

Electronic Supplementary Information

Integrated Synergy: PSF/PANI/GO Membranes for Dual-Action Textile Dye Detoxification

Anila Tabasum^{a1}, Amna Siddique^{a1}, Humaira Razzaq^{a*}, Hifza Nawaz^b, Shumaila Razzaq^c, Saba Tahir^a, Shaista Taimur^a, Nusrat Jabeen^a, Samreen Shehzadi^d

^a Department of Chemistry, University of Wah, 47070, Pakistan

Corresponding Author: humaira.razzaq@uow.edu.pk

^a Department of Chemistry, University of Wah, 47070, Pakistan

Corresponding Author: humaira.razzaq@uow.edu.pk

^b Department of Materials, University of Manchester, Oxford Road, Manchester, M13 9PL, UK;

^c Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

^d International Islamic university, Islamabad, Pakistan

^e Central Analytical Facility Division, Pakistan Institute of Nuclear Science & Technology, Islamabad, Pakistan

¹ Equal contribution

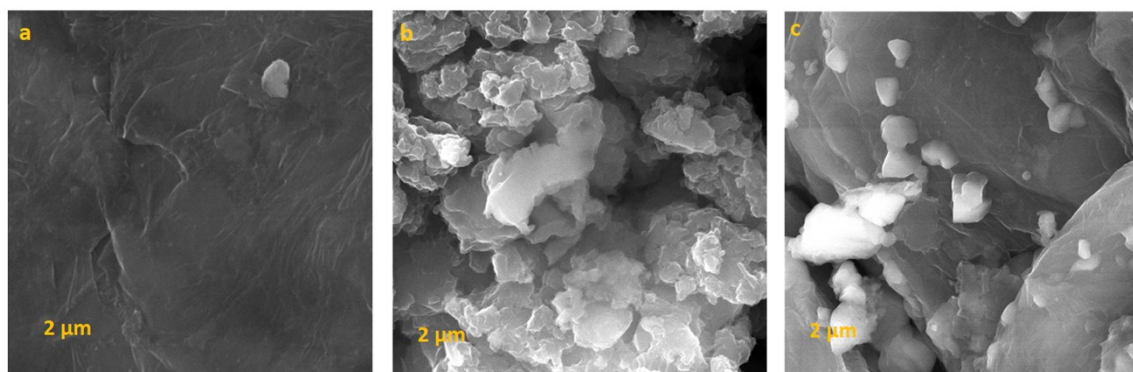


Fig. S1: SEM of a) GO b) PANI c) GO-PANI

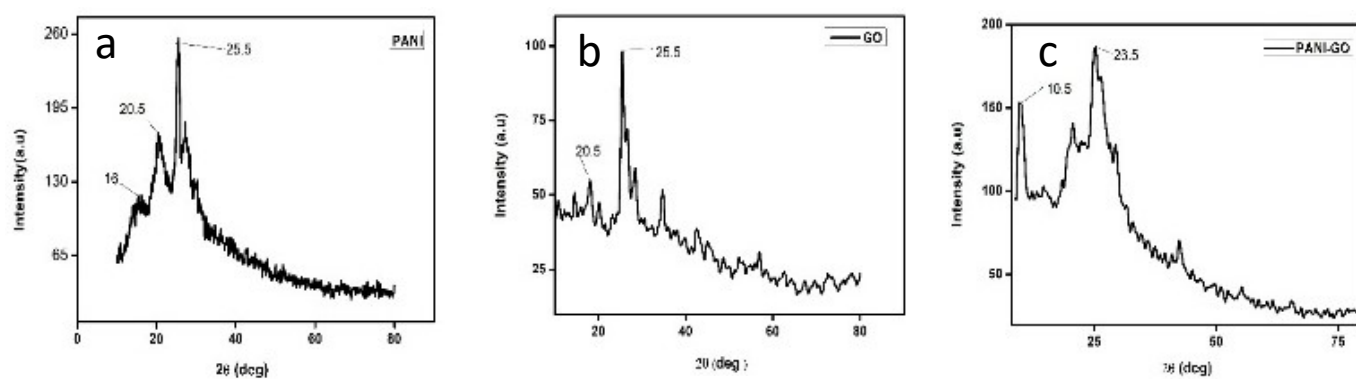


Fig. S2 : XRD of a) PANI b) GO c) PANI-GO

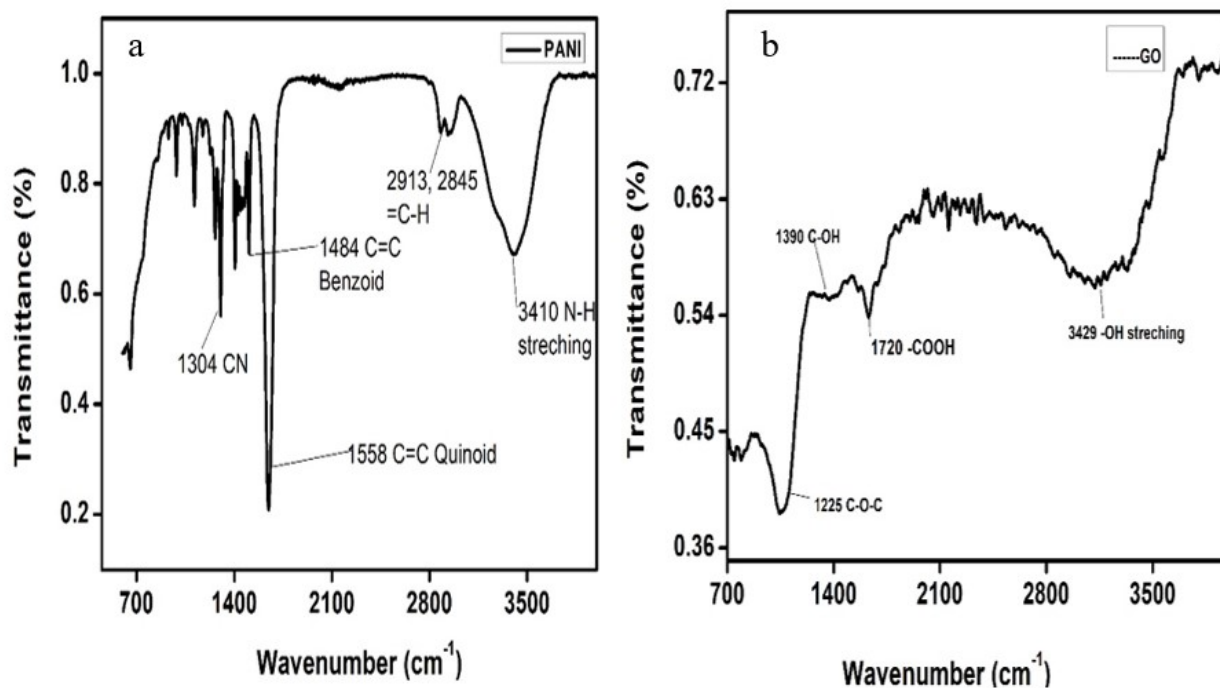


Fig S3: FT-IR of a) PANI b) GO

Table S1: Composition of pristine PSF, PSF/PANI Composite membranes

Membrane codes	PSF (wt.%)	PANI (wt.%)	NMP (wt.%)
P Pristine PSF	14	0	86
Pp1	13	1	86
Pp2	12	2	86
Pp3	11	3	86

Table S2: Composition/ codes of pristine PSF, PSF/PANI Composite membranes

Membrane	Membrane codes	PSF (wt.%)	PANI (wt.%)	GO (wt.%)
Pristine PSF	P	14	0	0
PSF/PANI/Graphene oxide	Pp2g0.5	11.5	2	0.5
PSF/PANI/Graphene oxide	Pp2g1	11	2	1
PSF/PANI/Graphene oxide	Pp2g1.5	10.5	2	1.5

1. Scanning Electron Microscopy-(SEM)

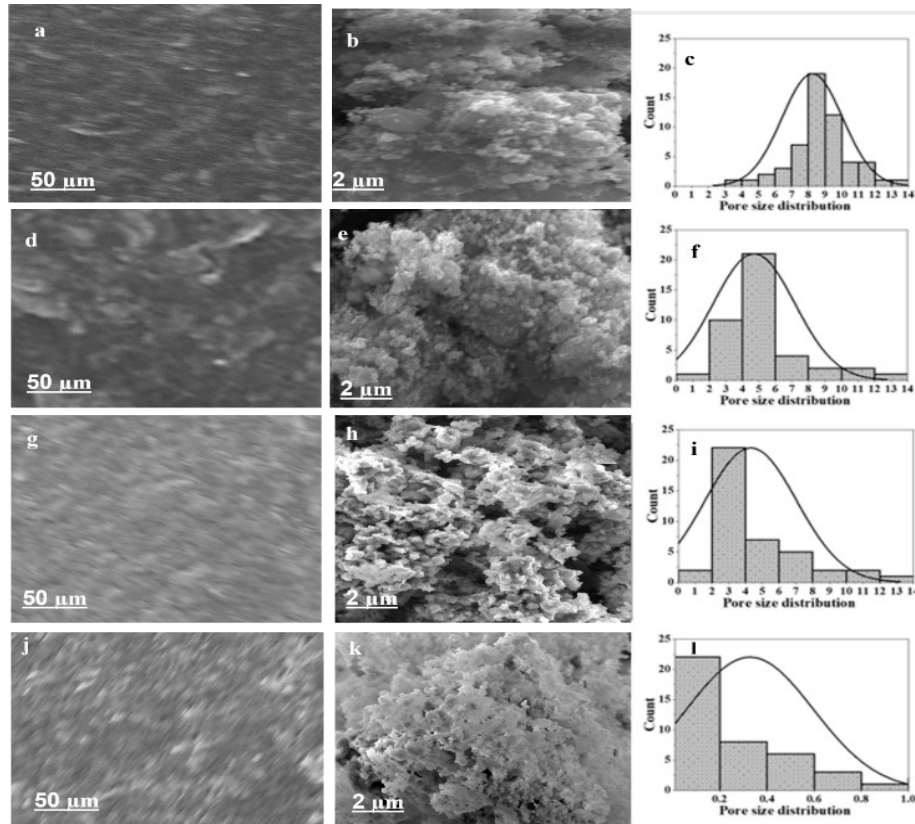


Fig. S4: (a) Surface morphologies of pristine PSF (b,c) Pore geometry analysis of Pristine PSF, (d) Surface morphologies of PSF/PANI 1wt% (e,f) Pore geometry analysis of Pp1, (g) Surface morphologies of PSF/PANI 2wt% (h,i) Pore geometry analysis of Pristine Pp2, (j) Surface morphologies of PSF/PANI 3wt% (k,l) Pore geometry analysis of Pristine Pp3.

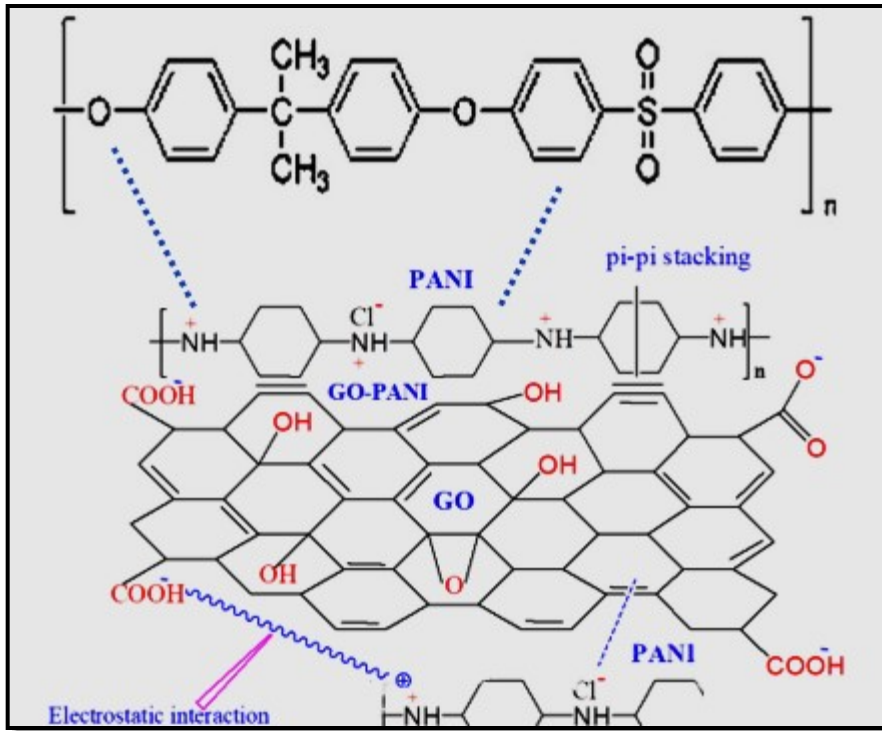


Fig. S5: Chemical interactions between PSF, PANI, and GO

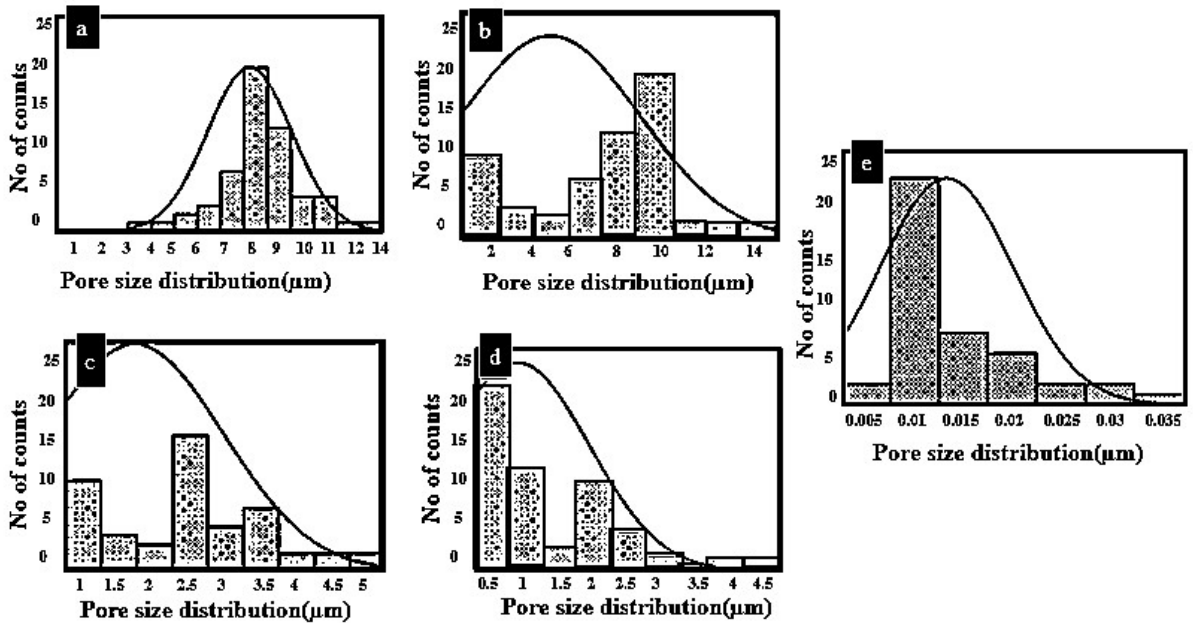


Fig. S6: a) Pore of Pristine PSF P, b) Pore of Pp2 (PSF:2wt.% PANI) c) Pore analysis of Pp2g0.5(PSF:2wt.% PANI:0.5wt.%GO) d) Pore analysis of Pp2g1(PSF:2wt.% PANI:1wt.%GO) e)Pore Pp2g1.5(PSF:2wt.% PANI:1.5wt.%GO)

These SEM images show that the addition of polyaniline to PSF increases the porosity and surface roughness of hybrid membranes. ImageJ software used for the determination of surface pore size and porosity by investigations of membrane's SEM images. According to these quantitative pore size calculations, the composite average pore diameter of membrane ranges from 0.5 to 3 μm , while the average surface pore size of pristine PSF membranes is 8 μm . The different concentration of PANI has reduced the pore size in hybrid membranes. The reduction in pore sizes of hybrid membranes is due to development of intermolecular chemical interactions such as van der Waals interactions and hydrogen bonding between polyaniline and poly sulfone. Razali et al. (2014) explained before that PANI behave as Fiber in membrane matrix and help to reduce the pore size. Fast solvents exchange is another reason for pore size reduction during phase inversion in the presence of hydrophilic polyaniline. Porosity in membranes induced by fast exchange of solvent and nonsolvent between polymer surface and water which results in formation of sponge like membrane structures. Continuous increase in PANI concentration causes trapping of PANI into pores of membranes and increase roughness and rejection properties of membrane.

Fig.S4(b, e, h, k). images show the binding and intermixing of nano filler in membrane matrix (PANI/PSF). In Fig.S4. it is very clear that PANI and PSF intermix with less pore formation while by increasing the concentration of PANI pore number increases into PSF. While 2 % addition increased the porosity of PSF and made it more hydrophilic. A detailed comparison with literature revealed that our prepared PSF nano composite membranes increase hydrophilicity by increasing porosity upto 3 μm size and membrane roughness to 2 wt% with addition of PANI Fig.2.(g, h, i). While further increase in concentration of PANI blocks the size of pores by reducing them 0.2 μm in size and makes it fragile Fig.S4.(j,k,l). So, the hybrid membrane with enhanced surface roughness and optimum pore size i.e., 2 wt% PANI (Pp2) was selected for further investigations.

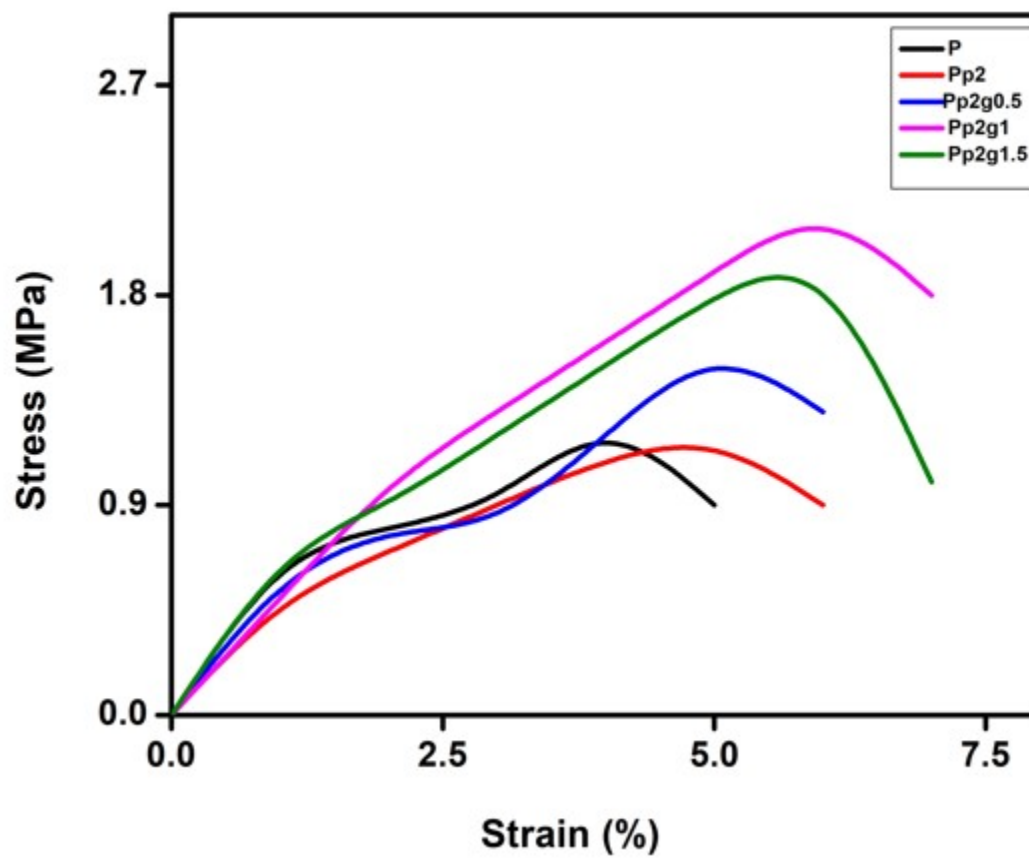


Fig. S7: Tensile stress strain curve for pristine PSF and composite membranes

Membranes	Temperature / % weight loss		
	P1	180 C° 3.8%	500 C° 29.8%
Pp1	182 C° 3.9%	584 C° 19.96%	799 C° 16.4%
Pp2	171 °C 3.3%	650 °C 22%	798 °C 8.5%
Pp3	150 °C 6%	614 °C 42%	799 °C 21%
Pp2g0.5	137 °C 5.2%	650 °C 48%	798 °C 8.6%
Pp2g1	146 °C 4.9%	690 °C 47%	799 °C 6.0%
Pp2g1.5	140 °C 4.6%	550 °C 43%	790 °C 7.0%

Table S3: Weight loss of PSF and Composite membranes at different temperature

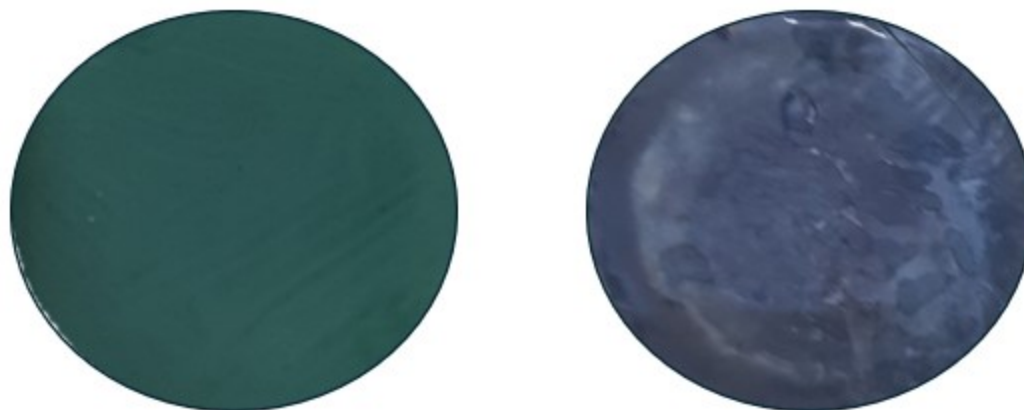


Fig. S8 : Figure of nanocomposite membrane before and after dye removal.

Table S4: Permeation proper ties of synthesized membranes:

Membrane code	PWF (Lm ⁻² h ⁻¹)	Membrane thickness (μm)	Average Pore diameter (μm)	Water Contact angle. (θ°)	Shrinkage Ratio (%)	Porosity (%)
P (Pristine PSF)	100	100	7±1	84°	23	53
Pp1	150	100 ± 0.33	3.5±1	70°	20	65
Pp2	250	115± 0.33	3±1	50°	20	67
Pp3	180	115± 0.33	2.78±1	60°	20	67
Pp2g0.5	498	118 ± 0.33	2.5±1	45°	16	73
Pp2g1	534	120 ± 0.58	0.5±1	37°	13	81
Pp2g1.5	500	120	0.01±1	50°	16	71

The Langmuir isotherm was plotted under optimized conditions of pH and removal efficiency.

1) Effect of pH

The influence of pH on the performance of the composite membrane was investigated, as depicted in Figure S9. The dye adsorption exhibited an increasing trend as the pH of the solution was varied from 3 to 11. This phenomenon can be attributed to the presence of negative ions (OH⁻) on the

membrane surface, which potentially interact with cationic dye molecules present on the membrane surface. The pH level plays a crucial role in modulating the functional groups, such as amino and hydroxyl groups, present on the PSF/PANI/GO composite membrane, which are responsible for adsorption [10]. At lower pH values, these functional groups become protonated, leading to a decrease in the electrostatic force of attraction between the positively charged surface of the PSF/PANI/GO composite membrane and the cationic dye molecules (MB). Conversely, as the pH value is increased from 3 to 11, the functional groups (hydroxyl and amino) on the surface of GO-PANI become deprotonated, thereby enhancing the removal efficiency of MB [11]. The pH of the real industrial dye wastewater sample was found to be basic, highlighting the practical relevance of these findings in real sample applications.

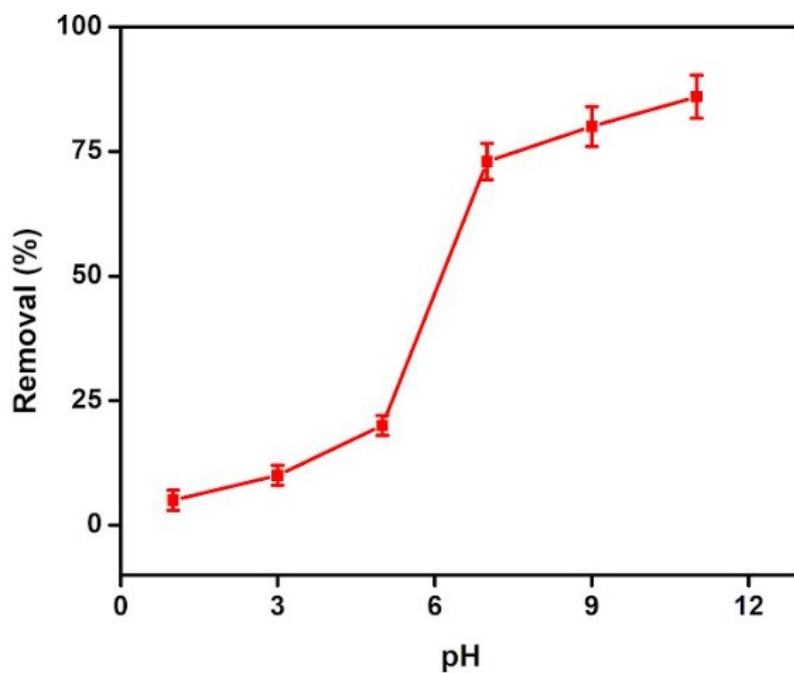


Figure S9: Effect of pH on adsorption of MB dye on Pp2g1 composite membrane (MB concentration=50mg/L, T=298K, weight of membrane= 0.5 g

1) Adsorption of PSF nanocomposite membrane:

The adsorption behaviour of a composite membrane made of PSF/PANI-GO was investigated. The dye adsorption capacities of pristine PSF, PSF/PANI, and PSF/PANI/GO membranes are presented in Figure S10. The adsorption experiments were conducted at a temperature of 298 K and pH ranging from 3 to 11 over a period of 24 hours, using an initial dye concentration of 50 mg/L of MB. The adsorption capacity of the pristine PSF membrane was determined to be only 2.5%. In contrast, the incorporation of PANI and GO fillers in Pp2, Pp2g0.5, and Pp2g1 membranes led to increased adsorption percentages of 44.9%, 63%, and 86%, respectively. This trend indicates that the adsorption capacity of the membranes is significantly influenced by the quantity of PANI and GO fillers. However, in the Pp2g1.5 membrane, a further increase in filler content resulted in a decrease in adsorption capacity to 79%. This reduction in adsorption can be attributed to an excess of GO, leading to agglomeration and a reduction in pore size, consequently diminishing the number of available adsorption sites in the composite membranes [9].

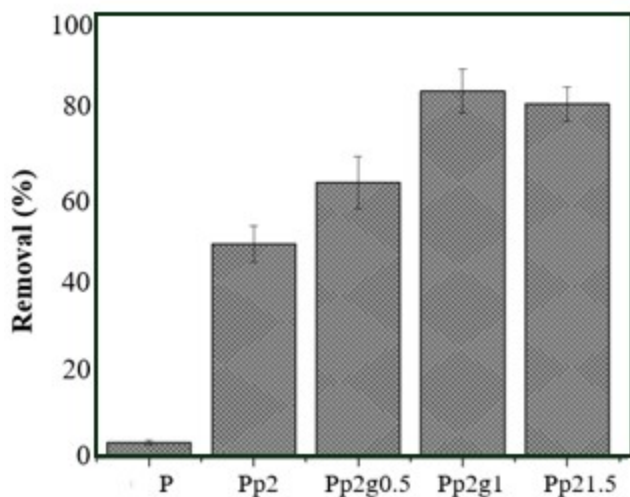


Figure S10: Composite membranes P, Pp2, Pp2g0.5, Pp2g1, Pp2g1.5 MB dye adsorption capacities. (pH=11)

2) Langmuir Adsorption Isotherm:

The Langmuir model suggests that active sites on the adsorbent surface are uniformly distributed, each having an equal attraction for adsorbate molecules. Consequently, a monomolecular layer forms on the surface. Additionally, the model assumes that adsorbed molecules do not interact with each other. The Langmuir isotherm equation, represented in linear form, is given below:

$$C_e/q_e = C_e/q_m + 1/q_m b \quad [1]$$

In the case of Pp2g1, the plot of C_e/q_e versus C_e yielded a straight line with an R^2 value of 0.99 for methylene blue, indicating the suitability of the Langmuir adsorption isotherm for the adsorption of MB on the nanocomposite membrane (0.5g) adsorbent. These results demonstrate that the adsorption of MB follows the Langmuir isotherm, as illustrated in Figure S11, Figure S12.

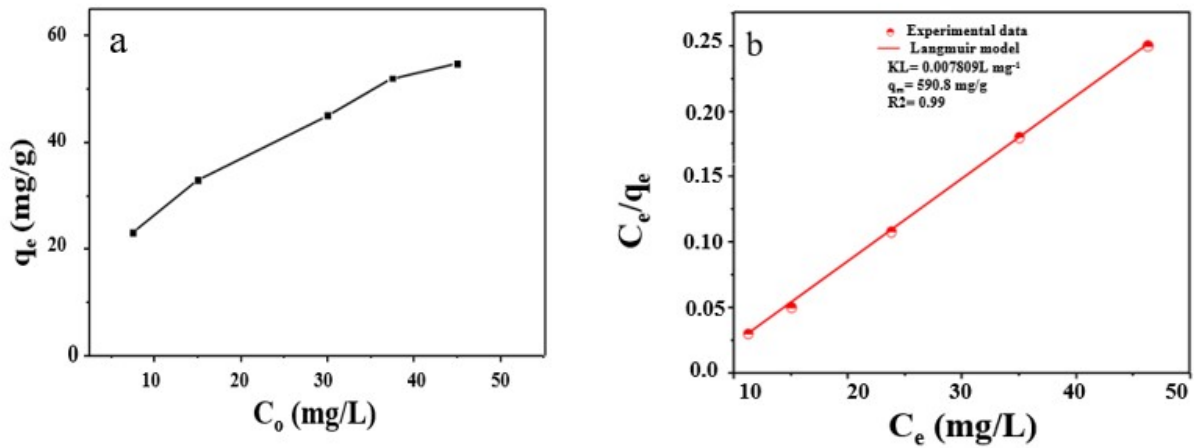


Figure S11: (a) The capacity of equilibrium adsorption of Pp2g1 composite membrane with different concentration of MB, (b) Langmuir adsorption isotherm.



WhatsApp Video
2023-07-04 at 8.21.3

S12: Video showing decolorization of MB dye by passing through ternary nano composite membrane (Pp2g1).