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by Wara Dyah Pita Rengga

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Chitosan/Silica/Polyethylene Glycol (Ch/Si/P) Composites Membrane as Selective Adsorbent of Rhodamine B from Aqueous Solution

F. WIDHI MAHATMANTI^{1*}, W.D.P. RENGGA², E. KUSUMASTUTI¹ and NURYONO³

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang 50229, Indonesia

²Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang 50229, Indonesia

³Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281 Indonesia

*Corresponding author: Tel: +62 8157709651; E-mail: widhimahatmanti@rocketmail.com; fwidhi_kimia@mail.unnes.ac.id

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In this research, chitosan/silica/polyethylene glycol (Ch/Si/P) composites membrane was used as selective adsorbent of rhodamine B from aqueous solution. This study involved by preparation Ch/Si/P composites membrane. The structure and surface morphology of Ch/Si/P composites membrane was characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy. Batch adsorption experiments were conducted with various contact time and rhodamine B concentrations to evaluate the adsorption kinetics and thermodynamics. Results show that adsorption fitted to Langmuir model and followed a kinetic model of pseudo-second-order. The adsorption capacity of rhodamine B onto the Ch/Si/P composites membrane is 0.052 mmol/g. The relative selective factor (α_i) values of rhodamine B/Cu and rhodamine B/Pb are 3.53 and 0.42. This means that rhodamine B can be determined even in the presence of Cu interference, but can't be determined in the presence of Pb interference.

Keywords: Adsorption, Rhodamine B, Chitosan, Silica, Polyethylene glycol, Membrane.

INTRODUCTION

Textile waste containing dye can provide its own problems for the textile dye harmful to living things, especially humans. Rhodamine B is one of the dyes used in the textile industry because the price is more economical and easily obtained. Rhodamine B is an important basis in the dyeing process in the textile and paper industries. Rhodamine B is highly toxic if exposed directly to the skin, eyes, or swallowing. The impact due to an exposure that occurs can be irritating to skin, eyes and gastrointestinal tract. Chronic effects on health that can cause cancer and liver dysfunction.

Several methods have been developed to reduce the levels of dyes from wastewater, such as chemical precipitation, coagulation, complexation, solvent extraction, ion exchange, adsorption and membrane separation [1-6]. From some of these techniques, adsorption and membrane separation is often used because it is relatively simple and relatively inexpensive cost required. The chitosan/silica/polyethylene glycol (Ch/Si/P) composites membrane prepared by mixing with silica isolated from rice husk ash (ASP) and polyethylene glycol (PEG) as a plasticizer. The addition of silica in the manufacture of chitosan-silica membranes increases the tensile strength and Young's modulus, the pore size of the membrane, the stability of the temperature rise. The addition of PEG in the manufacture of

chitosan membrane-silica-PEG increase the percentage of elongation and reduction in Young's modulus (more elastic and flexible membrane) and the properties of the membrane hydrophilicity [7,8]. The Ch/Si/P composite membrane with higher mechanical properties compared with chitosan membrane as indicated by the high value of per cent elongation and a low Young's modulus (membrane strong and stable). The process of using membrane separation and adsorption requires a powerful and flexible membrane so that the membrane is not easily torn upon use. The Ch/Si/P composite membrane is used to adsorb rhodamine B. Factors that influence includes pH, contact time, the initial concentration of the solution and selectivity is studied further.

EXPERIMENTAL

Chitosan with deacetylation degree of 83 % was supplied from CV Ocean Fresh Bandung, Indonesia, polyethylene glycol (m.w. 400), sodium silicate solution from rice hull ash silica (25 % SiO₂), sodium hydroxide pellet, HCl 37 %, acetic acid (2 % v/v), fumed HNO₃, rhodamine B, Cu(NO₃)₂·3H₂O, Pb(NO₃)₂ all in analytical grade were purchased from Merck.

pH meter (EUTECH Instrument Ecoscan), orbital Shaker (yellow line OS 10 basic), analytical balance (Denver Instruments), FTIR spectrometer (Shimadzu Prestige-21), scanning

electron microscope (SEM JSM-6360 LA) and A Shimadzu X-ray diffractometer (XRD) with Cu-K α radiation, spectrophotometry visible (Shimadzu 1240) was applied for the determination of rhodamine B concentration in the sample solution. Atomic absorption spectroscopy, AAS (Perkin-Elmer AA200), was applied for determination of Pb(II) and Cu(II) concentration in the solution.

General procedure:

Preparation of Ch/Si/P composite membrane: Chitosan 1 g was dissolved in 100 mL of 2 vol % acetic acid solution. Appropriate 0.8 g of rice hull ash silica and 0.5 g PEG were mixed with the chitosan solution and the mixture was thoroughly stirred until there was no air bubble in the solution. The membrane was obtained by casting the mixture on a glass plate and were allowed to evaporate the solvent under an ambient temperature for 3 days. Membranes were neutralized with a 5 % (w/v) NaOH solution after drying. Afterward, the membrane was washed with water to remove the remaining NaOH. Finally, the membrane was stored in a desiccator before use [7,8].

Characterizations of membrane: The surface morphology was investigated with scanning electron microscope after gold coating. The fractured cross-sections of the film were frozen in liquid nitrogen then broken and air dried. Fourier transform-infrared (FT-IR) spectra were obtained under dry air at a room temperature on KBr pellets in the range of 4000-500 cm $^{-1}$. An X-ray diffractometer was used to record the diffractograms of the films at 25 °C. The X-ray source was Ni-filtered CuK α radiation (40 kV and 30 mA). The dry films were mounted on a sample holder and the pattern was recorded in the reflection mode at an angle 2 θ over a range of 3.0200° to 70° at a speed of 5°/min.

Adsorption experiment: The adsorption experiment was performed using a batch method at various pH from 4 to 9. The solution pH was adjusted using HCl and NaOH solutions. An aqueous solution of 100 mg/L rhodamine B was shaken with 0.12 g membrane for 24 h at various pHs. The optimum pH was used to evaluate the kinetics parameter by varying the contact time (1, 2, 4, 8, 16, 24 and 26 h) and thermodynamics parameter by varying the concentration (50 to 250 mg/L). Selectivity of adsorption was evaluated on the data binary competitive rhodamine B and metal ion adsorption for rhodamine B/Cu(II) and rhodamine B/Pb(II) in aqueous solution. Sorbent (0.12 g) was equilibrated with 10 mL of solution containing 0.5 mmol/L of rhodamine B, 0.5 mmol/L of Cu(II) and 0.5 mmol/L of Pb(II) or 1 mmol/L of Cu(II) and Pb(II), respectively. The concentration of unadsorbed rhodamine B was measured by visible spectrophotometry. The concentration of unadsorbed metal ions were detected by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Characteristics of Ch/Si/P composites membrane: Mahatmanti *et al.* [7,8] studied FTIR spectra of Ch/Si/P composite membrane, peaks around 1240 and 842 cm $^{-1}$ were assigned to PEG indicating the presence of PEG after blending. The intermolecular interaction between chitosan and PEG should be ascribed to the hydrogen bond. Furthermore, C-O stretching

vibration from C-O-H of chitosan (1151 cm $^{-1}$) was shifted to low wavenumber. All these imply the existence of an attractive intermolecular interaction between chitosan and PEG, as suggested in the literature [9,10]. Hence, the intermolecular interaction between chitosan and PEG should be ascribed to the hydrogen bond.

The Ch/Si/P composites membrane give similar peaks with 2 θ around 9.80°, 20.445° and 10.46° which should be assigned to an amorphous solid structure [8,9]. The addition of silica and PEG in chitosan membrane does not change significantly the morphology agreed to the result reported by He *et al.* [9].

The morphology of the Ch/Si/P composites membrane is evaluated based on the scanning electron microscopy (SEM). Blending sodium silicate and polyethylene glycol with chitosan improves the porosity of membrane and the morphology however, shows no change significantly the porosity. The addition of PEG causes the pores in the Ch/Si/P composites membrane is reduced due to the physically trapped PEG on the solid surface. Polyethylene glycol is likely to accumulate on the top surface of the membrane, where maximum contact with water is possible during phase inversion [7,8,10,11]. This result supports the conclusion based on the FTIR spectra showed that the possibility of interaction between component molecules are very small and did not significantly affect material properties.

Adsorption of rhodamine B

Effect of pH: The pH factor is very important in the adsorption process especially for dye adsorption. The effects pH on the adsorption of rhodamine B onto Ch/Si/P composites membrane is shown in Fig. 1. The results showed the highest adsorption of rhodamine B at pH 7. The sorption of rhodamine B on the surface of the Ch/Si/P composites membrane is significantly influenced by the pH. It is attributed to that change in the pH of the solution results in forming different ionic species and different surface charge of the Ch/Si/P composites membrane. When pH lower than 7, the surface of the Ch/Si/P composites membrane is positive and has weakly interaction with rhodamine B cation. When pH higher than 7, the surface of the Ch/Si/P composites membrane is negative and has strongly interaction with rhodamine B cation. Alkaline pH value causes the negatively charged membrane surface while forming zwitterionic ion rhodamine B. Thus rhodamine B more easily adsorbed on the surface of Ch/Si/P composites membrane due to electrostatic attraction between rhodamine B with the surface of the membrane. Ion zwitterionic form of rhodamine B by Peng *et al.* [1] is shown in Fig. 2.

The efficiency of the adsorption process of rhodamine B will be greater as more easily rhodamine B is bound to the membrane surface. However, at pH 10 shows the results of adsorption of less than pH 9. This occurs because the state of the composite is already saturated (negatively charged) so that the maximum adsorption occurred at pH 7.

Kinetics adsorption: The effect of contact time on the adsorption of 50 mL of 100 mg/L rhodamine B at room temperature and optimum pH with 0.12 g Ch/Si/P membrane is shown in Fig. 3. It is obvious that the adsorption of rhodamine B on Ch/Si/P equilibrium is achieved within 24 h. The kinetics

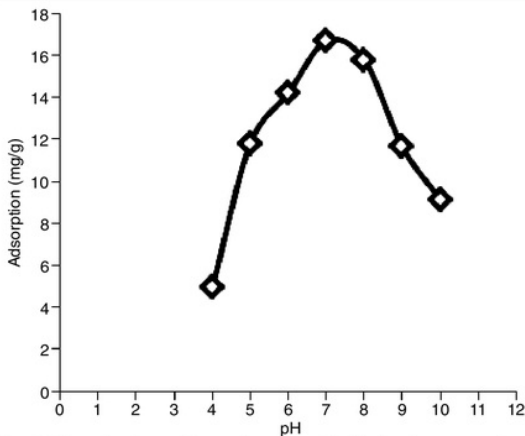


Fig. 1. Effect of various pHs on adsorption of rhodamine B onto membrane

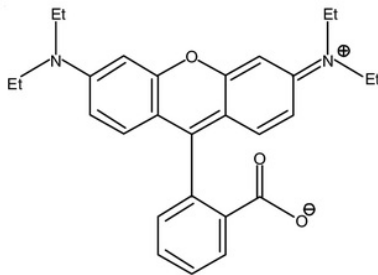


Fig. 2. Zwitterion rhodamine B

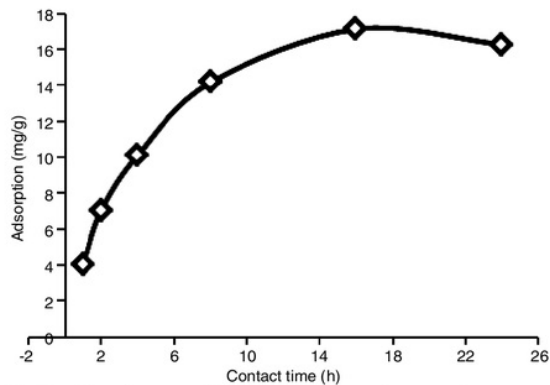


Fig. 3. Adsorption curve of rhodamine B onto membrane at various contact times

of rhodamine B adsorption have been described on the basis of the pseudo-first-order and pseudo-second-order models [12-17]. A simple kinetic model given by Lagergren is the pseudo-first order relation:

$$\frac{dQ}{dt} = k_1(q_e - q) \quad (1)$$

And the pseudo-second-order model is given by the following equation:

$$\frac{dQ}{dt} = k_2(q_e - q)^2 \quad (2)$$

where q and q_e are the adsorbed rhodamine B onto the membrane at time t and equilibrium, respectively. The k_1 and k_2 are the kinetic rate constants of pseudo-first-order and pseudo-second-order models, respectively. One can obtain a linear equation for the pseudo-first-order and pseudo-second-order modes by integrating eqns. 1 and 2, respectively:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \quad (4)$$

A fitting result for the kinetic models is given in Table-1. Pseudo-second-order model well represented the kinetic data on the basis of the excellent goodness of the fit (R^2) as well as the agreement of the equilibrium adsorption capacity predicted by the model (q_e) with the experimental ones. Pseudo-first-order model did not give an acceptable fit to the kinetic data. Moreover, equilibrium sorption capacity estimated by the first-order model was not comparable to the experiment ones.

TABLE-1

FITTING RESULTS OF THE PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETIC MODELS FOR ADSORPTION OF RHODAMINE B ONTO MEMBRANE

Pseudo-first-order Lagergren model			Pseudo-second-order kinetic model		
k_1 (h^{-1})	q_e (mmol/g)	R^2	k_2 ($g \text{ mmol}^{-1} h^{-1}$) (10^{-3})	q_e (mmol/g)	R^2
0.079	0.006	0.604	0.032	0.054	0.996

Adsorption isotherm models: The adsorption isotherm was studied by varying the initial concentration of rhodamine B (10 to 150 mg/L) at pH optimum. The effect of concentration of rhodamine B on the adsorption is shown in the Fig. 4. An adsorption isotherm describes the fraction of adsorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of rhodamine B by adsorbent was modeled using two adsorption isotherms [11, 8]. The Langmuir isotherm assumes mono-layer adsorption on a uniform surface with a finite number of adsorption sites that are saturable. Maximum capacity of adsorption is achieved when all the sites are saturated with adsorbates. The linear form of the Langmuir isotherm model is described as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (5)$$

where K_L is Langmuir constant related to the energy of adsorption and q_m is the maximum adsorption capacity (mg/g). The slope and intercept of a plot of C_e/q_e vs. C_e at different temperatures, were used to calculate q_m and K_L .

The Freundlich isotherm is applicable to both mono-layer (chemisorptions) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent. The linear form of Freundlich equation is expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where K_F and n are Freundlich isotherm constants related to adsorption capacity and adsorption intensity, respectively and C_e is the equilibrium concentration (mg/L). The Freundlich

Initial concentration		D (L/g)		α
Rhodamine B	Cu	Rhodamine B	Cu	Rhodamine B/Cu
0.5	0.5	105.779	29.9514	3.53
0.5	1	408.096	37.9074	10.766
Rhodamine B	Pb	Rhodamine B	Pb	Rhodamine B/Pb
0.5	0.5	28.7307	68.4015	0.4200
0.5	1	25.7049	15.8072	1.6262

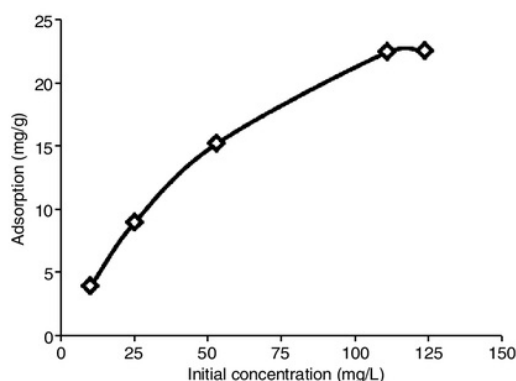


Fig. 4. Adsorption curve of rhodamine B onto membrane at various rhodamine B concentrations

isotherm constants K_F and n are determined from the intercept and slope of $\log q_e$ vs $\log C_e$.

The Langmuir isotherm provided much better fit to the equilibrium data compared with the Freundlich isotherm based on the higher R^2 values. Well representation of the equilibrium data by the Langmuir model supports the facts that the adsorption of rhodamine B on the Ch/Si/P composites membrane was favourable and homogeneous in nature. The calculated results for the Langmuir and Freundlich isotherm fitted to the equilibrium adsorption data at room temperature are given in Table-2.

Langmuir isotherm			Freundlich isotherm		
q_m (mmol/g)	K	R^2	K_F	n_F	R^2
0.052	78332	0.995	2.02	2.672	0.979

Selectivity of the Ch/Si/P composites membrane: Competitive adsorption of rhodamine B/Cu(II) and rhodamine B/Pb(II) for their binary mixture was also investigated in the batch system. Selectivity coefficient (α) was determined using eqn. 7 [19]:

$$\alpha_{(M1/M2)} = \frac{D_{M1}}{D_{M2}} \quad (7)$$

where D is distribution ratio $D = q/C_e$, q is adsorption capacity (mmol/g), C_e is the adsorbate concentration in the aqueous phase at equilibrium (mmol/L) and α is selectivity coefficient.

Competitive adsorption of rhodamine B/Pb(II) and rhodamine B/Cu(II) as selectivity coefficient is expressed in Table-3.

As can be seen in Table-3, selectivity coefficient (α) of rhodamine B/Pb(II) and rhodamine B/Cu(II) are 0.42 and 3.53. That means that rhodamine B can be determined even in the presence of Cu(II), but inverse rhodamine B can't be determined even in the presence of Pb(II).

Conclusion

The adsorption capacity of rhodamine B onto the Ch/Si/P composites membrane is 0.052 mmol/g. The relative selective factor (α) values of rhodamine B/Cu and rhodamine B/Pb are 3.53 and 0.42. The adsorption of rhodamine B described with pseudo-second order kinetic model and Langmuir adsorption isotherm. Further work is still going on to evaluate the probability of membrane to separate selected mixed rhodamine B and metal ions in flow system.

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