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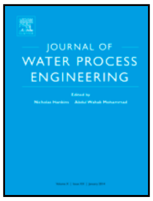

Impact of water chemistry, shelf-life, and regeneration in the removal of different chemical and biological contaminants in water by a model Polymeric Graphene Oxide Nanocomposite Membrane Coating

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ABSTRACT

The present study aims to investigate the impact of water chemistry, shelf-life and regeneration of a previously developed chitosan (CS)-polyethyleneimine (PEI)-graphene oxide (GO) nanocomposite membrane coating. Several studies have shown the development of coatings with multifuctionality in DI water but have negleted the effects of water chemistry, shelf-life and chemical regeneration of these nanocomposite coatings for the simultaneous removal of different biological and chemical water contaminants. This nanocomposite was selected for this investigation since it showed a broad removal capability. This nanocomposite showed removals of Cr(VI), Cu(II), and Pb(II) over 90% at 1 ppm initial concentration and nitrate >75% at 20 ppm initial concentration under DI water. Furthermore, the coated filters were effective in removing >3 logs of *E. coli* K12, *B. subtilis*, and *P. aeruginosa*. The integrity and performance of the modified filters were investigated against a wide range of water chemistries with different pH values, salinity, and total hardness. For water chemistries with pH 4–9, salinity 50–1000 ppm, and total hardness of 50–500 ppm as $CaCO_3$, at least one tested contaminant showed similar percentage removals indicating the potential use of the modified filters in these large ranges of water chemistry conditions. Based on that, the filters were used to treat representative samples of wastewater and seawater. The coated filters were able to remove suspended particles, bacteria, and heavy metals effectively. Later the potential for regeneration and the shelf-life of the coated filters were also investigated. For the regeneration, only 0.1 M HCl was able to desorb up to 40% of the adsorbed heavy metal, indicating that the filter can be partially regenerated. Accelerated experiments of shelf-life demonstrated that the modified filters lose their optimum performance around 9–12 months, indicating their potential for short-term storage without any specific preservation conditions.

1. Introduction

Water and wastewater treatment facilities can be an integral part of most municipalities. Depending on the sequence of treatment steps in the wastewater treatment facilities and different downstream treatment approaches of effluent water for drinking water; water treatment plants can be categorized as direct potable, indirect potable, and unplanned potable water reuse plants [1–3]. Direct potable water reuse plants are common in areas affected by water scarcity as opposed to indirect. In the first case, the treated wastewater is directly fed to the distribution system for potable reuse, while in the second case, the wastewater is left for a certain amount of time in a reservoir or natural ponds for natural purification [3,4]. In all cases, additional treatment is needed to purify the water, since the water may still be of poor quality for drinking purposes, due to diverse types and levels of contaminants present. Furthermore, in these systems, the water chemistry tends to be complex, which can make the treatment more complicated.

Polymers as adsorbents have been used widely, in both domestic and industrial applications for direct or indirect treatment of water. However, different polymers carry different contaminant removal capabilities based on their functionality, which creates a barrier for applications requiring removal of a wide range of water contaminants for water reuse. Therefore, the direction of research has moved toward incorporating nanomaterials with diverse polymeric materials to provide functional variety, structural strength, and stability. This approach has several advantages, such as enhanced adsorption capacity, selectivity, improved design flexibility, and potential for large-scale fabrication [5,6]. A special interest has drawn to natural polymers or biopolymers such as cellulose, lignin, hemicellulose, and chitosan (CS) to form graphene-based nanocomposites with enhanced or

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multifunctional properties [7–9]. Previous studies done by our research group and others have shown that it is easy to successfully disperse graphene-based nanomaterial into a polymer matrix yielding new multifunctional nanocomposites [7,8,10,11]. These nanocomposites also have shown to prevent biofouling, while being non-toxic to mammalian cells. Although, some researchers have investigated these nanocomposites with real water samples, we have very little understanding of how changes in the water chemistry would impact these nanocomposites, more importantly, how long these biopolymer nanocomposites can maintain their active coating layer after storage or chemical regeneration.

In a previous preliminary study [12], we developed, using a mathematical approach within response surface methodology (RSM), an optimized coating containing graphene oxide (GO) embedded into a polymeric matrix made of CS and polyethyleneimine (PEI) [12]. The preliminary results of this nanocomposite with spiked deionized water (DI) suggested the ability of this coating to remove positive and negative heavy metal ions. The preliminary results were based on only two differently charged heavy metals spiked in DI water. In the present study, we build upon these initial findings and confirm the ability of this coating to remove diverse range of contaminants such as nitrate, microorganisms, and other toxic heavy metals, not only in DI water, but also under complex water chemistries, after chemical regeneration, and after different storage times. In the present study, the removal efficiency by the coating was further analysed in a wide range of pH values, salinity, and hardness. The modified filters were used to treat representative wastewater and seawater samples spiked with heavy metals and microorganisms to quantify the performance of the modified filters with real-world water samples that have complex water chemistries. Finally, the shelf-life and capability of regeneration of the coated filters were investigated. This systematic study gives us an understanding of the impact of different types of water chemistries, as well as, shelf-life, and chemical regeneration impact on the treatment capability of graphene oxide-polymer based coatings. These parameters are essential for real life application of these and other biopolymer-based coatings described in the literature.

2. Methods

2.1. Materials

GO required to prepare the nanocomposite coating was synthesized starting from the graphite flakes ($< 45\,\mu m$) purchased from Sigma Aldrich (St. Louis, MO, USA), using the modified Hummer's method [13]. Chitosan (low molecular weight), polyethyleneimine (50 wt/wt % in water), and glutaraldehyde (25 v/v % in water) for the nanocomposite synthesis were also purchased from Sigma Aldrich. Glass microfiber (GMF) 691 (1.5 μm pore size) with 13 mm of diameter and 1.3 cm^2 of filtration area membranes used for the application of the coating was purchased from VWR international (Radnor, PA, USA). Chemicals used for the preparation of the different water chemistry conditions, as well as potassium dichromate ($K_2Cr_2O_7$, crystals, 99.8% assay) were purchased from Fisher Scientific (Hanover Park, IL, USA). Cupric nitrate ($Cu(NO_3)_2.3H_2O$ crystals, 98% assay), lead nitrate ($Pb(NO_3)_2$, 99.9% assay), cadmium sulfate ($CdSO_4$ crystals, 98% assay), nickel nitrate ($Ni(NO_3).6H_2O$ crystals), and sodium nitrate ($NaNO_3$ $>99\%$) were purchased from Sigma Aldrich. Other chemicals used to prepare the different water chemistries, such as sodium chloride crystals ($\geq$ 99.0% assay), sodium bicarbonate powder (99.5–100 % assay), acetic acid (99.7% w/w) were also purchased from Sigma Aldrich. All chemicals purchased were of analytical grade and the synthetic solutions were freshly prepared in deionized (DI) water, unless specified otherwise. We used bacterial strains of *Escherichia coli* K12, *Bacillus subtilis* and *Pseudomonas aeruginosa* that were stocked at −80 °C at the University of Houston. Bacteriophage MS2 (ATCC 15597-B1) and its bacterial host, *Escherichia coli* strain C-3000 (ATCC 15597) were purchased from American Type Culture Collection (Manassas, VA, USA).

2.2. Synthesis and characterization of CS-PEI-GO coated filters

GMF filters were coated with the optimum CS-PEI-GO composition as described in Bandara et al., 2019 [12]. Briefly, the GMF membranes were soaked in 0.04% CS solution for 30 min. Meanwhile, a solution containing 1.78% PEI, and 1500 ppm GO, and DI water were weighed in a separate glass vial and mixed thoroughly using a vortex mixer. A solution of 2% glutaraldehyde (GLA) was used as a crosslinker reagent. GLA was added to the above mixture and stirred thoroughly for one additional minute and poured onto a petri-dish. Next, CS coated GMF filters were carefully transferred to the homogenized mixture containing PEI-GO-GLA for dip coating for 30 min. Later, the coated filters were rinsed with DI water and air-dried overnight. Coated filters were characterized using attenuated total reflectance-infrared (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) to ensure successful coating and availability of various functional groups. ATR-FTIR analysis was carried out on dried coated filters with a Nicolet iS10 Mid Infrared FTIR Spectrometer (Thermo Fisher Scientific, USA) using air as the background. Raw spectra were processed and analyzed employing Omnic 8 (Thermo Fisher Scientific, USA) and Origin Pro8.5 (OriginLab, Northampton, MA). XPS analysis was done using a PHI 5700 X-ray photoelectron spectrometer. Wide and high-resolution scans were performed using pass energies of 23.5 eV and 187.8 eV, respectively. Raw spectra were further processed using the MultiPak V7.0.1 (ULVAC-PHI, Inc.) and Origin Pro8.5. For the SEM analysis, modified filter samples were fitted to a carbon double tape and gold-coated using a Desk V sputter (Denton Vacuum) during 40 s. Samples were analyzed with a FEI XL-30 FEG SEM (Philips) field emission scanning electron microscope [14].

2.3. Preparation of synthetic wastewater solutions

CS-PEI-GO coated filters were used to remove various contaminants from the water. First, the stock solutions of different synthetic wastewater solutions were made using DI water as the solvent. For the heavy metals, potassium dichromate ($K_2Cr_2O_7$, crystals, 99.8% assay), cupric nitrate $Cu(NO_3)_2.3H_2O$ crystals, 98% assay), lead nitrate ($Pb(NO_3)_2$, 99.9% assay), cadmium sulfate ($CdSO_4$ crystals, 98% assay) and nickel nitrate ($Ni(NO_3).6H_2O$ crystals) were dissolved in DI water to prepare 500 ppm stock solutions of Cr(VI), Cu(II), Pb(II), Cd(II) and Ni(II) metal ions. To prepare the 500 ppm nitrate stock solution, potassium nitrate (KNO_3 crystals) was used.

To prepare the bacterial wastewater solution, first, the desired bacterium was inoculated into 25 mL of liquid nutrient media: *E. coli* K12 and *B. subtilis* were grown in tryptic soy broth (TSB) media, while *P. aeruginosa* was grown in Luria broth (LB) media. All three bacteria were grown at 37 °C overnight in their respective media. Then, they were centrifuged at 10,000 rpm for 5 min to separate the bacterial cells from the media. Bacterial pellets were resuspended in 1x Phosphate Buffered Saline (PBS) solution with an optical density of 0.5 at 600 nm (OD600) using the Biotek Synergy 2 Multi-Mode Reader. Dilutions of 100-fold were used for actual filtrations. The solutions were made freshly for each filtration carried out. To prepare a liquid stock of bacteriophage, the host bacterium *E. coli* ATCC 15597 was inoculated in TSB media and processed as described earlier [15]. Detailed information about the bacteriophage stock preparation and enumeration are given in ESI text S3.

2.4. Contaminant removal experiments with synthetic wastewater solutions

Initial validation of the removal of different contaminants was done as dead-end filtrations in smaller volumes, such as 20 mL, using the CS-PEI-GO coated GMF filters. Larger volumes of 1 L were also used later to validate the contaminant removals in larger batches. For, Cr(VI), Cu(II) and Pb(II), initial concentrations of 1, 10 and 20 ppm were used while for Cd(II) and Ni(II), 1, 5 and 10 ppm were used as initial concentrations. For nitrate, 20, 40 and 60 ppm initial concentrations were used. Filtration experiments were carried out as batch experiments. All the heavy metals were analyzed using the flame atomic absorption spectrophotometry (AAS) AAnalyst 200 from Perkin Elmer, using chromium, copper, lead, cadmium and nickel lamps from Perkin Elmer. Five standard solutions were prepared as calibration standards with known heavy metal concentrations. The averages and standard deviations of triplicate measurements are reported for all measurements. Nitrate concentrations were measured with a Thermo Scientific™ Orion™ Nitrate Electrode equipped with a sure-flow combination electrode 9707BNWP. An ionic strength adjuster was added to nitrate samples based on the target nitrate concentration of each sample.

For the bacterial removal, bacterial solutions were passed through the modified filters. Bacterial concentrations of the filtrates and the initial solutions were measured using the drop plating method after serially diluting with PBS. For the bacteriophage removal, bacteriophage solutions were passed through CS-PEI-GO coated GMF membranes.[16] To measure the concentration (titer) of filtrates, the plaque forming units (PFU)/mL counts on double layer agar plating was used [33]. The filtrates were serially diluted with 1x PBS. Aliquots of 0.1 mL of these dilutions were mixed with 0.9 mL of six hours-old bacterial host and 3 mL of warm soft agar which was poured onto pre-solidified TSA plates and incubated at 37 °C. After about 24 h of incubation, higher dilutions of the filtrates resulted in countable plaques of bacteriophage on the lawn of bacteria. This number was counted and according to the dilution factor, bacteriophage concentration was determined as PFU/mL. For all these experiments, non-coated GMF membranes were used as the negative controls. All the experiments were done in three or more replicates. The results were averaged out and standard deviations were calculated.

2.5. Investigating effect of water chemistry on contaminant removal

Removal efficiencies of Cr(VI), nitrate, and *E. coli* K12 with varying water chemistries were investigated individually. Investigated water chemistry variables were pH, salinity, and hardness. Working synthetic wastewater solutions were prepared by diluting from the stock solutions prepared and by changing the water chemistry as mentioned below.

For the pH related experiments, the pH of the solutions was adjusted using 0.1 M HCl and 0.1 M NaOH. Solutions with pH 4–9 were used for the experiments. For salinity related experiments, sodium chloride (NaCl) was added to prepare solutions with desired salinity in the range of 0–1000 ppm. For the hardness related experiments, calcium carbonate ($CaCO_3$) was added to prepare solutions with 0–500 ppm hardness as $CaCO_3$. Initial concentrations of solutions were set at 10 ppm, 20 ppm, and 10^7 CFU/mL for Cr(VI), nitrate, and *E. coli* K12, respectively. The removals were quantified using the respective techniques mentioned above.

2.6. Wastewater sample collection and contaminant removal

The performance of the filters in real contaminated water with complex water chemistries was tested using representative wastewater and seawater. The representative wastewater contained 95% (v/v) bayou water and 5% (v/v) wastewater influent. More information about the collection of water samples and their characteristics can be found in the ESI text S4 and Table S1. Due to undetectable amounts of chromium or copper in the environmental samples, they were spiked with these metals before the filtration experiments to have 10 ppm of initial metal concentrations. Samples were also spiked with bacteriophage MS2 to investigate the effect on virus removal. These water sources, however, already contained microorganisms; therefore, no additional microorganisms were added for bacterial removal experiments. Heterotrophic plate count (HPC) was used to measure the number of bacteria before and after the filtration, employing the drop plating method [16]. Effect of filtration on solid removal was measured in terms of total dissolved solids (TDS) and total suspended solids (TSS) employing the gravimetric method [17].

2.7. Investigation of reusability of coated filters based on Cr(VI) adsorption

A set of adsorption and desorption experiments were performed to analyze the reusability of the coated filters. For these adsorption experiments, the Cr(VI) solution was prepared in DI water with 2 ppm initial concentration. One liter of Cr(VI) solution was filtered with the CS-PEI-GO coated GMF filters. Throughout the filtration, samples were collected every 10 mL intervals (until 250 mL) and every 15 mL interval (until 1000 mL) and was analyzed using AAS. The amount of Cr(VI) adsorbed (w_{ad}) in this step was calculated as follows:

$$\text{Amount of Cr adsorbed } (w_{ad}) = (C_i\text{-}C_e)V \tag{1}$$

Here, C_i is the initial concentration of the synthetic solution of Cr and C_e is the final Cr concentration of the filtrate. V is the total volume, which was 1000 mL in this case. Spent membranes were then treated with different desorption agents. A volume of 100 mL of these agents, namely 0.1 M HCl, 0.1 M NaOH, 0.1 M CH_3COOH, 0.1 M $NaHCO_3$, and 0.1 M NaCl were filtered through used membranes. Desorption was calculated as a percentage with respect to the amount of Cr adsorbed during the previous step as follows.

Here w_{de} is the desorbed Cr amount. Regenerated filters were again used for the Cr(VI) filtrations after being washed with 100 mL of DI water. Eq. (1) was used again to calculate the amount of Cr(VI) adsorption.

$$\%\ \text{Desorption} = \frac{w_{de}}{w_{ad}} \times 100\% \tag{2}$$

2.8. Accelerated aging of coated filters

A thermal aging process was employed to assess the effect of storing and aging of CS-PEI-GO coated filters. The accelerated aging was equivalent to 3–12 months of storage under room temperature at 24 °C. The aging procedure was carried out as suggested by ASTM F1980 and NBSIR 74-499 protocols [18,19]. ASTM-F1980 is the standard guide for accelerated aging of sterile barrier systems for medical devices; and NBSIR 74-499 is the protocol for accelerated aging for papers. Combining these two procedures, filters were stored at 55 °C for a calculated pre-determined period, accelerated aging time (AAT), which were calculated as follows:

$$\begin{aligned} &\mathit{Accelerated\ Aging\ time}\ (AAT) \\ &= \frac{\mathit{Desired\ Real\ Time}\ (RT)}{Q_{10}^{[(T_{AA}-T_{RA})/10]}} \end{aligned} \tag{3}$$

Here, the accelerated aging temperature (T_{AA}) is measured in °C. Common T_{AA} values are 50 °C, 55 °C, and 60 °C. The 55 °C was selected for corresponding to the average. Ambient temperature (T_{RT}) was measured in °C. The temperature typically varies between 20 °C–25 °C and can be interpreted as the storage temperature. In this study, it was 24 °C. The aging factor (Q_{10}) is unitless and this factor is typically between 1.8–2.5 with a value of 2.0 being the most common, which was selected for this calculation. After the aging, these filter membranes were analyzed using scanning electron microscopy (SEM) and were tested for Cr(VI), Cu(II) and *E.coli* K12 removal. The results were compared to the results with freshly coated filters. Also, the membranes were analyzed with ATR-FTIR to visualize the differences between the aged membranes.

3. Results and discussions

3.1. Characterization of CS-PEI-GO coted filters

The successful dip coating of the GMF filters with CS-PEI-GO nanocomposite was confirmed by the detailed characterization of the coating. SEM images shown in Fig. 1a and b, illustrates the appearance of the successful CS-PEI-GO coating on the fiber-like structure of the bare GMF membrane. As shown in the ATR-FTIR spectrum of the CS-PEI-GO coated filters in Fig. 1c, new peaks appeared at 1396, 1449, 1638, 2852, 2923, and 3359 cm^{-1} after the coating step. The peak at 1396 can be attributed to the CH— stretch from –$NHCOCH_3$ group from CS; while the peak at 1449 cm^{-1} was assigned to the C—H bending [14]. The peak at 1638 was assigned to the carbonyl stretching of the NHCO ——group or the carbonyl results from the cross-linking. Peaks at 2852 and 2923 cm^{-1} were assigned to CH vibrations from CH_2 and CH_3, respectively, which were originated from CS and PEI [20]. A broad peak was visible around 3100–3600 cm^{-1} range, the peak at 3359 cm^{-1} was attributed to —OH (from GO and CS) and -NH_2 (from CS and PEI) [14,20].

Fig. 1d and e show the deconvolution of the O1s and N1s peak of the high-resolution XPS spectra of CS-PEI-GO coating respectively. The deconvolution of the O1s core-level spectrum shows three major peaks with binding energies of 531.8, 532.9 and 534 eV. These binding energies were attributed to aliphatic C—OC, OH or CO groups and OCO ————═ groups mainly found in the GO structure. Deconvolution of N1s core-level spectrum has two major peaks at 397.6 and 399.8 eV binding energies, which can be assigned to imine and amine (N—H_2) groups, which are found in CS and PEI [10,21]. The C/O ratio for the bare GMF membrane showed a decreased from 7.5 to 1.1 for the CS-PEI-GO coating due to the presence of carbonaceous groups on the surface of the filter.

In summary, the characterization of CS-PEI-GO coated filters shows the successful coating procedure and availability of different functional groups from the components of the nanocomposites that are useful in contaminant removals. The synthesis was based on the optimized procedure already published [12]. In the previous investigation, the grafting efficiency, based on the thermogravimetric analysis, was estimated to be 27% on the coated membranes [12]. The change of water flux after the CS-PEI-GO coating was also determined and extensively explained in our previously published study [12]. In brief, the flow rate increased from 227 $Lm^{-1}s^{-1}$ to 411 $Lm^{-1}s^{-1}$ after the CS-PEI-GO coating, indicating that the incorporation of hydrophilic CS has facilitated the liquid flow through the pores.

3.2. Contaminant removal experiments with synthetic wastewater solutions

The coated filters were tested for the removal of various contaminants. Firstly, the CS-PEI-GO coating was optimized based on the heavy metals, Cr(VI) and Cu(II) removals. Results showed removal of both contaminants efficiently with 10 ppm concentrations [12]. For the other heavy metal contaminants tested in this study, analytical conditions for the AAS are shown in ESI Table S2. In this study, Cr(VI) and Cu(II) were further analyzed for the following concentrations: 1 and 20 ppm. These extreme concentrations were not previously analyzed in the coating optimization investigation [12].

To understand the effect of initial concentration, three different initial concentrations were selected for each heavy metal based on their respective linear ranges in the AAS instrument. This approach allowed us a more accurate quantification of the metals and also allowed us to achieve more realistic concentrations found in the environment, as shown in ESI Table S2. [22,23]. Based on the AAS linear ranges

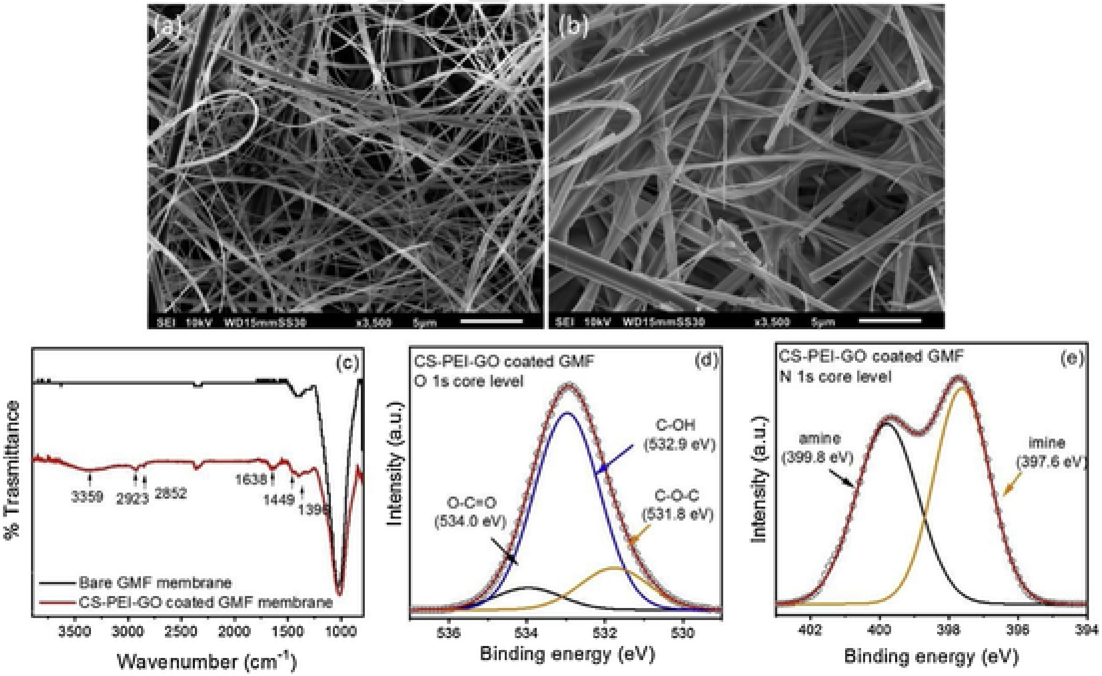

Fig. 1. SEM images of (a) bare GMF membrane, (b) CS-PEI-GO coated GMF membrane; (c) ATR-FTIR spectra showing important peaks of CS-PEI-GO coating; XPS spectra showing (d) deconvolution of O1s peak and (e) deconvolution of N1s peak.

for each metal, Cd(II) and Ni(II) were studied at 1, 5, and 10 ppm; while Cr(VI), Cu(II) and Pb(II) were studied at 1, 10, and 20 ppm. Fig. 2 summarizes the results of the removal experiments for heavy metals and nitrates.

CS-PEI-GO coated GMF filters were able to remove over 90% Cr(VI) (Fig. 2a), Cu(II) (Fig. 2b) and Pb(II) (Fig. 2c) at 1 ppm. Cr(VI) removal was consistent up to 20 ppm and reached 99% removals. However, Cu(II) and Pb(II) removals dropped when the initial concentration increased. For Ni(II), the highest removal of 62% was obtained for an initial concentration of 1 ppm, as shown in Fig. 2d. However, the coated filters were not very effective in removing Cd(II), as less than 15% removals were recorded for initial concentrations up to 10 ppm (Fig. 2e). Adsorption effect is affected by the size of the hydration radius. The smaller the hydration radius and the larger the charge density per area, the better will be the affinity of the metal for the adsorbent. Since Cd^{2+} exhibits a larger hydration radius (4.26 Å) compared to the other heavy metals, a reduced adsorption is observed with this metal than the others [24,25]. Nitrate is an inorganic contaminant, which is also regulated by EPA, with an allowable limit of up to 10 ppm maximum contaminant level (MCL) in drinking water. Experiments for nitrate were carried out for the initial concentrations between 20 and 60 ppm. CS-PEI-GO coated GMF filters showed maximum removals of 78% at 20 ppm (Fig. 2f), while the removal decreased with the increasing initial concentrations. Furthermore, since the number of adsorption sites remained the same, higher initial contaminant concentrations resulted in saturation of adsorption sites. In the heavy metal removal, CS and PEI play a major role. The mechanism of removal for the prepared filters involve the participation of the unshared electron pair present in the nitrogen atom of the amine group from the CS and PEI. This electron pair will form a donor bond with the unsaturated transition metals. Then, the hydroxyl and amine groups present, will capture the

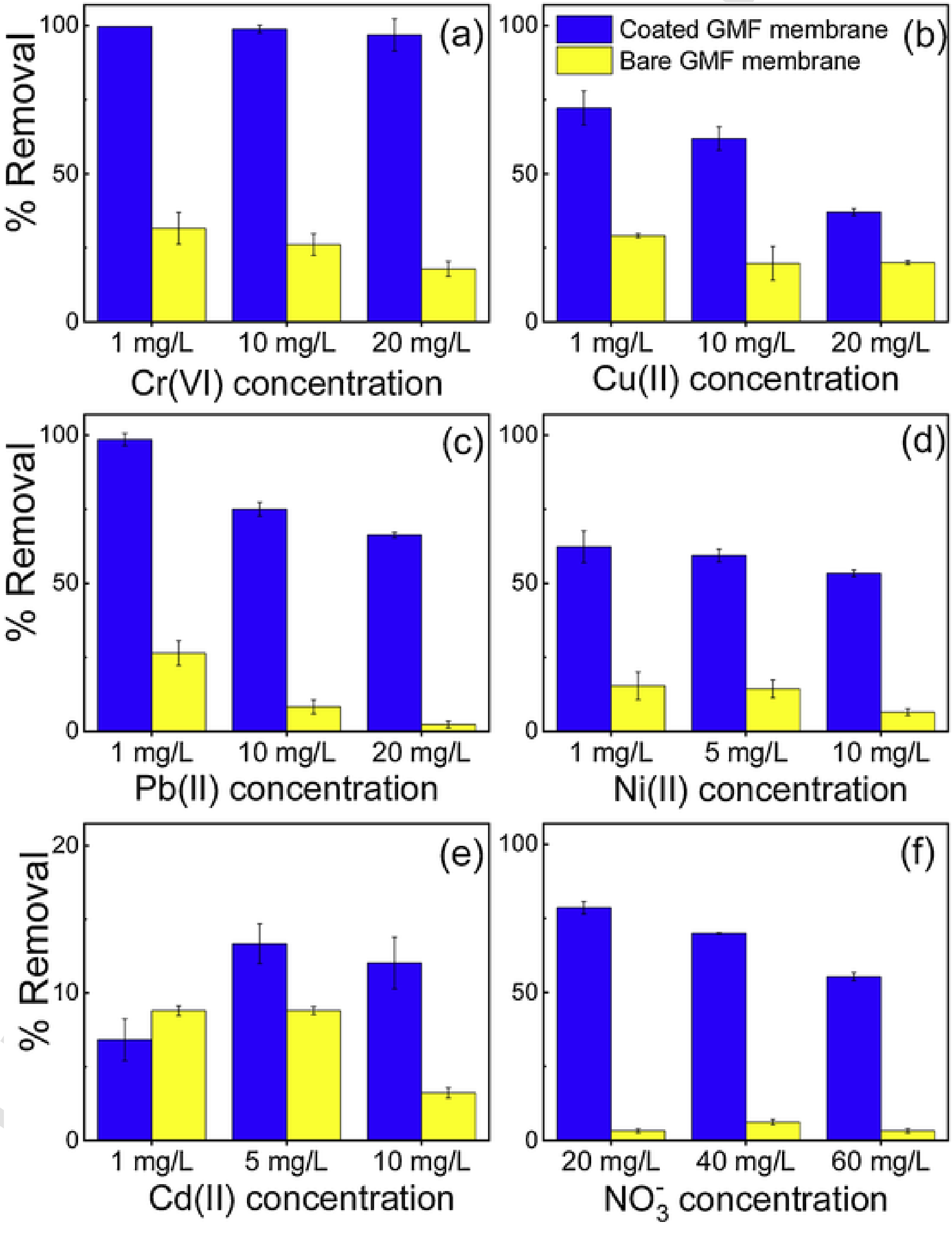

Fig. 2. Contaminant removals by CS-PEI-GO coated filters with synthetic solutions of (a) Cr(V), (b) Cu(II) (c) Pb(II), (d) Ni(II), (e) Cd(II) and (f) nitrate at various initial contaminant concentrations. The error bars represent the standard deviations.

metals while forming a shared bond between the metal and the amino groups of CS and PEI [26].

Results for microbiological contaminant removals are shown in Fig. 3. Bacterial removals were over 3 logs (or 99.9%) with CS-PEI-GO coated filters, for all three bacterial strains. *B. subtilis* was also removed with the non-coated filters. This can be understood as *B. subtilis* is a much larger bacteria compared to the other two types of bacteria used. *B. subtilis* is about 4–10 μm long and 0.25–1.0 μm in diameter, compared to the 1–2 μm length of *E. coli* K12 and 1–5 μm length of *P. aeruginosa* [27–29]. However, in the case of uncoated filters the mechanisms of removal are entirely sieving, i.e. based on the size of the bacterial cells and the pore structure of the bare membranes. However, for the CS-PEI-GO coated filters, the mechanism is driven by a combination of sieving and antimicrobial activity; therefore, recording much higher removals with bacteria [30,31]. The SEM images of the coated and uncoated filters taken after the *E. coli* K12 filtration are given in Fig. 4. This result shows how effective the coated filters entrapped and inactivated bacteria during filtration. It was not possible to see any bacteria retained on the bare membranes (Fig. 4a). For the modified filters, as shown in Fig. 4b, these bacterial cells seemed to be adsorbed and distorted, indicating that they could potentially be inactivated due to the antimicrobial properties of the GO. We can clearly see aggregation on the coated GMF membrane due to bacterial cell adsorption. Observation of distorted cells in the presence of GO is a well-studied phenomenon as GO tends to work as nano-blades and puncture bacterial cells [32,33]. Another possibility is the generation of reactive oxygen species, which could destroy the bacterial cells [19].

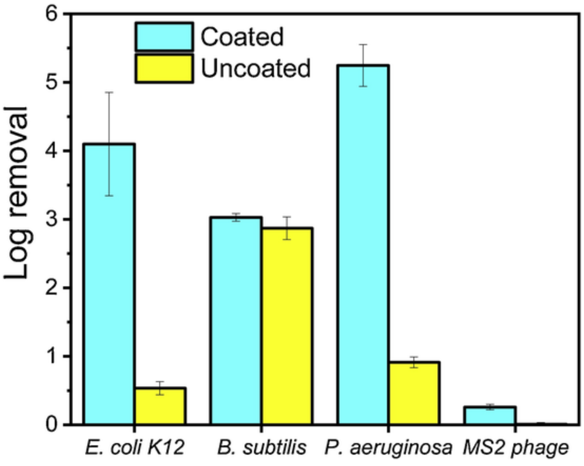

Fig. 3. Microbiological contaminant removal with CS-PEI-GO coated GMF filters. The error bars represent the standard deviations.

The nano-sized bacteriophage MS2 was not retained by the CS-PEI-GO coated GMF membranes. Fig. S2 showed the comparison between the coated and uncoated filters. We can see that even if the viruses could pass through the filter, some were inactivated, due to the antimicrobial properties of GO.

3.3. Effect of water chemistry on contaminant removal

For any water treatment technique, it is important to expect varying water chemistries of the source water. Hence, it is important to investigate the removal efficiency of any novel water treatment technique under different water chemistries in order to assure a high quality purification process [34,35]. In this study, effects of changing pH, salinity, and hardness on removal efficiencies of indicator contaminants were investigated. Therefore, we selected three different contaminants, such as a heavy metal (Cr(VI)), a microorganism (E. *coli* K12), and a nutrient contaminant (nitrate) for further study since these contaminants were shown earlier to have higher removals by the filter coating compared to the other studied contaminants. Fig. 5 shows the summary of results for removal of Cr(VI), nitrate, and *E. coli* K12.

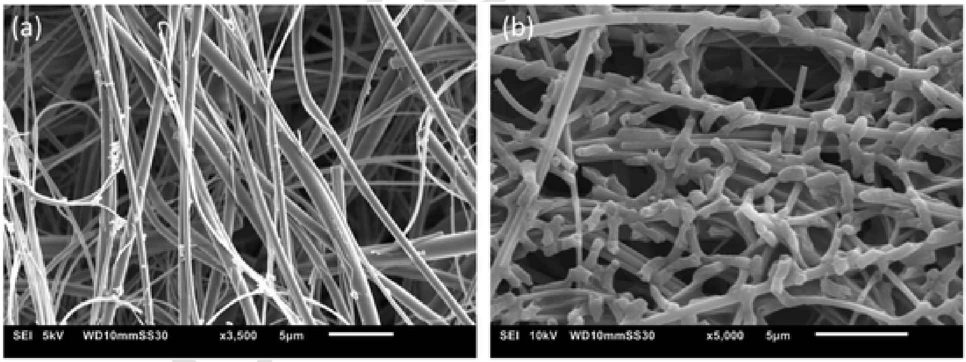

Fig. 4. SEM images of a) bare GMF membrane and b) CS-PEI-GO coated GMF membrane after the filtration of *E. coli* K12.

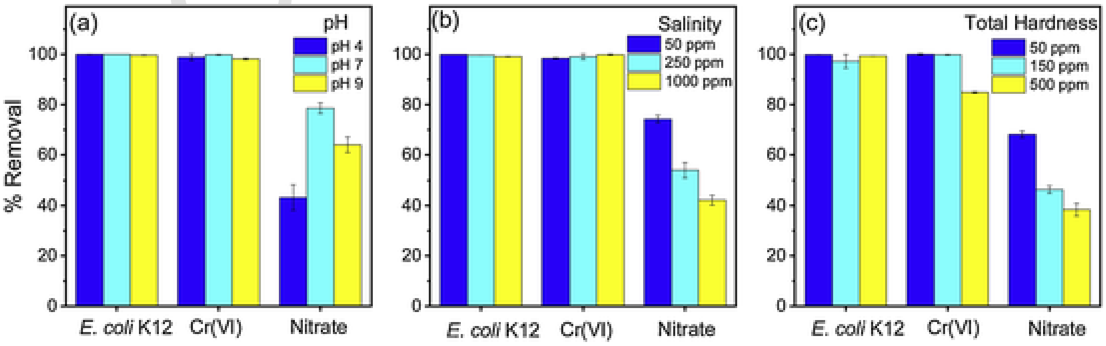

Fig. 5. Effect of (a) pH, (b) salinity and (c) hardness on contaminant removals. Ranges of pH 4–9, salinity of 50–1000 ppm and total hardness of 50–500 ppm as $CaCO_3$ were tested. Only the values for the extreme conditions and neutral water conditions are shown. The error bars represent the standard deviations.

The pH is a measure of acidity and basicity, which is affected by the natural environment or can be man-made. For instance, sources of pH changes can come from photosynthesis, microbial respiration in the water, dissolution of carbon dioxide, acid rain, acidic discharges, and mineral discharges [36]. Usually, for surface water systems, pH values range from 6.5 to 8.5, while for groundwater systems, the range is from 6 to 8.5 [37]. In this study, a range of pH 4 to 9 was tested representing the possible pH range for different water sources (Fig. 5a). Throughout for the selected pH range, the removal was always above 95% for Cr(VI) with the CS-PEI-GO coated filters. Although pH affected the active sites that are responsible for antimicrobial properties of the coating, no significant result is shown in the removal of *E. coli* K12 at various pH ranges [38,39]. Effect of the pH was more prominent in nitrate removal when acidic and basic conditions lowered the percentage nitrate removal significantly. In the case of anionic contaminants that are removed via electrostatic interactions with positively charged functional groups of the nanocomposites, pH lower than 5 was more favourable for removal [40–43]. Since more H^+ ions are in the solution at acidic pH, there were some restrictions in the free movement of nitrate ions toward the adsorption sites. With increasing pH, more OH^- ions are present in the solution, these ions compete with the nitrate ions; and hence, decrease the adsorption capacity of the filter [44]. Fig. S3 showed a decrease in the Zeta-potential at higher pH values, which suggested favorable adsorption of negatively charged species in lower pH values

Salinity is the mass of dissolved salts in a certain mass of water, measured in ppm (parts per million) or ppt (parts per thousand) or PSU (practical salinity units) [45]. Salinity often interferes with contaminant removals by claiming adsorption sites and competing with other contaminants in the source water. In general, for the surface and groundwater sources, salinities below 80 ppm are considered preferable for consumption, whereas salinities above 1000 ppm are considered to be poor in quality [45]. A range of 50–1000 ppm was used in this study. As shown in Fig. 5b, Cr(VI) removal remained consistent throughout the selected salinity range. Previously, it was shown that chlorides interfere with nitrate adsorption by suppressing nitrate uptake at elevated chloride concentrations [46]. Our results corroborate this nitrate removal trend with increasing salinity. Furthermore, Fig. 5b, showed no significant changes in bacterial removals with increasing salinity indicating salinity does not interfere with bacterial removal.

Total hardness is the amount of dissolved calcium and magnesium in the source water, measured in ppm as $CaCO_3$. It is common to see hardness cause problems in water treatment facilities and membrane technologies by aiding scaling on membrane surfaces [47,48]. Water sources can be categorized into different levels of total hardness: 0–60 ppm as $CaCO_3$ as soft water, 61–120 ppm as $CaCO_3$ as moderately hard, 121–180 ppm as $CaCO_3$ as hard and >180 ppm as $CaCO_3$ as very hard. [49,50] To represent all these categories, a range of 50–500 ppm as $CaCO_3$ of total hardness was tested in this study. Overall, hardness showed an inhibitory role for Cr(VI) and nitrate removals with increasing hardness, as shown in Fig. 5c. The addition of more carbonate in the initial solution resulted in reduction of acidity, therefore inhibiting electrostatic attraction of anionic contaminants [51].

In conclusion, the optimized CS-PEI-GO coating remained effective in a variety of water chemistries. Except for the source waters with very high total hardness, the CS-PEI-GO coated GMF filters presented consistent removals throughout the selected ranges of water chemistries, indicating the applicability of the modified coating with CS-PEI-GO for water purification applications. It is important to mention that in real water samples; the ranges of such water qualities can be narrow depending on the cleanliness and the water source used. However, the extreme conditions, such as high pH or high salinity, can be correlated to harsh environments that could occur in nature. Additionally, it is also important to understand how more complex water chemistries affect removals, therefore, the coated filters were tested to filter real environmental water samples.

3.4. The performance of the filters in real contaminated water with complex water chemistry

A representative wastewater sample containing 95% (v/v) bayou water and 5% (v/v) wastewater influent, as well as a water sample of seawater were filtered with the optimized CS-PEI-GO coated filters to observe the performance of the filters in more realistic conditions. Table S1 contains the physical and chemical characterization of the collected samples and Table S3 compile the removal data for all the experiments performed in wastewater and seawater. The removals can be interpreted as changes to physical and chemical properties as well as the contaminant removal. The initial treatment of the collected water was first determined via physical properties of the water, such as turbidity and TSS (Fig. 6). The seawater contained higher turbidity, which was 181 nephelometric turbidity unit (NTU), than the representative wastewater that contained 32 NTU. The filtrate of the latter resulted in 0.9 NTU on average, while the seawater filtrate presented a turbidity of 1.5 NTU. According to EPA's national primary drinking water regulations, turbidity should not exceed 1 NTU, if the treatment system contains conventional or direct filtration. At no time can the turbidity measurement go higher than 1 NTU. [23] In that sense, the filtrate produced from the representative wastewater was the closest to that limit (Fig. 6a).

From the gravimetric analysis, total dissolved solids (TDS) in the representative wastewater was reduced to 670 mg/L compared to the initial amount of 760 mg/L after the filtration with CS-PEI-GO coated filters (Fig. 6b). With respect to the EPA's drinking water regulations, recorded TDS was higher than the regulated limit of 500 mg/L. For the seawater, which contained a very high amount of TDS 33,500 mg/L compared to the representative wastewater. It only reduced to 30,000 mg/L after the filtration. This removal of about 3000 ppm for TDS was observed for the non-coated and CS-PEI-GO coated

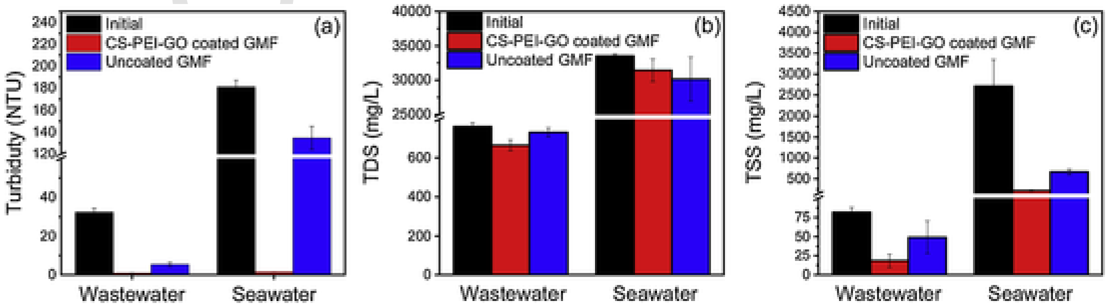

Fig. 6. Removal of (a) turbidity, (b) TDS and (c) TSS with representative wastewater and seawater samples when filtered with CS-PEI-GO coated GMF membranes. The error bars represent the standard deviations.

filters, therefore suggesting the limitation of the coating in removing TDS. In contrast, much larger suspended solids were well removed during the filtration (Fig. 6c). For the representative wastewater, the removal dropped to 18 mg/L from initial total suspended solids (TSS) amount of 82 mg/L. Seawater contained a much higher amount of TSS (2700 mg/L) and after filtration, it measured at 220 mg/L. In summary, the filtration alone was effective in removing TSS from the water, however, it was ineffective in removing dissolved solids, such as ions and salts.[39] Therefore it is important to use this type of modified membranes coupled with another treatment approach if the water contains considerable amounts of dissolved solids.

In the case of Cr(VI) and Cu(II) removals, they were similar for both seawater and representative wastewater, as shown in Fig. 7a and b. The Cr(VI) removals were slightly higher than the removals recorded with the experiments performed earlier with DI water. It is possible that organic matter in the water would also act as a flocculant, therefore, entrapping heavy metals such as Cr(VI) and Cu(II) in the flocs as they got removed from the water during filtration [52,53].

The tested water samples contained microorganisms measured in the form of heterotrophic plate count. Though no additional bacteria were added to the source water, they were spiked with bacteriophage MS2 to perform filtrations to investigate their removals. As shown in Fig. 7c, the filter was able to reduce 3.2 logs of the heterotrophic bacteria. It is important to note that HPC consist of a variety of culturable microorganisms present in water, which is essentially not a single bacteria, rather a mixture of bacterial species that will show a colonial growth on HPC agar plates [54]. Seawater contained less initial HPC (5.3×10^2 CFU/mL) compared to the representative wastewater (3.4×10^6 CFU/mL) and also showed reduced removals of HPC during the filtration. The modified filter was able to remove 3.1 logs in wastewater while for seawater, the removal was 2.7 logs.

However, with bacteriophage, more removal (2.8 logs) was recorded for the seawater, compared to 1.5 log removal in wastewater. Overall, MS2 removals were much higher than compared to the experiments with MS2 solutions made with DI water. It is possible that the solids in the source water have worked as a flocculant entrapping bacteriophage during the filtration and therefore, improving their removal. It is well known that the flocculation enhances the bacteriophage removal during filtrations [55].

3.5. Regeneration and reusability of the modified filters

The modified filters were used for filtration of larger volumes of 2 ppm Cr(VI), 2 ppm Cu(II) and 20 ppm nitrate solutions. Adsorption curves for each contaminant are shown in the Fig. 8. Unlike Cu(II) and nitrate, for Cr(VI), it took much longer time to saturate and exceed the MCL limit of the selected contaminant in the coated filters. These results show that the removal of different contaminants will vary with the coating. The possibility of regeneration and reusability of modified filters were also investigated.

Since the removal of Cr(VI) was more efficient, filters retaining Cr(VI) was further investigated for regeneration. It is important to highlight, however, that Cr(VI) concentration of the filtrate did not reach a saturation value even after filtrating 1 L, indicating there could be free sites still available for Cr(VI) adsorption. The used filters were treated with desorption agents that had diverse properties. As shown in Fig. 9, none of the desorption agents were able to remove more than 40% of the adsorbed amount of Cr(VI), indicating stronger complexation of Cr species to the adsorption sites during the filtration.

In addition, subsequent filtrations with Cr(VI) solutions with the desorbed modified filters showed lower Cr(VI) removals. The use of 0.1 M HCl was the most efficient solution for the regeneration of Cr(VI) adsorbed to the coating. As mentioned earlier, with adsorption sites available even after the 1st adsorption there were vacant adsorption sites that could remove Cr in the subsequent filtration. It is worth to note that regeneration of filter systems is important in industrial contexts, where more focus is given in enhancing the number of total adsorption sites by changing the physical and chemical properties of the coating materials.

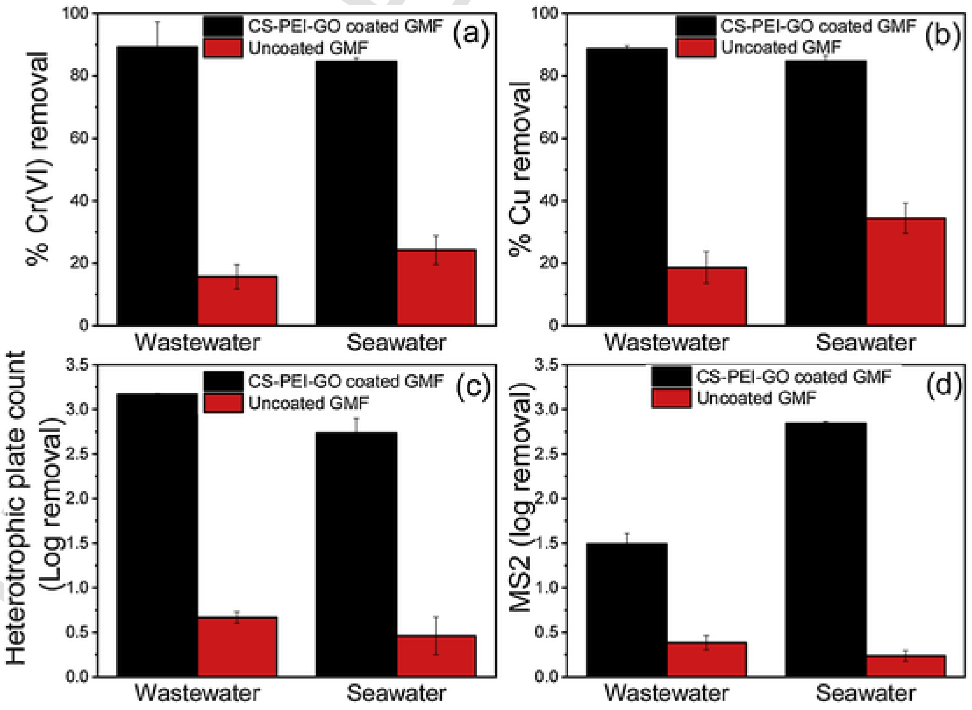

Fig. 7. Contaminant removals with environmental samples: (a) Cr(VI), (b) Cu(II), (c) heterotrophic plate count log removal and (d) MS2 log removal. The error bars represent the standard deviations.

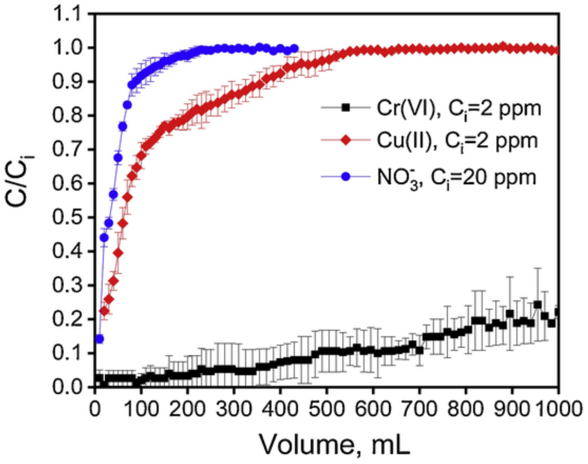

Fig. 8. Filtration of larger volumes of Cr(VI), Cu(II) and nitrate with CS-PEI-GO coated GMF membranes. The error bars represent the standard deviations.

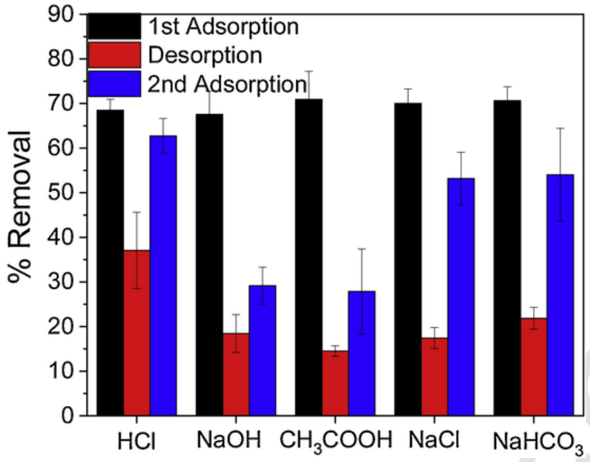

Fig. 9. Ability to regenerate the CS-PEI-GO coated filters used for Cr(VI) adsorption. None of the desorption agents were able to remove more than 40% of the adsorbed amount of Cr(VI) on average. Among the used desorption agents, 0.1 M HCl was the most efficient solution for the regeneration of Cr(VI) adsorbed to the coating. The error bars represent the standard deviations.

3.6. Accelerated aging of filters

Aging is another aspect that needed to be determined for the CS-PEI-GO coated filters as CS polymers is a natural polymer, which can be degraded over time [56]. Due to its degradability, it could affect the overall stability of the filter coating, therefore, it is better to quantify how long the performance of the coating remains unchanged under normal storage conditions. To investigate that, thermal accelerated aging was performed on the filters. Experiments were equivalent to storage times of up to 12 months. Aged modified filters were tested for Cr(VI), Cu(II), and bacterial removal and compared to the removals of freshly coated filters.

Fig. 10 illustrates the removals for the selected contaminants when treated with the aged filters. To determine statistically the significance of the removal changes, *t*-tests were carried out. This was done for both coated filters and respective uncoated filters in order to provide a clear insight of the differences in the filter matrix itself when stored for a long time, to be exact storing of 3, 6, 9 and 12-months periods.

When considering the Cr(VI) removal, CS-PEI-GO coated GMF membranes showed a significant drop in removal in 12 months, while the removal from uncoated GMF remained the same for up to 12 months (Fig. 10a). Data for Cu(II) removals suggest that the CS-PEI-GO coated GMF membranes show a significant drop in removal after 9 months of storage, however, bare GMF membranes did not show any significant change in terms of Cu(VI) removals (Fig. 10b). Similarly, when considering bacteria removals, a significant reduction was evident after storage for 9 months (Fig. 10c). Similarly, the bare GMF membranes also showed reduced removal trend after 9 months.

The preservation of the nanocomposite structure was confirmed by the ATR-FTIR and SEM images to ensure no significant structural or composition change after 12 months of aging was happening (Figs. S4 and S5). The SEM images showed no significative changes in the morphology of the nanocomposites compared to the “no aged” filter. Fig. S5 shows the ATR-FTIR results before and after 12 months aged. In the spectra, we can appreciate some loss of some of the functionalities for the CS-PEI-GO-GMF nanocomposites. The loss of some of the functional groups such as -O—H and -NH$_2$ can explain the efficiency loss in the heavy metal removal. Nonetheless, the removal of contaminants is still suitable before 9 months. The loss of efficiency is no more than 10%. Hence, it is safe to say that the coated filters were consistent in removing the tested contaminants compared to the freshly coated filters suggesting that around 9–12 months the CS-PEI-GO coatings started to show signs of decay.

In other words, this means that the coated filters can be used in the first 9 months without losing its removal efficiencies. However, it is also important to note that the method of aging used in this study is not a standardized method for coatings. We adapted the methods suggested in ASTM-F1980 standard guide and NBSIR 74-499, which were protocols developed primarily for the accelerated aging of sterile barrier systems for medical devices and for papers. In this case, heating was used as the aging technique, based on the Arrhenius equation, which explains that the higher temperatures result in higher reaction rates [57]. But in other terms, heating can also be considered as a physical crosslinking method, and therefore, higher fatigue temperatures could have adversely affected the performance of the filters, not only by aging alone [58]. It is important to note that modified filters could be stored under vacuum or acclimated conditions, which

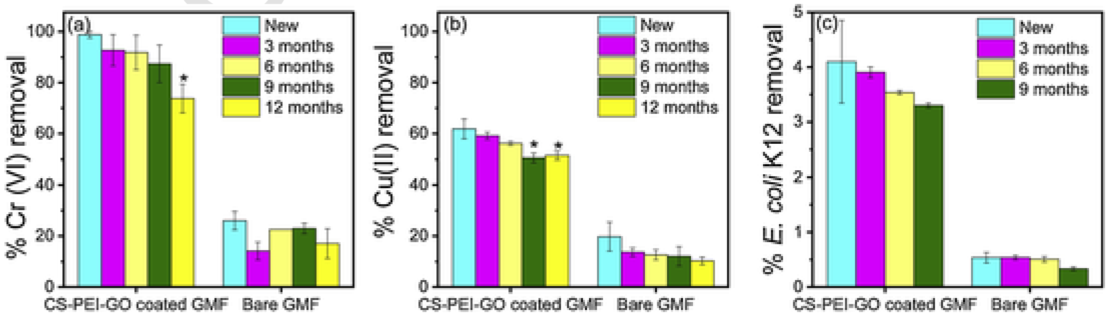

Fig. 10. Contaminant removal with aged filters (0–1 year), * corresponds to data which are statically significant compared to the removals of respective fresh membranes. The error bars represent the standard deviations.

could potentially extend the shelf-life of the coatings. However in in our experimental design, we did not investigate alternative methods to better preserve the coatings. On the contrary, our focus was to test them under the worst-case scenarios.

4. Conclusions

A previously optimized CS-PEI-GO coating on GMF membranes was investigated to understand the behavior of the coating with different water contaminants under a wide range of water chemistries. The coatings were effective in removing heavy metals, such as Cr, Cu and Pb, nitrate, and bacteria from the solutions containing these contaminants in DI water. The coating was tested under different water chemistries, pH, salinity, hardness, and alkalinity and shown to perform consistently for a wide range of water chemistries. Coated filters were investigated against real environmental waters, where they were effective in removing Cr, Cu, HPC and bacteriophage despite the presence of complex water chemistries. In the desorption studies, 0.1 M HCl was found to be the best desorption agent, however it was not very effective to regenerate all binding sites in the coating, indicating that the coating cannot be completely regenerated. The accelerated aging experiments indicated that the long-term storage of the coated filters is possible for up to 9 months without any special storing procedure (a vacuum or under dry or temperature regulated conditions). As a summary, CS-PEI-GO coating has emerged as a promising nanocomposite coating that can be used as a multifunctional water treatment technique. We were able to demonstrate that it can remove a variety of contaminants and is effective in many water chemistries. This coating can surely be used in practical applications for indirect potable reuse water treatments and in many other water treatment applications.

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Uncited references

[59–67].

Declaration of Competing Interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jwpe.2019.100967.

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