CLAIMS

1. A method of forming a semipermeable membrane having enhanced alkaline stability, comprising:

providing an ultrafiltration (UF) base support membrane made from a material selected from the group consisting of polyethersulfone (PES) and polysulfone (PS);

forming reactive moieties upon said UF base support membrane by immersing said UF base support membrane in a solution comprising polyethylenimine (PEI) and a condensate;

forming at least one first layer upon at least a portion of a surface of said UF base support membrane by immersing said UF base support membrane in a solution comprising PEI and a condensate subsequent to said step of forming reactive moieties upon said UF base support membrane, thereby forming a cross-linked skin on said surface of said base membrane; and,

forming a nanofiltration (NF) layer electrostatically bound to said UF base support membrane, said NF layer comprising at least one di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer, and at least one multifunctional amine having a molecular weight in the range of 400 to 750,000, provided that at least one of the di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer is not a di- or triazine monomer which is substituted only by Cl.

2. The method according to claim **1**, wherein said method comprises:

providing a modification solution comprising PEI and a condensate solution; and

forming at least one first layer upon at least portion of said UF base support membrane by immersing said UF membrane in said modification solution, thereby forming a cross-linked skin electrostatically bound to said surface of said UF membrane.

3. The method according to claim **2**, wherein said method comprises heating said modification solution to a temperature of about 50 ºC for about 1 hour.

4. The method according to claim **1**, wherein said method comprises repeating said steps of providing an ultrafiltration (UF) base membrane, forming reactive moieties upon said UF membrane, and forming at least one first layer upon at least a portion of a surface of said UF base support membrane *n* times, $n > 1$, thereby providing *n* layers.

5. The method according to claim **1**, wherein said method comprises performing said method at a temperature of between 60 °C and 90 °C, thereby actively increasing a rate of a cross-linking reaction between said reactive moieties upon said surface of said UF base membrane and said PEI.

6. The method according to claim **1**, wherein said method comprises forming at least one second layer upon said first layer by immersing said UF membrane in said PEI solution and said condensate solution in heat-treatment conditions in the range of about 60 °C to about 90 °C, thereby forming a cross-linked skin upon said first layer.

7. The method according to claim **1**, wherein said condensate is selected from the group consisting of cyanuric chloride, sulfanilic acid and any combination thereof.

8. The method according to claim **1**, comprising:

curing said first layer in alkaline solution at room temperature; and,

heating at about 90 °C following said step of curing, thereby completing a cross-linking reaction step.

9. The method according to claim **1**, wherein said step of providing said UF base support comprises providing a UF base support characterized by a molecular weight in the range of about 5 kD to about 30 kD.

10. The method according to claim **9**, wherein said step of providing said UF base support membrane comprises providing a UF base support membrane characterized by a molecular weight of about 20 kD.

11. The method according to claim **1**, comprising immersing said membrane in a 20% solution of acid in water at about 70 °C to about 90 °C for a period of about 18-24 hours.

12. The method according to claim **1**, wherein said step of immersing said UF support membrane in said solution comprises immersing said UF support membrane in a solution comprising about 0.05% to about 0.3% w/w of said condensate for about 1 to about 3 hours at a temperature of not more than about 70 °C.

13. The method according to claim **1**, wherein:

said solution comprises between about 0.1% and about 1% PEI;

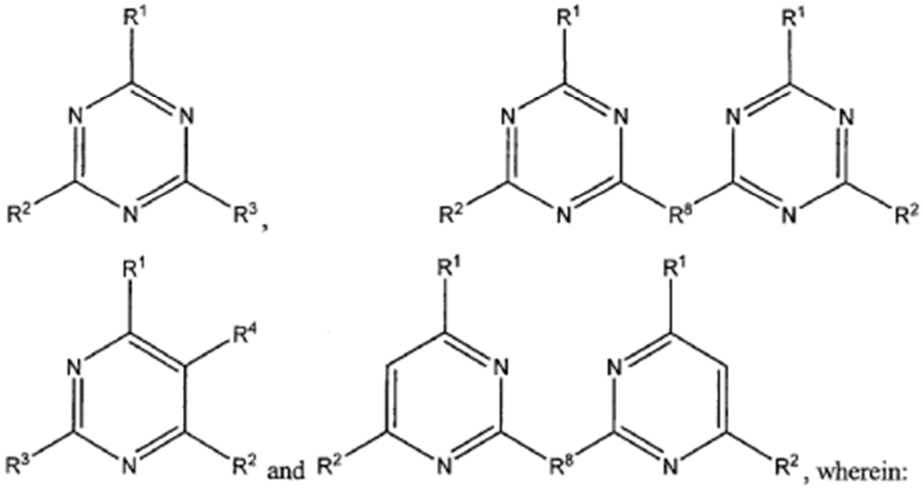
said steps of immersing said UF base support membrane solution are performed at room temperature; and,

said steps of immersing said UF base support membrane solution are followed by heat treatment at a temperature of about 70 °C to about 90 °C.

14. The method according to claim **1**, wherein said step of providing said first layer is performed using an alkaline feed solution having a pH of about 11.

15. The method according to claim **1**, wherein said solution comprises between about 0.1% and about 1% PEI.

16. The method according to claim **1**, wherein said diazine or triazine- containing monomer or oligomer is selected from the group consisting of:



wherein:

R^1 is independently selected at each occurrence from bromo, chloro, iodo, fluoro, -NHR^5, -OR^5 and SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R2 is independently selected at each occurrence from bromo, chloro, fluoro,

-NHR^5, -OR^5 and SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^3 is independently selected at each occurrence from bromo, chloro, fluoro,

-NHR^5, -OR^5 and SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^4 is selected from H, bromo, chloro, fluoro, -NHR^5, -OR^5 and SR^5, wherein

R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl; and

R^8 is independently selected at each occurrence from -NH_2- and -NH-A-NH- , wherein A is selected from $C_{1\text{-}2O}$ aliphatic moieties, $C_{6\text{-}10}$ aromatic moieties, and combinations thereof; provided that at at least two occurrences, R^1, R^2, R^3 and R^4,

taken together, are selected from bromo, chloro and fluoro, and further provided that when both R^1 and R^2 on a single ring are Cl, at least one of R^3 and R^4 is not Cl.

17. The method according to claim **1**, wherein said multifunctional amine has a molecular weight of in the range of 400 to 750,000.

18. The method according to claim **1**, wherein said method comprises forming a membrane having rejection of more than 95% glucose in 5% glucose feed solution.

19. The method according to claim **1**, wherein said membrane, after soaking in a 20% w/w aqueous NaOH solution at 40 °C, yields more than 97% glucose rejection.

20. The method according to claim **1**, wherein said membrane applied pressure of about 10 bars to 40 bars in 3.5% NaOH solution at 40^0C is in direct correlation with the membrane flux.

21. The method according to claim **1**, wherein said membrane, after soaking in a 20% w/w aqueous NaOH solution at 40 °C for a period of about 5 to 130 hours, yields more than 97% glucose rejection.

22. The method according to claim **1,** wherein said membrane, after soaking in a complex of Cu(EDTA) with 20% w/w NaOH solution, at 70 °C for a period of about 260 to 450 hours, yields more than 97% glucose rejection.

23. The method according to claim **1**, wherein said membrane after soaking in 1% w/v $NaAlO_2$ in 3.5% w/w sodium hydroxide solution at about 40 °C to about 60 °C for about 240 hours, yields more than 80% glucose rejection.

24. A semipermeable membrane having an enhanced alkaline stability, said semipermeable membrane comprising a nanofiltration (NF) layer and characterized by:

said NF layer comprises a matrix which is electrostatically bound to an UF base membrane comprising a polymer selected from the group consisting of PES and PS; and,

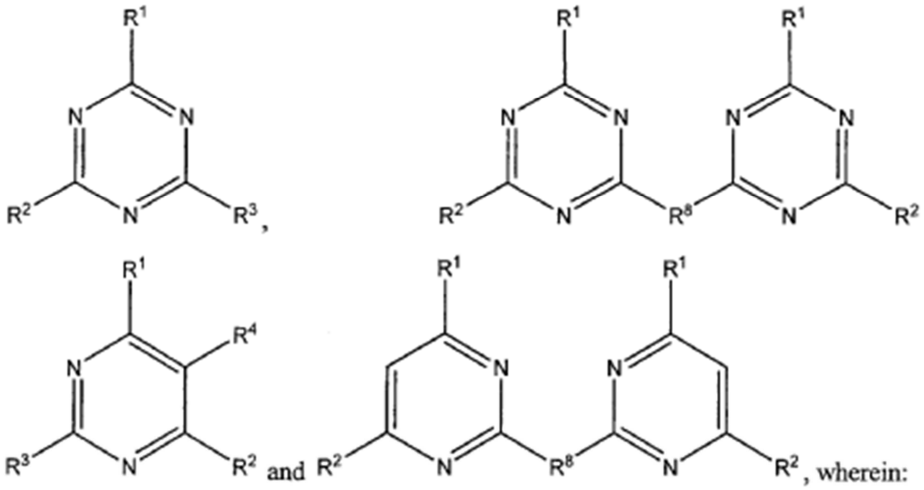
said NF layer contains a matrix that has been formed from at least one substrate selected from the group consisting of di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer, at least one multifunctional amine having a molecular weight in the range of about 400 to about 750,000, provided that at least one of the di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer is not a di- or triazine monomer which is substituted only by Cl.

25. The semipermeable membrane according to claim **24**, wherein said NF layer, when exposed to 20% w/w NaOH solution at about 40 ºC for 140 days, maintains glucose rejection of about 95%.

26. The semipermeable membrane according to claim **24**, wherein said NF layer, when exposed to 10% w/w NaOH at 70 ºC for about 450 hours, removes at least 97% of Cu(ETDA) at a flux greater than 21 LMH from a feed solution of 0.4% w/w Cu(ETDA) in 10% NaOH when the feed solution is applied to said NF layer at a feed pressure of about 30 bar and a temperature of 25 ºC.

27. The semipermeable membrane according to claim **24**, wherein said NF layer, when exposed to 1% w/v $NaAlO_2$ at 40ºC for about 240 hours, removes at least 85.4% of impurities from a feed solution of 3.5% NaOH when the feed solution is applied to said NF layer at a feed pressure of 15 bars and a temperature of about 25 ºC.

28. The semipermeable membrane according to claim **24**, wherein said diazine or triazine-containing monomer or oligomer is selected from the group consisting of:



and , wherein:

R^1 is independently selected at each occurrence from bromo, chloro, iodo, fluoro, -NHR^5, -OR^5 and -SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^2 is independently selected at each occurrence from bromo, chloro, fluoro, -NHR^5, -OR^5 and -SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^3 is independently selected at each occurrence from bromo, chloro, fluoro, -NHR^5, -OR^5 and -SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^4 is selected from H, bromo, chloro, fluoro, -NHR^5, -OR^5 and -SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl; and,

R^8 is independently selected at each occurrence from -NH_2- and -NH-A-NH- , wherein A is selected from C_{1-2O} aliphatic moieties, C_{6-10} aromatic moieties, and combinations thereof; provided that at at least two occurrences, R^1, R^2, R^3 and R^4, taken together, are selected from bromo, chloro and fluoro, and further provided that when both R^1 and R^2 on a single ring are Cl, at least one of R^3 and R^4 is not Cl.

29. An alkaline stable semipermeable membrane comprising a nanofiltration layer electrostatically bound to an ultrafiltration layer, prepared by:

providing an ultrafiltration (UF) base support membrane made from a material selected from the group consisting of polyethersulfone (PES) and polysulfone (PS);

providing a modification solution comprising PEI and condensate;

forming at least one first layer upon at least one portion of said UF base support membrane by immersing said UF membrane in said modification solution thereby forming a cross-linked skin on the surface of said UF membrane; and,

forming a nanofiltration (NF) layer upon said UF base support membrane, said NF layer comprising at least one di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer, and at least one multifunctional amine having a molecular weight in the range of 400 to 750,000, provided that at least one of the di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer is not a di- or triazine monomer which is substituted only by Cl.

30. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane is prepared by a method comprising immersing said UF membrane in a solution containing PEI and condensate to form reactive moieties upon said UF membrane.

31. The alkaline stable semipermeable membrane according to claim **30**, wherein said membrane is prepared by a method comprising actively increasing a cross-linking reaction between said reactive moieties upon the surface of said UF base membrane and said PEI at room temperature and further by elevating temperature in the range of about 60 °C to about 90 °C.

32. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane is prepared by a method comprising repeating said steps of providing an ultrafiltration (UF)

base membrane, forming reactive moieties upon said UF membrane, and forming at least one first layer upon at least a portion of a surface of said UF base support membrane *n* times, *n* > 1, thereby providing *n* layers.

33. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane is prepared by a method comprising forming at least one second layer upon said first layer by immersing said UF membrane of step in said solution comprising PEI and condensate, thereby forming a cross-linked skin upon said first layer.

34. The alkaline stable semipermeable membrane according to claim **29**, wherein said condensate is selected from the group consisting of cyanuric chloride, sulfanilic acid, and any combination thereof.

35. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane is prepared by a method comprising curing at least said first layer in alkaline solution.

36. The alkaline stable semipermeable membrane according to claim **29**, wherein said UF base support membrane is characterized by a molecular weight in the range of about 5 kD to about 30 kD.

37. The alkaline stable semipermeable membrane according to claim **36**, wherein said UF base support membrane is characterized by a molecular weight of about 20 kD.

38. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane is prepared by a method comprising forming at least one layer upon at least a portion of said UF base support membrane in an environment having a pH in the range of about 2 to about 14.

39. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane is prepared by a method comprising curing said membrane in alkaline solution following a heat treatment at about 90 °C in order to complete a cross-linking reaction step.

40. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane is prepared by a method comprising immersing said base stable semipermeable membrane in 20% solution of acid at about 70 °C to about 90 °C for a period of about 18 to 24 hours.

41. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane is prepared by a method comprising immersing said UF support membrane in aqueous solution containing about 0.05 to about 0.3% w/w of said condensate for about 1 to 3 hours at a temperature of not more than 70 °C.

42. The alkaline stable semipermeable membrane according to claim **29**, wherein said said membrane is prepared by a method comprising immersing said UF base support membrane in a solution comprising about 0.1% to about 1% polyethylenimine (PEI) solution, followed by heat-treatment at a temperature of about 70 °C to about 90 °C.

43. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane is characterized by a rejection of at least 95% glucose in a 5% glucose feed solution.

44. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane, in applied pressure of about 10 bars to 40 bars at a room temperature is in direct correlation with the membrane glucose rejection.

45. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane, after soaking in 20% w/w NaOH solution at 40^0C, yields more than 97% glucose rejection.

46. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane in applied pressure of about 10 bars to 40 bars in 3.5% NaOH solution at 40 °C is in direct correlation with the membrane yield flux.

47. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane, after soaking in a complex of Cu(EDTA) with 20% w/w NaOH solution at 70 °C for a period of about 260 to 450 days, yields more than 97% glucose rejection.

48. The alkaline stable semipermeable membrane according to claim **29**, wherein said membrane, after soaking in 1% w/v $NaAlO_2$ in 3.5% w/w sodium hydroxide solution at 40 °C to 60 °C, yields more than 80% rejection for about 240 hours.

49. A method of forming a semipermeable membrane having enhanced stability to solvent and acid, comprising:

providing a ultrafiltration (UF) base membrane made from a material selected from the group consisting of polyethersulfone and polysulfone;

forming reactive moieties upon said UF base membrane by immersing said UF membrane in a condensate solution;

immersing said UF base support membrane of in a solution comprising PEI, thereby forming a cross-linked skin on the surface of said base membrane; and,

forming a nanofiltration (NF) base membrane comprising at least one di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer, and at least one multifunctional amine having a molecular weight in the range of 400 to 750,000, provided that at least one of the di-, tri- or tetra-halo substituted diazine or

triazine-containing monomer, oligomer or polymer is not a di- or triazine monomer which is substituted only by Cl, wherein said NF base membrane is electrostatically bound to said UF base membrane.

50. The method according to claim **49**, comprising actively increasing a cross-linking reaction between said reactive moieties upon the surface of said UF base membrane and said PEI .

51. The method according to claim **50**, wherein said step of actively increasing a cross-linking reaction is at room temperature or by elevating temperature to the range of about 60 °C to about 90 °C.

52. The method according to claim **49**, comprising repeating said steps of providing an ultrafiltration (UF) base membrane, forming reactive moieties upon said UF membrane, and forming at least one first layer upon at least a portion of a surface of said UF base support membrane *n* times, $n > 1$, thereby providing *n* layers.

53. The method according to claim **49**, wherein said UF base membrane is made from a material that is not crosslinked.

54. The method according to claim **49**, comprising forming at least one first layer upon said UF base support membrane by immersing said UF base support membrane of step (c) in said solution comprising PEI for functionalizing said support membrane surface.

55. The method according to claim **49**, comprising forming at least one second layer upon said first layer by immersing said UF membrane in said PEI solution and said condensate solution following said step of immersing said UF base support membrane of in a solution comprising PEI, thereby forming a cross-linked skin on said first layer.

56. The method according claim **53**, comprising curing said at least first layer in alkaline solution having a pH of about 11.

57. The method according to claim **49**, wherein said condensate is selected from the group consisting of cyanuric chloride, sulfanilic acid, and a combination thereof.

58. The method according to claim **49**, comprising curing said support membrane in alkaline solution followed by heat treatment at 90 °C in order to complete the cross-linking reaction step.

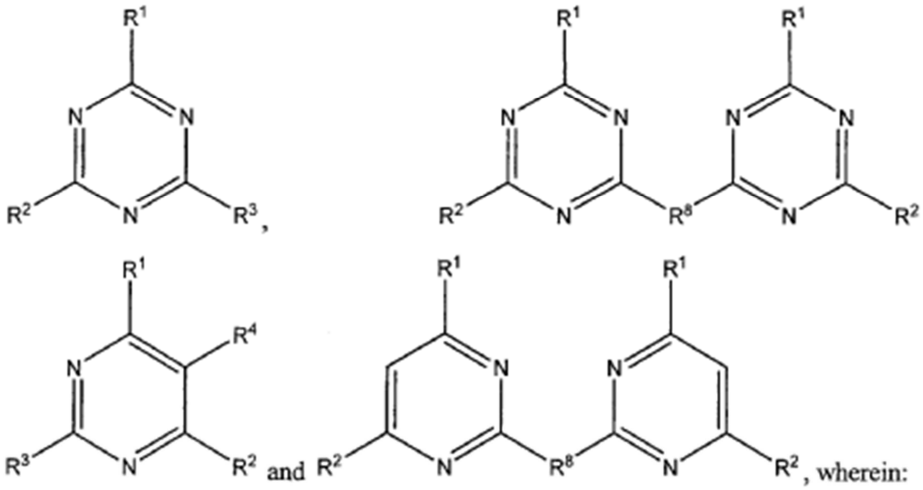
59. The method according to claim **49**, wherein said step of forming second layer is performed at a room temperature or in heat-treatment conditions in the range of about 60 °C to about 90 °C.

60. The method according to claim **49**, wherein said method comprises treating said solvent and acid stable semipermeable membrane in 20% solution of acid in water at about 70 °C to 90 °C for a period of about 18-24 hours.

61. The method according to claim **49**, wherein said solvent and acid stable semipermeable membrane is characterized as rejecting more than 95% glucose in a 5% glucose feed solution.

62. The method according to claim **49**, wherein said step of immersing said UF base support membrane in said solution comprising PEI comprises immersing said UF base support membrane in a solution comprising about 0.1% to about 1% PEI followed by heat treatment at a temperature of about 70 °C to about 90 °C.

63. The method according to claim **49**, wherein said diazine or triazine- containing monomer or oligomer is selected from the group consisting of:



R^1 is independently selected at each occurrence from bromo, chloro, iodo, fluoro, -NHR^5, -OR^5 and -SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^2 is independently selected at each occurrence from bromo, chloro, fluoro, -NHR^5, -OR^5 and -SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^3 is independently selected at each occurrence from bromo, chloro, fluoro, -NHR^5, -OR^5 and -SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R^4 is selected from H, bromo, chloro, fluoro, -NHR^5, -OR^5 and SR^5, wherein R^5 is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl; and

R^8 is independently selected at each occurrence from $-NH_2-$ and -NH-A-NH- , wherein A is selected from C_{1-20} aliphatic moieties, C_{6-10} aromatic moieties, and combinations thereof; provided that at at least two occurrences, R^1, R^2, R^3 and R^4, taken together, are selected from bromo, chloro and fluoro, and further provided that when both R^1 and R^2 on a single ring are Cl, at least one of R^3 and R^4 is not Cl.

64. The method according to claim **49**, wherein said multifunctional amine has a molecular weight of in the range of 400 to 750,000.

65. The method according to claim **49**, wherein said membrane after soaking said membrane in 20% w/w H_2SO_4 at 90 °C for a period of about 24 to 300 hours yields more than 96% glucose rejection.

66. The method according to claim **49**, wherein said membrane, after soaking said membrane in 100% w/w N-methylpyrrolidone (NMP) at 60^0C for a period of about 24 to 300 hours yields more than 96% glucose rejection.