Challenges and Advances in Chemical Science
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Challenges and Advances in Chemical Science Vol. 1

This book covers key areas of chemical science. The contributions by the authors include mesopores, confined systems, bistability, curves of states, adsorption hysteresis, lifetime of metastable states, bistability, pfitzinger reaction, beckmann rearrangement, chitosan, tetraethyl orthosilicate, polyethylene glycol, membrane, adsorption, alkaline catalyst, biodiesel, degumming, water degummed linseed oil, transesterification, fluorine compound, chloride compound, bromine compound, sulfur oxides, japanese industrial standards, flue gas analysis, ion chromatography, power functions complex, stability theory, evolution equations, bifurcation theory, stable focuses, stable cycles, parameter eigenvalues, nanoholes, densely branched morphology, diblock copolymer thin films, crystalline diblock copolymer, X-ray scattering, whey proteins, whey protein concentrates, ultrafiltration, diafiltration, water quality index. This book contains various materials suitable for students, researchers and academicians in the field of chemical science.

Chapters

A New Theory and Its Applications: Fluids in Mesopores
Harald Morgner

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Abstract ⌄   View Article

Time Dependent Aspects of Adsorption: Evaluating the Lifetimes within the Hysteres Loop
Harald Morgner

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Abstract ⌄   View Article

Exploration of Newer Possibilities to the Synthesis of Diazepine and Quinoline Carboxylic Acid Substituted Analogues of Benzothiazolo Condensed Oxocarbazoles a Oxoazacarbazoles of Medicinal Interest
Vatsala Soni, Meenakshi Sharma, Vaishali Soni, Shiv Lal Soni

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Chitosan-silica- polyethylene Glycol (Ch/Si/P) Solid Membrane for Removal of Cu(II), Zn(II) and Cd(II) Ions from Aqueous Solutions

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ABSTRACT

Chitosan is interestingly thought to be used as raw material to make membrane for it has functional group of $-NH_2$ and $-OH$ that is easy to modify. Chitosan membrane has weakness like low mechanical properties. To overcome those weaknesses, silica is added on chitosan membrane synthesis to improve chitosan membrane stability. In membrane synthesis process, plasticizer is used to improve mechanical properties, maintain integrality, and avoid holes and crackness. Polyethylene Glycol plasticizer addition is expected to increase physical and mechanical properties and hydrophilic properties on membrane surface significantly therefore metal ion solution can easily diffuse through chitosan-silica-PEG membrane. In this research, it is done chitosan-silica-PEG (Ch/Si/P) membrane synthesis with tetraethyl orthosilicate (TEOS) that is used as silica source then the membrane is used as adsorbent for ion Cu(II), Zn(II) and Cd(II) by batch method. Research shows that adsorption with batch method to all membranes is optimum pH for metal ions Cu(II) and Zn(II) = 6, Cd(II) = 5.5. Adsorption for ions Cu(II), Zn(II) and Cd(II) in membrane tends to follow Langmuir isotherm model. Generally, it can be said that Ch membrane ability on all adsorption metal ions increases with silica or PEG addition. Adsorption capacity value for Ch/Si/P membrane in µmol/g for ion Cu(II), Zn(II) and Cd(II) in order are 262, 183, and 107 µmol/g. Generally, in adsorption kinetic data there is a tendency of coefficient score of R^2 linearity that is higher in the second order of pseudo kinetic model.

Keywords: Chitosan; tetraethyl orthosilicate (TEOS); polyethylene glycol; membrane; adsorption.

1. INTRODUCTION

At the beginning of the 20th century, it has been widely developed the use of membranes that have high thermal and mechanical stability for metal ion separation. Several polymeric materials have been developed to make such membranes, such as cellulose, polysulfone, polypropylene and polyvinyldifluoride derivatives. Chitosan has been used in biomedical and biotechnological research as a membrane synthesis material since it has several characteristics like hydrophilic, non-toxic, biologically compatible and biodegradable. The process of swelling chitosan powder to becomesolution, beads, gel, and membrane, has been done by several researchers in order to optimize the ability of chitosan adsorption on heavy metal ions as well as in wider application.

Chitosan [poly (2-amino-2-deoxy-D-glucose)] is a second abundant natural polymer after cellulose. According to No and Mayers [1], in general the outer skeleton of marine animals contains 15-40% chitin, 20-40% protein, 20-50% $CaCO_3$ and other components such as pigments, fats and metal salts. Skeletal waste of marine animals has the potential to be isolated into chitin. Chitin is a linear polymer of an N-acetyl-2-amino-2-deoxy-D-glucopyranose (N-acetyl-D-glucosamine) monomer unit. The main

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derivative of chitin is chitosan that is produced from chitin deacetylation using NaOH. Chitosan is interestingly to be made use of as the basic material of membrane synthesis because it has functional group of -NH$_2$ and -OH which is easy to modify. Chitosan membrane has a weakness for instance low mechanical properties that is shown by the tensile strength value, low elongation percentage and Young Modulus high value [2,3].

Organic polymer membranes have some weaknesses such as low mechanical properties, unstable at high temperatures and extreme pH and easily decomposed in organic solvents. To overcome these weaknesses, inorganic materials are used as alternative. Inorganic materials are more stable at high temperatures and extreme pH and can survive in organic solvents.

Inorganic compound such as silica is added in chitosan membrane synthesis to improve the stability of chitosan membrane by forming crosslinks with silica through the formation of hydrogen bonds between chitosan structure with silica [3,4]. Silica source that is used by the previous researchers in chitosan-silica membrane synthesis polydimethyl siloxane (PDMS) [5], tetraethyl orthosilicate (TEOS) [4], sodium silicate that is isolated from rice husk ash [6,7] and commercial sodium silicate [8].

Earlier researchers [3,5,9] report that the production of chitosan-silica membranes with sol-gel process shows that the more silica is added, the produced membranes do not meet the expected quality. This condition is indicated by the produced chitosan-silica membrane that has tensile strength value, the percentage of elongation that has not increased significantly. The tensile strength test, elongation percentage and Young Modulus are used to evaluate characteristic and stability of the membrane [10].

In membrane synthesis, plasticizers are used to improve mechanical properties, maintain wholeness and avoid holes and cracks. In the membrane matrix, the addition of plasticizer is expected to reduce the intermolecular link among chitosan molecules therefore it weakens the intermolecular strength. According to Zhang et al. [11]; He et al. [12]; Rodriques et al. 2014, plasticizers are generally polyol molecules including sorbitol, glycerol and polyethylene glycol (PEG). The mechanical, physical and chemical stability of the membrane will have an effect when the membrane is applied to the separation process. The addition of PEG plasticizer is expected to improve physical and mechanical properties, as well as hydrophilic characteristic on the membrane surface significantly so that the metal ion solution diffuses easily through the chitosan-silica-PEG membrane.

According to Muzarelli 1977, the metal ion bonding in chitosan can be through the formation of chelates which means that -NH$_2$ (amine) and -OH (hydroxide) groups that join metal ions or through a combination of ion exchange, sorption and chelate formation. The bonding mechanism that occurs depends on the metal ion that is interacted. The main functional groups of -NH$_2$ and -OH are active groups that have the ability to interact with metal ions. The – NH$_2$ group is a stronger ligand than the -OH ligand. In the spectrochemical series for ligand strength, -OH group is located on the left side of -NHCO- and -NH$_2$ group. This assumption has been reported by (Muzarelli 1977; Tsezoz et al. 1982) as in their research, they state that metal ion linking to chitin and chitosan is dominated by -NHCO- and -NH$_2$ groups.

This work presents the production of chitosan-silica-PEG (Ch/Si/P) membrane with Tetraethyl orthosilicate (TEOS) that is used as a source of silica and its characterization to identify the mechanical properties, morphology, crystallinity, thermal stability, functional group, and hydrophilicity. The precursor TEOS is an organically substituted alkoxylan, CH$_3$Si (OCH$_3$)$_3$ is more reactive than the same alkoxylan without binding to an inorganic compound (Na$_2$SiO$_3$) under acidic conditions. The acidity of the silanol groups increases with the number of Si-O-Si bonds at the silicon atom. The membrane is used as adsorbent for Cu(II), Zn(II), and Cd(II) ions with batch method. The adsorption properties of Cu(II), Zn(II) and Cd(II) ions onto the chitosan-silica-PEG (Ch/Si/ P) membrane were studied. The effects of different conditions such as solution pH, contact time and initial ion concentration on the adsorption capacities of membranes were investigated respectively. In addition,the kinetics and adsorption equilibrium Cu(II), Zn(II) and Cd(II) ions on the chitosan-silica- PEG (Ch/Si/ P) membrane were analyzed by fitting experimental data in various kinetics and isotherm models.

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2. EXPERIMENTAL

2.1 Materials

The materials used in this study are (a) chitosan purchased at CV Ocean Fresh Bandung, Indonesia (b) chemical components used are acetic acid, HCl, NaOH, TEOS (Merck), PEG BM 400, $Cu(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ as ingredients to make solution of Cu(II), Zn(II) and Cd(II) ions in which all are p.a qualified and aquabides

Equipment required for the membrane preparation includes: dryers, analytical balance (Denver) with precision of 0.001 grams, pH meter (Ecoscan), Whatman 42 filter paper, glass plate with size 20 cm x 20 cm, and other supporting tools such as polyethylene bottles and glass equipments. Equipment for membrane characterization includes: a set of membrane mechanical properties test equipment (Pearson Panke Equipment Ltd), IR Spectrophotometer (Shimadzu FTIR-8201PC) with accuracy of 1/1000 transmittance percentage, a set of SEM tools (JEOL JSM-6360 LA), a set of X ray diffractometer Shimadzu 6000 tool, a set of *Differential scanning Calorimetry* (DSC), and a set of Thermogravimetry Analysis (TGA) Linseis STA PT 1000 tool. The equipment required for the adsorption process includes: orbital shaker (Yellow line OS 10 basic), atomic absorption spectroscopy/SSA (Perkin-Elmer AA200) is used to measure the amount of metal ions in solution, other additional tools such as polyethylene bottles and glass equipments.

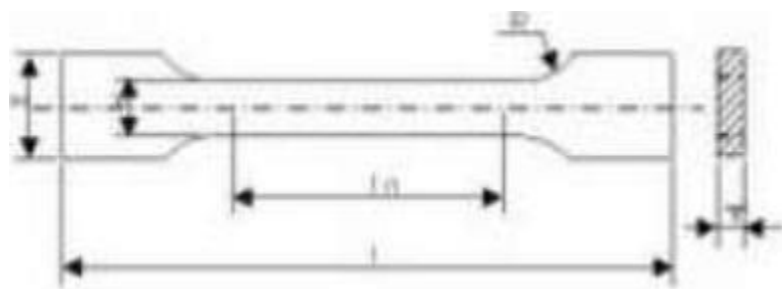### 2.2 Preparation of Ch/Si/P Solid Membrane

The preparation of chitosan-silica membrane with TEOS, the silica source, is conducted based on the conventional procedure [13,2,14] with some modifications. Silica soles are made firstly by mixing TEOS and commercial silicate natrium and ethanol in plastic beaker. HCl that acts as catalyst is mixed with water, then this mixture is added to the TEOS/ethanol mixture, then stirred using stirrer magnetic for 30 minutes at 60°C. The comparison of TEOS mole : ethanol : water : HCl is 1 : 2 : 2 : 0.01.

TEOS weight is varied to investigate the effect of TEOS-chitosan ratio on the quality of produced membrane. Variations were performed by weight ratio of chitosan/TEOS 1:0.0, 1:0.1, 1:0.2, 1:0.3, 1:0.4, 1:0.5, 1:0.6, 1:0.7, 1:0.8, 1:0.9, 1:1.0 and 1:1.5. The silica sol is then mixed into 1% chitosan solution (one gram of chitosan is dissolved into 100 ml of 2% acetic acid (v/v), the mixture is stirred constantly for 24 hours at room temperature until homogenous solution is produced). The solution mixture of chitosan and silica sol is then stirred for 15 minutes at room temperature until homogenous solution is reached. The solution is then poured gently on a glass plate and is leveled using a stirring bar.

The glass plate is inserted into the dryer with temperature of 30°C and air humidity of 80% to evaporate the solvent. After the membrane is dry, the membrane is immersed in 5% NaOH for 2hours then washed by using aquades to remove residual solvent. The produced membrane is then stored in desiccator. The membrane is tested for mechanical properties to determine the value of tensile strength, percentage of elongation and Young Modulus. The membrane that have the highest tensile strength value is the chitosan-silica mass composition used to synthesis chitosan-silica-PEG membrane. The amount of PEG added to the chitosan solution mixture and the silica sol is: 0.1; 0.15; 0.20; 0.25; and 0.50 g. The chitosan-silica-PEG membrane is tested for mechanical properties to determine the value of tensile strength, elongation percentage and Young Modulus.

2.3 Characterization of Ch/Si/P Solid Membrane

1. Tensile strength test, elongation percentage and Young Modulus of chitosan-silica-PEG membrane with standard ASTM D638-03 method using Pearson Panke Equipment Ltd. The dried sample is cut according to the following picture:

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Description: sample length is 110 mm, width 75 mm. Tensile speed 10 mm/minute, the test is conducted 3 times repetition for the same sample. On the measurement of tensile strength, elongation value percentage will be known. Young modulus is the ratio of strength value attraction to elongation percentage.

2. Morphological test on the surface and cross section of the membrane is using Scanning Electron Microscope (SEM). Before being tested, samples are coated with gold, they are scanned with magnification 2500 times and 5000 times.
3. Crystallinity Test on the membrane is using X-Ray Diffractometer. Samples are tested at 25°C, Cu ray source filtered with Ni with Kα radiation (40 KV and 30 mA). Samples are tested at 5.0 (°)/minute rate from 5° to 40° (2 Θ).
4. Thermal stability test of the membrane uses the Differential Scanning Calorimetry (DSC) method. As much as 10 mg sample is tested starting from room temperature to 400°C with heating rate of 10°C/minute at atmospheric pressure.
5. Functional groups test on the membrane that is based on qualitative test result is using Fourier Transform Infrared (FTIR) Spectrophotometer. The samples are cut into small pieces then the KBr pellet is then tested at the wave numbers of 300-4000 cm^{-1}.

Swelling Index (SI) measurement: membrane of a certain weight is immersed in 50 mL on a buffered solution which varied from 4.0-11.0 for 24 hours then SI value is calculated using the following formula,

$$SI\ (\%) = \frac{Ww - Wd}{Wd\ x\ 100} \tag{1}$$

Explanation: Ww = weight after being soaked, Wd = initial weight [15].

Membrane code and chitosan/silica/PEG composition ratio used in the adsorption process are presented in Table 1.

Table 1. Ratio of chitosan, silica and PEG compositions to synthesis membranes

Membrane code	Chitosan (g)	Silica (g)	PEG (g)
Ch	1	0.00	0.00
Ch/Si	1	0.80	0.00
Ch/Si/P	1	0.80	0.50

Adsorption in the *batch* system is conducted on individual Cu(II), Zn(II) and Cd(II) ions. The effect of pH solution on the adsorption of metal ions is assessed with membrane of ± 0.12 grams cut into 10 parts. The membrane is immersed in 50 mL of Cu(II), Zn(II), and Cd(II) solutions at concentration of 25 mg/L in pH 4- 9 variation and is boiled for 24 hours. Influence of contact time on metal ion adsorption, the membrane is immersed into 50 ml of Cu(II), Zn(II) and Cd(II) with concentration of 25 mg/L at the optimum pH of each metal ion. All solutions are boiled for 1, 2, 4, 8, 16, 24 and 26 hours. Influence of initial solution concentration on metal ion adsorption, membrane is immersed into 50 mLof Cu(II), Zn(II) and Cd(II) with concentration of 5-70 mg/L at optimum pH and shaken for 24 hours. The solution is separated with a membrane and then tested its metal ion content with SSA.

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3. RESULTS AND DISCUSSION

3.1 The Mechanical Properties

The membrane is tested for its mechanical properties to determine attraction value (Tensile Strength, stress), Percent Elongation (strain) and Modulus Young with standard ASTM D638-03 method using Pearson Panke Equipment Ltd. The result of mechanical properties test is presented in Fig. 1 and Fig. 2. In Fig. 1, it can be seen that silica concentration addition increases Tensile Strength value of the membrane, in the addition of 0.7-0.8 g of silica membrane it has maximum Tensile Strength. In the addition of 0.9 g of silica the Tensile Strength value decreases significantly.
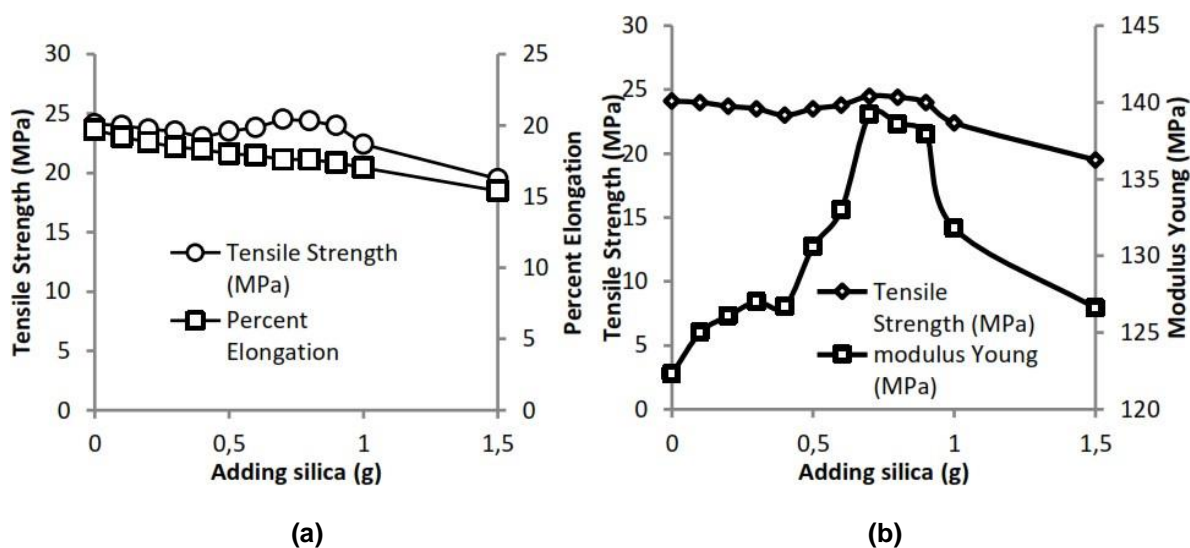

(a)   (b)

Fig. 1. The effect of silica addition to (a) Tensile Strength and Percent Elongation, (b) Tensile Strength and Modulus Young

Generally, silica addition increases the Tensile Strength and decreases Percent Elongation. An increase in membrane Tensile Strength accompanied by a decrease in Percent Elongation causes an increase in the Modulus Young. The increased Modulus Young indicates membrane stiffness, whereas Modulus Young decrease indicates the membrane gets more flexible. According to the research result [3], chitosan membrane has a tensile strength value of 32.0 MPa and 19.3% Elongation. The addition of 0.8 g TEOS increases the Tensile Strength to 33.2 MPa and 20.1% Elongation. The addition of mixture 0.8 g VTES and 3.2 g TEOS decrease Tensile Strength value to
30.3 MPA and 17.7% Elongation. According to Pandis et al. [15] on the increasing of silica addition, it has a negative effect on the rise of mechanical properties. Based on the properties mechanical test result, in chitosan-silica-PEG membrane synthesis with silica source from TEOS is used with chitosan-silica mass ratio (1:0.8).

The test result of mechanical properties in PEG addition is presented in Fig. 2.

Commonly, PEG addition increases Percent Elongation but Tensile Strength of the membrane decreases insignificantly. PEG addition resulted in the dropping value of Modulus Young significantly which means that membrane viscosity increases significantly. Chitosan/silica/PEG composition (1:0.8:0.5) on membrane synthesis is the optimum composition, due to the minimum of Modulus Young, maximum Percent Elongation and no significant decrease of Tensile Strength significantly thatindicate elastic and strong membrane. It is in accordance with the research of Enescu et al. [5], PEG is plasticizer used to improve mechanical properties, maintaining wholeness and hopefully avoiding holes and cracks. In membrane matrix, plasticizer addition is expected to reduce intermolecular bond among chitosan molecules so it weakens intermolecular strength [11,12].

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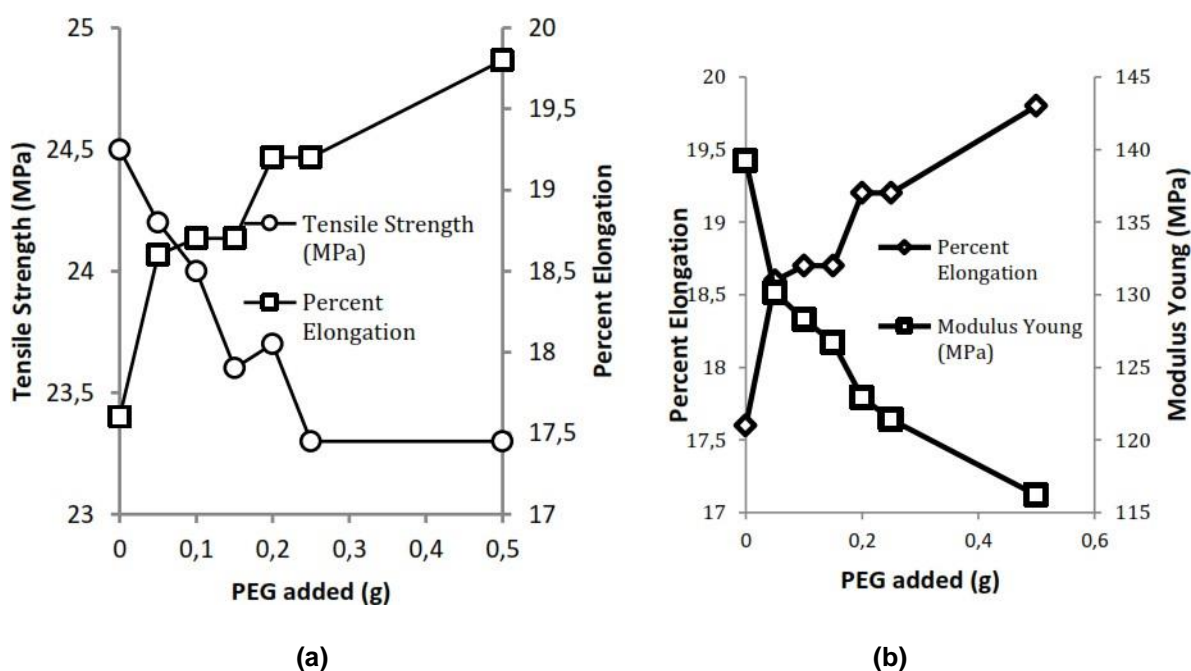
(a)

(b)

Fig. 2. PEG addition influence on (a) Tensile Strength and Percent Elongation (b) Tensile Strength and Modulus Young

3.2 Membrane Morphology

Membrane morphological test is performed by using SEM photograph. The result of membrane surface and cross section imaging using SEM photograph can be seen in Fig. 3.
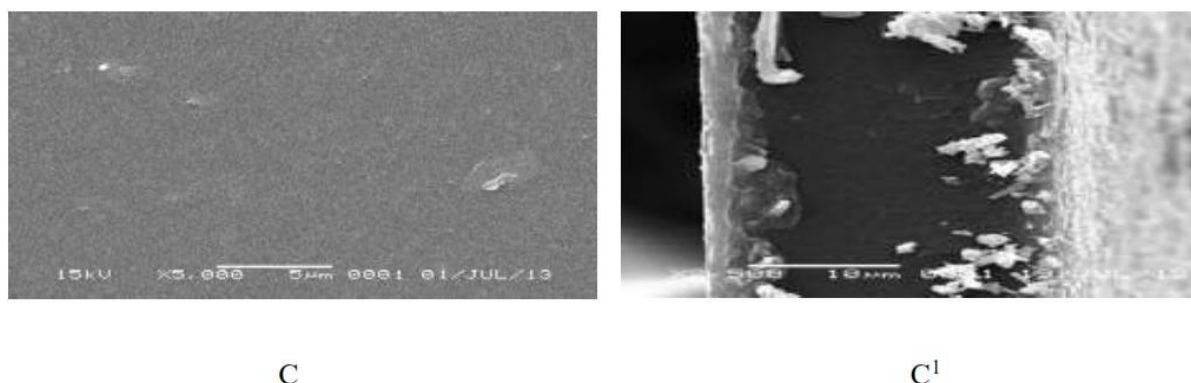

A

A¹

B

B¹

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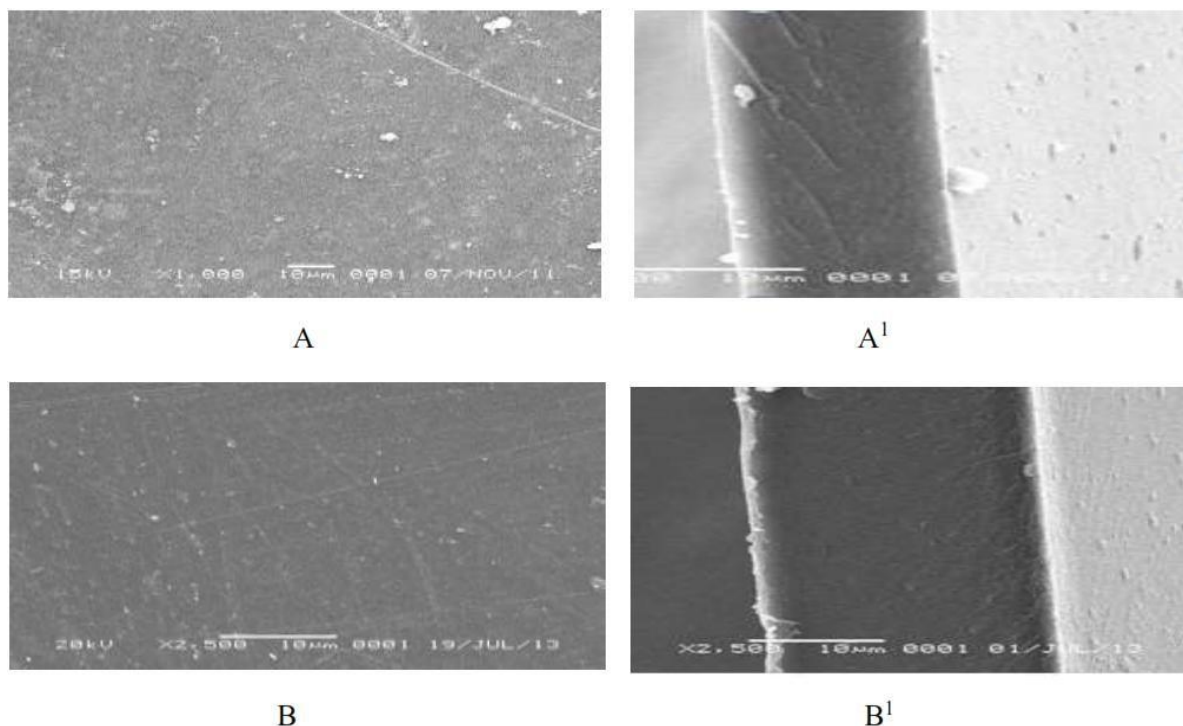
Fig. 3. SEM photographs of the surface and cross section of membrane Ch (A and A[1]), Ch/Si (B and B[1]), and Ch/Si/P (C and C[1])

Chitosan membrane on its surface is softer, compared to the surface of chitosan membrane added with TEOS that looks more rough. SEM test result that is obtained is in line with previous research result that explains chitosan membrane has uniform and non-porous morphological structure (Rutnakurpituk et al. 2006). This result is also in line with mechanical properties especially tensile strength value, the higher the concentration of silica added, the tensile strength increases. In certain compositions (the ratio of chitosan-silica= 1:0.8) to the maximum tensile strength value, in the next silica addition tensile strength value decreases, it is perhaps physically the silica will make pores due to its porogenous properties (Liu et al. 2005).

In PEG addition, it reduces pores. It is possible to be found in PEG addition, PEG molecules are attached and trapped in membrane pores physically [11]. This result is supported by He et al. [12] who states that there is no chemical interaction between chitosan and PEG although hydrogenbonding between chitosan and PEG is possible to happen.

In TEOS precursor, the morphology and characteristic of the obtained material are controlled by many parameters that affect sol-gel process. In acid media, TEOS monomers are hydrolyzed faster than partially hydrolysis of more Si-O-Si bonded compounds. The rapid formation of silanol groups immediately forms primary balls and joins chitosan polymer chain. It causes the produced membrane has more homogenous and smaller pore size distribution.

The inclusion of the PEG polymer in the membrane matrix results in smaller pore size distribution for all membranes with different silica sources. The integration of PEG polymers on membrane matrix is possible to happen because PEG is trapped and agglomerated on the membrane surface and through hydrogen bonds formation along chitosan chain. The trapped PEG polymers along membrane matrix causes increased membrane elasticity, it is proved with the increase of elongation percentage on the membrane mechanical properties.

3.3 Membrane Crystallinity

The result of XRD analysis on Ch/Si/P membrane is presented in Fig. 4. Peak $2\Theta= 9.26°$; $20.4°$; and $22.1°$ indicates chitosan, while peak $2\Theta= 10.1°$; $20.3°$; $21.9°$ indicates chitosan-silica.

In PEG addition, the peaks of $2\Theta= 10.1°$ and $20.4°$ in chitosan-silica membrane decrease in its intensity and has a widened peak that indicate that chitosan-silica membrane crystallinity decreasesto amorph. According to He et al. [12]; Dakroury et al. [16], silica addition causes crystal structure to change to be amorphic by the appearance of peak at $2\Theta= 23.0°$. PEG concentration addition further decreases membrane crystallinity and changes the peak 2Θ to be $19.3°$. The effect of PEG additionon the chitosan membrane crystal structure is possible because of the interaction between chitosan and PEG through hydrogen bonds formation [12]. Hydrogen bonding formation destroys part ofchitosan crystal structure. Generally, produced membrane has an amorphic properties. According to Certier et al. 1990, chitosan has two crystalline forms namely form I and form II. The crystal form I is

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an orthorhombic that has cell unit with a= 7.76 Å, b= 10.9 Å, and c= 10.3 Å. The strongest reflection at 2Ө= 11.5° is a reflection from area (100). Crystal form II is also orthorhombic that has cell unit with a= 4.40 Å, b= 10.0 Å, and c= 10.30 Å. The strongest reflection that appears at 2Ө= 20.2° also corresponds to the reflection from the area (100).
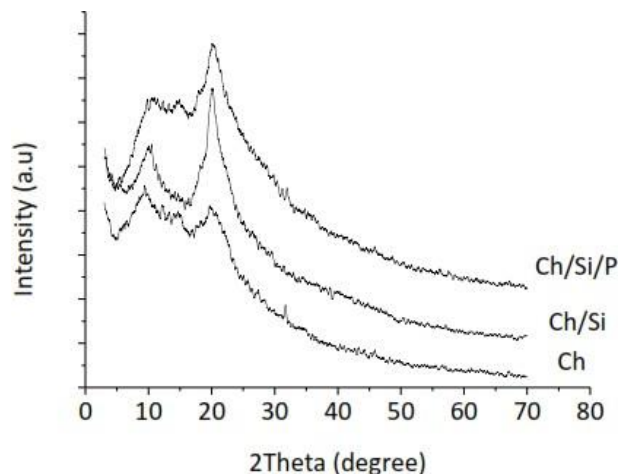

Fig. 4. Diffractogram of membrane Ch, Ch/Si, and Ch/Si/P

The change in *basal spacing* value (d) is used to study the distance shift between atoms in chitosan crystals after interacting with silica and PEG. The basal spacing value (d) on chitosan membrane is (9.54., 4.35., and 4.04) Å. Silica addition to membrane matrix is characterized with the increase of 2Ө and decrease of d value as follows: 8.83., 4.42., and 4.09. The d value decrease in chitosan-silica membrane matrix is possible as the result of silica particles that are largely trapped in membrane matrix thus it makes the distance between hydrogen bonds in O-3 --- O-5 and O-6 --- N-2 molecules decreases (Certier et al. 1990; Kumirska et al. [17]). PEG addition in chitosan-silica membrane matrix is marked with a decrease of 2Ө and an increase of d as follows: 8.89., 6.96. The increasing of d value in chitosan-silica-PEG membrane matrix is possible as a result of PEG polymer is bound to chitosan polymer chain through the formation of hydrogen bonds among molecules then it will reduce intermolecular hydrogen bonds that is shown with an increase of hydrogen bonds distance in O-3--O-5 and O-6--N-2.

3.4 Membrane Thermal Stability

Thermal stability test using DSC obtained glass transition temperature (T_g) data, T_g test result is still a controversial topic [12]. The main reasons may be due to chitosan properties such as crystallinity, molecular weight, deacetylation degree and chitosan source and chitosan extraction method have an effect on T_g value (Netto et al, 2005). Chitosan has an unclear T_g value, but some researchers have calculated the T_g value of chitosan in the range of 161-203°C. The glass transition temperature (T_g) is the temperature at which amorphous material is melted, whereas the melting point (T_m) is the temperature at which the crystalline material is melted. T_m is measured from the peak temperature when endotherm or exothermic processes happen. Material of metals and pure organic, there is no temperature peak from endothermic processes but derives from extrapolation of initial temperature (To) from endothermic and exothermic processes [18]. Thermogram DSC of chitosan-silica-PEG membrane is shown in Fig. 5.

DSC Thermogram is divided into 2 processes, they are endotherm processes that occurs at temperature 40-140°C and exothermic processes that occur at temperature 250-320°C. According to Liu et al. [18], at endothermic process it happens evaporation and absorption of water molecules, volatile components and hydrophilic groups. In exothermic process, degradation and membranecomponents breakdown occur. The complete test result using DSC is presented in Table 2.
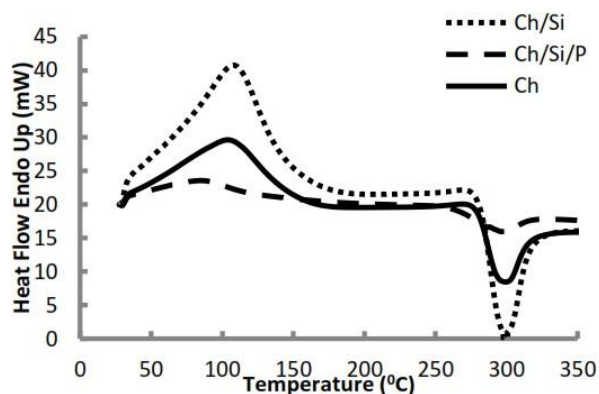
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Fig. 5. DSC Thermogram of membrane

Table 2. Data tabulation of membrane DSC thermogram

Membrane	Endotherm Phase				Exotherm Phase			
	T_0 (°C)	T_m (°C)	T_g (°C)	ΔH(J/g)	T_0 (°C)	T_m (°C)	T_g (°C)	ΔH(J/g)
Ch	66.41	106.12	143.07	209.34	260.58	297.74	317.56	-180.15
Ch/Si	77.88	109.72	140.78	216.10	282.03	299.39	317.49	-209.85
Ch/Si/P	50.54	87.43	121.77	62.81	270.98	296.08	316.44	-63.17

Generally, the result of DSC thermogram in chitosan-silica-PEG membrane, the value of T_0, T_m and T_g in Ch/Si membrane in exothermic phase increases compared to Ch membrane. It is due to hydrogen bonds increase that is formed between chitosan and silica. The increase in hydrogen bonds number causes molecular structure to be stable, due to hydrogen bonds formation between chitosan and silica [18,19]. Another factor that causes To, Tm and Tg values of Ch/Si membrane to increase is the reduced of polymer free volume as a result of silica increasing amount trapped in the membrane. The value of T_0, T_m and T_g in Ch/Si/P membrane on the exothermic phase decreases compared to the Ch/Si membrane. It is due to PEG addition to the membrane that occurred in agglomeration and trapped physically on the membrane surface. Other factors causing T_0, T_m and T_g values on the decreased Ch/Si /P membrane are possible as a result of polymer free volume. The free volume polymer is the polymer volume that is not occupied by polymer molecules. The higher the free volume, there will be more space for molecule to move. This result is also supported by the increaseof basal spacing value (d) in the test using XRD. Reduced solubility of chitosan, silica and PEG in membrane matrix makes the membrane becomes more amorphous structure, which is characterized by the declining of T_g value of Ch/Si/P membrane compared to Ch/Si membrane (Rodriques et al. 2014; Martiques et al. 2010).

3.5 Functional Group Analysis on Membrane

The analysis of functional group change is done by using FTIR spectroscopy. FTIR spectra result is presented in Fig. 6.

Fig. 6 shows that stretching bands of O-H and N-H on chitosan overlap in an area of 3000-3600 cm^{-1}. Absorption of C=O and CONH is present at wave numbers 1631 cm^{-1} and 1547 cm^{-1}. The absorption band of C-OH is also found at 1631 cm^{-1} and 1030 cm^{-1} and absorption band of C-O-C is found at 1150 cm^{-1}, indicating chitosan existence. The absorption band at 3278 cm^{-1} is an interaction of carbonyl group in chitosan with silica in natrium silicate. Specifically shown in the region of 1000-1250 cm^{-1} for existence of chitosan of Si-O-Si and Si-O-C in 1069 cm^{-1} and 795 cm^{-1}. This absorption is found in chitosan-silica membrane. The interactions among functional groups in the membrane are found in the presence of changes in typical absorption intensity of the -OH and -NH group. Generally, infrared spectra of chitosan-silica membrane shows an increase in -OH groups absorption at wave numbers around 1080 cm^{-1}. It is due to -OH groups addition of chitosan and natrium silicate. The shift in -OH group absorption towards smaller wave number on membrane shows the interaction between -

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OH groups in silica and -NH on chitosan (although it is not significant). In PEG addition it causes -OH group (3425 cm^{-1}) and amide (1651 cm^{-1}) of chitosan shift to lower wave numbers (though it is not significant). Interaction between chitosan and PEG derives from intermolecular hydrogen bonds of chitosan and PEG. This result is in line with the research of He et al. [12] who states that there is no chemical reaction between chitosan and PEG, although it is possible to form hydrogen bonds between chitosan and PEG. This result is also supported by thermal stability analysis results which states that PEG addition decreases the value of T_0, T_m and T_g on the Ch/Si/P membrane on exothermic phase.
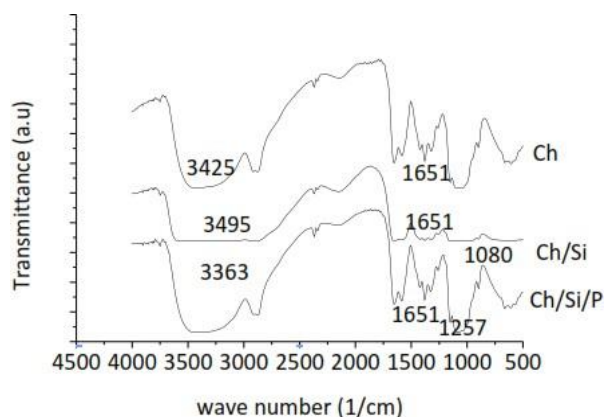
Fig. 6. FTIR spectra membrane

3.6 Membrane Hydrophylicity Properties

The hydrophilic properties of the produced membrane is tested by immersing the membrane in a buffer solution with a pH of 2.0-11.0 for 24 hours. The Swelling Index (SI) value is calculated using equation 1. Test result on membrane hydrophilicity is presented in Fig. 7.
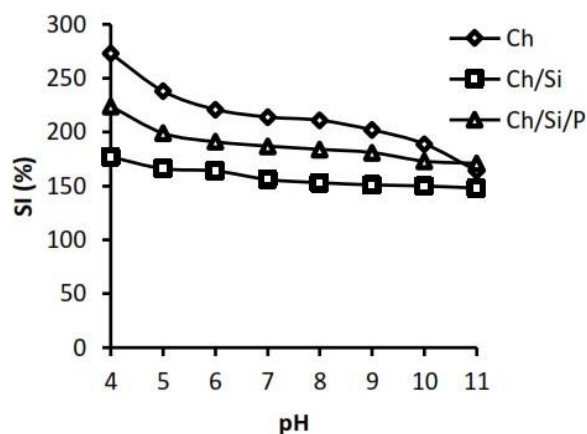
Fig. 7. Swelling Index (SI) value at various pH variations in membrane solution

Fig. 7 shows that in a strongly acidic solution it causes high Swelling Index value. The high Swelling Index value results in a soluble membrane at pH 2,0 to pH 3,0. It is due to acidic solution, -NH$_2$ group protonation on chitosan is changed into -NH$_3^+$ which acts as a weak base. Dissolution mechanism occurring in the membrane is thought to be due to acid reaction in solvent with the weak base in the -NH$_3^+$ group. Under the solution condition that is neutral and slightly alkaline, the Swelling Index value decreases along with the increasing of pH solution. A decrease in H$^+$ concentration causes protonation of -NH$_2$ group decreases that does not occur along the chitosan chain, therefore it causes solvent to be easily diffused in membrane [18]. Generally it can be concluded that the increase of

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silica concentration decreases hydrophilicity and increasing PEG concentration increases hydrophilicity characteristic along with pH value increase. PEG is a polymer that has large number of -OH and is hydrophilic so that absorption to water gets increased [18].

3.7 Proposed Structural Formula

Proposed formula for Ch/Si/P membrane structure based on mechanical character and XRD data, it is proposed that the -OH group in silica has crosslinking with -NH_2 and -OH groups in chitosan polymer and trapped in membrane matrix. Also for PEG molecules, PEG enters the membrane matrix by forming hydrogen bonds along the polymer chain as well as being trapped in the membrane matrix. The presence of silica in the membrane matrix causes the membrane free volume to decrease, whereas the presence of PEG in the membrane matrix increases the matrix free volume as a result of PEG forming hydrogen bonds along the chitosan polymer chain. The proposed structural formula is presented in Fig. 8.
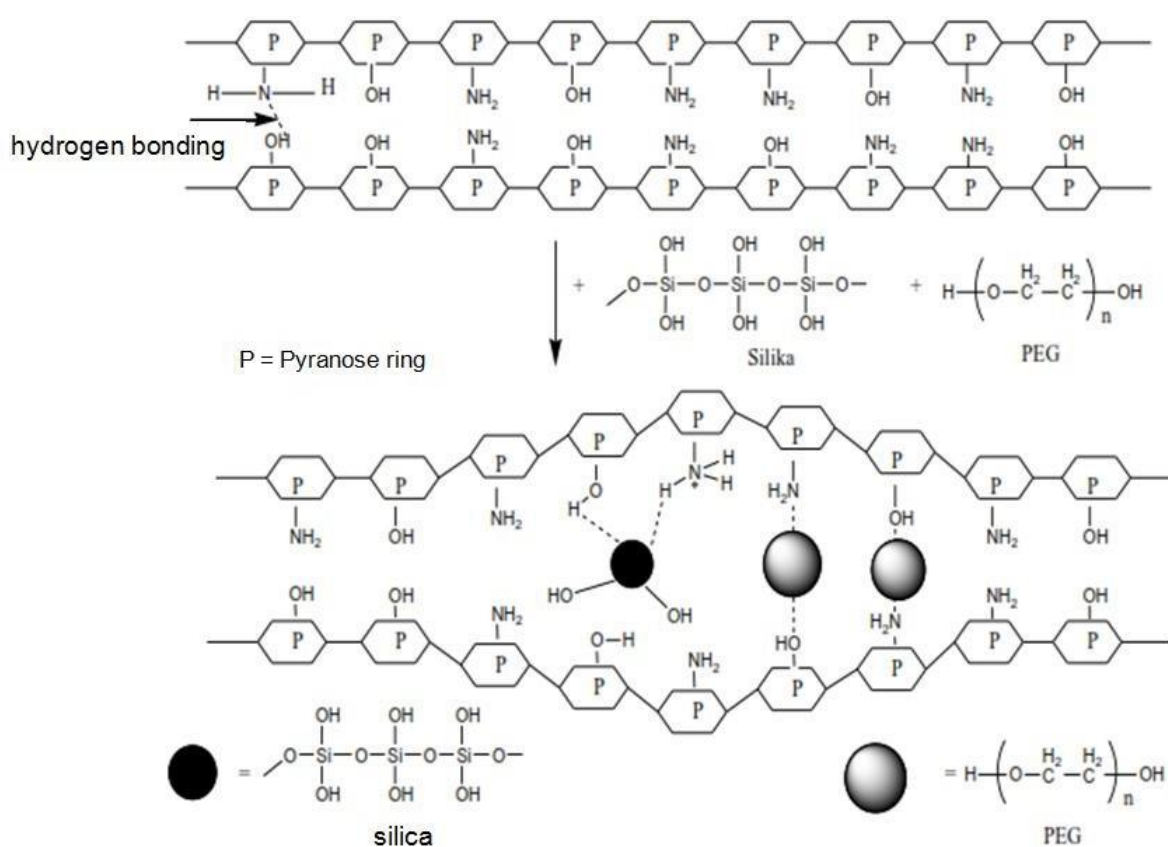
Fig. 8. Proposed structural membrane matrix

3.8 Removal of Cu(II), Zn(II) and Cd(II) Ions by Membrane

3.8.1 Effect of pH solution to metal ion adsorption by membrane

Membrane adsorption capacity of Cu(II), Zn(II) and Cd(II) ions is strongly influenced by the pH of metal ion solution. pH variation is to examine pH effect on adsorption of some metal ions is done inthe range of 4-9. It is due to < 4 pH all membranes are soluble in the solution. Comparison of Cu(II), Zn(II), and Cd(II) adsorption of on the solution pH variation to the membrane Ch, Ch/Si, and Ch/Si/P is presented in Fig. 9. It is commonly perceived that the higher of the pH, then metal ions adsorption increases and reaches optimum condition at pH range 5-6, then decreases at a pH above 6. Concretely, it can be seen of visible characteristic of each adsorbed metal ion on all membranes, ion

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Cu(II) and Zn(II) are adsorbed optimally at pH= 6. Ion Cd(II) is adsorbed optimally at pH 5-6. With an assumption that metal ions adsorption by all membranes involves the active site of -NH2 on the surface adsorbent, then at pH 2-3 (high acidity), it occurs protonated group of -NH2 on chitosan turned into NH_3^+ that acts as a weak base. Dissolution mechanism that occurs at the membrane may be due to the occurrence of acid reaction in a solvent with a weak base in the group of - NH_3^+ [15]. At pH 4-5 active sites tend to be protonated by the acid so that it is positively charged. It leads to a decreased adsorption of the adsorbate since it is thought to occur electrostatic repulsion interaction between active site of $NH3^+$ with metal ions which are both positively charged.

(a)

(b)   (c)
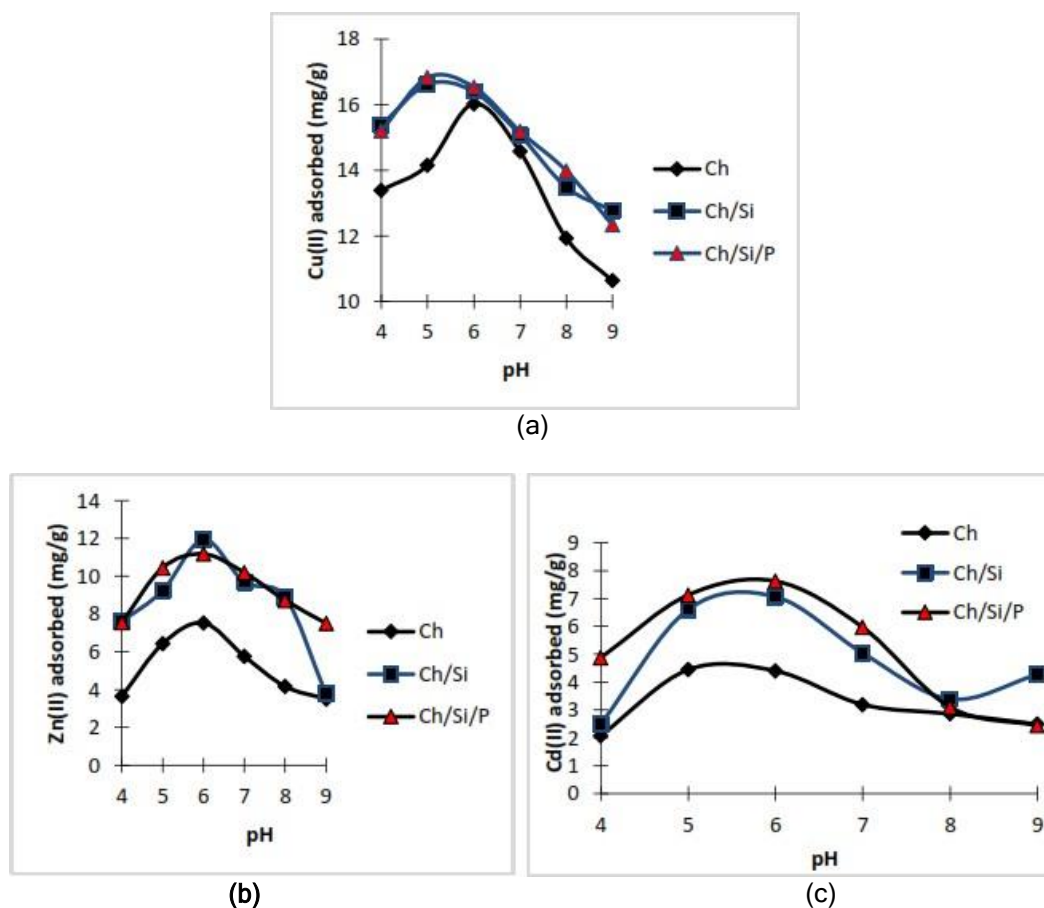
Fig. 9. Comparison of metal ion adsorption (a) Cu(II), (b) Zn(II), and (c) Cd(II) on solution pH variation to all membranes

According to Reirad et al. 2012; Byungryul An and Jae-Woo Choi [20]; Sahebjamee et al. [21]; Le et al. 2018) a mechanism which is possible to occur in metal ions adsorption is as follows:

$$R\text{-}NH_2 + H^+ \longrightarrow R\text{-}NH_3^+ \tag{2}$$

$$R\text{-}NH_2 + Cu^{2+} \longrightarrow R\text{-}NH_2\, Cu^{2+} \tag{3}$$

$$R\text{-}NH_3^+ + Cu^{2+} \longrightarrow R\text{-}NH_2\, Cu^{2+} + H^+ \tag{4}$$
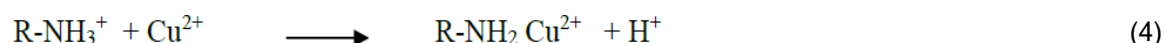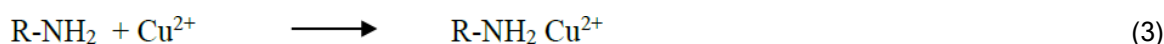
The increase in pH lower levels of protonated group - NH2 on the surface of membrane followed with a decrease in partial positive charge, therefore an increase in pH tends to increase the adsorption of metal ions. In relatively high pH, the amount of adsorbed metal ions decreases. It is expectedbecause the formation of metal hydroxide ions precipitate as a result of exceeding value of Ksp in

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solution [15,22]. Thus the optimum pH used to study interaction time effect and metal ions initial concentration is as follows: pH= 6 for Cu(II), and Zn(II), pH= 5.5 for ion Cd(II).

3.8.2 Effect of contact time to metal ion adsorption by membrane

In this research, kinetic parameters obtained by interacting each metal ion at optimum pH, room temperature and time variation of 1-26 hours. The observation of time effect for each metal ion in all membranes is presented in Fig. 10.

(a)

(b)

(c)
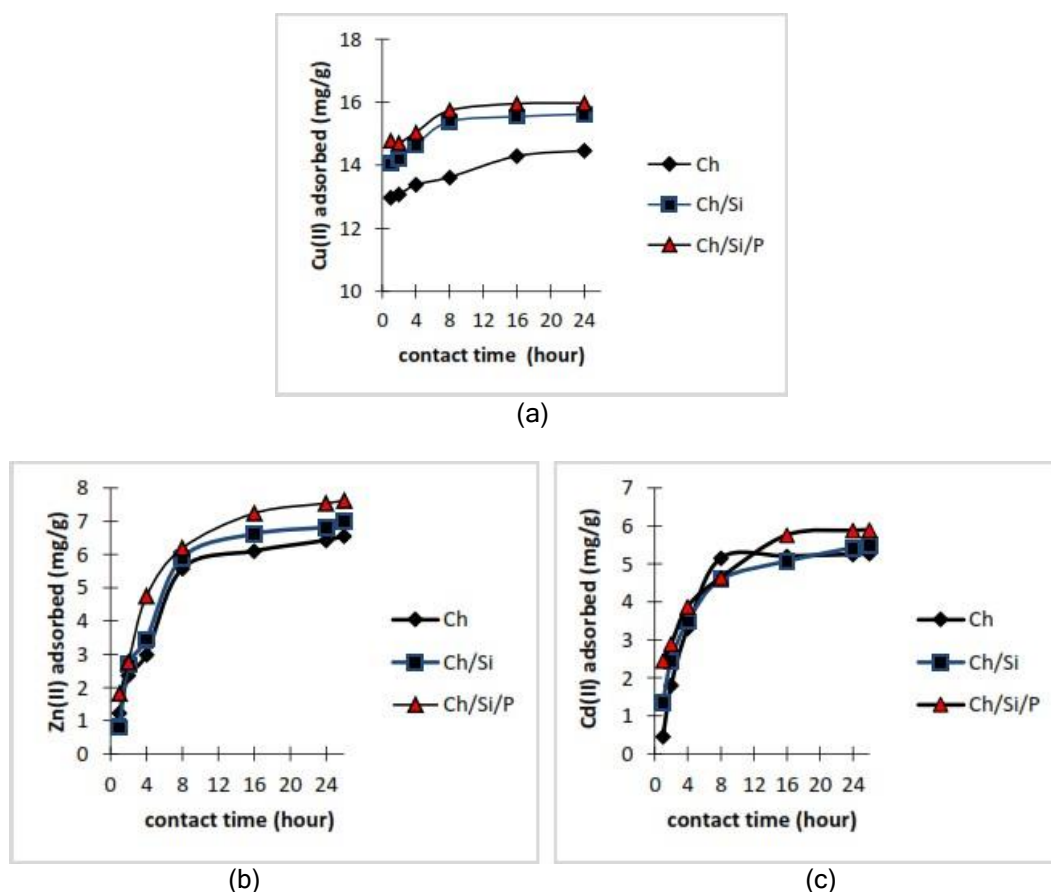
Fig. 10. Effect of contact time on metal ions adsorption on membrane (a) Cu(II), (b) Zn II) and (c) Cd(II)

Fig. 10 shows that generally adsorption of Cu(II), Zn(II) and Cd(II) in Ch membrane or Ch/Si membrane and Ch/Si/P membrane quickly lasts for 4 hours. At contact time between 1-16 hours there is an increase in adsorbed metal ions number, while during 16-26 hours time no increase is significantly found. It indicates that there has been a balance between metal ions adsorbed number by the amount of metal ions remaining in the solution.

Based on this phenomenon it can be predicted that the amount of adsorbed adsorbate is parallel with the number of active sites on membrane that has not bonded with the adsorbate. The more of active sites on the membrane that are not bonded with adsorbate, the more adsorption occurs more easily and vice versa. At the beginning of interaction, there are many empty active sites so that there are much adsorbat which quickly bonded to membrane. At the time of long lasting interaction, there is less vacant positions so that the amount of bonded adsorbate declines. Based on Fig. 10, adsorption data at various times of interaction can be processed using pseudo-first-order kinetics model proposed by Lagergren and pseudo-order kinetic model proposed by Ho. Some researchers have previously used Lagergren's pseudo first-order kinetics equation and pseudo-order kinetics 2 equation (Ho) to

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evaluate kinetics model prevailing tendency in metal ion adsorption process by the adsorbent-based chitosan [23,24,25].

Lagergren's pseudo first order kinetics equation:

$$\log (q_e - q_t) = \log q_e - (k_1/2{,}303)\, t$$

notes: q_e = The number of adsorbate at equilibrium (mmol g^{-1}) q_t= the number of adsorbate at time t (mmol g^{-1}), t= time (hours), k_1= pseudo-order rate constants 1 (hour^{-1}). Pseudo-order kinetics equation 2 (Ho): $\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$

Notes: q_e is the number of adsorbate at equilibrium (mmol g^{-1}), q_t is the number of adsorbate at the time t (mmol g^{-1}), t is the time in hours and k_2 is the second order rate of constant pseudo (mmol g^{-1}h^{-1}).The data result processing using pseudo first-order kinetic Lagergren's equation and pseudo-order kinetics 2 (Ho) equation are presented in Table 3.

Table 3. Kinetic parameters of pseudo-first-order kinetics model and pseudo-two-order in metal ion adsorption process by membrane

Ion	Membrane code	Lagergren's pseudo-first- order kinetic model			pseudo-second- order kinetic model		
		k_1 (/h)	q_e (mmol/g)	R^2	K_2 (g/mmol/h) x 10^{-3}	q_e (mmol/g)	R^2
Cu(II)	Ch	0.03	0.24	0.89	0.36	9.27	0.99
	Ch/Si	0.05	0.16	0.88	0.49	10.0	1.00
	Ch/Si/P	0.06	0.10	0.87	0.55	10.2	1.00
Zn(II)	Ch	0.10	6.22	0.71	0.04	5.15	0.99
	Ch/Si	0.12	7.91	0.99	7.48	0.06	0.99
	Ch/Si/P	0.16	7.21	0.99	15.20	0.03	0.99
Cd(II)	Ch	0.09	4.77	0.55	0.02	6.77	0.99
	Ch/Si	0.05	2.08	0.81	0.05	6.90	0.99
	Ch/Si/P	0.07	2.81	0.99	0.06	7.25	0.99

Table 3 is obtained from the research data that is correlated according to kinetics pseudo first order Lagergren's model equation and pseudo-order 2 (Ho) kinetics model equation, that are in order for Cu(II), Zn(II), and Cd(II). Value data correlation factor R^2 contained in Table 3 provides some significant data between the results obtained through pseudo first-order kinetic model and the Lagergren's pseudo second-order kinetic model. In general there is a tendency of correlation factor value R^2 that is higher on pseudo second-order kinetic model.

Some of these phenomena illustrate that despite the pseudo second-order kinetic model significantly works on some metal ion-membrane interactions, but there is a metal ion-membrane interactions that are suitable following Lagergren's pseudo first order kinetics model. In pseudo second-order kinetic model, the value of q_e (equilibrium adsorption) is more suitable with the value of q_e experimental result. Kinetic constant value in pseudo second order model (k_2) increases along with silica and PEG added number. It indicates that kinetically adsorption rate increases with silica and PEG addition. In Table 3 it shows k_2 value is smaller than k_1 value it indicates reaction goes slowly since in adsorption reaction it happens metal ion-adsorbent through chelate formation. It is consistent with previous research result [26,27,22]. According to Cheng et al. [27], Cu(II) adsorption on transparent chitosan modified thin membrane (MCTTM) tends to follow pseudo second order kinetics model. k_1 value is greater than k_2 value. According to Ghaee et al. [16], Cu(II) adsorption to the chitosan-silica membrane tends to follow pseudo second order kinetics model. Chitosan-silica membrane with ratioof 6:1 increases k_2 value to be doubled compared to chitosan membrane. Kinetic data shows that 24 hour contact time is the time to achieve equilibrium. At the beginning of adsorption process, the speed

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of adsorption process is controlled by mass transfer process on membrane surface and afterwards adsorption process is controlled by diffusion mass on the inside of membrane [22].

3.8.3 Effect of initial metal ion concentration on metal ion adsorption by membrane

Thermodynamic study is conducted to determine adsorption isotherms type from membrane as an adsorbed membrane on metal ions. Observation of initial concentration effect on each metal ion adsorption in all membranes is presented in Fig. 11. The observation on all metal ions and all membranes shows an increasing number of adsorbed metal ions along with the increasing concentration of metal ions. At higher concentrations, the increase in metal ions concentration is not accompanied by metal ions adsorption increase significantly. Adsorption data evaluation using Langmuir's isotherm adsorption model and Freundlich's isotherm adsorption model is done by transforming data into variables that correspond to Langmuir and Freundlich's linear isotherm equation models. Langmuir and Freundlich's isotherm parameters data are presented in Table 4. Obtained R^2 value can be used to track conformance with Langmuir and Freundlich's adsorption isotherm model. In Table 4 it is shown that Langmuir's isotherm model provides conformity to most interactions between metal ions and membranes.

(a)

(b)

(c)
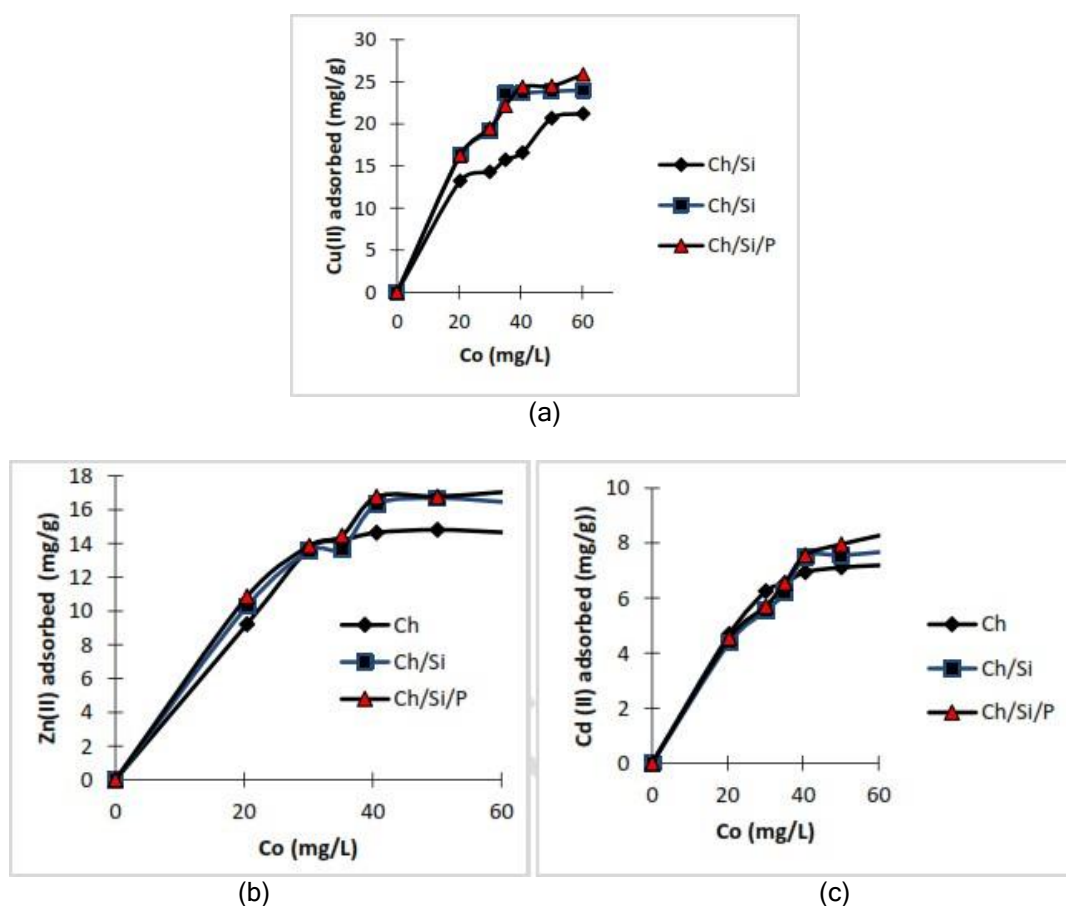
Fig. 11. Influence of the initial concentration on metal ion adsorption in (a) Cu(II), (b) Zn(II) and (c) Cd(II) membranes

Phenomenon occured in interaction of Cu(II), Zn(II), and Cd(II) metal ions with active sites on membrane is in accordance with Langmuir's isotherm model. Langmuir's isotherm concept states that the increase in concentration followed by the increasing amount of adsorbed substance so as to achieve equilibrium quantity. Langmuir's adsorption theory suggests that on adsorbent surface there are certain number of active sites is parallel with adsorbent surface area. In the state of active sites that has not been saturated by adsorbate, there will be an increase in adsorption. Adsorbate

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increasing concentration that is interacted does not increase the amount of adsorbed adsorbate when active sites have been saturated by the adsorbate. If this trend occurs, then metal ions interaction involved on the surface of each adsorbent monolayer/one layer. It happens in interaction between Cu(II), Zn(II), and Cd(II) membranes and Ch membrane, Ch/Si membranes, and Ch/Si/P membranes. Metal ion adsorption on an adsorbent is influenced by several factors, for example, the ability of adsorbent, metal ion size, and environment in adsorption process. The adsorbent ability can be seen through two different sides namely the active group and the pore size of adsorbent. It appears that adsorption capacity value at all membranes follows the order of Cu(II) > Zn(II) > Cd(II). In accordance with HSAB concept, metal ions Cu(II) and Zn(II) are medium acid, Cd(II) is a soft acid. Active group of – NH_2 is the most dominant active sites of all membranes and in accordance with HSAB concept, -NH_2 group is a hard base.

Table 4. Langmuir and Freundlich isotherm parameter

Ion	Membrane code	Langmuir Isotherm			Freundlich Isotherm		
		q_e ($\mu mol/g$)	ΔG (KJ/mol))	R^2	K_F	n_F	R^2
Cu(II)	Ch	247	-23.3	0.99	5.33	3.70	0.96
	Ch/Si	249	-31.3	0.99	12.1	12.3	0.99
	Ch/Si/P	262	-31.3	0.99	12.6	14.0	0.99
Zn(II)	Ch	156	-25.9	0.99	4.45	4.27	0.81
	Ch/Si	181	-25.1	0.99	5.24	4.56	0.94
	Ch/Si/P	183	-25.5	0.99	5.82	5.15	0.98
Cd(II)	Ch	95.0	-29.0	0.99	2.22	2.64	0.95
	Ch/Si	98.0	-23.2	0.99	2.34	2.72	0.98
	Ch/Si/P	107	-23.0	0.99	2.39	2.62	0.98

Adsorption of Cu(II) on all membranes have the highest adsorption capacity values compared to the metal ions Zn(II) and Cd(II). Based on data, the value of ionic radius: Cu(II) = 0,57 Å, Zn(II) = 0,74 Å, and Cd(II) = 0,95 Å. [28]. Ion Cd(II) has larger ionic radius than Cu(II) and Zn(II) so that its polarization strength is the biggest and behaves as soft acid. It results in an ionic bond Cd(II) with -NH_2 group on membrane that is not as strong as in Cu(II) and Zn(II). It appears the value of all metal ions adsorption capacity of the membrane increase following the sequence Ch/Si/P > Ch/Si > Ch. In all membranes, there are active -NH_2 group membranes that are dominant and act as a hard base. Adsorption capacity improvement on Ch/Si membrane compared to Ch due to the increasing membrane pore size with silica addition. Increased pore size of the membrane causes an increase in surface area, the greater the surface area of the membrane then the active group of -NH_2 on membrane surface which can be bonded by metal ions also increases [29,30]. This results is consistent with the research of [19] silica particles increase to be three-part proved increases Cu(II) adsorption to be doubled.

Adsorption capacity of all the metal ions in Ch/Si/P membrane is the highest compared to Ch membrane and Ch/Si membranes. The increase in adsorption capacity is caused by the increase in - OH functional groups that derive from PEG. PEG addition results in hydrophilic character increase. The ability to absorb water increases with PEG addition, it results in membrane surface ability increase to bond metal ions dissolved in water media. Porogen is not the only factor causes an increase in capacity but also other factors such as membrane wettability character or membrane hydrophilicity character [22,31,32].

4. CONCLUSION

Based on the data obtained from chitosan-silica-PEG membrane characterization, it can be concluded that silica source that is commonly used affects Ch/Si produced membrane characteristic. Generally, silica addition in Ch/Si membrane synthesis increases its tensile strength, Young Modulus, pore size distribution, and stability against temperature and decreases elongation percentage value and hydrophilicity character, but does not affect crystallinity and functional groups change on membrane. PEG addition on Ch/Si/P membrane synthesis increases elongation percentage, Young Modulus and hydrophilicity properties and pore size distribution reduction but does not affect crystallinity, stability

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against temperature and functional groups change on the membrane. In adsorption with batch system, for all membranes is obtained optimum pH for metal ion Cu(II) and Zn(II) = 6, Cd(II) = 5.5. Cu(II), Zn(II) and Cd(II) adsorption in membrane tends to follow Langmuir's isotherm models. Generally, it can be said that Ch membrane adsorption capability against all metal ions increases with silica and PEG addition. Ch/Si/P membrane adsorption capacity µmol/g value to Cu(II), Zn(II), and Cd(II) respectively is 262, 183 and 107 µmol/g. Commonly, in adsorption kinetics data there is a tendency of linearity coefficient R^2 value that is higher on pseudo second-order kinetic model.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. No HK, Meyers SP. Preparation and characterization of chitin and chitosan – A review. Journal Aquatic Food Production Technology. 1995;4;27-52.
2. Liu Y-L, Yu-Huei S, Juin-Yih L. *In situ* crosslinking of chitosan and formation of chitosan-silica hybrid membranes using γ-glycidoxypropyltrimethoxysilane as a crosslinking agent. Journal Polymers. 2004;45:6831-6837.
3. Yeh J-T, Chin-Lai C, Kuo-Shien H. Synthesis and properties of chitosan/SiO_2 hybrid materials. Materials Letters. 2007;61:1292-1295.
4. Al-Sagher F, Muslim S. Thermal and mechanical properties of chitosan/SiO_2 hybrid composites. Journal Nanomaterials. 2010;7. Article ID: 490679.
5. Enescu D, Viorica H, Rodinel A. Polymethylsiloxane modified chitosan. Part III: Preparation and characterization of hybrid membranes. Carbohydrate Polymers. 2009;76:268-278.
6. Zulti F, Kiagus Dahlan, Purwantiningsih Sugita. Adsorption of waste metal Cr(VI) with composite membranes (chitosan-silica rice husks). Makara. 2012;16(3):163-168.
7. Mahatmanti FW, Nuryono, Narsito. Adsorption of Ca(II), Mg(II), Zn(II) and Cd(II) on chitosan membrane blended with rice hull ash silica and polyethylene glycol. Indonesian Journal of Chemistry. 2016;16(1):45-52.
8. Mahatmanti FW, Nuryono, Narsito. Physical characteristics of chitosan based film modified with silica and polyethylene glycol. Indonesian Journal of Chemistry. 2014;14(2):131-137.
9. Chen AH, Ceng-Yu Y, Chia-Yun C, Chia-Yuan C, Chia-Wen C. The chemically crosslinked metal-complexed chitosans for comparative adsorptions of Cu(II), Zn(II), Ni((II) and Pb(II) ions in aqueos medium. Journal Hazardous Materials. 2009;163:1068-1075.
10. Zou H, Shihshan W, Jian Shen. Polymer/Silica nanocomposites: Preparation, characterization, properties and applications. Chemical Reviews. 2008;108:3893-3957.
11. Zhang M, Li XH, Gong YD, Zhao NM, Zhang XF. Properties and biocompatibility of chitosan films modified by blending with PEG. Biomaterials. 2002;23:2641-2648.
12. He L-H, Xue R, De-bin Y, Liu Y, Song R. Effects of blending chitosan with PEG on surface morphology, crytallization and thermal properties. Chinese Journal Polymer Science. 2009;27(4):501-510.
13. Park S-B, Jin-Oh Y, Ham-Yong P, Seung Joo H, Woo-Sik K. A novel pH sensitive membrane from chitosan-TEOS IPN; Preparation and Its Drug Permeation Characteristics. Biomaterials. 2001;22:323-330.
14. Choi S-S, Lee SG, Im SS, Kim SH, Koo YL. Silica nanofibers from eelectrospinning/sol-gel process. Materials Science Letters. 2003;22:891-893.
15. Pandis C, Sara M, Joana M, Apostolos K, Joao FM, Jose LGR. Chitosan-silica hybrid porous membranes. Materials Science Engineering C. 2014;42:553-561.
16. Dakroury GA, Abo ‑ Zahra Sh. F, Hassan HS, Fathy NA. Utilization of silica–chitosan nanocomposite for removal of [152+154] Eu radionuclide from aqueous solutions. Journal of Radioanalytical and Nuclear Chemistry. 2020;323:439-455.
17. Kumirska J, Czerwicka M, Kaczynski Z, Byhowska A, Brzozowski K, Thoming J, Stepnowski P. Application of spectroscopic methods for structural analysis of chitin and chitosan. MarineDrugs. 2010;8:1567-1636.

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18. Liu D, Zehui L, Yi Z, Zhenxuan L, Kumar R. Recycled chitosan nanofibril as an effective Cu(II), Pb(II) and Cd(II) ionic chelating agent: Adsorption and desorption performance. Carbohydrate Polymers. 2014;111:469-476.

19. Ebisike K, Okoronkwo AE, Alaneme KK. Synthesis and characterization of Chitosan-silica hybrid aerogel using sol-gel method. Journal of King Saud University – Science. 2020;32:550-554.

20. Byungryul An, Jae-Woo Choi. An experimental application of four types of chitosan bead for removal of cationic and anionic pollutants. Water Air Soil Pollution. 2019;230:314.

21. Sahebjamee N, Soltanieh M, Mousavi SM, Heydarinasab A. Removal of Cu^{2+}, Cd^{2+} and Ni^{2+} ions from aqueous solution using a novel chitosan/polyninyl alcohol adsorptive membrane. Carbohydrate Polymers. 2019;210:264-273.

22. Salehi E, Madaeni SS, Rajabi L, Vatanpour V, Derakhsan AA, Zinadini S, Ghorabi Sh., Monfared HA. Novel chitosan/poly(vinyl) alcohol thin adsorptive membranes modified with amino functionalized multi-walled carbon nanotubes for Cu(II) removal from water preparation, characterization, adsorption kinetics and thermodynamics. Separation Purifcation Technology. 2012;89:309-319.

23. Popuri SR, Vijaya Y, Veera, Boddu M, Abburi K. Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads. Bioresources. Technology. 2009;100:194-199.

24. Dinu MV, Dragan ES. Evaluation of Cu^{2+}, Co^{2+} and Ni^{2+} ions removal from aqueous solution using a novel chitosan/clinoptilolite composite: Kinetics and isotherms. Chemical Engineering Journal. 2010;160:157-163.

25. Kavianinia I, Paul GP, Nadia GK, David RKH. New hydrogels based on symmetrical aromatic anhydrides: Synthesis, characterization and metal Ion adsorption evaluation. Carbohydrate Polymers. 2012;87:881-893.

26. Ghaee A, Shariaty-Niassar M, Barzin J, Matsuura T. Effect of chitosan membrane morphology on copper ion adsorption. Chemical Engineering Journal. 2010;165:46-55.

27. Cheng Z, Xiaoshuai L, Mei H, Wei M. Adsorption kinetic character of copper ions onto a modified chitosan transparent thin membrane from aqueous solution. Journal Hazardous Materials. 2010;182:408-415.

28. Martell AE, Hancock RD. Metal complexes in aqueous solutions. Plenum Press, New York; 1996.

29. Shi P, Hu X, Duan M. A UIO-66/tannic acid/chitosan/polyethersulfone hybrid membrane like adsorbent for the dynamic removal of dye and Cr (VI) from water. Journal of Cleaner Production. 2021;290:125794.

30. Nikiforova TE, Kozlov VA, Telegin FY. Chemisorption of copper ions in aqueous acidic solutions by modified chitosan. Materials Science & Engineering B. 2021;263:114778.

31. Saber-Samandari S, Gazi M, Yilmaz O. Synthesis and characterization of chitosan-graft-poly (N-allyl Maleamic Acid) hydrogel membrane. Water Air Soil Pollution. 2013;224:1624.

32. Marques JS, Pereira MR, Sotto A, Arsuaga JM. Removval of aqueous Copper(II) by using crosslinked chitosan films. Reactive and Functional Polymers. 2019;134:31-39.

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Any other remarkable point(s):

Research publication in reputed journals include:

Physical characteristics of chitosan based film modified with silica and polyethylene glycol. Indonesian Journal of Chemistry. (2014). url:https://jurnal.ugm.ac.id/ijc/article/view/21249/13954

Chitosan Membrane with Blending with Rice Hull ash Silica and Polyethelene Glycol for Cu(II) in aqueous solution. Advanced Materials Research. (2015) url:Doi: 10.4028/www.science.net/AMR.123.169

Adsorption of Ca(II), Mg(II), Zn(II), and Cd(II) on Chitosan Membrane Blended with Rice Hull Ash Silica and Polyethylene Glycol. Indonesian Journal of Chemistry. (2016) url: http://pdm-mipa.ugm.ac.id/ojs/index.php/ijc/article/view/1043/1156

Porous Chitosan-silica-polyethylene Glycol Membrane for Dinamic Adsorption of Binary Mixtures Cu(II) and Zn(II) Ions. International Journal of Materials, (2017). url:http://www.ijmmm.org

/index.php?m=content&c=index&a=show&catid=47&id=337

Chitosan/Silica/Polyethylene glycol (Ch/Si/P) Composites Membrane as Selective Adsorbent of Rhodamine B from Aqueous Solution. (2017). url:http://dx.doi.org/10.14233/ajchem.2017.20157

Conference Procedings (first Author)

Adsorption of Pb(II) ion from aqueous solution onto chitosan/silica/polyethylene glycol (Ch/Si/P) composites membrane. (2017). http://iopscience.iop.org/1757-899X/172/1/012019

Preparation and Characterization of Composite Membrane Chitosan-Silica-Polyethylene Glycol. (2018).doi:10.4028/www.scientific.net.382.3

Dynamic adsorption of mixtures Rhodamine B, Pb(II), and Zn(II) ions composites Chitosan-Silica-Polyethylene Glycol membrane. (2018). http://iopscience.iop.org/1088-899X/349/1/012022

Synthesis and Characterization of Chitosan Based Superabsorbent Polymer Modified with Acrylic Acid and Acrylonitrile forPb(II) Metal Ions Removal from Water. (2020). https://doi.org/10.1063/5.0005748

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