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REMOVAL OF CHROMIUM (VI) AND COBALT IONS FROM AQUEOUS SOLUTION USING HYPERBRANCHED POLYETHYLENEIMINE IMPREGNATED AG-GO MIXED MATRIX MEMBRANE

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Abstract
The current study looks at the synthesis and optimization of performance of polyamide nanofiltration membranes engineered with silver-graphene oxide (Ag - GO) and hyperbranched polyethyleneimine (HPEI) to selectively remove hexavalent chromium (Cr(VI)) and cobalt(II) (Co^{2+}) ions on aqueous media. The treatment of Ag - GO into the polyamide layer was aimed at polishing membrane surface chemistry, expanding hydrophilic regions, and controlling the electrostatic characteristics so as to increase rejection rates within pH variation. Extensive characterization involving measurement of water contact angle and zeta potential established that incorporation of nanoparticles had a great effect on the wettability of surfaces and distribution of charges, thus making interactions between ions and the membrane more responsive. The performance testing showed that the B4 with an optimized level of Ag+GO had the most favorable trade-off between the permeate flux and the selectivity, having 91 percent removal of Cr(VI) and up to 99 per cent rejection of Co 2 + at neutral pH. The latter was explained by a well-balanced system between an increase in hydrophilicity, robustness of electrostatic repulsion or attraction (depending on ion charge), and a less unfavorable pore framework. Though water flux was slightly higher on the B5 membrane, its selectivity was worse, which is related to the agglomeration of nanoparticles, and, thus, to the importance of controlled loading of nanomaterials. Taken together, the findings substantiate the fact that prudent nanoscale engineering has the potential of fundamentally transforming the functionality of membranes which is a feasible option in regard to the effective treatment of industrial effluents that might have toxic heavy metals. Not only does the study highlight the prospect of Ag -GO-modified membranes in environmental cleanup, but also provides a conceptual foundation of the next-generation nanofiltration systems that can be described as having higher adaptability, stability and separation efficiency.

INTRODUCTION

The issue of water pollution has become one of the most urgent environmental problems, which can be explained by the increased level of industrialization, population growth, and constant influx of untreated effluents into the natural water bodies.(Aliabadi, 2016) Metal plating, mining, textile manufacturing,

pigment manufacturing, fertilizer manufacturing, and chemical processing industries have discharged large amounts of wastewater which includes toxic heavy metals. They are not biodegradable and therefore build up in the soils, sediments and biological matrices and have long lasting effects on the eco-system and human health.(Hesamedini & Bund, 2018) Chromium and cobalt are the most serious of all the number of heavy metals that are observed in the polluted water due to their high toxicity, mobility and persistence. There are two main stable oxidation states of chromium one being trivalent chromium [Cr(III)] and the other one is hexavalent chromium [Cr(VI)].(Islam et al., 2023) Cr(VI) is significantly more toxic and can serve as a strong oxidizing agent and carcinogen, being able to cause renal dysfunction, liver malfunction, respiratory issues and serious skin irritation. Cobalt is also a commonly occurring element in industrial effluents and this can cause cardiovascular related complications, genetic mutations and pulmonary diseases when taken in large quantities.(Nqombolo, Munonde, Makhetha, Moutloali, & Nomngongo, 2021) They are very widespread in drinking water, agricultural soils, and water bodies which highlight the urgency to develop effective and affordable removal technologies. The traditional treatment methods- chemical precipitation, coagulation-flocculation, ion exchange and adsorption have been used to get rid of heavy metals. Whereas the processes may reduce concentrations of metals to some extent, in many cases they require high amounts of chemicals, produce secondary sludge or have relatively low efficacy in low-concentration systems.(Seid & Gonfa, 2022) Many scholars have shown much interest in membrane-based separation processes in recent years, based on the high selectivity, low energy consumption, operational simplicity, and a possibility to eliminate contaminants without phase transition. However, nanofiltration (NF) has been identified as one of these methods and has emerged as a hopeful technique in the process of removing heavy-metals due to the ability of the NF membrane to reject multi-valent ions and organic molecules at moderate pressures and allows higher permeation flux.(Belcaid, Beakou, El Hassani, Bouhsina, & Anouar, 2021) However, there is frequent foulings in commercially available NF membranes, limited hydrophilicity and reduced performance under severe wastewater matrices. These drawback has seen scientists explore more innovative nano compositions membranes, which include functional nanoparticles to increase separation rates, mechanical strength and antifouling properties.(Silva & Oréfice, 2023)

Graphene oxide (GO) is a material that has already gained significant attention among scientists due to its large surface area, large number of oxygen-containing functional groups on it and high dispersibility in polymer matrices. GO also increases the hydrophilicity of membranes, facilitates the transport channels of water and provides more active membrane sites to react with the metal ions. Silver nanoparticles (AgNPs) are known to have antimicrobial and ability to reduce membrane fouling due to bacterial growth.(Rahmani, Pourmadadi, Zandi, Rahdar, & Baino, 2022) This is due to the fact that their amalgamation can produce an amalgamation of nanomaterials with better physicochemical properties, increased chemical stability, and more defouling resistance. Hyperbranched polyethyleneimine (HPEI) is also a branched polymer with a high density of amine groups, which is of interest because of its excellent binding properties to metal ions, and because it can be used to stabilise metal nanoparticles in polymer networks. Since it can be incorporated into membrane matrices, HPEI may strengthen the hydrophilicity of membranes, charge, and capacity to bind metal-ions.(Passi & Pal, 2023) The use of AgGO nanoparticles through mixed-matrix membranes (MMMs) has shown the possibility to enhance the removal of metal-ions and permeation activity. MMMs bring on board polymeric flexibility and that of a nanofiller, thus providing a mechanism that can be used to overcome the trade-offs between flux and rejection characteristically experienced with the conventional membranes. In this study, a mixed-membrane membrane was produced by using cellulose acetate (CA) and hyperbranched polyethylene implicate (HPEI) and impregnated with different concentrations of Ag-GO nanoparticles. The production of the membrane was through solution-casting process, which allows a closer control of the dispersion of nanofiller and architecture of the polymer. To achieve this, two

steps were followed: Ag -GO nanoparticles were firstly synthesized, then the nanoparticles were incorporated into the CA -HPEI matrix to produce modified membranes as shown in B1 -B5, with B0 representing the unaltered membrane.(Armstrong et al., 2023) The structural and surface properties of the made membranes were tested by employing comprehensive characterisation methods. The functional groups were monitored by using Fourier-transform infrared spectroscopy (FTIR) and confirmed the effective introduction of the nanomaterials. Scanning electron microscopy (SEM) was able to give insights on the morphology of the surface and cross-sectional structure, whereas atomic force microscopy (AFM) was able to measure the surface roughness.(Kandasamy, Selvaraj, Kumarappan, & Murugesan, 2022) Contact -angle values were used to assess the hydrophilicity of the membranes, and zeta -potential measurements were made to analyze the charge of surface of membranes under different pH conditions. The parameters play a decisive role in the efficiency of membrane processes, especially when it comes to contact with contaminants of the charged nature, including Cr(VI) and Co ions.(Song, Tao, Zhang, & Li, 2024) Removal efficiency was measured using nanofiltration experiment in regard to pH equilibrium, metal concentration and filtration period. The findings showed that Ag +GO modified membranes had significantly elevated removal efficiencies and flux values, as compared to the actual membrane. B4 of the modified membranes showed the best performance with an 91per cent Cr(VI) ion removal and 97per cent Co ion removal in pH 7. These improvements were attributed to the increased and augmented hydrophilicity, augmented roughness of surfaces, more even distribution of nanoparticles, and augmented electric interactions amid the metal ions and membrane. Such results highlight the possibility of using Ag -GO integrated CA/HPEI mixed-matrix nanomembranes to be effective and sustainable when it comes to heavy-metal removal in contaminated wastewater.

Materials and Methods

Materials

All the reagents used were in the state of analysis and were used in their unpurified form. Cellulose acetate was chosen as the polymer base since it is stable, high in forming a film and phase inversion. Polyethyleneimine comes in hyperbranched form hence with numerous amine sites, which has the capacity to bond metals and improve hydrophilicity on the surface. A silver nitrate, graphene oxide powder, and formaldehyde were used in the production of the Ag-GO nanocomposite. PH adjustment was done using sodium hydroxide and hydrochloric acid, and potassium dichromate and cobalt(II) chloride were used to prepare chromium(VI) and cobalt(II) stock solutions. Polymer dissolving and casting solvents were made afresh. All the synthesis, washing, and nanofiltration were done using distilled water.

Synthesis of Graphene Oxide

Graphene oxide has been produced differently through the modified oxidation route to ensure good surface concentration of oxygen functionalities. The potassium permanganate was added gradually to graphite powder into a sulfuric acid solution that was under controlled mixing. Close attention was paid to the exothermic nature of the reaction in order to avoid overheating. After the oxidation, deionized water and hydrogen peroxide were introduced to curb the reaction and eliminate surplus oxidants. The resulting GO suspension was centrifugally washed several times until the pH centrifugation was in the neutral regime. The GO powder was dried and the resulting powder was rich in hydroxyl, epoxy and carboxyl groups and these groups later assisted in anchoring of silver nanoparticles and dispersing them in the polymer matrix.

Synthesis of Silver Nanoparticles

Silver nanoparticles had been made through the chemical reduction. An established sample of AgNO3 was dissolved in deionized water to produce the precursor solution. A reducing agent was added drop by drop and constant stirring took place to reduce Ag + ions to metallic silver. Color change of the reaction mixture was achieved and the presence of nanoparticles was seen. The suspension was allowed to age until all the reduction occurred and washed repeatedly to remove any unreacted ions as well as dried. The obtained nanoparticles were round and had a good fitting with GO sheets.

Preparation of Silver–Graphene Oxide Nanocomposite (Ag–GO)

In order to make Ag+GO nanocomposite, the solution of GO in distilled water was prepared through sonication to develop a stable colloid solution. This dispersion was then incubated with the AgNO3 solution so that Ag + ions can be adsorbed on the oxygenated surface of GO. A reducing agent was added gradually, formaldehyde. Ag nanoparticles were grown on the GO surface producing a uniform decoration of GO sheets with silver. The reaction was stirred at a longer period until the usual color change was a sign of reduction. Agglomeration of the Ag-GO with a variety of washing and dried produced a hybrid substance, which has higher hydrophilicity, antimicrobial characteristics, and metal ion binding sites when used in membranes.

Preparation of CA/HPEI Casting Solution

Casting solution was made by dissolving cellulose acetate in the chosen system solvent subjected to constant mechanical stirring. After a good solution was obtained HPEI was added in identical measured loads to obtain uniform distribution of the amine rich polymer into the CA matrix. The mixture was stirred, several hours until all the components were dissolved. The incorporation of the HPEI was necessary to enhance the communication of Ag -GO nanosheets as well as increase the surface charge of the resulting membranes.

Incorporation of Ag–GO into the Polymer Matrix

To prepare a number of mixed-matrix membranes, several Ag-GO nanocomposites of varied amounts were added to the CA/HPEI solution. The small volume of solvent used to disperse the nanocomposite minimized agglomeration and in which the nanocomposite was pre-dispersed and ultrasound. Adding of the dispersion was done slowly to polymer solution with high stirring in order to get even dispersal. This cycle was replicated with every load of nanocomposite to be used to have membranes named B1-B5. A control was made of neat membrane without nanocomposites (B0). The casting mixtures were then degassed to dislodge the air bubbles in the mixtures before filming.

Membrane Casting by Phase Inversion

The membranes were made by conventional method of phase-inversion. Wetting agent solution was added into homogeneous casting solution then cast on clean glass plate and spread to a defined thickness using casting knife. The wet film was then plunged in a coagulation bath with distilled water. Solidification took place as the solvent diffused out and water diffused into the polymer matrix to give an asymmetric membrane structure. The resulting membranes were peeled carefully, washed many times to take away the left-over solvent and free floating particles and then stashed in fresh water pending subsequent characterization.

Characterizations of Synthesized membrane

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to recognize the presence of functional groups and the presence of CA, HPEI, GO, and AgAg-GO in the membranes. Membrane samples were then dried, and a scan done over the suitable wavenumber range. The acetyl group, amine functional and GO oxygen group peaks were observed. The change in positions of peaks or observance of new peaks denoted the interaction between the polymer matrix and the nanofillers.

Scanning Electron Microscopy (SEM)

SEM was used to study the surface and cross-sectional morphologies of the membranes. Samples which had been dried were sputter-coated with a light conducting layer to avoid charging. SEM imaging gave a high level of visualization in structure of pore, top-layer density, nanoparticle dispersion and change of structure in pristine and modified membranes. Slices of cross-sections were broken at liquid nitrogen temperature and provided clean edges upon which probing could be performed.

Atomic Force Microscopy (AFM)

To measure the surface roughness/topographical variations of the membranes using AFM. The samples were placed on the AFM stage and tapped in tapping mode. The three-dimensional images of the result were used to obtain roughness values and demonstrate the effect of Ag-GO loading on the membrane topography. As roughness increased it

tended to correlate with better water permeability and better metal ion interaction.

Thermogravimetric Analysis (TGA)

TGA was carried out to determine thermal stability and decomposition behavior. Controlled heating of samples was done and weight loss patterns documented. Variations in neat and modified membranes suggested the Ag-GO effect on thermal behavior, polymer decayed and structural integrity. X-ray Diffraction (XRD) Crystalline phases such as the existence of silver nanoparticles in the nanocomposites membranes were ensured by XRD analysis. Metallic silver-like sharp peaks and polymer wide peaks were also evidence of successful incorporation of nanoparticles.

Contact Angle Measurement

Measurements of the water contact angle were made in order to measure hydrophilicity at the surface. Water droplets were put on membrane surfaces and the recorded angle at the end of equilibrium. Nanocomposite-loaded membranes decreased the contact angles which characterized increased hydrophilicity as well as the water-membrane interactions.

Zeta Potential Measurement

Zeta potential analysis was utilized in determining the surface charge of the membranes. It was conducted on the electrolyte solutions with varying pH values in the samples. The obtained profiles of zeta potentials showed the presence or absence of a positive or negative charge of the membrane surface at the respective pH. Rejection behaviour was explained by the presence of electrostatic interactions between charged surfaces and metal ions.

Nanofiltration Setup

A nanofiltration system operating at laboratory scale with an object of testing the membranes was fitted in that case using a high-pressure cell. Membranes were fabricated to the desired size and put on a filtration cell and compacted with an initial pressure to stabilise flux. The solutions of chromium(VI) and cobalt(II) with known concentrations were filtered using the membranes under the pressure after being compacted. Volumes of permeate were recorded after fixed intervals in order to determine flux.

Metal ion removal experiments

The performance of the rejection was measured in relation to chromium(VI) solution, and cobalt(II) solution in distilled water. The pH level of them was altered using dilute base or acid. The concentration of the feed was measured spectrophotometrically as well as the permeate concentrations. The influence of the pH, starting metal concentration, perception pressure, loading of nanocomposites, and filtration time was examined. Percentage of rejection and flux values were determined on all the membranes and repeated assays on the same tests ensured reproducibility.

Results and Discussions

Fourier Transform Infrared Spectroscopy (FTIR)

The chemical composition of the pristine and Ag–GO -modified membrane was confirmed by using FTIR analysis in order to identify any changes in the functional groups of the membrane after the addition of nanoparticles. The spectrum of the unmodified cellulose acetate (CA) membrane (B0) showed clear peaks typical of CA such as a strong absorption band at 1735 cm^{-1} restrictions of C=O stretching vibrations of the acetyl moiety, and maxims at 1235 cm^{-1} and 1030 cm^{-1} of C–O–C stretching vibrations. These bands supported the canonical structural qualities of CA. The existence of HPEI in the blended membrane was evidenced by the existence of the broad NH region at 3200-3500cm -1 and 1580-1650cm -1, which are the primary and secondary amine groups, respectively. After the inclusion of AgAgGO nanoparticles into the membranes of B1-B5, there was a discernible spectral change. A minor shift and strengthening of the OH/NH stretching band was an indication of hydrogen-bonding between the HPEI and oxygenated functional groups on graphite oxide (GO), and the CA matrix. The C=O stretching motif in the spectrum had minor red-shifts which was evidence of increased interactions of molecules between the polymer chains and the nanocomposite. Other weak bands in the 600-800 cm -1 region of the modified membranes were explained by out-of-plane C-H vibrations affected by GO layers. In spite of the poor IR-activity of Ag nanoparticles, their presence indirectly altered the intensities of the peaks by interacting with the functional groups of the surface

of GO. Taken together, the FTIR information led to the positive incorporation of HPEI and Ag-GO into the CA scaffold. The shifts in the characteristic peaks as well as changes in the intensity of the bands indicated a strong binding between the polymer and the nanomaterials, hence supporting the growth of the structural stability as well as the performance obtained in the subsequent filtration experiments.

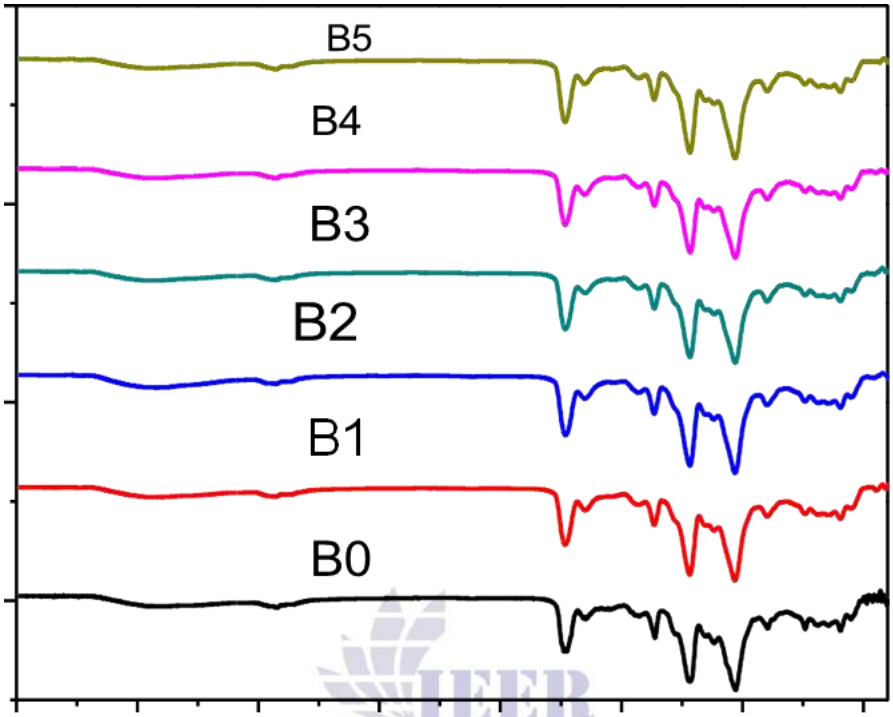

Figure 3. 1 FTIR spectra of Pristine (B0) and Ag-GO modified mixed matrix membrane B(1-5)

Scanning Electron Microscopy (SEM)

SEM was used to examine the morphology of the pristine and Ag+GO modified membrane of poly(ε - caprolactone) CA by interrogation of the surface and cross-sectional morphology. The photographs of the unaltered CA membrane (B0) showed that its surface was not very rough, but rather compact, which is typical of phase-inversion membranes with a low level of pore formation. The morphology was cross-sectional, and thus with a high density of skin externally covered by a porous under layer, and thus with uniform membrane formation. Augmentation by the incorporation of Ag 0 GO nanocomposites led to the appearance of morphological changes in the row of masks B1B5. The membrane surface became increasingly rough and more textured which suggested an increase in the dispersion of the nanomaterials in the polymer matrix. Graphene oxide sheets and silver nanoparticles enhanced micro- porosity through breaking of CA chain packing creating more nano- channels that moved water. The highest Ag GO loadings on the membranes, especially B4, had the sampled nanoparticles designed evenly without any visible aggregation, indicating that CA/HPEI was well-compatible with the nanofillers. The increased roughness and appearance of the micro-ridges was associated with the increase in the value of flux valued when filtration tests were conducted. SEM images of the modified sintered membrane taken cross-sectionally indicated a further open and connected porous network as compared to B0. Their pores were longer and more defined, which suggested that the phase-separation dynamics is modulated through Ag-GO thus hastening the process of solvent nonsolvent exchange. This produces a less stressful sublayer that is preferable to greater permeability. Notably, no cracks, voids, or clusters of nanoparticles were observed, which led to the conclusion of the homogeneous incorporation

and structural integrity of the membranes. To sum up, when using agglomeration on the membrane the morphology of the membranes is largely boosted through the use of agglomeration to elevate the roughness of surfaces and porosity that in return leads to a significant boost in the performance of nanofiltration.

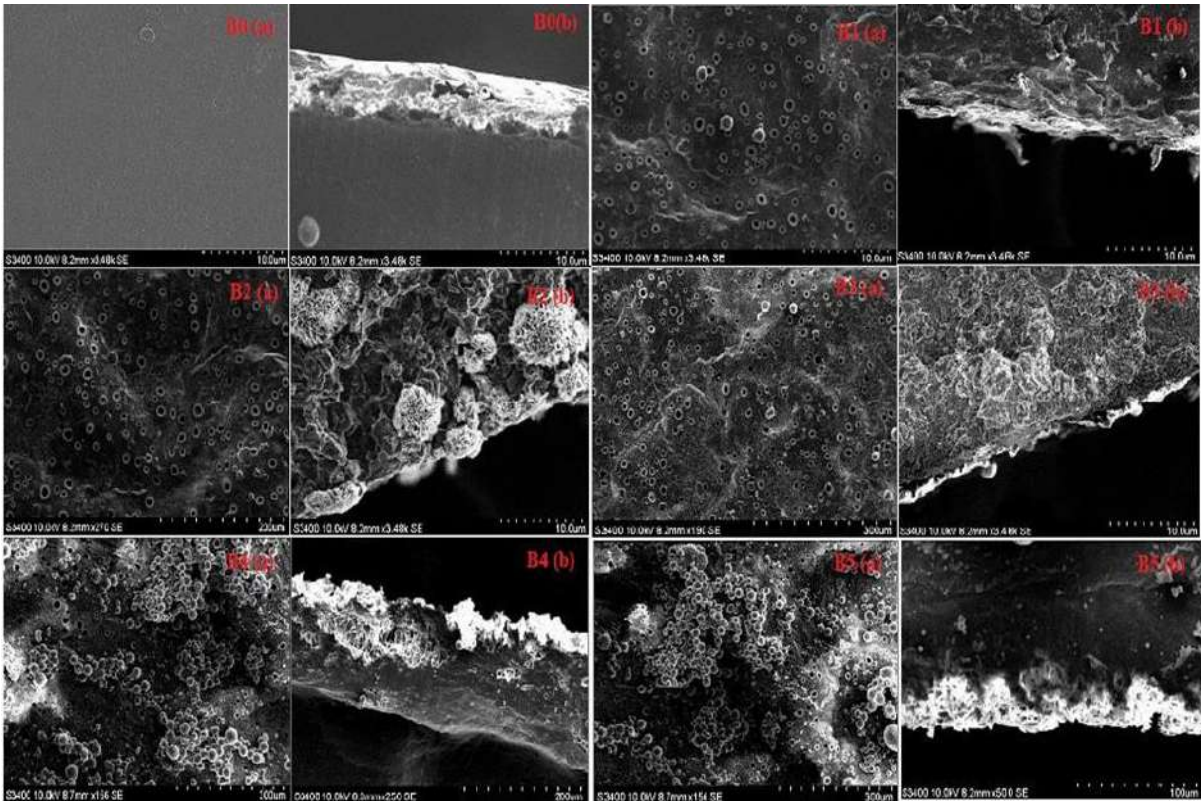

Figure 3. 2 Surface images of pristine and Ag-GO modified mixed matrix membrane: (a) top surface and (b) cross section at different magnifications

Atomic Force Microscopy (AFM)

The AFM analysis was done to measure the changes in both surface topography and roughness of the pristine and the Ag-GO-modified membranes. The CA membrane (B0) was unmodified implying that it had a comparatively smooth and homogenous surface; this is indicated by low roughness measurements which describe the tight polymeric structure of the B0. Ag-GO incorporation provoked apparent changes in the surface morphology; the treated membranes were found to have a higher roughness with more pronounced peaks and depressions, denoting that the nanocomposite destroyed the organized structure of CA chains and produced a more textured surface. The roughness of the membrane B4 has been found to be the highest of all the specimen indicating an optimal distribution of Ag-GO into the polymer matrix. Roughness augmentation is useful, since it enhances the effective surface area on which water transportation and contact between the membrane surface and metal ions can be strongest. In general, the AFM findings indicate that the incorporation of Ag-GO significantly increases the surface properties of membranes, which ultimately leads to the improvement of permeability and rejection.

Membrane Sample Name	Weight of Ag-GO (wt %)	Root mean square roughness RMS (nm)
B0	0	185.68
B1	0.2	240.36
B2	0.4	279.34
B3	0.6	331.29
B4	0.8	429.22
B5	1	392.5

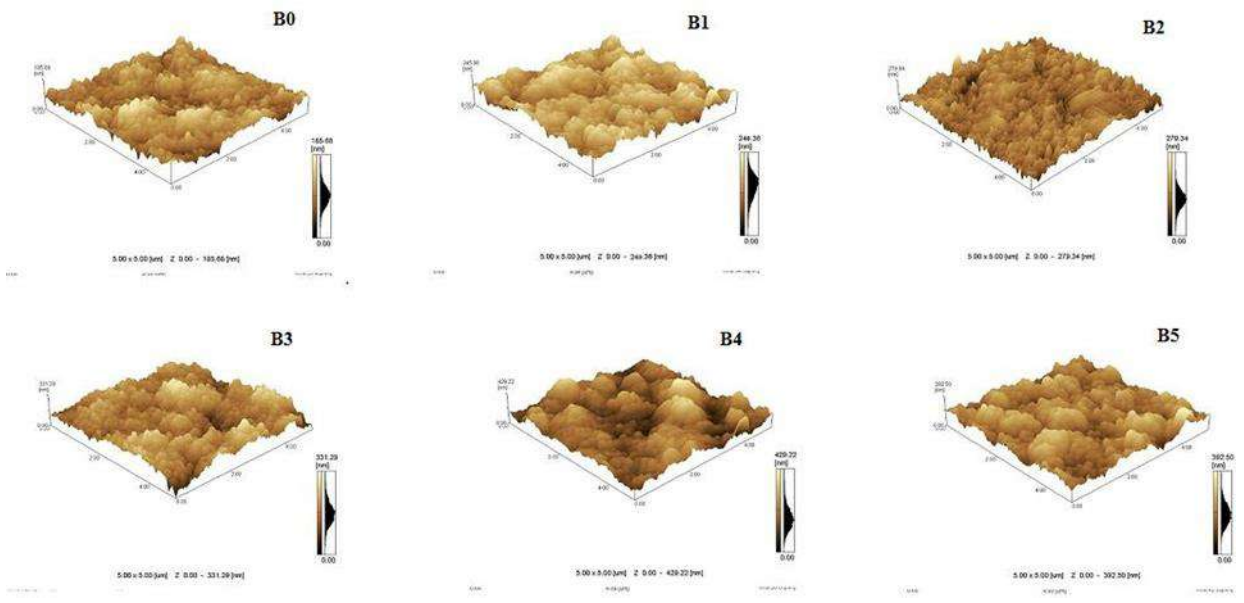

Figure 3. 3 depict the 3D AFM images of pristine (B0) and Ag-GO modified mixed matrix membranes B (1-5)

Water Contact Angle

The water contact angle analysis offered a slightly but important view of the surface properties of the membranes explaining the extent to which each of the membranes being analyzed accommodated water. The contact angle of the pristine membrane (B0) was about 67 0, which can be regarded as evidence of its relatively impaired hydrophilicity. When Ag-GO was introduced and the concentration of it was increased

by adding equal amounts of B1 up to B5, the measurement of the contact angles significantly dropped and took the values of 48 degree with B4 and 46 degree with B5. This orderly weakening is an indication of a highly increased affinity of surfaces to water. The existence of the silver-graphene structure, as well as the polar -NH 2 functional properties of the HPEI, acted as hydrophilic sites and thus attracted water molecules and thus enhanced permeability. Of the sampled samples, the strongest hydrophilic behavior was observed in B5 which had the lowest contact angle and therefore receptive topology on its surface. The combination of the downward trend of the contact angles together supports the idea that the addition of Ag-GO significantly increases the wettability of the membranes- a major quality in order to attain effective nanofiltration outcomes.

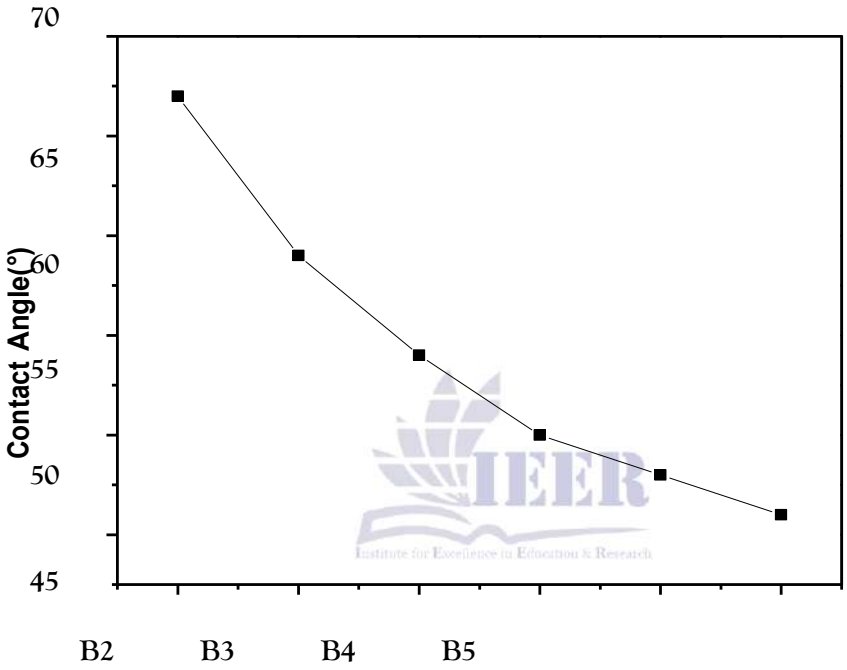

Figure 3. 4 Different contact angle values of pristine and Ag-GO mixed matrix membrane B (1-5)

Zeta Potential

The zeta potential readings were used to map the electrostatic distribution of the membranes which characterized the range of modification of the surface charges with pH and the changes in response to incorporation with Ag GO. The purest membrane (B0) showed a positive response at acidic and homogeneous conditions (pH 2, 5, 7) and was sharply negative at a higher alkalinity level (pH 10 - 41.11 m V). The pattern changed with the Ag-GO modified membranes (B1-B5): at lower pH, the membranes were negative and progressed to a more negative value as the environment moved towards neutrality and alkalinity. The existence of the positive charge at acidic pH could be explained by the protonation of -NH and -NH 2 groups of HPEI and increased when Ag-GO was introduced in the polymer structure. Fluids As the pH was increased, the functional groups eventually lost protons and the availability of oxygen rich Ag -GO facilitated the adsorption of -OH groups, which consequently caused the zeta potential to move into the negative sphere. The highest concentration of Ag GO in membrane B5 had the most intense negative charge at high pH indicating greater surface deprotonation and concentration of -OH groups. These electrostatic changes are critical to the ion–membrane processes: they control how ions and membranes interact, how repulsive or attractive forces influence the dynamics,

and eventually determine the efficiency at which Cr(VI) and Co 2+ are eliminated during nanofiltration. The procedure can be termed as a silent electrical-dance, which guides the separation act.

Zeta Potential (mv)

Sample Name	pH 2	pH 5	pH 7	pH 10
B0	7.12	4.42	3.46	-41.11
B1	36.66	34.74	- 31.76	-40.7
B2	26.32	29.71	-28.11	-32.61
B3	25.56	27.62	-26.67	-28.18
B4	24.76	26.31	-21.52	-26.78
B5	25.52	27.86	-22.42	-30.45

Membrane Performance

Membrane Performance for Cr(VI) Ions Removal

The elimination of Cr(VI). Tell-Tale The elimination of Cr(VI) ions showed an exquisitely coordinated interaction between the charge on the membranes and speciation of chromium in varying pH regimes. Cr(VI) is present in various anionic species, namely HCrO 4 -, CrO 4 2 -, and Cr 2 O 8 -, the preponderance of which decreases with the pH of the solution. The rejection of these species is strongly governed by the electrostatic repulsion as these species are negatively charged. The pure membrane (B0) had fewer negatively charged domains and there were fewer functional groups that could repel the anionic chromium species. As a result, its efficiency of rejection was low. The density of oxygen-containing groups on the membrane surface and protonated amines was on the rise as Ag-GO introduced B1 and followed by B2, B3 and B4. These working groups were functional equivalents of the electrostatic signposts, which increased the repulsive strength between the membrane and the negatively charged ions of Cr (VI). The optimum dispersion of the nanoparticles, great hydrophilicity, increased negative potential with appropriate conditions of operation, and balanced pore arrangement noticed Membrane B4 as the best performer with 91 20. The close to ideal surface charge plus uniformity of the structure allowed the rejection of Cr(VI) ions to occur effectively. Nonetheless, B5 exhibited a slight decrease in the removal even at increasing nanoparticle loading. This effect was due to the agglomeration of Ag -GO sheets, resulting in a broken surface uniformity and obstructed selective paths and a decrease in effective electrostatic landscapes needed to maintain the constant Cr (VI) repulsion. On the whole, the pH pattern showed that bat environments with neutral to slightly alkaline conditions allowed the most active removal since the form of chromium was CrO 4 2 -,

and the membrane contained enough negative charges to repel the specimen.

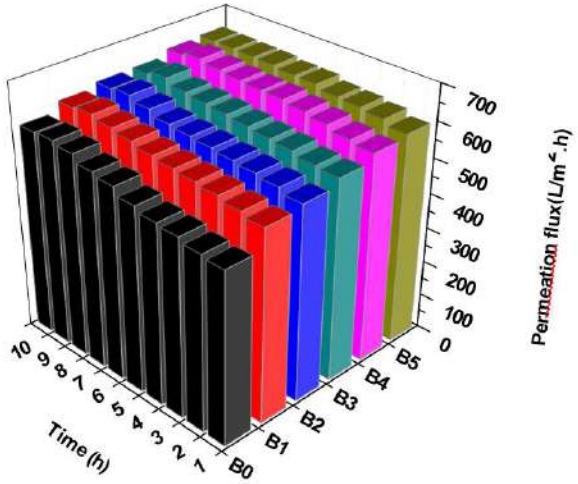

Figure 3. 5 Effect of pH on removal of Chromium Cr (VI) ions

Membrane Performance for Cobalt Ion Removal

Electrochemical unfolding No, cobalt removal involved a completely new story. In contrast to Cr(VI), cobalt ions are present as Co +, a positive ion in the form of Co (NO 3) 2. This switched the repelling electrostatic process to the attracting one and the contribution of the protonated amine groups of the membrane was quite significant. When in acidic, and neutral environment, the HPEI sequences on the surface of the membrane get enriched with protons, becoming positively charged. By introducing Ag-GO, there is easy access of these functional domains because of higher surface roughness and wettability. Consequently, the affinity of the modified membranes towards cobalt ions was tremendously higher. Adsorptive and electrostatic forces then directed Co 2+ ions to the membrane surface interface, after which they could be rejected by a size-based hindrance and selective partitioning. Again, membrane B4 came out as the leading performer with as much as 99 percent cobalt removal in neutral pH where the ratio between protonation, pore size, and hydrophilicity was optimal. The pure membrane was sluggishly trailing with much lower rejection which demonstrated the significance of Ag -GO to improve the interaction of charges as well as the morphology of the membrane. Whereas B5 held more Ag -GO, its performance decreased due to agglomeration that decreased uniform dispersion of active positions. This decreased the uniformity of the electrostatic interactions and made its selectivity mechanism less effective. But B5 provided a higher flux margin because of more pore openness- which is compensated by lower rejection capability.

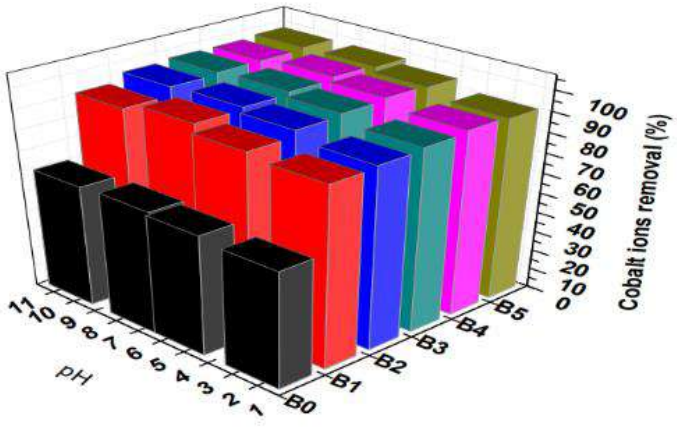

Figure 3. 6 Effect of time (hr) on permeation flux of Cr (VI) ions

Membrane Performance for Cobalt Ion Removal

Flux measurements were also helpful in understanding the effects of structural and chemical changes on the overall behavior of membranes. In both Cr(VI) and Co 2+ tests, the permeation flux continued to increase steadily in the early stages (below or about 9 hours). This early increase was due to the fact that the membrane pores were clean, wet and void of any deposited ions. At this stage, a decrement in flux was recorded which was ascribed to two broad phenomena: Pore blockage in which deposited or adsorbed ions covered transport channels partially. The polarization of concentration, in which ions became concentrated around the membrane surface, and this created a resistance layer that decreased the rate of flow of the solvent. The optimal flux removal balance was found to be in Membrane B4 under all the conditions. It was capable of maintaining a constant water flow and yet blocking ions due to its optimized hydrophilicity, fine pore distribution and stable surface charge. B5 that was more open in structure and had the greatest flux, but a low level of selective rejection, which meant that size and charge exclusion controls were compromised by excessive nanoparticles loads.

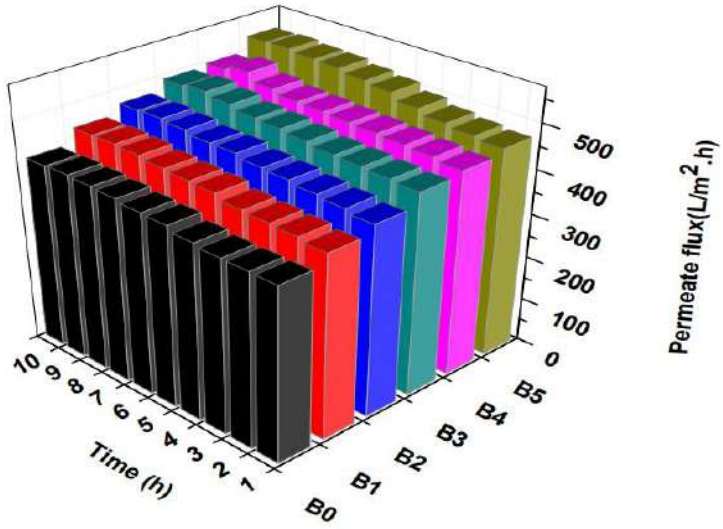

Figure 3. 7 Impact of pH on removal of Cobalt ions

Sample Name	Rm (x 10-10 m-1)	Jw(L/m^{2} h)	ε %	rm (nm)	thickness (µm)
B0	0.86	489.6	78.4	32.6	48.72
B1	0.67	642.1	76.3	30.5	45.21
B2	0.52	648.6	75.2	28.6	42.67
B3	0.48	652.78	74.6	27.2	40.28
B4	0.39	660.89	73.2	25.4	38.76
B5	0.41	641.2	72.1	24.8	35.29

Conclusion

This paper shows that application of Ag–GO and HPEI on a polymeric membrane varies its surface energy, charge distribution and pore structure leading to improvement of its filtration performance. The gradual loss in the degree of contact with the water, the dynamic adjustment of the zeta potential at variable pH and increased hydrophilic nature are all the signs that the introduced nanomaterials effectively reengineered the membrane interface. Out of the constructed variants, the B4 membrane continuously delivered the best balanced performance, showing strong hydrophilicity, a maintained negativity at the surface at the relevant PH of the experiment, a high Cr(VI) rejection and high Co 2 + removal. Despite the increased permeate flux caused by the increase in nanoparticle loading in B5 it also reduces selectivity because nanoparticle agglomeration occurs, which emphasizes the fact that optimization is the determinant leading to membrane efficiency rather than overloading. Overall, it can be highlighted with the findings that controlled integration of nanoscale can significantly improve the performance of membranes in the treatment of polluted water. Such understandings lead to future generation nanofiltration systems,

more responsive, rather selective, and capable of handling difficult industrial contaminants.

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