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1 **pH-Responsive Nano-Structured Membranes Prepared from Oppositely** 2 **Charged Block Copolymer Nanoparticles and Iron Oxide Nanoparticles**

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16 **Abstract**

17 Nanostructured (hybrid) membranes combining properties of inorganic and polymeric materials is an
18 integral part of the field of separation technology. Mixed matrix membranes were prepared from
19 oppositely charged inorganic (INPs) and polymeric (PNPs) nanoparticles using spin coating method. Four
20 different types of PNPs were prepared. Poly(2-dimethylaminoethyl methacrylate)-*b*-(methyl
21 methacrylate)) and poly((methacrylic acid)-*b*-(methyl methacrylate)) diblock copolymers were prepared
22 via RAFT dispersion polymerization in ethanol at 70°C. Quaternized poly(2-(dimethylamino) ethyl

23 methacrylate)-*b*-poly (benzyl methacrylate) and poly(potassium 3-sulfopropyl methacrylate)-*b*-poly
24 (benzyl methacrylate) block copolymers were prepared using aqueous RAFT emulsion polymerization
25 method at 70°C. The inorganic iron oxide nanoparticles (INPs) were either coated with [3-(2-
26 Aminoethylamino)propyl] trimethoxysilane (TPED) via Dimercaptosuccinic acid (DMSA) using stab
27 exchange. Transmission electron microscopy (TEM) and Dynamic light scattering (DLS) analysis were
28 performed to examine the size and morphology of the prepared polymeric and inorganic nanoparticles.
29 Scanning electron microscope (SEM) and Atomic Force Microscope (AFM) images were obtained to
30 analyze the topography and thin film formation on the nylon support. Detailed filtration experiments were
31 carried out to evaluate the effect of pH on the performance of the membrane.

32 **Keywords:** pH-responsive membranes, Block copolymer nanoparticles, Iron oxide nanoparticles,
33 Surface charge, SEM, AFM, Filtration

34 **1. Introduction**

35 Since the last few decades, polymeric membranes have played an essential role in separation and
36 purification technologies. However, there are certain limitations of these membranes posed by their
37 mechanical stability, particularly for thin-film membranes, and chemical resistant [1]. Mixed matrix
38 membranes have been evolved as a potential alternative to polymeric membranes because of their
39 superior mechanical properties by choosing suitable components [2, 3]. The fabrication method for such
40 composite membranes consists of incorporation of inorganic nanoparticles into a polymeric matrix.
41 Several types of inorganic materials have been reported so far in the literature to prepare these hybrid
42 membranes including mesoporous materials [4], carbon nanotubes (CNTs) [5], zeolites [6, 7], metal-
43 organic frameworks (MOFs) [8], and metal oxides [9, 10]. The most exciting feature of these hybrid
44 membranes is that they exhibit merits of both phases (organic and inorganic materials), such as
45 mechanical stability and pressure resistance comes from inorganic phase while flexibility, low cost, and
46 processability results from the polymeric material [11]. Apart from giving higher mechanical stability, the
47 incorporation of nanoparticles also provides other unusual characteristics such as photochemical,
48 magnetic and antimicrobial properties, which results in advanced applications of such hybrid membranes
49 [12].

50 A critical challenge for the advancement of membranes is to have higher permeability and reasonable
51 selectivity in a single membrane. This challenge comes with the requirement of selective and thin-film
52 membranes in addition to the high porosity and regular porous structure [13]. Amphiphilic block
53 copolymers have gained so much attraction, as a potential solution to challenges mentioned above
54 because of their capability to self-assemble into ordered nanostructures, i.e., porous materials [14, 15].
55 Pore size and structure of membrane can easily be tuned by playing with the type and morphology of
56 block copolymers, which eventually tunes the flux, and the selectivity of the membranes. These
57 fascinating self-assembling copolymers have increased the scope of application such as purification in
58 food and pharmaceutical industry [16], water treatment [17], drug delivery [18], data storage [19] and

59 hemodialysis [20]. So far, different methods including extrusion, spin coating, and bulk evaporation have
60 been developed to prepare membranes from block copolymers [21]. The major drawback of these
61 methods is the requirement of post-fabrication steps to make porous structures in the thin films. Recently,
62 this problem has been solved by combining two phenomena, self-assembly of block copolymers with the
63 non-solvent induced phase separation (NIPS), to produce exceptionally isoporous asymmetric membranes
64 without the need of any post-fabrication step to create porosity [22].

65 Recently, stimuli-responsive membranes have gained attention due to their switchable physicochemical
66 and barrier properties [23]. These new membranes can modify their mass transfer and interfacial
67 properties in response to the external stimuli including direct ones (i.e., pH, temperature and ionic
68 strength [24, 25]) and newly developed remote or indirect triggers (i.e., light, magnetic and electric fields
69 [26, 27]). The main objective for the preparation of stimuli-responsive membranes is to have the
70 reversible changes in addition to the high selectivity at a faster rate. The conformational changes in the
71 functional groups of responsive polymers, either in bulk membrane or at the surface, give rise to the
72 stimulus response. The process of responsiveness in such membranes usually occurs in two steps [28]: (i)
73 morphological changes in polymer, on microscopic level, in response to the stimuli (ii) intensification of
74 these microscopic morphological transformations into macroscopic changes that can be measured as
75 different membrane properties. As compared to other external stimuli, pH responsiveness provides more
76 alternatives for materials and their application fields, making it a new and useful approach.

77 Zhang et al. [29] described the production of pH-sensitive membranes by mixing ethylcellulose with
78 poly(N-isopropyl acrylamide-co-methacrylic acid) nanoparticles, produced via aqueous dispersion
79 polymerization method. The prepared membranes were coated with the layers of polyelectrolyte to
80 prevent the separation of nanoparticles from the membrane surface. Nunes et al. [30] prepared the pH-
81 responsive membranes having self-assembly of metal-block copolymer complexes using NIPS technique.
82 The structure of the thin film was manipulated by using different stability constants of series of metal-
83 polymer complexes. The most vigorous pH response was evident for the membranes having pores of

84 nano-meter size. The effect of pH on the pore sizes of hybrid membranes was also reported by Tufani et
85 al. [31]. These composite membranes were synthesized by the surface modification of the pore walls with
86 pH-responsive block copolymer via initiated chemical vapor deposition (iCVD). pH responsiveness of the
87 prepared membranes was tested under various pH values by using different permeates such as polyacrylic
88 acid (PAA), nanoparticles, and BSA protein. Recently, Fan et al. [32] reported the development of pH
89 sensitive smart gating membranes by efficiently incorporating poly(*N,N'*-dimethylamino-2-ethyl
90 methacrylate) (PDMAEMA) microgels, as functional gates, into poly(ether sulfone) (PES) membrane
91 through liquid-induced phase separation technique. The prepared membranes displayed positive pH-
92 responsive behavior in an acidic environment whereas in a basic environment, negative pH-responsive
93 behavior was evident.

94 Recently, we developed a novel method to synthesize thin-film membranes from sequential spray coating
95 of self-assembled block copolymers nanoparticles [33]. Spray coating is a convenient approach to prepare
96 thin layers involving two mechanisms, bulk movement in the spray and random spreading in the liquid
97 film [34]. The anionic and cationic block copolymers were produced using Reversible Addition
98 Fragmentation Chain Transfer (RAFT) aqueous emulsion polymerization method which, self-assembled
99 spontaneously into spherical nanoparticles in the presence of water through polymerization induced self-
100 assembly. The results revealed the fine-tuning of polymeric layer thickness by controlling the number of
101 deposited layers. Formation of porous and defect free membranes was also confirmed by imaging
102 analysis. In our previous studies [14, 35-37], we also reported the preparation of nanocomposite
103 membranes with particular pore sizes, by using already produced colloidal stable solutions. By
104 movement using this method, membrane of desired pore size could be easily synthesized by first
105 preparing the nanoparticles of a particular diameter which will assemble to give a porous membrane with
106 the desired properties. The final properties of the developed membranes were also manipulated by playing
107 with the type of nanoparticles [14, 37]. We reported the preparation of nanocomposite membranes from
108 block copolymer nanoparticles of different morphologies (worms, spheres, and vesicles) and

109 functionalized iron oxide nanoparticles [36]. The results showed a prominent effect of the amount of
110 functionalized INPs and pH values on the mechanical stability of membranes. Application of the
111 magnetic field also showed an increase in the flux due to the movement of the magneto-responsive iron
112 oxide nanoparticles [37].

113 In this study, new strategies to prepare inorganic nanoparticles (INPs) and polymeric nanoparticles having
114 positive and negative surface charges are being developed. Thin-film membranes are synthesized by the
115 combination of positive inorganic nanoparticles (INPs) coated with [3-(2-Aminoethylamino)propyl]
116 trimethoxysilane (TPED) and negative diblock copolymeric nanoparticles (PNPs) such as PMAA₆₄-
117 PMMA₄₀₀ and by combining negative INPs coated with Dimercaptosuccinic acid (DMSA) and positive
118 PNPs (PDMAEMA₈₀-PMMA₅₀₀). Another set of polymeric nanoparticles having positive and negative
119 surface charges (PQDMA₂₃-PBzMA₃₀₀ and PKSPMA₃₆-PBzMA₃₀₀), previously prepared in our group
120 [33], is also mixed with inorganic nanoparticles coated with the opposite charges to make thin-film
121 membranes. In contrast to our previous studies, functionalization of INPs is done on the core of the
122 particle instead of a polymeric chain on the surface. Furthermore, pH-sensitive (PMAA and PDMAEMA)
123 and non-pH-sensitive (PQDMA and PKSPMA) block copolymer nanoparticles are utilized in this study to
124 assess the effect of pH on the membrane performance. Using these four types of PNPs along with the two
125 pH sensitive INPs allow preparation of membranes from PNP/ INP pairs where both nanoparticles are
126 sensitive to pH as well as pairs that only the INP has pH sensitivity. This large combination of
127 nanoparticles permits the preparation of pH sensitive membranes with different pore sizes and flux
128 values. The nanoparticles are characterized by Transmission Electron Microscopy (TEM) and Dynamic
129 Light Scattering (DLS). Nanocomposite membranes are analyzed by using Atomic Force Microscopy
130 (AFM), Scanning Electron Microscopy (SEM), and filtration tests at different pH values.

131 **2. Results and discussion**

132 **2.1. Synthesis and characterization of the block copolymer nanoparticles (PNPs) and** 133 **inorganic nanoparticles (INPs)**

134 In our previous study [36], we synthesized mixed matrix membranes from negatively charged PMAA-*b*-
135 PMMA block copolymer particles with different morphologies (prepared through polymerization induced
136 self-assembly) and positively charged iron oxide nanoparticles coated with quaternized poly(2-
137 dimethylamino)ethyl methacrylate. The effect of particle morphology (spheres, worms, and vesicles),
138 added amount of inorganic particles and pH values on filtration and mechanical performance of the
139 prepared membranes were evaluated. It was demonstrated that the membranes from spherical NPs in the
140 presence of high enough positively charged magnetic nanoparticles had the best performance with a pore
141 size of 2–20 nm. The positively charged INPs increased the mechanical stability of the final membrane
142 due to electrostatic attractions.

143 In this work, following a similar methodology, a library of charged spherical polymeric nanoparticles
144 (pH-responsive and non-pH responsive) is prepared. Reversible Addition Fragmentation Chain Transfer
145 (RAFT) ethanolic dispersion and aqueous emulsion polymerization methods are used to synthesize
146 positively and negatively charged diblock copolymer nanoparticles through polymerization induced self-
147 assembly (PISA) method. The cationic diblock copolymer particles are synthesized by using cationic
148 steric stabilizer (macro-chain transfer agent) based on poly(2-dimethylaminoethyl methacrylate)
149 (PDMAEMA), and a core-forming hydrophobic block based on poly(methyl methacrylate) (PMMA). The
150 second cationic block copolymer nanoparticles are prepared by using a macro-chain transfer agent based
151 on quaternized poly(2-(dimethylamino) ethyl methacrylate) (PQDMA), and a hydrophobic core based on
152 poly(benzyl methacrylate) (PBzMA). On the other hand, the anionic diblock copolymer nanoparticles are
153 prepared using an anionic stabilizer of PMAA, and a hydrophobic core of PMMA. Similarly, the second
154 anionic copolymer nanoparticles were made from an anionic poly(potassium 3-sulfopropyl methacrylate)
155 (PKSPMA) stabilizer and a hydrophobic core of PBzMA. All four block copolymer nanoparticles formed
156 spherical nanoparticles in ethanol or water under polymerization induced self-assembly (PISA) regime.

157 DLS study of PDMAEMA₈₀-PMMA₅₀₀ nanoparticles presented broad size distribution and stable spheres
158 with an average hydrodynamic diameter of 28.8 ± 1.3 nm with the polydispersity index of 0.9 and width
159 of 25.5 ± 0.3 nm (from TEM analysis) (Fig. S1C). DLS investigation of PMAA₆₄-PMMA₄₀₀ nanoparticles

160 also indicated narrow size distribution, and stable spheres with an average hydrodynamic diameter of 22.8
161 ± 1.7 nm, the diameter of these nanoparticles from TEM investigation is about 18.9 ± 1.1 nm (Fig. S1D).
162 Furthermore, PMAA₆₄-PMMA₄₀₀ bearing negative surface charge, due to the presence of polymethacrylic
163 acid groups on their surface, with a zeta potential of -38 ± 2.0 mV at pH 8. The PDMAEMA₈₀-PMMA₅₀₀
164 particles had positive surface charge (zeta potential value of 28.9 ± 5.0 mV at pH 8 (Table S1)) due to the
165 presence of the amine groups. DLS measurements of PQDMA₂₃-PBzMA₃₀₀ nanoparticles revealed narrow
166 size distribution and stable spheres with an average hydrodynamic diameter of 40 nm whereas a narrow
167 size distribution and stable spheres with an average hydrodynamic diameter of 45 nm were obtained for
168 PKSPMA₃₆-PBzMA₃₀₀ nanoparticles. TEM analysis showed a diameter of 26.4 ± 1.1 nm and 28.8 ± 0.5
169 nm for PQDMA₂₃-PBzMA₃₀₀ and PKSPMA₃₆-PBzMA₃₀₀ nanoparticles, respectively (Figs. S1E & S1F).
170 The charged inorganic nanoparticles were synthesized via previously reported methods [39, 40].
171 Positively charged iron oxide nanoparticles bearing amino groups (INPs-TPED), and the negatively charged
172 particles had succinic acid groups on their surface (INPs-DMSA) (Fig. 1). DLS measurements of INPs-
173 TPED nanoparticles showed narrow size distribution and solid spheres having an average hydrodynamic
174 diameter of 57.4 nm. The TEM analysis of the nanoparticles proposed diameter of 3.1 nm (Fig. S1A).
175 DLS characterization of INPs-DMSA also displayed narrow size distribution and stable spheres with an
176 average hydrodynamic diameter of 25.4 nm, whereas the diameter from TEM analysis was 1.0 nm (Fig.
177 S1B).

178

179 **2.2.Synthesis and Characterization of Hybrid Membranes**

180 To prepare the casting solutions, oppositely charged PNP and INP were mixed at different ratios (Fig. 1).
181 To avoid precipitation of the oppositely charged nanoparticles, the isoelectric point (IEP) of each
182 PNP/INP pair was determined, and the PNP: INP ratios were kept below the IEP of each pair (see Table
183 1). The casting solution mixtures were stirred at room temperature for 24h. This solution mixture was
184 then vortexed 10-15 minutes before membrane casting. Spin coating was used to deposit a thin layer of

185 the nanoparticles on commercial nylon support with an average pore diameter of 0.2 μm . The prepared
186 hybrid membranes were analyzed using AFM, SEM and filtration test.

187 **Table 1.** Summary of amounts of nanoparticles required for preparation of the membrane casting solutions

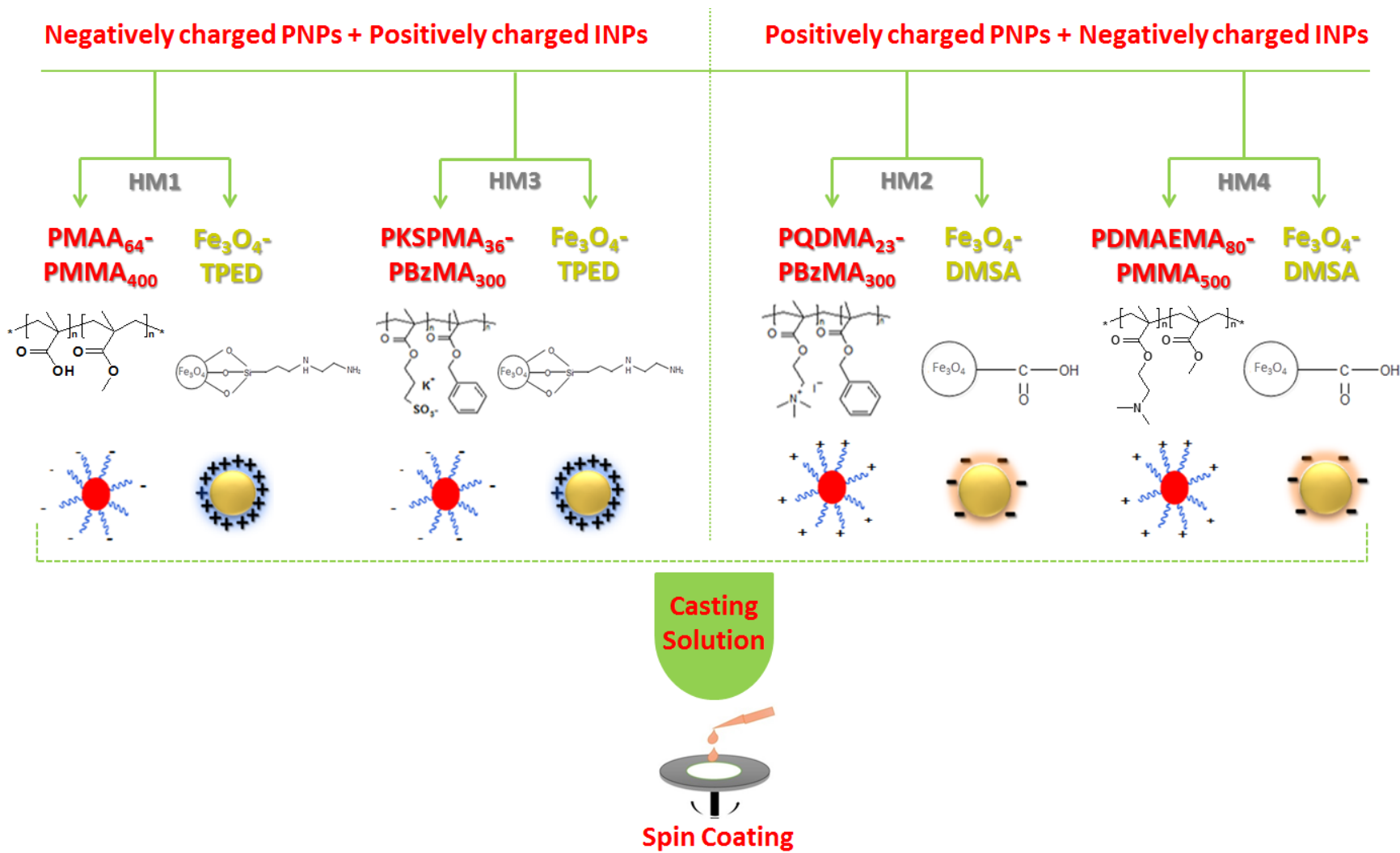
Sample ID	Sample Membranes	Inorganic Nanoparticles (INPs)*				Polymeric Nanoparticles (PNPs)			
		Amount of INPs to get the isoelectric point (mL)		Amount of INPs to get the isoelectric point (mL)		Amount of PNPs to make membrane solution (mL)			
		Fe ₃ O ₄ -DMSA	Fe ₃ O ₄ -TPED	Fe ₃ O ₄ -DMSA	Fe ₃ O ₄ -TPED	PDMAEMA ₈₀ - PMMA ₅₀₀	PMAA ₆₄ - PMMA ₄₀₀	PQDMA ₂₃ - PBzMA ₃₀₀	PKSPMA ₃₆ - PBzMA ₃₀₀
HM1	PMAA ₆₄ - PMMA ₄₀₀ - Fe ₃ O ₄ -TPED	-	1.4	1.2	-	-	0.5	-	-
HM2	PQDMA ₂₃ - PBzMA ₃₀₀ - DMSA- Fe ₃ O ₄	3.0	-	-	2.6	-	-	0.5	-
HM3	PKSPMA ₃₆ - PBzMA ₃₀₀ - TPED- Fe ₃ O ₄	-	2.6	2.0	-	-	-	-	0.5
HM4	PDMAEMA ₈₀ - -PMMA ₅₀₀ - Fe ₃ O ₄ -DMSA	1.0	-	0.8	-	0.5	-	-	-

188 * Concentration of Fe₃O₄-DMSA stock solution = 2.14 mg/mL

189 * Concentration of Fe₃O₄-TPED stock solution = 1.27 mg/mL

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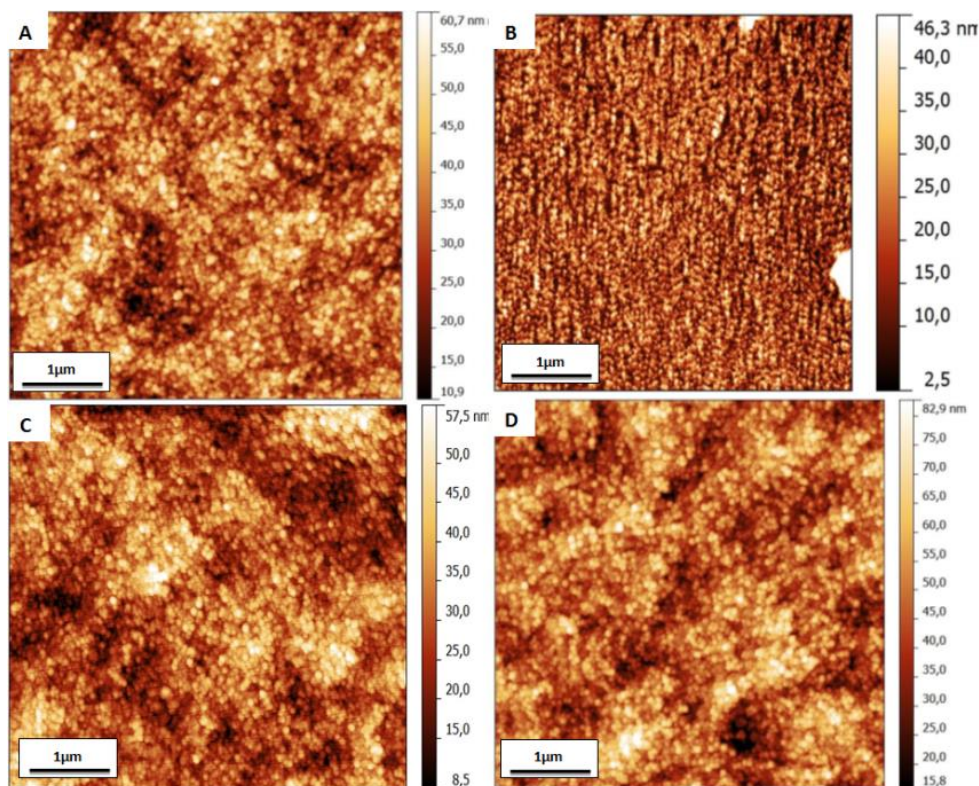
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193 **Fig. 1.** Schematic representation of nanostructured membrane prepared from oppositely charged PNPs and INPs

194 Fig. 2 shows the topography of the prepared four nanostructured membranes. These AFM images clearly
195 show the spherical morphology of the PNP nanoparticles and also confirm the compact packing of the
196 PNPs with no visible alteration due to the presence of the INPs.

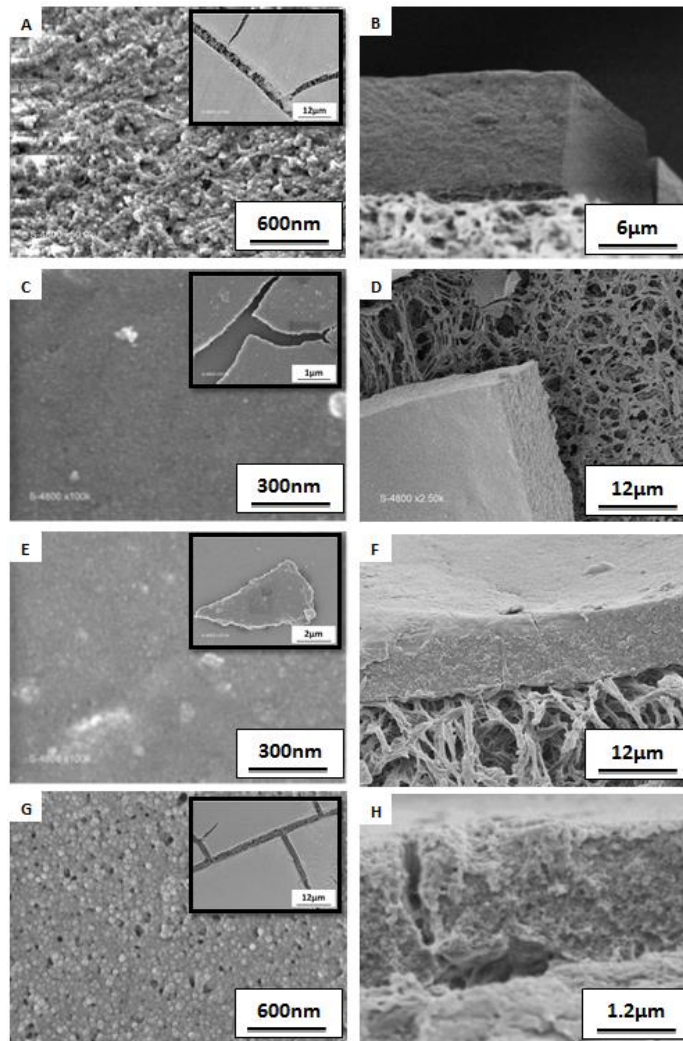


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198 **Fig. 2.** Atomic force microscopic images of the membranes (A) **HM1** (B) **HM2** (C) **HM3** and (D) **HM4**.

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200 The SEM images of all four membranes (**HM1-4**, Fig. 3) display the formation of defect-free active
201 layers. The thickness of the top layer of membrane containing PMAA₆₄-PMMA₄₀₀ and INPs-TPED is
202 about 1.82 μm while membrane containing PDMAEMA₈₀-PMMA₅₀₀ and INPs-DMSA has top layer
203 thickness of 1.84 μm. Similarly, PQDMA₂₃-PBzMA₃₀₀ and PKSPMA₃₆-PBzMA₃₀₀ nanoparticles based
204 membranes have top layer thickness of 1.89 μm and 1.56 μm, respectively.



205

206 **Fig. 3.** SEM images of (A, C, E, and G) top surface and (B, D, F and H) cross-section of (A, B) **HM1**, (C, D) **HM2**,
 207 (E, F) **HM3** and (G, H) **HM4** membranes. Insets present the images of the top surface with lower magnification.

208 It is apparent that the void among the congested nanoparticles gives rise to the porous structure.

209 Theoretical pore size was estimated using a straightforward model based on the hexagonal arrangement of

210 mono-disperse spheres [35]. Here, the average diameter of the PMAA₆₄-PMMA₄₀₀ and PDMAEMA₈₀-

211 PMMA₅₀₀ spherical nanoparticles are 18.9 nm and 25.5 nm, respectively as measured from TEM images.

212 The calculated pore diameter is considered to be 0.4142 times of a sphere diameter (Fig. S2). The

213 estimated pore size for **HM1** membrane is 7.8 nm, while for **HM4** membrane is 10.5 nm. By performing

214 the same calculation, the estimated pore size for **HM2** membrane is 10.9 nm, whereas for **HM3** membrane

215 this value is 11.9 nm (Table 2). The pore diameter calculations were based on particle diameters measured

216 from TEM images as the membranes are at semi-dry state; hence, the particle size should be closer to dry
 217 state rather than the hydrodynamic diameter at colloidal state. During the calculations, the INPs diameter
 218 was not considered since they are much smaller as compared to the PNPs. HM2 to HM4 membranes
 219 show similar pore size compared to HM1. The shells of the PNPs used in these membranes are made of
 220 permanently charged polymeric chains (strong poly-acid and base). The presence of permanent charge in
 221 a polymer chain forces them to be in an extended and rigid configuration rather than the entangled and
 222 collapsed state. In the block copolymer, the extended ionic block will be much more solvated compared to
 223 a collapsed polymeric chain resulting in the formation of more hydrated nanoparticle shell hence a bigger
 224 nanoparticle size and pore diameter.

225 **Table 2.** Theoretical pore sizes of the prepared membranes calculated using Eq. in Fig. S4.

Sample ID	PNPs size (nm)	Pore size (nm)
HM1	18.9	7.8
HM2	26.4	10.9
HM3	28.8	11.9
HM4	25.5	10.5

226

227 The prepared membranes were also tested for pure water filtration. The filtration cycles (repeated three
 228 times) were all performed on the same membrane. The membranes were fitted in a filtration cell with a
 229 diameter of 2.5 cm and a volume of 10 mL. Each membrane was conditioned for 2 hours at 3.5 bar, and
 230 then water flux was recorded to reach an equilibrium state. For filtration under pressure, the filtration cell
 231 was filled with water and linked with a pressurized water reservoir. Upon collection of data, Darcy's law
 232 was used to calculate the flux (J_v) and permeability (L_p) values using the following equations [41]:

233
$$J_v = \frac{V_p}{t S}$$

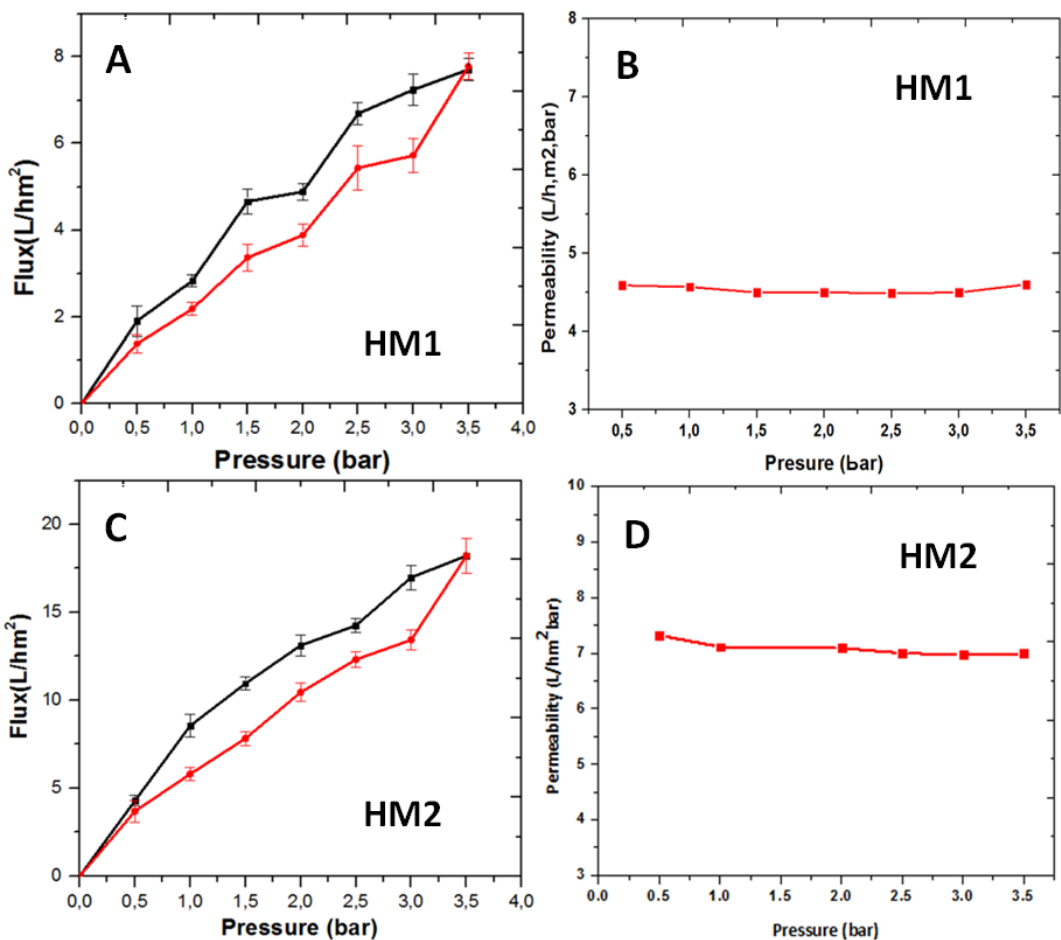
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$$L_p = \frac{J_v}{\Delta P}$$

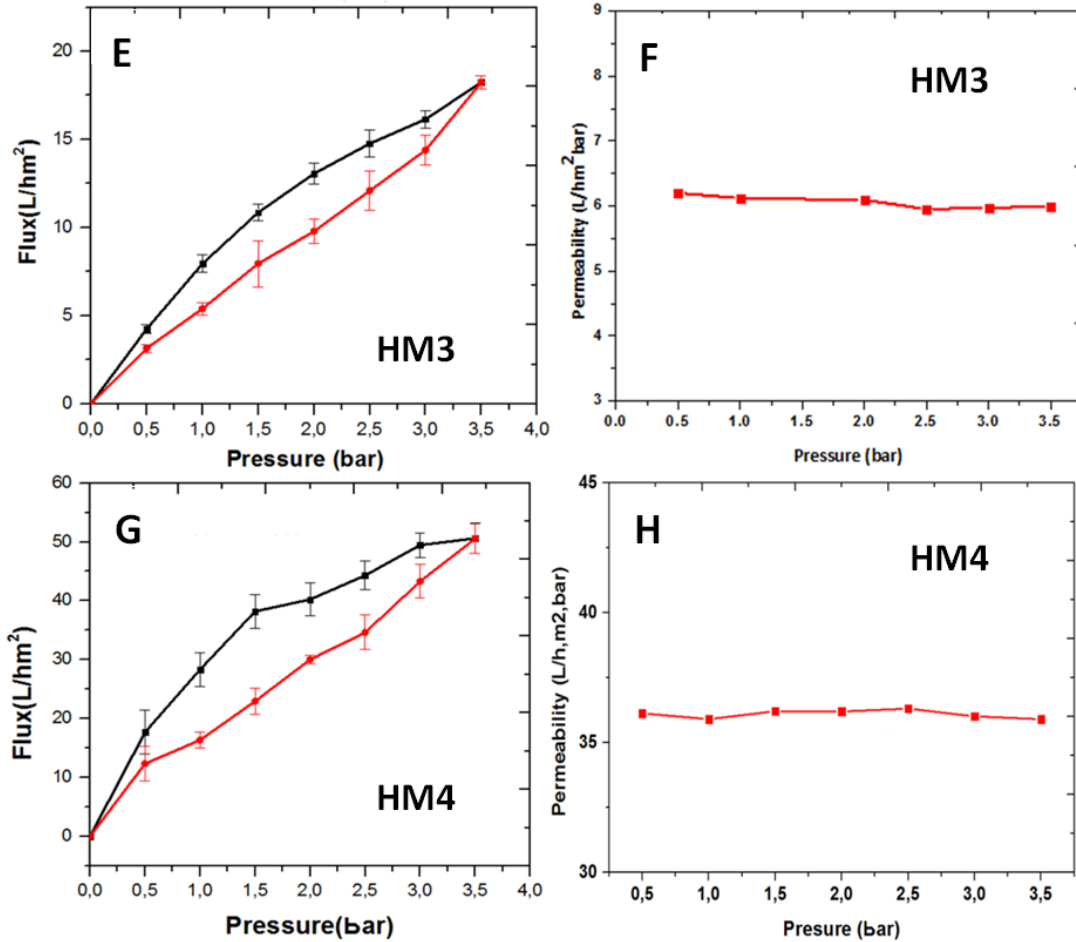
where, V_p corresponds to the volume of water going through the membrane (L), t represents time (h), S denotes the surface of the membrane (m^2), and ΔP is water pressure (bar).

Water flux (J_v) was calculated at different pressure intervals between 0 and 3.5 bar. At each pressure, 20 minutes equilibrium time was allowed before recording the data, followed by a 20 minutes recording. In all four cases, the water flux plots versus pressure show an almost linear increase (Figs. 5A, 4C, 4E & 5G). Figs. 5B, 5D, 5F, and 5H show that the permeability is almost constant as a function of applied pressure which also verifies the stability of the prepared membranes under tested conditions. For **HM4** membrane, at 3.5 bar the calculated flux was 50.8 L/hm² and the resultant permeability was 36.2 L/hm²bar whereas for **HM1** membrane, at 3.5 bar the calculated flux was 7.69 L/h.m², and the resultant permeability was 4.60 L/hm²bar. In the same way, for **HM3** membrane, at 3.5 bar the calculated flux was 18.7 L/hm² with the permeability of 4.52 L/hm²bar and for **HM2** membrane, at 3.5 bar the calculated flux is 18.3 L/hm² with the permeability of 5.34 L/hm²bar. These flux values were lower than the values already reported in literature for PMAA-PMMA based membranes having PMAA-*b*-PQDMAEMA coated INPs [36, 37] which may be due to the fact that the INPs used in this study are stabilized using small molecules as compared to the INPs used in the previous study which had hairy shell structure (stabilized with positively charged polymer chains with an average size of 7 nm). These particles were less prone to aggregation because of the presence of the charged polymer chain. However, the INPs stabilized using only an acid or amine group (INP-DMSA and INP-TPED) aggregated readily as it could be seen from the data presented in Table S1. The average size measured from TEM images (dry state) show particle diameters of 1 and 3 nm for the negatively and positively charged particles respectively. While DLS measurements in solution, gave diameters of 25 and 57 nm for the same particles. Such a big difference in size could only be due to particle aggregation. Therefore, if the INPs present in the membrane dope solutions are aggregated (i.e. larger diameters) they would possibly clog some of the

258 membrane pores reducing the apparent pore size, resulting in lower flux values. This aggregation could
259 also be the reason behind the small hysteresis observed in the flux curves. If the INPs are aggregated, they
260 would interact less with the polymer chains stabilizing the PNPs. This could influence the cohesion of the
261 particles brought about by the electrostatic forces due to the presence of oppositely charged nanoparticles.
262 Weaker cohesion would lead to lower stability of the membrane active layer that could be slightly pushed
263 into the support layer under water pressure (during filtration).



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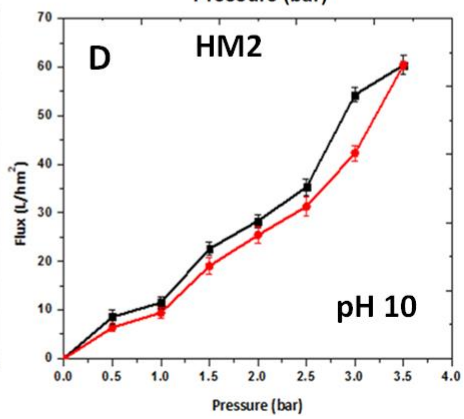
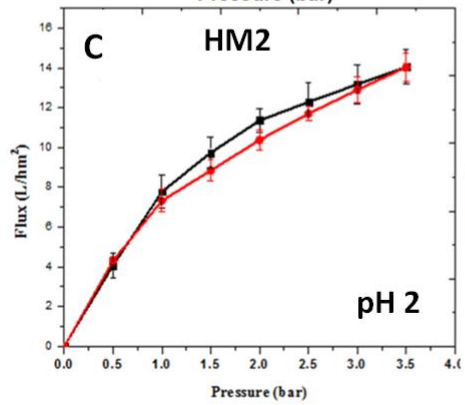
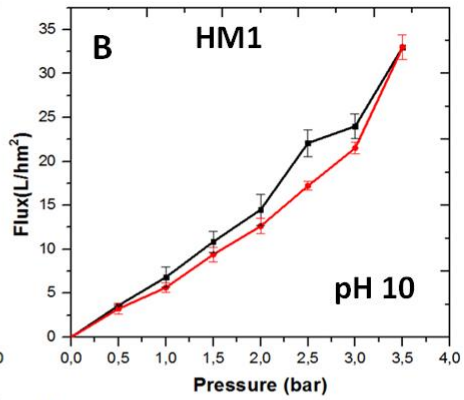
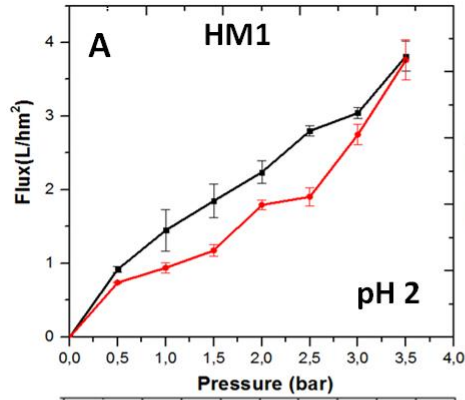


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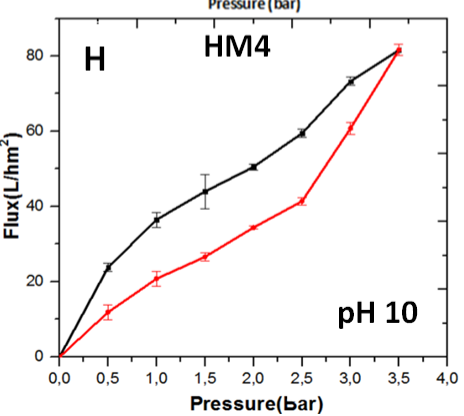
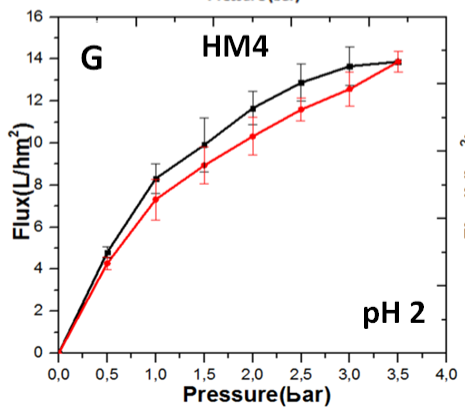
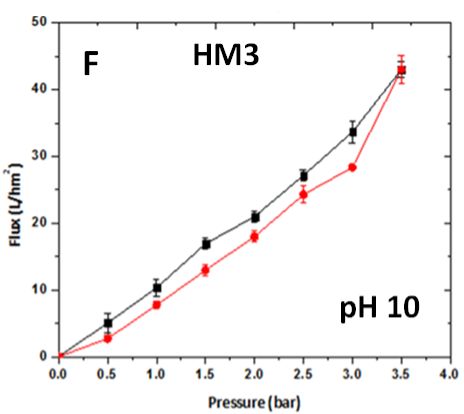
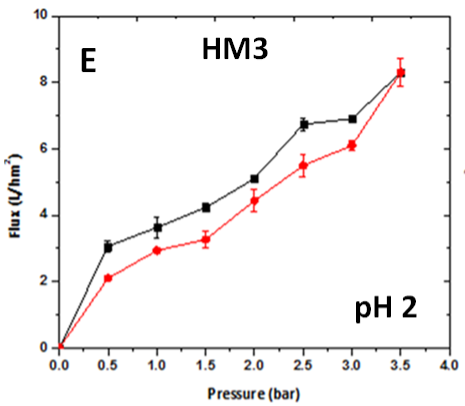
266 **Fig. 5.** (A, C, E, and G) Water flux (J_v) and (B, D, F, and H) Permeability (L_p) as a function of pressure for
 267 nanostructured membranes (A, B) **HM1** (C, D) **HM2** (E, F) **HM3** and (G, H) **HM4** at pH of 7. The reported values
 268 are the average of three different measurements, and the bars represent the standard deviation. Blackline is pressure
 269 ramp up, and the red is the ramp down.

270

271 PMAA₆₄-PMMA₄₀₀ and PDMAEMA₈₀-PMMA₅₀₀ polymeric nanoparticles are pH-sensitive because of the
 272 presence of PMAA and PDMAEMA on their surface. So are the inorganic nanoparticles used, as they
 273 bear either -COOH (DMSA, pK_a 1 = 2.9, pK_a 2 = 4.5) or -NH₂ (TPED, pK_a = 8) functionalities. To see
 274 the effect of the pH change on the pore size of the nanostructured membranes, filtration tests at acidic and
 275 basic pH values were performed. Feed solutions with pH values below and above the pK_a of PDMAEMA
 276 and PMAA (7.4-7.8 and 6.1, respectively) [36, 42] were used for filtration (pH 2 and 10). The flux shows
 277 the increasing trend as a function of applied pressure for both acidic and basic pH values (Fig. 6A-H).



278



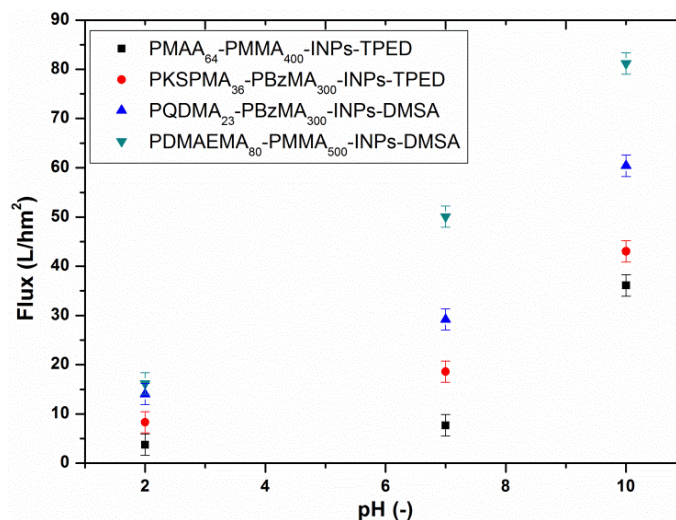
279

280 **Fig. 6.** Water flux (J_v) as a function of pressure for (A, B) **HM1** membranes, (C, D) **HM2** membranes, (E, F) **HM3**
281 membranes and (G, H) **HM4** membranes, at (A, C, E and G) pH 2 and (B, D, F and H) pH 10. The values are the
282 average of three different measurements, and the bars represent the standard deviation. Blackline is pressure ramp
283 up, and the red is a ramp down.
284
285

286 The flux increases progressively from 3.5 L/hm² at 1.0 bar to 34.6 L/hm² at 3.5 bar for pH 10 in case of
287 **HM1**, while for **HM4** membrane flux increases gradually from 22.3 L/hm² at 1 bar to 81.2 L/hm² at 3.5
288 bar for pH 10. Likewise, the flux increases from 11.5 L/hm² at 1.0 bar to 60.4 L/hm² at 3.5 bar for pH 10
289 in case of **HM2**, whereas for **HM3** membrane flux increases from 10.33 L/hm² at 1 bar to 43.03 L/hm² at
290 3.5 bar for pH 10. The SEM analysis of hybrid membranes was also performed after filtration tests and
291 the micrographs revealed no signs of deformation on the active layer (Fig. S5).

292 To be able to compare the membranes together, the maximum flux values recorded at 3 different pH (2, 7
293 and 10) at 3.5 bar were plotted in one single figure (Fig. 7). The flux values were at lowest when the
294 water pH was 2. The flux values are lower for prepared membranes at pH 2 as compared to the values at
295 pH 10. This is because at pH 2 there is only a small number of charges present since pH 2 is below the
296 pKa of all the used functional nanoparticles (PNP and INP). As the number of apparent charge on the
297 surface of the nanoparticles increase ($\text{pH} \geq 10$) the flux value increases sharply. This is most likely due to
298 the repulsive forces generated between the packed particles forcing them to move. This stands out more in
299 membranes made from nanoparticles coated with PDMAEMA as stabilizer (with highest flux values at all
300 3 pH values tested). For this nanoparticle pair (PDMAEMA-PMMA and INP-DMSA) there is no pH
301 value where both particles are charged. This means that the cohesion between the PNP particles is at its
302 minimum due to same charge repulsion.

303 The changes in flux brought about by pH could be very useful to tune the pore size according to the
304 filtration regime/ range. If membrane with bigger pore size is required a cycle of filtration with water at
305 pH 10 could be performed prior to the actual sample filtration. Another simple method to tune the pore
306 size would be to soak the membrane in water with a certain pH value.



307

308 **Fig. 7.** Water flux as a function of pH for different nanostructured membranes at 3.5 bar. Black color represents
 309 PMAA₆₄-PMMA₄₀₀-INPs-TPED (HM1 membrane), red color represents PKSPMA₃₆-PBzMA₃₀₀-INPs-TPED
 310 (HM3 membrane), blue color represents PQDMA₂₃-PBzMA₃₀₀-INPs-DMSA (HM2 membrane) and green color
 311 represents PDMAEMA₈₀-PMMA₅₀₀-INPs-TPED (HM4 membrane).

312

313 Conclusion

314 In summary, iron oxide nanoparticles were prepared by polyol method and functionalized with [3-(2-
 315 Aminoethylamino)propyl] trimethoxysilane (TPED) and Dimercaptosuccinic acid (DMSA) to achieve the
 316 positive and negative charges on their surface. PDMAEMA₈₀-PMMA₅₀₀ and PMAA₆₄-PMMA₄₀₀
 317 copolymer nanoparticles were prepared via RAFT-PISA synthesis method in ethanol while PKSPMA₃₆-
 318 PBzMA₃₀₀ and PQDMA₂₃-PBzMA₃₀₀ copolymer nanoparticles in water. High conversions were attained
 319 within 24 hours. DLS analysis showed their spherical features, and TEM images represented well-defined
 320 nanoparticles. Cationic and anionic nanoparticle pairs were effectively utilized to synthesize thin-film
 321 membranes by spin coating method on a nylon support. SEM and AFM analysis revealed the formation of
 322 porous and defect-free membranes. Pressure-driven water filtration tests, using prepared membranes,
 323 were performed at different pH values. Since the pK_a value of polymethacrylic acid (PMAA) on the
 324 surface of PNPs is about 6.1 and for PDMAEMA on the surface is in the range of 7.4-7.8, therefore, feed
 325 solutions of two different pH values, 2 and 10, were used and the filtration experiments were performed.
 326 For neutral pH (7), the membranes HM1 displayed the flux of 7.69 L/hm², while HM4 membranes

327 showed the flux of 50.8 L/hm² at 3.5 bar of pressure. In the same way, for HM3 membranes, at 3.5 bar,
328 the flux was 15.4 L/hm² and for HM2 membranes, at 3.5 bars, the calculated flux was 21.3 L/hm². The
329 highest recorded flux was 81.2 L/hm² for HM4 nanostructured membranes at the pressure of 3.5 bars and
330 pH 10, which was linked with the deprotonation of the amine groups resulted in higher water flux. When
331 the pH value was below the pK_a value (pH 2) lower flux values were observed for all the investigated
332 membranes which were attributed to the existence of a fewer number of charges for interaction. The
333 filtration tests also verified the mechanical stability of studied membranes under the investigated pressure
334 range (0-3.5 bars). The prepared nanostructure membranes were found to have a pore size in a nano-
335 metric range following lower limit of ultrafiltration and upper limit of nano-filtration. The adequate
336 bonding of positively and negatively charged particles (PNPs and INPs) resulted in the enhanced
337 mechanical stability of the prepared membranes. In future work, the magneto-responsive behavior of
338 these hybrid membranes can further be examined.

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