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Studies on Rhodamine B dye transport through supported liquid membrane from basic aqueous solutions using phenol as membrane phase

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ABSTRACT:

The aim of this work is to investigate the transport of Rhodamine B across supported liquid membrane under various experimental conditions. The phenol was mixed with xylene which acts as carrier in membrane phase. A flat sheet polytetrafluoroethylene (PTFE) membrane was impregnated with xylene in phenol. The flux value of Rhodamine B increased with increasing dye concentration in the feed phase. The maximum permeability $(1.80 \times 10^{-5} \text{ m/s})$ of RB dye was observed using 0.8 mol/L phenol in xylene. The effect of pH on feed phase, carrier concentration on the membrane phase, stirring speed and strip phase concentration has been determined. Finally, the stability and reusability of the impregnated membrane has been investigated.

Keywords: Feed phase; phenol; kinetics; Rhodamine B; transport.

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1. Introduction:

Synthetic dyes are generally aromatic organic compounds, which are widely used in various industries such as textile, leather, paper and food industries in order to color and/or dye their products [1]. As a result, large amount of dye wastewater is released from industries and these colored effluents contaminated the aquatic, surface and ground water system [2]. Presence of trace amount of dyes in drinking water (< 5 ppm) is considered to be toxic and not suitable for human consumption, pose serious threat to the eco-system [3]. Hence, it is highly necessary to remove dyes from wastewater, before it is being released into the environment. There are many conventional treatment techniques currently used for the removal of dyes from wastewater that includes adsorption [4-9], photochemical degradation [10-12], ozone treatment [13, 14], coagulation [15-17], Fenton's reagent [18-20], solvent extraction [21-23] and liquid membrane process [24, 25] etc.

Among different dyes, Rhodamine B and Rhodamine 6G are considered as the important dyes in the basic dyes category [26, 27]. It was earlier used as a colorant in textiles and as water tracer fluorescent. Recently, it is used for coloring paper, ink manufacturing, plastics, sprit based coatings boards and craft's, mosquito coils, laboratory reagent and bamboo wood etc. RB is harmful if swallowed by human beings and animals, caused irritation to the skin, eyes and respiratory tract.

Liquid membrane (LM) is one of the attractive and alternative treatment techniques for the removal of dyes from wastewater [28]. The major drawback of LM process is loss of organic phase in the successive cycles which seriously hampers its larger scale applicability. Furthermore, formation of emulsion at the interface greatly affects the transport and/or removal

of pollutants from the feed phase. Supported liquid membrane (SLM) is an emerging technique, which gives us the real solution for the above mentioned problems. SLM has a three-phase system with an organic phase (LM) placed between two aqueous phases. The organic phase (extractant) is immobilized by capillary forces in the pores of hydrophobic membrane, while the feed (donor) and the stripping (acceptor) solutions are placed on opposite sides of the membrane. Mass transfer in SLM extraction comprises diffusion of the solute of interest from the bulk of the donor phase to the donor/(organic phase) interface, partitioning of the solute between the donor phase and the organic phase, diffusion of the solute through the organic phase to the (organic phase)/acceptor interface, and its re-extraction into the acceptor phase.

Usually, SLM is based on hydrophobic organic solvent immobilized in a polymeric hydrophobic membrane separating two aqueous solutions. Several different polymeric membrane supports have been used such as polypropylene (PP), polytetrafluoroethylene (PTFE) etc. SLM have been widely used in order to separate and recover heavy metals [29-32], peptide [33, 34] and dyes [35, 36] etc. Catechins have been recovered from tea leaves through hollow fiber supported liquid membrane (HF-SLM) using medicinal grade ethanol as stripping agent. Tributyl phosphate (TBP) in n-decane was used as a carrier component in LM [37]. Similarly, separation of synthetic dye Rhodamine 6G and water was investigated using mixture of organic liquids in a SLM [38]. In addition, the transport of cationic dyes, methyl violet and RB from aqueous synthetic dye solution using Di (2-ethylhexyl) phosphoric acid (D2EHPA) as carrier was reported by Hajrabeavi et al [39]. D₂EHPA has been widely used to remove organic and inorganic pollutants in LM and SLM process. D₂EHPA is a bidentate ligand and shows high removal efficiency for the removal of inorganic metal ions rather than organic pollutants [40].

dyes. SLM has the advantage of selective removal and concentration in single stage, low inventory of the organic phase used, low energy consumption, thus have great potential for reducing cost significantly [41]. However, the instability of the liquid membrane in the pores of the inert membrane support (carrier lost) is the main disadvantage. In the present study phenol is used as an extractant. Compared to D2EHPA, phenol is cheaper and it also extracted the dye very effectively.

In this paper, the recovery of textile dye like RB from wastewater has been investigated using PTFE supported membrane impregnated with phenol-xylene carrier and the results are discussion details. PTFE membrane was used as flat sheet membrane (47 mm diameter) with sub microns porosity for the removal of RB at ambient condition. The other parameters included the transport time, lifetime of the membrane and mechanism of the transport.

2. Materials and Methods

2. 1. Reagents and solutions

Hydrochloric acid (35%), n-hexane (99.0%), xylene (\geq 98.5%), toluene (99.0%), benzene (99.5%), phenol (99.5%) and Rhodamine B (99.9%) were purchased from Merck, S D Fine and Fisher scientific suppliers and used without any further purification. Dye solutions were prepared using double distilled water.

2.2. Instrument

The pH of the dye solution was measured with a pH meter, Elico model-LI 120 with a combined electrode. An Elico SL 159 UV visible spectrometer was used for absorbance measurements. REMI 1 MLH magnetic stirrer was used for stirring. The Whatman PTFE plain

membrane with a pore size of 0.45 μ m, thickness 18 μ m and 47 mm diameter, obtained from GE Healthcare UK Ltd (Made in Germany) was used in this study.

2.3. Membrane preparation

PTFE flat sheet membranes were used for the transport of RB. The polymeric PTFE membrane was impregnated with a carrier solution containing phenol in xylene for 24 h before use. The polymeric support was taken out from the carrier solution and then this membrane was clamped into the SLM cell.

2.4. SLM transport experiments

The SLM experiment was carried out in a glass cell consisting of two cubic compartments and separated by the microporous membrane impregnated with phenol in xylene. The feed phase containing 140 mL of 50 mg/L aqueous dye solution at $pH = 11 \pm 0.1$ and strip phase containing 140 mL of 8 mol/L acetic acid solutions were taken in SLM reactor. Agitation was performed in both (feed and strip) compartments by using Teflon coated magnetic pellets of 12 mm length. After different time intervals, 2-3 mL of sample was taken from feed as well as strip chamber and then the dye concentration was measured spectrophotometrically at 554 nm. If the absorbance of sample exceeded 0.900 the samples were diluted with double distilled water. The experimental setup of SLM is given in Fig. 1.

The percentage of transport of dye was calculated as using the following Eq. (1)

Transport (%) =
$$[Dye]_{f,0}$$
- $[Dye]_{f,t}/[Dye]_{f,0}$ -----(1)

The following equation measures the quantity of a dye transported through a specific area of membrane surface in given unit of time.

 $\log\{[Dye]_{f,t}/[Dye]_{f,0}\} = -A/2.303V Pt -----(2)$

where $[Dye]_{f,t}$ is the dye concentration in feed phase at time t, $[Dye]_{f,0}$ is the dye concentration in feed phase at initial time, A is the area of membrane (cm²), V is the volume of feed phase (m³), t is the time (min or sec) and p is the permeability (m/s).

The dye flux was obtained by following equation [42]

 $J = - V/A dc/dt \qquad \dots (3)$

3. Results and Discussion

3.1. Influence of diluent on the transport

The experiments were carried out with different diluents such as xylene, toluene, benzene, n-hexane and kerosene. Among them it was found that xylene is a very efficient diluent along with phenol for transport of RB dye from aqueous feed phase into aqueous strip phase as shown in Table 1. The maximum permeability $(1.805 \times 10^{-5} \text{ m/s})$ was obtained when membrane was impregnated in xylene and also xylene is less toxic when compared to benzene and toluene. Higher efficiency is due to the polar nature of xylene, which firmly binds in to the polar nature of phenol and facilitates the transport of RB dye. The polarity of the diluent is the most decisive factor to determine effectiveness as a membrane medium [43], but on the other hand, membrane stability vs. rapid transport is the major choice to be made in choosing a membrane diluent [44]. Viscosity of the diluents also plays a significant role in the transport of RB dye. Less viscous diluents easily lose its stability in the pores of the membrane and also its long term stability is highly questionable. In contrary, highly viscous diluents restrict the mobility of the pollutants. Viscosity of xylene is 0.812 cP at 20 °C, which highly suitable for the transport of RB dye when compared to toluene (0.601 cP at 20 °C), benzene (0.55 cP at 20 °C) and n-hexane (0.297 cP at 20 °C). Whereas, highly viscous nature of kerosene (1.601 cP at 40

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°C) greatly reduces the mobility of the RB dye and displays least efficiency when compared to other diluents.

The diffusion coefficient can be calculated by using the following equation [45]

 $D = 7.4 \times 10^{-8} \frac{(M_{cl})^{1/2} T}{\eta (V_m)^{0.6}} \qquad -----(4)$

Where D is the diffusion coefficient (cm² s⁻¹), M_d is diluent molar mass (g mol⁻¹), T is the absolute temperature (K), η is the viscosity of the diluent (mPa s) and V_m is the molar volume of solute phenol at its boiling temperature (cm³ mol⁻¹). From the results, diffusion coefficient D is inversely proportional to permeability [46] values of RB dye shown in Table 1. Even though kerosene has low D, it might be its viscosity greater (i.e. approximately three times of xylene at 40 °C) hence permeability decreases. Therefore xylene was used for further studies and similar observations made by other researcher too [47-49].

3.2 Influence of the pH on the feed phase

The transport studies were carried out at different pH such as 8.0, 9.0, 10.0, 11.0 and 12.0 \pm 0.1 in the feed phase and samples were collected at different time intervals. The pH of the feed solution was adjusted using 0.1 N and 0.5 N NaOH. All the reactions were carried out for the fixed reaction time of 240 min. The percentage of transport increases with increasing pH of the feed phase as shown in Fig 2. The transport efficiency was found as follows: 36.0% for pH 8.0 \pm 0.1, 56.0% for pH 9.0 \pm 0.1, 78.0% for pH 10.0 \pm 0.1, 96.0% for pH 11.0 \pm 0.1 and 92.0% for pH 12.0 \pm 0.1. From the experimental results permeability was calculated and given in Table 2. It shows that the permeability was increased from 0.250×10^{-5} to 1.805×10^{-5} m/s with increasing pH up to 11.0 ± 0.1 and then the permeability was decreased. At a low pH, the permeation process may be governed mainly by the low distribution coefficient at the feed interface, which generates

a little concentration gradient through the membrane cross section [50]. At pH 12 or greater than 12, the competition between the OH⁻ ions and RB dye for phenol molecules keeps the permeability low. At pH 11.0 \pm 0.1, it is seen that complexation is more favored and thus transport efficiency increases [51]. Therefore, the maximum transport of RB dye 96.0% was achieved at pH 11.0 \pm 0.1 and this pH was recommended for further studies.

3.3. Influence of RB dye concentration on the feed phase

In order to investigate the influence of initial concentration of RB in the feed phase, three different dye concentrations like 50, 75, 100 mg/L were taken. Usually, the percentage of transport of dye decreases with the increasing dye concentration and the same results were reported by other researchers [39]. Fig 3 shows that the transport efficiency decreases from 96.0% to 85.0% and further to 70.0% with increasing RB dye concentration from 50 to 75 and then 100 mg/L, respectively. The dye concentration was increased from 50 to 100 mg/L RB, the permeability decreased from 1.805×10^{-5} to 0.675×10^{-5} m/s and flux value increased from 1.12×10^{-6} to 1.68×10^{-5} mg cm⁻² s⁻¹. The permeability and flux values were given in Table 3.

This is in accordance with equation (5), where flux (f) is directly proportional [52] and permeability is indirectly proportional [53] to RB dye concentration in the feed phase. This shows that the dye concentration range of 50 to 100 mg/L of RB in feed solution no saturation of the carrier and also similar results were observed [48].

3. 4. Influence of the phenol concentration on the membrane phase

The concentration of extractant is an important parameter influencing the transport efficiency of target compounds [54]. An experiment was conducted with xylene in absence of

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phenol in membrane phase, and found no transport of RB for long time (6 h), this indicates that phenol plays a vital role in transport of RB. In order to analyze the effect of carrier concentration on RB transport, phenol with different concentrations (0.2, 0.4, 0.6, 0.8 and 1.0 mol/L) was used and the results were calculated and given in Fig 4. It is revealed that the permeability was increased from 1.03×10^{-5} to 1.80×10^{-5} m/s with increase of phenol concentration from 0.2 to 0.8 mol/L. The permeability did not change with any further increase of phenol concentration. At lower phenol concentration, the permeability was low which might be because the phenol concentration on the membrane pores was not appreciable for the transport of RB. Hence the carrier concentration of 0.8 mol/L was fixed for further studies. The carrier based LM can be compared its efficiency with the previously reported carriers as shown in Table 4. It reveals that the new developed phenol based carrier is least time consuming and highly efficient for the transport of RB.

3.5. Influence of the time on the transport

Experiments were conducted for a dye concentration of 50 mg/L, a stirring speed of 400 rpm, strip phase concentration of 8.0 mol/L of acetic acid and pH 11.0 ± 0.1 was maintained at different time intervals. The results are presented in Fig. 5. It shows that the transport efficiency increases with increasing time. In feed phase, the dye concentration decreased indicating that the dye was successfully transported from aqueous feed phase into strip phase. The maximum transport efficiency (96.0 %) was achieved at 240 min. With further increase in time there was no appreciable change in the concentration of dye in the aqueous feed as well as strip phases. Hence transport time of 240 min was recommended for further studies.

3.6. Influence of stirring speed on the transport

To investigate the effect of stirring speed on transport of RB, stirring speed was varied from 200 rpm to 800 rpm while other experimental conditions were kept at the optimum condition. The results given in Table 5, reveals that the transport efficiency increases with increase in stirring speeds in bulk feed and strip solution up to 500 rpm and then decreases gradually. The maximum transport efficiency (96.0%) was obtained at 500 rpm. Beyond 500 rpm, the transport efficiency decreases and similar results have been reported [57]. This indicates that the aqueous boundary layer thickness is diminished continuously with increasing stirring speed and turbulence caused by stirring, resulting from displacement of carrier from the membrane pores [39, 57, 58].

3.7. Influence of acetic acid concentration on the stripping phase

In this part of the study, acetic acid concentrations such as 5, 6, 7, 8 and 9 mol/L were used in order to determine the effect of acid concentration in strip phase on RB transport. The percentage of transport of RB for each acetic acid concentration is shown in Fig. 6. It shows that the percentage of transport increases with increasing acetic acid concentration. This can be explained by using the rate of stripping reaction (R_s) made the following equation [59].

$R_s = K_s [AcOH] \qquad ----(6)$

 $[RB-OPh]_{org} + [CH_3COO^{-}H^+]_{aq} \longrightarrow [CH_3COO^{-}RB^+]_{aq} + [PhOH]_{org} \dots (7)$ Where, R_s is stripping reaction rate, K_s is rate constant of stripping reaction and [AcOH] is acetic acid concentration. From the equilibrium reaction (7), when the concentration of acetic acid is increased from 5.0 to 8.0 mol/L, the reaction will shift forward, resulting in an increase in percentage of RB stripping. This can be explained by Le Chatelier's principle [60, 61]. However, at concentrations of stripping agents higher than 8 mol/L, the percentage of stripping remained constant. This was because of being obstructed by concentration polarization [62-64] as well as

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being limited owing to the amount of complex species which reacted with the stripping solution at m/s interface [65]. According to the molecular kinetic interpretation by Stokes and Einstein, the increase in high stripping concentration leads to lower diffusion coefficient [66, 67]. The highest percentage of transport (96.0%) was achieved at 8.0 mol/L. With further increase in acetic acid concentration, there was no appreciable transport of dye. Hajarabeevi et al. also observed similar results using a stripping reagent with the pH of 2.5, for the transport of RB and methyl violet (MV) [39].

3.8. The mechanism of transport

The suggested mechanism for the transport of RB through SLM which was operated in this study is shown schematically in Fig. 7.

- In basic medium, phenol is converted into phenoxide anion which interacts well with cationic dye at feed/membrane (F/M) interface. Hence the ion-pair complex is formed between cationic RB and anionic phenoxide ion.
- ✤ At the membrane/strip (M/S) phase, in an acidic medium the phenoxide ion abstracts a proton and ion-pair complex is broken. Also the cationic RB is diffused into strip phase.
- ◆ The neutral carrier diffuses back into membrane phase where the cycle starts again.

The kinetics of transport process across SLM can be given by a first order reaction with respect to dye concentration [39]. The permeability (p) can be calculated by using equation 2. A plot of log $[Dye]_{f,t}/[Dye]_{f,0}$ against time gave a straight line which is shown in Fig. 8. From the Fig. 8 we found permeability (p) value by using the relationship y = mx + c. The permeability (p) value was calculated and found to be 6.0×10^{-5} m/s.

3.9. The lifetime of membrane

The preliminary test of stability was carried out in order to check the lifetime of the membrane. The stability of PTFE-phenol in xylene system was studied. The lifetime of the membrane was evaluated by several consecutive experiments for (240 min) 4.0 h performed without re-impregnation of carrier. The results are presented in Table 6. After the third run, the transport efficiency of RB suddenly decreased. It might be because loss of phenol into the aqueous phase, the contact of the membrane pores with air during the time of experimental set up [51], less viscosity and wetting of support pores by aqueous phase [68]. After the 5th run, regeneration of the membrane was achieved by re-impregnating the phenol-xylene system.

4. Conclusion

As result of this study, it was determined that RB dye can be effectively separated from aqueous solutions through a flat-sheet SLM process containing the membrane liquid prepared from a mixture of phenol in xylene. The flat sheet PTFE membrane that offers excellent product uniformity, strength and chemical stability. The effect of various parameters such as pH of the feed phase, carrier concentration, stirring speed, time, dye and stripping acid concentration on the transport RB dye was examined. Under the optimum conditions (feed phase concentration of 50 mg/L of RB, strip phase concentration of 8.0 mol/L of acetic acid, pH 11 \pm 0.1, 0.8 mol/L of phenol in xylene on the membrane phase and stirring speed 500 rpm at room temperature), the maximum permeability of 1.805 \times 10⁻⁵ m/s was obtained. The optimized condition and suggested mechanism of the transport of RB dye through SLM impregnated in phenol-xylene system can be applied for the removal of dye from the industrial wastewater.

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Figure Captions:

Fig 1. Schematic diagram of SLM cell.

Fig. 2 Effect of pH of the feed phase (Experimental conditions: Feed phase = 50 mg/L, receiving phase = 8.0 mol/L acetic acid, extractant concentration = 0.8 mol/L, stirring speed = 400 rpm and time = 240 min).

Fig. 3 Effect of dye concentration on the feed phase (Experimental conditions: strip phase = 8.0 mol/L acetic acid, extractant concentration 0.8 mol/L, stirring speed = 400 rpm, pH 11.0 ± 0.1 and time = 240 min).

Fig. 4 Effect of phenol concentration on membrane phase (Experimental conditions: Feed phase = 50 mg/L, strip phase = 8.0 mol/L acetic acid, stirring speed = 400 rpm, pH 11.0 ± 0.1 and time = 240 min).

Fig. 5 Effect of time on transport (Experimental conditions: feed phase = 500 mg/L, strip phase = 8.0 mol/L acetic acid, extractant concentration 0.8 mol/L, stirring speed = 400 rpm and pH 11.0 ± 0.1).

Fig. 6 The effect of acetic acid concentration on strip phase (Experimental conditions: Feed phase = 50 mg/L, extractant concentration = 0.8 mol/L, stirring speed = 400 rpm, pH 11.0 ± 0.1 and time = 240 min).

Fig. 7 The proposed mechanism of RB dye transport through SLM

Fig. 8 Kinetics of cationic dye transport in SLM







Fig 2



Fig 3







Fig 5













Fig 8

Table 1. Effect of diluent (Experimental conditions: Feed phase = 50 mg/L, strip phase = 8.0 mol/L acetic acid, extractant concentration = 0.8 mol/L, stirring speed = 400 rpm, pH 11.0 \pm 0.1 and time = 240 min).

| Diluent | Polarity | Density (g/mL) | Viscosity (cP, 20 °C) | [dye] _f in mg/L | [dye] _s in mg/L | Permeability (×10 ⁻⁵ m/s) | Diffusion Coefficient (×10 ⁻⁵ cm/s) |
|----------|----------|-------------------|--------------------------|-------------------------------|-------------------------------|---|--|
| Xylene | 0.074 | 0.870 | 0.812 | 2.0 | 48.0 | 1.805 | 1.876 |
| Toluene | 0.099 | 0.867 | 0.601 | 4.0 | 46.0 | 1.416 | 2.360 |
| Benzene | 0.111 | 0.876 | 0.550 | 5.0 | 45.0 | 1.290 | 2.375 |
| Hexane | 0.012 | 0.655 | 0.297 | 12.5 | 37.5 | 0.589 | 4.616 |
| Kerosene | - | 0.795 | 1.601 | 30.0 | 20.0 | 0.289 | 1.204 |

| pH of the feed phase (± 0.1) | Permeability (×10 ⁻⁵ m/s) | |
|------------------------------|--------------------------------------|---|
| 5 | 0.250 | _ |
| 6 | 0.460 | |
| 7 | 0.849 | |
| 8 | 1.805 | |
| 9 | 1.415 | |
| | | |

Table 2. The permeability at different pH on the feed phase

Table. 3 Effect of dye concentration on the feed phase (Experimental conditions: strip phase = 8.0 mol/L acetic acid, extractant concentration 0.8 mol/L, stirring speed = 400 rpm, pH 11.0 ± 0.1 and time = 240 min).

| RB dye conc (mg/L) | [dye] _f in mg/L | [dye] _s in mg/L | Permeability (×10 ⁻⁵ m/s) | Flux (×10 ⁻⁶ (mg cm ⁻² s ⁻¹) |
|--------------------------|-------------------------------|-------------------------------|---|---|
| 50 | 2.0 | 48.0 | 1.805 | 1.12 |
| 75 | 11.25 | 63.75 | 1.064 | 6.30 |
| 100 | 30.0 | 70.0 | 0.675 | 16.8 |

| Carrier | Cationic dye | Transport time (min) | Transport of dye (%) | Reference |
|---------------------|-------------------|-------------------------|-------------------------|---------------|
| D ₂ EHPA | RB | 420 | 90.0 | [39] |
| | Methyl violet | 540 | 94.2 | |
| Cyanex 301 | Methylene blue | 420 | 85.0 | [55] |
| D2EHPA/ M2EHPA | Methylene blue | 420 | 62.0 | [56] |
| Phenol | RB | 240 | 96.0 | Present study |

Table. 4 Comparative study of phenol with other carriers used for different dyes.

Table 5. The effect of stirring speed (Experimental conditions: Feed phase = 50 mg/L, strip phase = 8.0 mol/L acetic acid, extractant concentration 0.8 mol/L, pH 11.0 ± 0.1 and time =240 min).

| Stirring speed (rpm) | [dye] _f in mg/L | [dye] _s in mg/L | % of transport |
|-------------------------|----------------------------|----------------------------|----------------|
| 200 | 12.5 | 37.5 | 75 |
| 300 | 9.0 | 41.0 | 82 |
| 400 | 5.0 | 45.0 | 90 |
| 500 | 2.0 | 48.0 | 96 |
| 600 | 3.0 | 47.0 | 94 |
| 700 | 5.5 | 44.5 | 89 |
| 800 | 7.0 | 43.0 | 86 |

Table 6. The lifetime of the SLM (Experimental conditions: Feed phase = 50 mg/L, strip phase = 8.0 mol/L acetic acid, extractant concentration = 0.8 mol/L, stirring speed = 400 rpm, pH 11.0 ± 0.1 and time 240 min).

| No. of runs | % of transport | Permeability (×10 ⁻⁵ m/s) |
|-------------------|----------------|--------------------------------------|
| 1 | 96.0 | 1.805 |
| 2 | 95.5 | 1.725 |
| 3 | 94.0 | 1.576 |
| 4 | 60.0 | 0.286 |
| 5 (Reimpregnated) | 96.0 | 1.805 |