

Dynamic adsorption of mixtures of Rhodamine B, Pb (II), Cu (II) and Zn(II) ions on composites chitosan-silica-polyethylene glycol membrane

F W Mahatmanti^{1*}, W D P Rengga², E Kusumastuti¹, Nuryono³

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

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

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

*widhimahatmanti17@gmail.com,

Abstract. The adsorption of a solution mixture of Rhodamine B, Pb (II), Cu (II) and Zn(II) was studied using dynamic methods employing chitosan-silica-polyethylene glycol (Ch/Si/P) composite membrane as an adsorptive membrane. The composite Ch/Si/P membrane was prepared by mixing a chitosan-based membrane with silica isolated from rice husk ash (ASP) and polyethylene glycol (PEG) as a plasticizer. The resultant composite membrane was a stronger and more flexible membrane than the original chitosan-based membrane as indicated by the maximum percentage of elongation (20.5 %) and minimum Young's Modulus (80.5 MPa). The composite membrane also showed increased mechanical and hydrophilic properties compared to the chitosan membranes. The membrane was used as adsorption membrane for Pb (II), Cu (II), Cd (II) ions and Rhodamine B dyes in a dynamic system where the permeation and selectivity were determined. The permeation of the components was observed to be in the following order: Rhodamine B > Cd (II) > Pb (II) > Cu (II) whereas the selectivity was shown to decrease the order of Cu (II) > Pb (II) > Cd (II) > Rhodamine B.

Introduction

The textile industry is one of the few developed industrial sectors in Indonesia. One aspect that needs to be considered in the textile industry is the waste that can pollute the environment, especially water. Textile industry waste is dominated by dyestuff pollution due to the use of both natural and synthetic dyes in the production process. The commonly used colors in the textile industry are Rhodamine B dyes to color silk, wool, and synthetic materials. Rhodamine B dyes are basic dyes which are chloride or oxalic salts of organic bases. These dyes can be Zwitterionic, having both positive and negative electrical charges in the same structures. Regularly found metal ions in textile industry waste are mainly As (III), Cd (II), Cr (III), Pb (II), Cu (II), and Zn (II).

The dye intensity and the content of metal ions in the textile waste can be reduced physically, chemically and biologically. Chemically, several methods have been reported to be used by researchers to reduce pollution in textile industry waste including coagulation-flocculation, electrochemical



oxidation, adsorption and membrane filtration [1]. Membrane technology is considered an effective chemical way to reduce dye pollutants and metal ions in waste. Therefore, this paper reports the investigation of the effectiveness of a composite membrane Ch/Si/P for the permeation and selectivity of dyes and cations for potential use in the textile waste treatment.

Materials and Methods

Materials

Materials used were NaOH, HCl, Rhodamine B and nitrate salts of Pb (II), Cu (II) and Cd (II); purchased from Merck and used as received without purification., Pearson Panke equipment Ltd for measuring the mechanical parameters and Thermogravimetric Analysis (TGA) (Perkin-Elmer TGA-7) for evaluating thermal stability. Spectrophotometry visible (Shimadzu 1240) was applied for the determination of Rhodamine B concentration in the sample solution. Atomic absorption spectroscopy, AAS (Perkin-Elmer AA 200), was applied for the determination of Pb (II), Cd (II) and Cu (II) concentration in the solution.

Methods

Preparation of composites Ch/Si/P membrane

Chitosan solution 1 wt % was prepared by dissolving 1 g of chitosan in 100 mL 2 % (v/v) acetic acid solution. An appropriate amount of sodium silicate from isolated rice hull ash with the different mass ratio (0.1-1.5 g) were mixed with 100 mL 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 was allowed to evaporate the solvent under an ambient temperature for three days. The membrane was 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. The optimum ratio mass of chitosan to silica is obtained from the membrane giving the highest tensile strength. The same work was carried out by adding varying the mass of PEG (0.05-0.50 g) on chitosan-silica to evaluate the effect of PEG content on the membrane properties.

Characterization of composites Ch/Si/P membrane

The mechanical properties of the membrane in dry state were performed at 25°C using a universal material testing instrument with a crosshead speed of 10 mm/min. The results were presented in mean values of three independent measurements. Thermo-gravimetric (TG) data was performed for a 10 mg sample from room temperature to 400 °C at a heating rate of 10 °C/min in a dynamic (30 mL/min) synthetic air atmosphere. For determination of swelling index (SI), a procedure reported by [2] was used. The pH-dependent on swelling properties of the film, pre- weighed dry samples was immersed in buffer solutions at pH of 2.0-11.0. After 24 h, the swollen films were removed, excess water was bottled from the surface, and then were weighted. The following equation was used to determine SI.

$$SI (\%) = [(w_w - w_d) / w_d] \times 100 \%, \quad (1)$$

with w_w and w_d are the sample weights after swelling for 24 h and dry state, respectively. In each specimen, three samples were tested.

Preparation of solution mixture:

An aqueous mixture of Rhodamine B, Pb (II), Cu (II) and Cd (II) was prepared by mixing two mmol of each chemical into a 1000 mL volumetric flask and adding distilled water to the mark. The solution was shaken to ensure a complete dissolution and mixing.

Test the ability of Ch/Si/P membrane as an adsorptive membrane of metal ions and dye.
Test of membrane capability as metal ions separating membrane was carried out on a solution containing

Rhodamine B and Pb (II), Cu (II) and Cd (II) metal ion by dynamic system. The sample used is sample of metal ion solution and artificial dye. The metal ions solution and the dye with a concentration of 2 mmol/L are included in the diffusion cell consisting of the chamber A and B. The chamber A contains a solution which contains no metal ions, whereas chamber B contains a solution containing both metal ions and dyes. The diffusion test was carried out using the cell set up presented schematically in Figure 1.

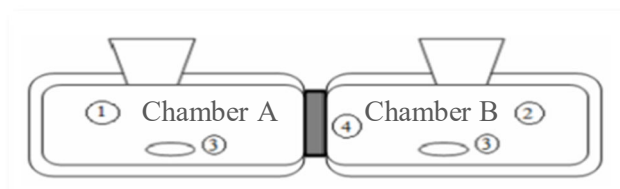


Figure 1. Diffusion cells for dynamic system adsorption test where (1) Chamber A containing the solution of metal ions/dye, (2) Chamber B containing distilled water, (3) Magnetic stirrers, (4) Ch/Si/P composites membrane

Chambers A and B were filled with the solution mixture (50 mL) and distilled water (50 mL), respectively, with constant stirring. The two chambers were separated with the Ch/Si/P membrane of 0.16 mm thickness. Every 2 hours for 24 hours a sample of solution in both chambers A and B was collected and tested in an Atomic Absorption Spectrometer (AAS) and UV-Visible spectrophotometer to determine the concentrations of metal cations and the Rhodamine B. The tests for the ability of the membrane as an adsorbent were carried out for each of the metal ion solutions separately, as mixture of metal ions and as mixture of dyestuff with metal ions.

Results and Discussion

Membrane characterization

The membranes were tested for mechanical properties to determine their tensile strength, stress, strain and Young's Modulus following ASTM D638-03 using Pearson Panke Equipment Ltd. The tensile strength was determined by measuring the maximum voltage that can be retained by a material when stretched or withdrawn before the material is broken. Tensile strength is commonly used in designing the part of a ductile and brittle structure that is not static. In all materials, in the early stages of the tensile test, the relationship between the load or force is proportional to the length of the material, in which the ratio of stress and strain is constant. Stress is the load divided by the cross-sectional area of the material (F/A), and the strain is the length increase divided by the initial length of the material ($\Delta L/L$). Stress and strain comparisons are always fixed, formulated as Young's Modulus. The test results of mechanical properties are presented in Figures 2(a) and 2(b).

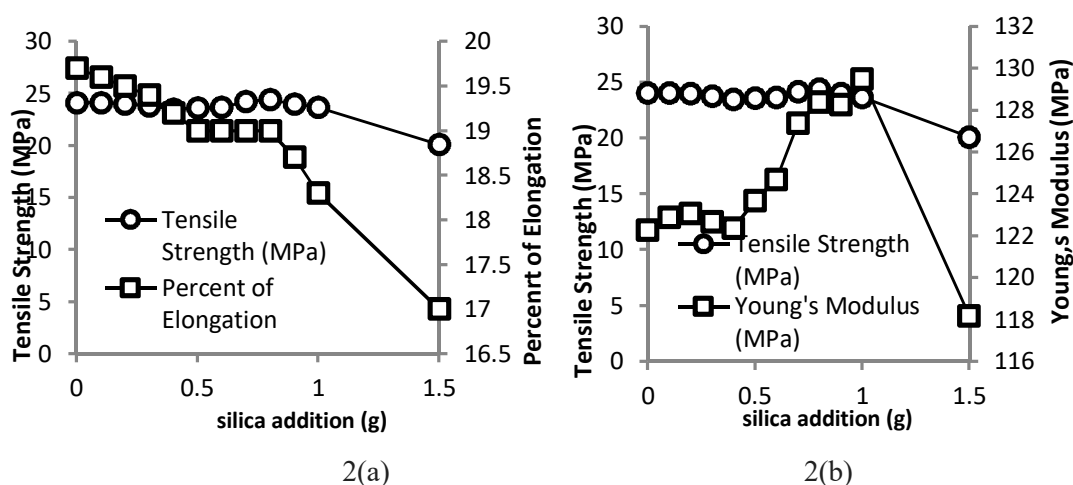


Figure 2. Effect of adding silica to (a) Tensile strength and Percentage of elongation, (b) Tensile stress and Young's Modulus

The tensile strength of membrane tends to decrease with the increase of the chitosan-silica ratio up to 1.0:0.8; at the higher content of silica, the tensile strength drastically decreases. The optimum ratio showing the highest tensile strength is 1.0:0.8. The addition of silica more than 0.8 g ratio of chitosan, both properties above deteriorate supporting a conclusion that silica may harden and toughen chitosan. The percentage of elongation decreases with increasing the silica content. The high silica content would bring chitosan-silica membranes to high inorganic characters such as the brittleness and makes low elongation at break. The test results revealed that formation chitosan-silica membranes did not bring positive effect on improving the mechanical properties of the membrane. The addition of silica-enhanced the membrane character of being more inorganic, harder and more fragile [3]. According to [4] increasing silica content would result in a negative effect on the mechanical properties.

The effect on the mechanical properties of the addition of PEG is presented in Figure 3(a) and 3(b). In general, the addition of PEG increased dramatically the percentage of elongation up to a maximum of 21 % at 0.2 g of PEG addition followed by a slight decrease beyond the maximum, but the tensile strength of the membrane decreased slightly. The addition of PEG resulted in a significant drop of Young's Modulus indicating that the viscosity of the membrane increased significantly. Considering the minimum Young's Modulus, the maximum percentage of elongation, no significant drop of tensile strength indicating elastic and strong membrane, the optimum composition of Chitosan/silica/ PEG was indicated to be 1: 0.8: 0.5. This is in agreement with the report by [5]. PEG as a plasticizer could improve mechanical properties, maintaining wholeness and avoiding holes and cracks. In the membrane matrix, the addition of a plasticizer is expected to reduce the intermolecular bonds between the chitosan molecules thereby weakening the intermolecular forces [6-7].

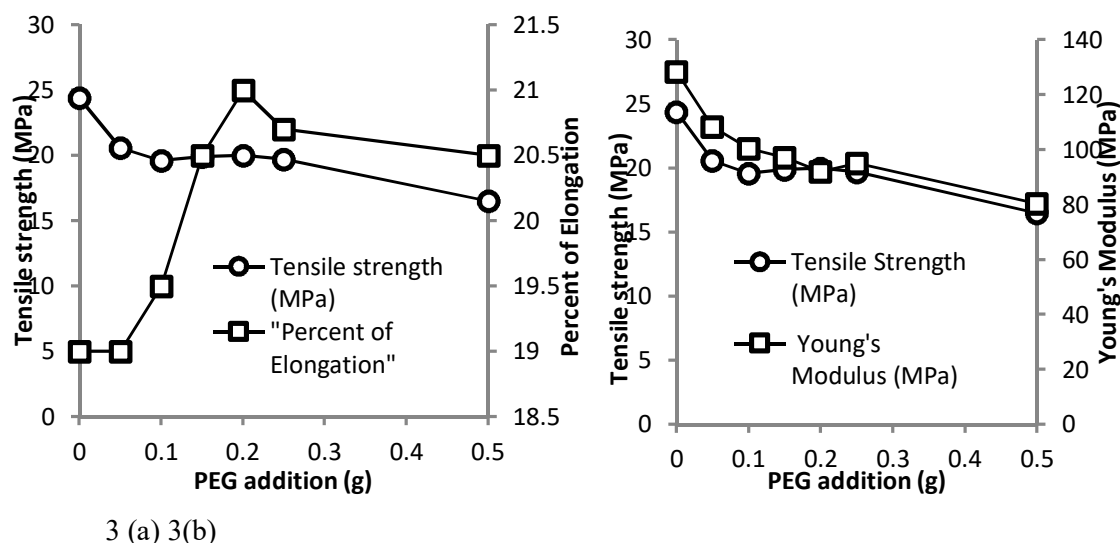


Figure 3. Effect of polyethylene glycol (PEG) addition to (a) Tensile strength and percentage of elongation, (b) Tensile strength and Young's Modulus

The addition of PEG plasticizer in membrane material has been reported by several researchers. [6] added PEG with 6000 and 8000 weight molecular on the manufacture of chitosan membranes. In the addition of PEG with 6000 weight molecular with chitosan ratio: PEG (2: 1), the value of tensile strength decreased from 5.5 to 4.2 MPa. Addition of PEG with 6000 weight molecular and chitosan ratio: PEG (4: 1) increase tensile strength value to 7 MPa. Also PEG with 8000 weight molecular produces membranes with mechanical properties equal to the membrane with the addition of PEG 6000 weight molecular. [8] use PEG because of its non-toxic, biocompatible and biodegradable nature. Through mixing technique, PEG is commonly added to chitosan as an effort to improve membrane elasticity. According to [9], the addition of PEG to the chitosan-silica membrane with PDMS as a source of silica tends to increase chitosan dispersion with PDMS. This indicates that increase in PEG increases drastically the membrane flexibility, due to the formation of hydrogen bonds between chitosan molecules with PEG [10].

The thermal properties of the membranes were measured by TG presented in Figure 4. The weight loss takes place in two stages. The first stage starts at 60 °C with a weight loss of 10 %. The second stage begins at 240 °C and reaches a maximum at 380 °C with a weight loss of 41.4 % [11]. For chitosan membrane, chitosan-silica membrane and chitosan-silica-PEG, the first stage of decomposition occurs between ambient and 200 °C being accounted for around 14 % weight loss, corresponding to dehydration of the membranes. The second stage of decomposition which starts from around 200 to 550 °C is attributed to a weight loss due to the decomposition of the polymeric network [11-13]. For the chitosan-silica film, the second stage starts from 240 to 550 °C with the weight loss of 60.0 %. Blending chitosan-silica with PEG, the second stage starts from 240 to 550 °C with the weight loss of 62.2 %. As the amount of PEG is increased, the intra-molecular interactions between the terminal hydroxyl groups of PEG predominate, the attractive bonds are inhibited, the blend becomes incompatible, and as a consequence, the thermal stability of the chitosan and chitosan-silica membranes is lower than that of chitosan-silica-PEG one. This result is contradicted with result reported by [14]. It was observed that thermal stability of chitosan blending PEG is higher than that of chitosan, but thermal stability decreases at a too high mass ratio of chitosan to PEG.

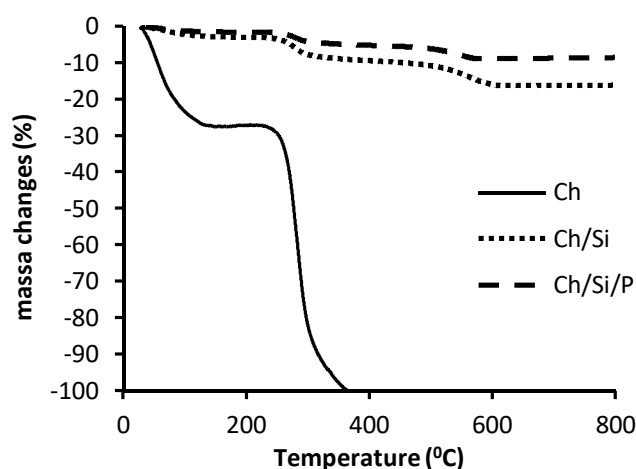


Figure 4. TGA thermograms of the membranes

The hydrophilic properties of the membranes were tested by immersing the membrane in a buffer solution with a pH of 2.0-11.0 for 24 hours. Test results on membrane hydrophilicity indicated by the values of the swelling index (SI) are presented in Figure 5. In Figure 5 it can be seen that in a strongly acidic solution, the value of the Swelling Index was high. The high Swelling Index value results in a *hydrophilic* membrane at pH 2.0 to pH 3.0. In an acidic solution, the protonation of the $-NH_2$ groups on chitosan produces $-NH_3^+$ which is a weak base. The dissolution mechanism occurring in the membrane is thought to be due to the acid reaction in the solvent with the weak base in the $-NH_3^+$ group. In neutral and slightly alkaline solutions, the Swelling Index value decreased. In general, it can be concluded that the increase of silica concentration decreased the hydrophilicity and the increase of PEG concentration increased the hydrophilicity characteristic along with the increase of pH value. PEG is a polymer having a sufficiently large number of $-OH$ and is hydrophilic [15], explaining this observation.

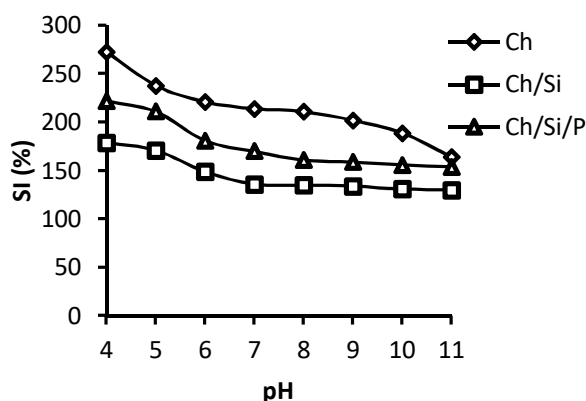


Figure 5. The Swelling Index (SI) of membranes at various pH

The separation process using a membrane is a separation process at a very small molecular or particle level. The membrane can move one component faster than the other based on the physical and chemical properties of the membrane and the separated component. The displacement may occur due to differences in pressure (ΔP), concentration (ΔC), electrical potential (ΔE) and temperature (ΔT).

Membrane selectivity is the ability of the membrane to pass a component relative to the other, expressed by rejection coefficient (R) [16]. The transport of ions and molecules through the membrane can occur through passive or active transportation. A passive transport does not require energy such as diffusion, facilitated diffusion and osmosis. The basic principles of transport through the membrane are based on the tendency of molecules to occupy space evenly. Molecules at high concentrations have a greater pressure, and each molecule tends to always move because of its kinetic energy content. Thus naturally there is a tendency of molecules at high concentrations to move to low concentrations. An active transport uses energy as it is transported through the membrane that resists the natural tendency of concentration difference.

In this study, the Ch/Si/P membrane was studied for its transport properties of Cu (II), Pb (II), Cd (II) and Rhodamine B dyes by calculating the rejection coefficient (R) to determine the selectivity. The membrane capability test as a separating membrane is performed for each of the metal ion solutions, metal ion mixture and dyestuff mixture with metal ions. The amount of absorbed metal ions and dissolved metal ions (permeated) were determined using AAS and UV-Vis.

Membrane selectivity is expressed by rejection coefficient (R), also called % removal, a fraction of the concentration of a non-penetrating membrane or. Rejection coefficient (R) is defined as:

$$R = (1 - \frac{C_p}{C_f}) \quad (2)$$

where: C_p is the permeated concentration and C_f is the feed concentration.

The results of the study on the transport properties of Rhodamine B and all metal ions on the Ch/Si/P membrane are presented in Tables 2-5.

Table 2 Percentage of permeated Rhodamine B for individual and mixed solutions

Contact time (h)	Permeated Rhodamine B (%)	
	Individual	Mixed
0	0.0	0.0
8	96.0	78.0
16	95.3	78.0
24	85.0	75.0

Table 3 Percentage of permeated Pb (II) for individual and mixed solutions

Contact time (h)	Permeated Pb (II) ion (%)	
	individually	mixed
0	0.0	0.0
8	2.4	5.0
16	6.1	3.7
24	6.03	3.5

Table 4 Percentage of permeated Cu (II) for individual and mixed solutions

Contact time (h)	permeated Cu (II) ion (%)	
	individually	mixed
0	0	0
8	13.7	0.5
16	24.1	0.31
24	24.9	0.27

Table 5 Percentage of permeated Cd (II) for individual and mixed solutions

Contact time (h)	permeated Cd (II) ion (%)	
	individually	mixed
0	0	0
8	24.5	90.2
16	18.6	39.7
24	18.4	39.7

Tables 2-5 revealed that the order of permeability of the dye and metal cations is as follows: Rhodamine B > Cd (II) > Pb (II) > Cu (II). Permeated ions are the ions that pass through the membrane as a result of the equilibrium of concentration, and the size of the molecule is smaller than the pore size of the membrane. The Rhodamine B molecule successfully penetrates the Ch / Si / P membrane before it is attached to the pore wall of the membrane. Membrane selectivity can be illustrated as rejection coefficient (R). The Rejection coefficient (R) can be calculated by using equation 2. Table 2-5 is calculated the value of R can be written in Table 6-9.

Table 6 Percentage of removed Pb (II) ion for individual and mixed solutions

Contact time (h)	Removed Pb (II) ion (%)	
	Individual	Mixed
0	0.0	0.0
8	97.6	95.0
16	93.9	96.4
24	93.97	96.5

Table 7 Percentage of removed Cu (II) ion for individual and mixed solutions

Contact time (h)	Removed Cu (II) ion (%)	
	individually	mixed
0	0	0
8	86.3	99.5
16	75.9	99.7
24	75.1	99.6

Table 8 Percentage of removed Cd (II) ion for individual and mixed solutions

Contact time (h)	Removed Cd (II) ion (%)	
	individually	mixed
0	0	0
8	75,5	90.2
16	81,4	60.3
24	81,6	60.3

Table 9 Percentage of removed Rhodamine B for individual and mixed solutions

Contact time (h)	Removed Rhodamine B (%)	
	individually	mixed
0	0	0
8	4	22
16	4.7	22
24	15	25

The results displayed in Tables 6-9 showed that Cu (II) ions were the most adsorbed ions compared to Rhodamine B dyes or other ions. The adsorbed portion as a result of equilibrium concentrations in the two membrane chambers may then be ion bound by an active group present on the membrane surface as well as on the inside of the membrane. Cu (II) ions are easily bonded to membrane walls compared to Rhodamine B dyes or other metal ions. Table 6-9 also indicates that Cu (II) ions are the largest adsorbed ions compared to Rhodamine B dyes or other ions. The adsorbed portion as a result of the equilibrium concentration in the two membrane chambers then the ion may be bound by the active group present on the membrane surface as well as on the inside of the membrane. Cu (II) ions are easily bonded to membrane walls compared to Rhodamine B dyes or other metal ions.

In general, metal ions were hydrated by the presence of water to form metallic aquo, $M(H_2O)_n$ which increased the size of the moiety. By the concept of HSAB, Cu (II) ion is middle acids that tend to bind to the $-NH_2$ group which is a hard base compared to Cd (II) ion which is a softer acid. This result is consistent with previous research reported by [17] that the selectivity of the composite membrane which is capable of forming complex compounds with metal ions, was in the order of $Cu(II) > Hg(II) > Zn(II) > Cd(II) > Ni(II) > Co(II), Ca(II)$. According to the HSAB concept, the ability to form complexes depends on the size and hardness of the metal ions. Disadvantages of membrane technology include: flux and selectivity because the membrane process occurs flux phenomenon inversely proportional to the selectivity. The higher the flux often results in decreased selectivity and vice versa.

Conclusion

In the study of adsorption of Rhodamine B dyes, Pb (II), Cu (II), and Cd (II) ions using Ch/Si/P membrane, the permeability of the membrane increases following the order of Rhodamine B > Cd (II) > Pb (II) > Cu (II). The selectivity of the membrane increases following the order of $Cu(II) > Pb(II) > Cd(II) > Rhodamine\ B$.

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