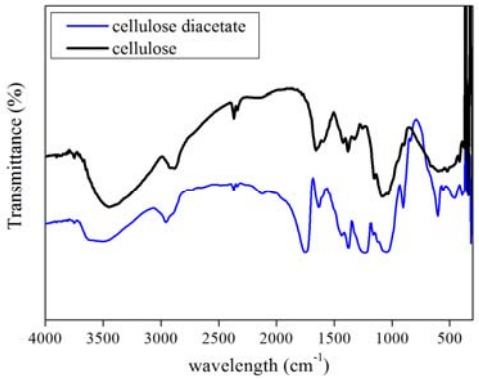


Fig. 1 FTIR spectra of cellulose and cellulose diacetate.

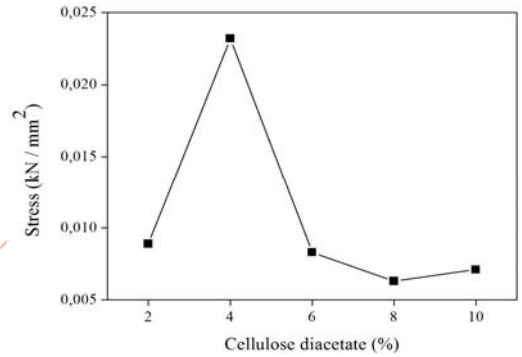


Fig. 2 The relationship of cellulose diacetate concentration with stress of composite membrane.

Membrane with optimal concentration of cellulose diacetate (4%) was made to composite membrane with various concentrations of TiO_2 and the characterization of permeability (flux) and rejection on the cell composite membrane were performed with a dead end filtration.

The relationship between TiO_2 concentration with flux and rejection of composite membrane are described in **Figure 3**. The largest flux value was 1242.03 L/m^2.day at the addition of 0.20% TiO_2. The increasing of TiO_2 concentration, the decresing fluks value will be obtained. It is due to increasing of TiO_2 bonding structure so total and distribution of pores reduced and caused feed of flow rate to be obstructed and flux decline [12]. The greatest rejection coefficient is shown in addition of 0.3% TiO_2 with a rejection coefficient of 97.70%. Increasing concentration of TiO_2 which was bounded to the composite membrane in a photocatalytic reactor showed rejection values increase as more TiO_2 degradation using 5 ppm of NaLS solution. Flux decline can also occur due to fouling on the surface and composite membrane pores. Foulings occur due to the accumulation of particle-bait is irreversible [13] and accumulation of solutes in the pore blocking and narrowing the feed rate to the process so that the filtration flux value decreases.

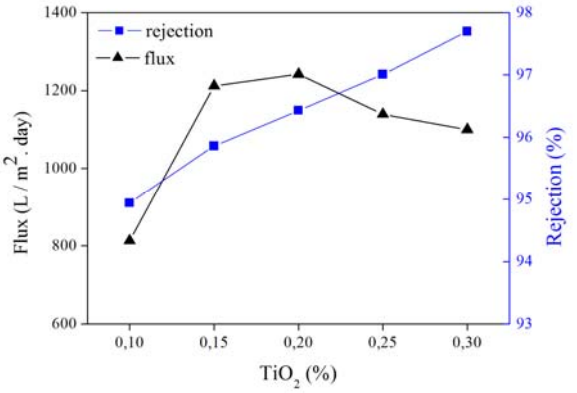


Fig. 3 The relationship of TiO_2 concentration with flux and rejection of composite membrane.

The mechanical properties analysis of chitosan composite membrane - cellulose diacetate - TiO_2 values obtained stress and strain which are described in **Figure 4**.

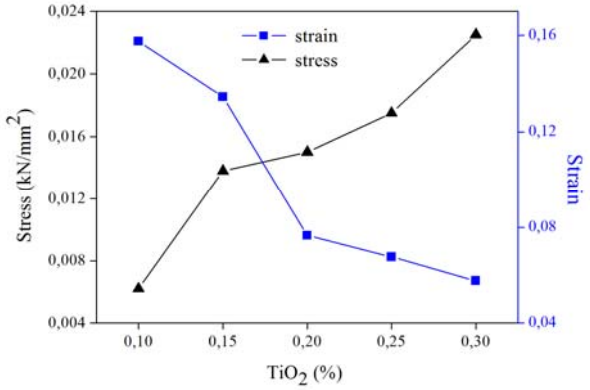
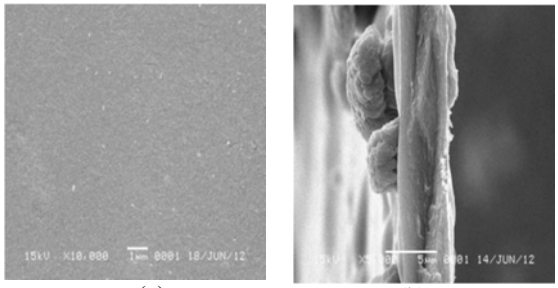


Fig. 4 The relationship of TiO_2 concentration with stress and strain of composite membrane.

Stress is the force required to break the composite membrane cross-sectional area perpendicular to the direction of gravity. **Figure 4** shows the effect of TiO_2 on the value of the stress and strain. The more the addition of TiO_2, the higher the mechanical strength of the composite membrane. This is due to that TiO_2 may increase bond strength of composite membrane structure. The greater the stress value of composite membrane, the better power to accept force without damaging the composite membrane [9]. The highest stress value owned by chitosan - cellulose diacetate - TiO_2 composite membrane with 0.30% TiO_2 concentration with a value of 0.3906 kN/mm^2. The optimum composite membrane was obtained by 3% chitosan, 4% cellulose diacetate and 0.3% TiO_2.

The morphology of optimum composite membrane was analysed by SEM. This analysis was used to determine the cross-section, pore distribution and pore size on the composite membrane surface. The morphology of optimum composite membrane is described in **Figure 5**.

Figure 5(a) shows that pore on the surface of the composite membrane of chitosan-cellulose diacetate-TiO_2 is not clearly enough. It caused the composite membrane obtain from natural polymer and the energy was used in the SEM is very high. In **Figure 5(b)**, the composite membrane cross-sectional images shows that the composite membrane has a porous structure.



(a) (b)

Fig. 5 SEM results of (a) the composite membrane surface and (b) the cross section.

FT-IR analysis on composite membrane with the addition of cellulose diacetate was done to determine the bonding that occurs in the composite membrane by the addition of cellulose diacetate chitosan and chitosan composite membrane - cellulose diacetate - TiO_2 by comparing the FT-IR spectra of the composite membrane. The composite membrane spectrum is described in **Figure 6**.

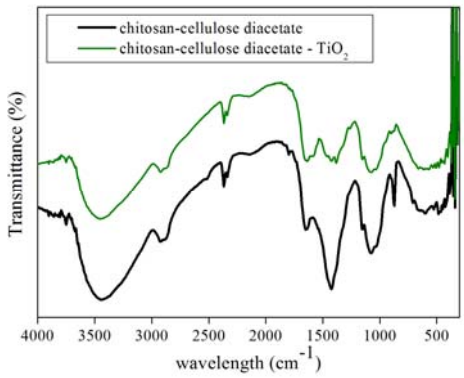


Fig. 6 The FTIR spectra of composite membrane of chitosan - cellulose diacetate-TiO_2.

Figure 6 shows FTI-R spectra of cellulose diacetate-chitosan membrane and chitosan - cellulose diacetate - TiO_2 composite membrane. Cellulose diacetate- chitosan membrane spectrum showed that streching vibration band of CO at 1072.42 cm^{-1} is sharper which is characteristic of cellulose diacetate and vibration band of NH amine at 1635.64 cm^{-1} which is characteristic of chitosan. The composite membrane did not show the presence of CN at ≈ 1400 which is seen in the cellulose diacetate- chitosan membrane at 1427.32 cm^{-1}. Ti-O bonding on TiO_2 shown at 509 cm^{-1}. The presence of bonding beetwen TiO_2 and chitosan in the composite membrane was indicated from Ti-N bonding at 370.33 cm^{-1} and 339.47 cm^{-1}. The spectrum was resulted from the existence of chemical bond between

TiO_2 and chitosan in composite membrane of chitosan – cellulose diacetate - TiO_2.

3.4 Application of composite membrane of chitosan-cellulose diacetate-TiO_2 for waste detergent treatment

The optimum synthesized composite membrane was applied to waste detergent treatment. Detergent waste tretment using composite membrane obtained rejection coefficient 95.39% and flux 832.93 L/m^2.day. High rejection coefficient is caused by Ti-N bonding between TiO_2 with chitosan on the composite membrane. Presence TiO_2 on composite membrane produce ·OH radical which can degrade detergent waste and pore on the membrane can hold the detergent waste at a moment before degrade by TiO_2. Based on the result the composite membrane, it is effective to treat detergent waste because the rejection coefficient is more than 90% that is 95.39% [14].

4. CONCLUSION

The composite membrane of chitosan-cellulose diacetate-TiO_2 was prepared using inversion phase method which evaporate the solvent after the membrane printing process in a Petri dish. The optimum composite membrane was obtained with the concentration of chitosan 3%, cellulose diacetate 4% and TiO_2 0.3% . Characteristics of composite membrane chitosan -cellulose diacetate - TiO_2 include the thickness of 0.01 mm, stress at 0.0225 kN/mm^2, strain and Young's modulus of 0.0576 and 0.3906 kN.mm^2, flux at 1099.95 L/m^2.days and composite membrane rejection was 97.70%. TiO_2 concentration variations affected the mechanical properties and performance of chitosan composite membrane -cellulose diacetate-TiO_2. The greater concentration of TiO_2, the greater mechanical properties and composite membrane rejection. Chitosan composite membrane-cellulose diacetate-TiO_2 can be applied to the waste detergent treatment with high filtration effectiveness 95.39%.

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