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Novel adsorptive ultrafiltration membranes derived from polyvinyltetrazole-co-polyacrylonitrile for Cu(II) ions removal

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ABSTRACT

Novel adsorptive ultrafiltration membranes were manufactured from synthesized polyvinyltetrazole-co-polyacrylonitrile (PVT-co-PAN) by nonsolvent induced phase separation (NIPS). PVT-co-PAN with various degree of functionalization (DF) was synthesized via a [3 + 2] cycloaddition reaction at 60°C using a commercial PAN. PVT-co-PAN with varied DF was then explored to prepare adsorptive membranes. The membranes were characterized by surface zeta potential and static water contact angle measurements, scanning electron microscopy as well as atomic force microscopy (AFM) techniques. It was shown that PVT segments contributed to alter the pore size, charge and hydrophilic behavior of the membranes. The membranes became more negatively charged and hydrophilic after addition of PVT segments. The PVT segments in the membranes served as the major binding sites for adsorption of Cu(II) ions from aqueous solution. The maximum adsorption of Cu(II) ions by the membranes in static condition and in a continuous ultrafiltration of 10 ppm solution was attained at pH = 5. The adsorption data suggest that the Freundlich isotherm model describes well Cu(II) ions adsorption

on the membranes from aqueous solution. The adsorption capacity obtained from the Freundlich isotherm model was 44.3 mg g^{-1} ; this value is higher than other membrane adsorption data reported in the literature. Overall, the membranes fabricated from PVT-co-PAN are attractive for efficient removal of heavy metal ions under the optimized conditions.

Keywords: PVT-co-PAN polymer; adsorptive membrane; copper adsorption; dynamic ultrafiltration; regeneration.

1. Introduction

The scarcity of fresh water is raising concern worldwide with the increase of industrial activities and environmental pollution [1]. Industrial wastewater is a major source for spreading heavy metal ions (Copper (Cu), nickel (Ni), lead (Pb), mercury (Hg) and chromium (Cr)) pollution in the accessible water sources [2-4]. Heavy metals are harmful at high concentration and they have a tendency to accumulate in living organisms. Among these heavy metals, Cu is an important trace element for the progress of plants, animals and human beings [5]. However, the contamination of aqueous systems by copper creates considerable risks to the environment in developing countries where the regulations are not strict. The accumulation of Cu higher than the permissible limit (1.3 mg/L , according to Environmental protection agency) in the human body can be responsible for kidney damage, severe irritation of the gastrointestinal and nerve systems [5,6]. Therefore, the removal of Cu(II) ions from contaminated water and aqueous solutions is of great interest for the researchers working in water treatment technology.

Reverse osmosis (RO), nanofiltration (NF) and electrodialysis (ED) have been explored for removal of metal ions from contaminated water [7-9]. RO is used to concentrate metal ions from aqueous solutions by allowing permeation of water, but the isolation of dissolved ions is further required. ED has been explored for separation of monovalent ion from multivalent ions in a

mixture solution. However, metal ions solutions of low concentration are necessary for an efficient use of this process [9]. Due to these reasons, it is desirable to develop an alternate process to separate similar sized and charged metal ions present in aqueous or wastewater solutions.

Adsorbents based on functionalized polymers have been reported as effective materials for specific binding of similar charged metal ions [3,10]. Chen et al. reported a polyvinyltetrazole-grafted resin for removal of heavy metal ions from aqueous solution. The grafted resin was efficient for removal of Cr(III) and Cu(II) ions [3]. Thus, adsorption has been considered as an efficient and economical alternative for removal of metal ions from aqueous/wastewater solutions. The use of adsorbents in fixed-bed columns or other flow-through system may have diffusional limitations for removal of heavy metal ions such as , the pressure drop can be high for columns with small particles and long desorption times might be required [11].

In the view of above mentioned difficulties, researchers have reported adsorptive membranes for removal of metal ions from aqueous/wastewater solutions. The adsorptive membranes hold specific functional groups on the surface, which can bind the metal ions through ion exchange or surface complexation, even though the pore size of these membranes is larger than the size of the metal ions [5,12-16]. Weidman et al. reported nanostructured adsorptive membranes for binding of Cu(II) ions from aqueous solutions. The nanostructured membranes were fabricated using a polyisoprene-b-polystyrene-b-poly(N,N-dimethylacrylamide) triblock polymer by self-assembly and nonsolvent induced phase separation. Subsequently, acid hydrolysis was conducted in 6 M HCl solution to introduce carboxylic acid ($-\text{COOH}$) groups. The membranes had high Cu(II) ions binding capacity, which did not change after regeneration in acidic aqueous solution [12]. The polymer used for the fabrication of these membranes was

synthesized by a tedious method and is not readily available. Farjadian et al. functionalized propylene microfiltration membranes via grafting a layer of poly(aminoethyl methacrylate) brushes using a UV polymerization technique. The active sites for adsorption of Cu(II) ions were created by further chemical reaction between free amino groups of comb-like brush layer and salicylaldehyde. Schiff-base anchored membranes were effective for capturing Cu(II) ions from aqueous solution under optimized experimental conditions [14]. Hence, the functionalized adsorptive polymeric membranes can be suitable for effective removal of metal ions from aqueous/wastewater solutions either by static or dynamic adsorption. Polyacrylonitrile is an extensively used polymer for fabrication of micro- and ultra-filtration membranes because of low cost, high mechanical strength and good solvent stability [17]. The nitrile ($-\text{CN}$) groups of PAN are easily modified via hydrolysis and a [3+2] cycloaddition reaction at elevated temperature for adsorption of heavy metal ions [3,18]. Recently, tetrazole groups were grafted on the resin by conducting a [3+2] cycloaddition reaction at 40°C. The tetrazole moieties anchored resin had the capability to adsorb metal ions in excess quantity compared with the unfunctionalized resin [3].

By considering the above beneficial facts related to adsorptive membranes and the tetrazole groups, efforts in this study were made to fabricate novel adsorptive ultrafiltration membranes using PVT-co-PAN with varied degrees of functionalization. The adsorptive membranes containing various amount of PVT segments have been prepared from 12 wt% PVT-co-PAN polymer solution in N,N-dimethylformamide by water induced phase separation. The membranes were characterized in detail to examine their charge behaviour, surface morphology and hydrophilicity. The fully characterized membranes were then applied in adsorptive removal of Cu(II) ions from aqueous solution in static and dynamic adsorption at a specific pH.

2. Experimental

2.1. Chemicals and reagents

PAN was supplied by Kelheim Fibers GmbH, Germany. Sodium azide (NaN_3), ammonium chloride (NH_4Cl) and copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$) were purchased from Sigma–Aldrich. Lead nitrate ($\text{Pb}(\text{NO}_3)_2$) and tetrahydrofuran (THF) were acquired from Fisher Scientific. Dimethyl sulfoxide (DMSO), N,N–dimethylacetamide (DMAc), N,N–dimethylformamide (DMF), N-methyl-pyrrolidone (NMP) and chloroform (CHCl_3) were received from Sigma–Aldrich and used without purification. All other chemicals and reagents were of analytical grade. DI water purified with a Milli-Q system (Millipore, Inc.) was used in this study.

2.2. Synthesis of polyvinyltetrazole-grafted PAN

Polyvinyltetrazole–grafted PAN (PVT–co–PAN) was synthesized by a [3+2] cycloaddition reaction of nitrile groups of PAN with NaN_3 at 60°C [18]. The detailed protocol for synthesis of PVT–co–PAN is included in **Section S1** of ESI.

2.3. Membrane preparation

PVT–co–PAN based porous membranes were prepared by water induced phase separation. 12 g PAN or PVT–co–PAN polymer was dissolved in 88 ml of DMF under mechanical stirring at 50°C for 24 h to obtain the casting solution. This solution was further ultrasonicated for 30 min and left unstirred for at least 6 h to degas the solution. Afterward, the solution was cast onto a glass plate using a casting knife with a gate height of 200 μm . After 30 s evaporation of solvent at room temperature (RT), the glass plate along with polymer solution film was immersed in a DI water coagulation bath until the membrane was detached. The prepared membrane was taken out

and kept in water bath for 24 h to remove traces of solvent. The same procedure was adopted to fabricate other membranes from PVT-co-PAN with varied degree of functionalization (4.2, 12 and 24%). The membranes were stored in DI water before characterization and further use. The prepared membranes are denoted as membrane M0, M1, M2 and M3, respectively.

The hollow fiber membranes were fabricated using a laboratory spinning apparatus as described in a previously published paper [19]. The bore fluid and polymer solution flow were carefully controlled during the spinning process. The bore fluid was pumped using a HPLC pump (Knauer Scientific Instruments, Germany). The dope flow was regulated through a nitrogen pressure-induced flow controlled by a digital thermal mass flow meter (Bronkhorst, El-flow, Germany). The hollow fiber was prepared at 5 ml min⁻¹ bore flow (DI water) and 12 wt% polymer (PVT-co-PAN) solution flow at 3 ml min⁻¹. DI water was used as the bore fluid and the fiber was precipitated in a rotating water bath at 23°C. An air gap of 10 cm was used between spinneret and water bath. The relative humidity in the air gap was 55%. Finally, the fibers were placed in DI water for minimum two days to remove any residual solvent and the hollow fibers were dried at 23°C for 24 h.

2.4. Characterization of membranes

The detailed procedure to determine water uptake, contact angle, zeta potential, bound and free water fraction (%) of the membranes are given in Section S2 of ESI. The surface morphology of the membranes was assessed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. The experimental details are included in **Section S2** of ESI.

2.5. Preparation of metal ion solutions

The stock solution (100 ppm) of Cu(II) and Pb(II) ions were prepared separately by dissolving an appropriate amount of Cu(NO₃)₂ · 2.5 H₂O and Pb(NO₃)₂ salt in DI water. Cu(II)

and Pb(II) ions solution of various concentration (5, 10, 20 and 40 ppm) were obtained after proper dilution with DI water.

2.6. Batch adsorption experiments

The batch adsorption experiments were conducted to determine adsorption capacity of the membranes for removal of Cu(II) and Pb(II) ions from aqueous solutions. Batch experiments were performed in 25 ml capacity glass vials containing 20 ml solution of 10 ppm Cu(II) or Pb(II) ions at pH = 5 and 4.1 cm² membrane (~10 mg). The glass vials were kept on a shaker for 24 h at RT. Thereafter, the membrane samples were taken out and the concentration of Cu(II) or Pb(II) ions in the supernatant solutions was determined using a Varian 720-ES inductively coupled plasma–optical emission (ICP–OES) spectrometer. The adsorption of Cu(II) or Pb(II) ions (%) by the membranes was calculated using eqn (2):

$$Adsorption(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 is the initial concentration and C_e is the equilibrium concentration of Cu(II) or Pb(II) ions (ppm). In addition, the equilibrium adsorption capacity of the membranes was calculated with help of eqn (3):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (3)$$

where q_e is the equilibrium adsorption capacity (mg g⁻¹), m is the weight of the dried membrane (mg), and V is the volume of the adsorbate solution (L).

The effect of pH on the adsorption capacity of the membranes for Cu(II) ions was studied in the pH range from 2 to 5 by adding the membrane (~10 mg) into the vial containing 20 ml solution of 10 ppm Cu(II) ions. The pH of the solution was adjusted using 1 M HCl solution and the concentration of Cu(II) ions in the remaining solution after 24 h adsorption was determined.

Batch adsorption kinetic experiments were carried out for membranes at fixed concentration of Cu(II) ions (10 ppm) at pH = 5 for different time intervals (0, 4, 12 and 24 h). The initial concentration of Cu(II) ions solution was varied from 5 to 40 ppm to evaluate adsorption isotherms. Desorption of Cu(II) ions from the used membranes was examined in a batch mode with 0.25 M EDTA or HCl solutions. The copper loaded membranes were added into the vials containing 20 ml solution of 0.25 mM EDTA or HCl. The vials with membranes were then placed on a shaker for 24 h to desorb Cu(II) ions. The concentration of Cu(II) ions in the desorption solutions was determined using ICP–OES spectrometer.

2.7. Water permeability

An Amicon cell 8100 (Millipore Corp., USA) connected to a 1 L reservoir and pressurized with nitrogen gas was applied to obtain the pure water permeability of the membranes at 1 bar feed pressure. Prior to the measurements, the membrane samples ((3.9 cm²) were compacted by filtering DI water for 30 min at 2 bar feed pressure. Thereafter, DI water was filtered using the membrane for 30 min at 1 bar and the weight of the collected permeate was measured on a digital balance (Mettler Toledo Inc., UK). The water permeability of the membranes was calculated as follows:

$$P = \frac{V}{tA\Delta p} \quad (4)$$

where V is the volume of DI water (L), t is the permeation time (h), A is the area of the membrane and Δp is the feed pressure (bar). The water permeability of the hollow fibers was determined according to the previously published paper [19].

2.8. Dynamic ultrafiltration of Cu(II) ions solution

A 10 ppm Cu(II) solution was used to determine the adsorption capacity of the membranes in a dynamic ultrafiltration at 1 bar feed pressure. The reservoir and the UF cell were filled with 10

ppm copper solution of pH = 5 and ultrafiltration experiments were conducted for 8 h at 1 bar feed pressure. At the end of each experiment, the concentration of Cu(II) ions in permeate and retentate samples were determined by a ICP–OES spectrometer. The adsorption capacity of the membranes for Cu(II) ions was calculated from the change in concentration of Cu(II) ions in solution before and after ultrafiltration. Moreover, the adsorption capacity of hollow fiber membranes was estimated by filtering 10 ppm Cu(II) ions solution for 8 h at 0.6 bar feed pressure using small hollow fiber modules [19].

3. Results and discussion

Tetrazoles are heterocyclic compounds in which a five-membered ring contains one carbon and four nitrogen atoms; these compounds can be synthesized *via* a [3+2] cycloaddition of the nitrile group with sodium azide at elevated temperature. The tetrazole groups on the chains of PAN were grafted through a [3+2] cycloaddition of the nitrile group with sodium azide at 60°C (**Scheme 1**). The degree of functionalization (DF) of PAN was monitored by conducting the reaction for 4, 8 and 12 h at 60°C and the DF was calculated from the difference in weight of PAN before and after functionalization. The obtained values are tabulated in **Table S2** of ESI. The DF of PVT-co-PAN increased gradually with reaction time and the highest DF was attained after 12 h. Elemental analysis results are presented in **Table S2** of ESI. The content of N (%) increased whereas the content of C (%) and H (%) was decreased with increase in reaction time. The viscosity of the polymer solutions was measured using a Brookfield CAP 2000 viscometer (Brookfield Engineering Laboratories, Inc.). The viscosity gradually declined with increase in DF of PVT-co-PAN (*cf.* **Table S2**, ESI). However, the reduction in viscosity was minor at 24% DF, this could be due to a slight polymer degradation after 12 h.

3.1. Physicochemical and instrumental characterizations

The water uptake, free and bound water fraction values of the membranes are reported in **Table S3**. The detailed discussion is provided in supporting information. The water contact angle values declined with increasing amount of PVT segments in the matrix of the membranes (**Fig. 1**). This is associated with a formation of a tight hydration layer on the surface of membranes through the binding of water molecules by PVT segments (*cf. above discussion*). The surface free energy values for membranes are also presented in **Fig. 1**. The surface free energy increased with content of PVT segments in the matrix of the membranes. The lowest water contact angle ($\sim 41^\circ$) and the maximum surface free energy was attained for membrane M3 due to its improved hydrophilicity. The obtained results suggest that the hydrophilicity of the membranes was influenced by the amount of PVT segments.

The average zeta potential values for membranes with varied amount of PVT at pH = 3, 5 and 7 are presented in **Fig. S6** of ESI. The zeta potential of the membrane M0 at pH = 3 is positive and the zeta potential values of this membrane are negative at pH = 5 and 7. The zeta potential values for membrane M1, M2 and M3 are higher than that of the membrane M0 at pH = 5 and 7. This can be attributed to the change in charge behaviour of PVT moieties with solution pH. TZH moieties become negatively charged with change in pH from 3 to 5 due to the deprotonation of TZH moieties [20]. The deprotonation of PVT occurred and the membranes became negatively charged when pH was changed from 3 to 5. Thus, a negative zeta potential was achieved for membrane M1, M2 and M3 at pH = 5. In addition, the zeta potential of the membranes depended on the amount of PVT and the highest zeta potential value was achieved for membrane containing maximum amount of PVT (M3). Furthermore, PVT moieties in the matrix of membranes could be more deprotonated with change in pH from 5 to 7 because pK_{a2} of TZH is 4.92 [20]. Thus, the zeta potential values for membrane M1, M2 and M3 was increased with

increase in pH. The zeta potential values for membrane M3 were -29.7 and -44.3 mV at pH = 5 and 7 (**Table S3**, ESI).

Fig. 2 shows the surface SEM images of the membranes with varied content of PVT and the fabricated membranes have microporous surfaces. The membrane M0 has uniform microporous surface with high number of pores. However, the number of pores in the skin layer of the membranes is reduced with increase in amount of PVT. The porosity of the membranes decreased which led to decline in their water permeability. The membrane M3 seems to be more compact than the membrane M0. The slow precipitation of the hydrophilic polymer solution might be one reason for simultaneously decline in number of pores and porosity at high amount of PVT in the matrix of membranes.

3.2. Adsorption capacity of the membranes

The adsorption capacity of the membranes for Cu(II) and Pb(II) ions was investigated with 10 ppm solution of metal ions (Cu(II) or Pb (II)) at pH = 5. The obtained results are presented in **Fig. 3**. The membranes containing PVT segments had a significantly higher adsorption for Pb(II) and Cu(II) ions than the pristine membrane M0. This confirms that the introduction of PVT segments in the matrix of membranes indeed improved the adsorption of Cu(II) and Pb(II) ions from aqueous solution at pH = 5. It was also observed that the adsorption of metal ions by the membranes was enhanced with increasing content of PVT segments. This can be attributed to increase in active sites for adsorption of metal ions with PVT segments in the membranes (*cf.* **Table S2** and **Fig. S6** of ESI). The maximum adsorption of Cu(II) and Pb(II) ions was 98.5 % and 51 % for membrane M3. Moreover, the adsorption of Cu(II) ions was higher than the adsorption of Pb(II) ions under similar experimental conditions. The difference in adsorption capacity of the membranes might be due to the different electrostatic behaviour of the negatively

charged five-membered tetrazole moieties with Cu(II) or Pb(II) ions at pH = 5. Because of high adsorption of Cu(II) ions by the membranes, all other studies were explored in details for adsorption of Cu(II) ions from aqueous solution.

The pH is an important parameter that affects adsorption capacity of PVT containing membranes because the pH of the solution does not only influence the ionic speciations but also the dissociation of tetrazole moieties in the matrix of membranes [3,21,22]. The adsorption capacity of the membranes was determined and the obtained values are depicted in **Fig. S7** of ESI. The adsorption capacity (mg g^{-1}) of the membranes towards Cu(II) ions was enhanced with increase in pH from 2 to 5. The maximum adsorption of Cu(II) ions by the membranes was obtained at pH = 5. The variation in adsorption capacity of the membranes at varied pH could be relevant to the characteristic of tetrazole moieties in the matrix of membranes. Tetrazole (TZh) is an amphoteric compound in which the protonation occurs in two steps (*i.e.*, $\text{TZh}^{2+} = \text{TZh} = \text{TZh}^-$, $\text{pK}_{\text{a1}}: 0.8 \pm 0.1$, $\text{pK}_{\text{a2}}: 4.73 \pm 0.1$) in acidic and basic medium [20]. Tetrazole moieties in the membranes were protonated at high acidic pH = 2 and therefore, the active sites for adsorption of Cu(II) ions were reduced. The adsorption of Cu(II) ions on the membranes at pH = 4 occurred via chelation due to the formation coordination bond after deprotonation of TZh_2^+ moieties [3,22]. TZh moieties in the membranes were converted into the negatively charged five-membered rings as the pH changed from 4 to 5. Thus, the strong adsorption of Cu(II) ions on the membranes at pH = 5 occurred via electrostatic interactions (*cf.* **Fig. 4**). The obtained results clearly show the maximum adsorption of Cu(II) ions at pH = 5.

Fig. 5 shows the adsorption of Cu(II) ions by the membranes with time. The adsorption of Cu(II) ions increased with time and the equilibrium time for maximum adsorption of Cu(II) ions was obtained in about 24 h. The adsorption of Cu(II) ions by the membranes depended on the

metal ion concentration in solution (**Fig. 6 A**). The adsorption of Cu(II) ions gradually declined with increase in concentration of Cu(II) ions. This is correlated to the availability of binding sites in the membranes for adsorption of Cu(II) ions. The adsorption of Cu(II) ions was high at low concentration because the binding sites were available in excess for copper adsorption. The membrane M3 adsorbed 98.7% copper from 5 ppm solution at pH = 5.

3.3. Adsorption isotherms

The adsorbed amount of Cu(II) ions (mg g^{-1}) at varied concentration (ppm) are presented in **Fig. S8** of ESI. The adsorption isotherms for copper adsorption by the membrane M3 are shown in **Fig. S9** of ESI as a representative example. The Langmuir isotherm model presents a homogeneous system with single layer adsorption. The Langmuir isotherm model is given as follows [23]:

$$\frac{1}{q_e} = \frac{1}{K_L q_{\max}} \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (5)$$

where $q_{\max}$ is the maximum adsorbed amount of Cu(II) ions by the membranes at equilibrium (mg g^{-1}) and K_L is the Langmuir constant.

The Freundlich isotherm model is used to describe a heterogeneous system usually in multiple layer adsorption. The Freundlich isotherm model is given as follows [24]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where K_F and n are the Freundlich constants. The Langmuir and Freundlich isotherm models were applied and the obtained parameters are tabulated in **Table 1**. The Freundlich isotherm model fitted well for the adsorption of Cu(II) ions (the correlation coefficient; R^2 : 0.9434, 0.9898 and 0.978). The adsorption of Cu(II) ions by the membranes is heterogeneous. The K_F and n values for membrane M3 was 44.2 mg g^{-1} and 4.97, which are the highest values. The

adsorption capacity of the membrane M3 (44.2 mg g⁻¹) is higher compared with other reported membranes in the literature (**Table 2**) [2,13,25-27].

3.4. Desorption of Cu(II) ions in various solutions

For practical application of the membranes, it is necessary to regenerate the membranes in a suitable desorption solution for reuse [4,25,28]. Both HCl and EDTA (0.25 mM) solutions were used for desorption of Cu(II) ions from the membranes. The obtained results are presented in **Fig. 6B**. EDTA and HCl solution desorbed Cu(II) ions, but the 0.25 mM EDTA solution was more effective. About 96 % Cu(II) ions were desorbed from membrane M1 when this membrane was kept in a 0.25 mM EDTA solution for 24 h. The rate of desorption of Cu(II) ions from high copper loaded membrane M2 and M3 was slightly reduced in 0.25 mM EDTA solution.

3.5. Performance of the membranes

The water permeability was measured to evaluate the effect of PVT segments in the matrix of the membranes. The obtained data are presented in **Fig. 7**. As can be seen, the water permeability of the membranes steadily decreased with increasing content of PVT segments. This is attributed to the decreased porosity of the membranes at high content of PVT segments. The water permeability of the membrane M0 was 353 L m⁻² h⁻¹ bar⁻¹, this is highest value due to the high number of pores in the matrix of the membrane M0 (*cf.* **Fig. 2**). The water permeability of the membrane M3 was 153 L m⁻² h⁻¹ bar⁻¹, which is the lowest value of the prepared membranes. The water permeability of the membranes is appropriate for their efficient use in filtration processes at low feed pressure. The well characterized membranes were explored in ultrafiltration experiments of 10 ppm Cu(II) ions solutions at pH = 5 and 1 bar feed pressure to find their binding capacity for Cu(II) ions. The Cu(II) ions binding capacity of the membranes

after 8 h filtration is presented in **Fig. 7**. It can be visualized that the binding capacity of the membranes consistently increased with the amount of PVT segments. The digital photographic images of the membrane M3 before and after ultrafiltration of 10 ppm Cu(II) ions solution as well as desorption in 0.25 mM EDTA solution are shown in **Fig. S10** of ESI. The membrane M3 has an off-white color before ultrafiltration of the copper solution; the membrane color turned to a light blue after filtration because of the binding of Cu(II) ions as shown in middle of **Fig. S10**. This observation confirms high binding capacity of the membranes towards Cu(II) ions during a dynamic filtration. The color of the membrane changed again from light blue to off-white after desorption of Cu(II) ions in 0.25 mM EDTA solution (*cf.* **Fig. S10 (C)**). Thus, the fabricated membranes had good regeneration capability in EDTA solution.

The binding of Cu(II) ions by the membrane M0 was negligible because the binding sites were not available for adsorption Cu(II) ions from aqueous solution. The maximum binding capacity of the membrane M3 for Cu(II) ions was 134.4 mg g⁻¹ after 8 h filtration of 10 ppm solution at pH=5. The increment in active adsorption sites of the membrane M3 was responsible for high binding of Cu(II) ions. The obtained binding capacity of the membrane M3 for Cu(II) ions is higher than the other reported adsorptive membranes in the literature [13,25,29]. Efforts were also made to further enhance binding capacity of the membranes using a highly functionalized PVT-co-PAN. However, the fabrication of the membranes from more than 24 % functionalized PVT-co-PAN was not possible. The binding of Cu(II) ions by the membranes in a continuous ultrafiltration of 10 ppm solution was higher than the binding capacity of the membranes in a static adsorption. It is reported that the external and internal binding sites of the adsorptive membranes in co-adsorption/filtration process can be well utilized by considering an advantage of convective flow in an adsorption system compared with slow diffusion mechanisms

in the batch adsorption [30]. A similar phenomenon occurred during binding of Cu(II) ions by the membranes from 10 ppm solution at 1 bar feed pressure. The binding capacity of the membrane M3 was the highest because Cu(II) ions were tightly bound in excess by external and internal available binding sites of this membrane. These results confirm an efficient binding of copper ions by the membranes in a dynamic filtration of copper solution under the optimized conditions.

3.6. Hollow fiber membranes

PVT-co-PAN with 12% DG was used to prepare hollow fiber membranes by dry-wet spinning. The cross-section, wall and the surface SEM images of the hollow fiber is shown in **Fig. 8**. The wall thickness was $\sim 78 \mu\text{m}$ and the inner diameter was $\sim 1.24 \text{ mm}$. A skin layer appeared on both sides of the membrane wall and a spongy sublayer was attained. Exchange of DMF solvent with DI water took place fast from an internal side of the nascent hollow fiber when the polymer solution was extruded through the spinneret. Then, the exchange started from the outside of the membrane after immersion in the coagulation bath. Thus, a porous wall formed in the middle of the fiber. The porous wall of the membrane can be altered by manipulating the wall thickness and the air gap. The permeability and binding capacity of the hollow fiber membrane was determined after 8 h filtration of 10 ppm solution containing Cu(II) or Pb(II) ions using a hollow fiber module at 0.6 bar feed pressure. The obtained results are presented in **Fig. 9**. The binding capacity of the hollow fibers for Cu(II) and Pb(II) ions was 43.7 and 26.5 mg g^{-1} . The permeability of the hollow fiber membrane for Cu(II) and Pb(II) ions solution was 17.6 and 14.8 $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. These values are much lower than the flat sheet membranes. Therefore, it is important to optimize the membrane fabrication conditions to obtain better permeability and high binding capacity hollow fiber membranes.

4. Conclusions

PVT-co-PAN was synthesized successfully via a [3+ 2] cycloaddition reaction at 60°C. The degree of functionalization of PVT-co-PAN depended on the reaction time; 4.2, 12 and 24% functionalized polymers were obtained after 4, 8 and 12 h reaction at 60°C. The FTIR, NMR and elemental analysis data confirmed grafting of PVT moieties on PAN. The fabricated membranes were porous and the surface pore size altered after introducing PVT segments. The membrane M-3 had lower porosity and the same trend was attained for water permeability. The membranes were hydrophilic and water adsorbed by the membranes through hydrogen bonding interactions. It was observed that the adsorptive membranes were highly selective for adsorption of Cu(II) ions over Pb(II) ions under similar experimental conditions. The maximum binding capacity of the membrane M3 in a static adsorption was 44.3 mg g⁻¹. Freundlich adsorption isotherm explained well the adsorption of Cu(II) ions by the membranes. The membranes were regenerated effectively in 0.25 mM EDTA solution and could be reused. The binding capacity of the membranes in a dynamic ultrafiltration of 10 ppm solution at 1 bar feed pressure and pH = 5 was higher than that of membrane M0. The binding capacity of the membrane M3 after 8 h filtration was 134.4 mg g⁻¹, which is the highest value due to the highest amount of PVT segments in the membrane. Hollow fiber membrane prepared from 12% functionalized PVT-co-PAN was mechanically stable and successfully used in filtration of 10 ppm metal ions solution. The binding capacity of hollow fibers for Cu(II) ions was 43.7 mg g⁻¹. However, the permeability of the hollow fiber membrane is lower than flat sheet membranes. Therefore, optimization of the parameters would be necessary to obtain high water permeability hollow fiber membranes using the functionalized polymer.

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References

- [1] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, *Nature* 452 (2008) 301–310.
- [2] A. Ghaee, M. Shariaty-Niassar, J. Barzin, T. Matsuura, Effects of chitosan membrane morphology on copper ion adsorption, *Chem. Eng. J.* 165 (2010) 46–55.
- [3] Y. Chen, M. He, C. Wang, Y. Wei, A novel polyvinyltetrazole-grafted resin with high capacity for adsorption of Pb(II), Cu(II) and Cr(III) ions from aqueous solutions, *J. Mater. Chem. A* 2 (2014) 10444–10453.
- [4] K.K.R. Tetala, D.F. Stamatialis, Mixed matrix membranes for efficient adsorption of copper ions from aqueous solutions, *Sep. Purif. Technol.* 104 (2013) 214–220.
- [5] M. Jiang, J. Wang, L. Li, K. Pan, B. Cao, Poly(N,N-dimethylaminoethyl methacrylate) modification of a regenerated cellulose membrane using ATRP method for copper(II) ion removal, *RSC Adv.* 3 (2013) 20625–20632.
- [6] A.B. Dichiaro, M.R. Webber, W.R. Gorman, R.E. Rogers, Removal of copper ions from aqueous solutions via adsorption on carbon nanocomposites, *ACS Appl. Mater. Interfaces* 7 (2015) 15674–15680.

- [7] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science* 333 (2011) 712–717.
- [8] L. Ouyang, R. Malaisamy, M.L. Bruening, Multilayer polyelectrolyte films as nanofiltration membranes for separating monovalent and divalent cations, *J. Membr. Sci.* 310 (2008) 76–84.
- [9] J. Lambert, M. Avila-Rodriguez, G. Durand, M. Rakib, Separation of sodium ions from trivalent chromium by electrodialysis using monovalent cation selective membranes, *J. Membr. Sci.* 280 (2006) 219–225.
- [10] X.P. Zhang, F.Q. Liu, C.Q. Zhu, C. Xu, D. Chen, M.M. Wei, J. Liu, C.H. Li, C. Ling, A.M. Li, X.Z. You, A novel tetraethylenepentamine functionalized polymeric adsorbent for enhanced removal and selective recovery of heavy metal ions from saline solutions, *RSC Adv.* 5 (2015) 75985–75997.
- [11] R.J. Gohari, W.J. Lau, E. Halakoo, A.F. Ismail, F. Korminouri, T. Matsuura, M.S.J. Gohari, M.N.K. Chowdhury, Arsenate removal from contaminated water by a highly adsorptive nanocomposite ultrafiltration membrane, *New J. Chem.* 39 (2015) 8263–8272.
- [12] J.L. Weidman, R.A. Mulvenna, B.W. Boudouris, W.A. Phillip, Nanostructured membranes from triblock polymer precursors as high capacity copper adsorbents, *Langmuir* 31 (2015) 11113–11123.
- [13] E. Salehi, S.S. Madaeni, L. Rajabi, V. Vatanpour, A.A. Derakhshan, S. Zinadini, S. Ghorabi, H.A. Monfared, Novel chitosan/poly(vinyl) alcohol thin adsorptive membranes modified with amino functionalized multi-walled carbon nanotubes for Cu(II) removal from water: Preparation, characterization, adsorption kinetics and thermodynamics, *Sep. Purif. Technol.* 89 (2012) 309–319.

- [14] F. Farjadian, S. Schwark, M. Ulbricht, Novel functionalization of porous polypropylene microfiltration membranes: via grafted poly-(aminoethyl methacrylate) anchored Schiff bases toward membrane adsorbers for metal ions, *Polym. Chem.* 6 (2015) 1584–1593.
- [15] H. Yoo, S.Y. Kwak, Surface functionalization of PTFE membranes with hyperbranched poly(amidoamine) for the removal of Cu^{2+} ions from aqueous solution, *J. Membr. Sci.* 448 (2013) 125–134.
- [16] M. R. Kotte, A. T. Kuvarega, M. Cho, B.B. Mamba, M.S. Diallo, Mixed matrix PVDF membranes with in situ synthesized PAMAM dendrimer-like particles: A new class of sorbents for Cu(II) recovery from aqueous solutions by ultrafiltration, *Environ. Sci. Technol.* 49 (2015) 9431–9442.
- [17] N. Scharnagl, H. Buschatz, Polyacrylonitrile (PAN) membranes for ultra- and microfiltration, *Desalination* 139 (2001) 191–198.
- [18] M.R. Huang, X.G. Li, S.X. Li, W. Zhang, Resultful synthesis of polyvinyltetrazole from polyacrylonitrile, *React. Funct. Polym.* 59 (2004) 53–61.
- [19] R. Hilke, N. Pradeep, P. Madhavan, U. Vainio, A.R. Behzad, R. Sougrat, S.P. Nunes, K.–V. Peinemann, Block copolymer hollow fiber membranes with catalytic activity and pH-response, *ACS Appl. Mater. Interfaces* 5 (2013) 7001–7006.
- [20] G.I. Koldobskii, V.A. Ostrovskii, Acid-base properties of five-membered nitrogen-containing heterocycles, *Chem. Heterocycl. Compd.* 5 (1998) 469–480.
- [21] Y. Wang, H. Chen, Y. Xu, J. Sun, L. Bai, R. Qu, D. Wang, L. Yu, Synthesis of polyvinyltetrazole resin by combination of RAFT polymerization and click chemistry for adsorption of Hg(II), *J. Macromol. Sci. Part A: Pure and Appl. Chem.* 52 (2015) 707–712.

- [22] S. Yan, M. Zhao, G. Lei, Y. Wei, Novel tetrazole-functionalized absorbent from polyacrylonitrile fiber for heavy-metal ion adsorption, *J. Appl. Polym. Sci.* 125 (2012) 382–389.
- [23] S. Deng, R. Bai, J.P. Chen, Aminated polyacrylonitrile fibers for lead and copper removal, *Langmuir* 19 (2003) 5058–5064.
- [24] H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.* 57 (1906) 385–470.
- [25] Z.Y. He, H.L. Nie, C. Branford-White, L.M. Zhu, Y.T. Zhou, Y. Zheng, Removal of Cu^{2+} from aqueous solution by adsorption onto a novel activated nylon-based membrane, *Bioresour. Technol.* 99 (2008) 7954–7958.
- [26] A.R. Cestari, E.F.S. Vieira, J.D.S. Matos, D.S.C. dos Anjos, Determination of kinetic parameters of Cu(II) interaction with chemically modified thin chitosan membranes, *J. Colloid Interf. Sci.* 285 (2005) 288–295.
- [27] Y. Bao, X. Yan, W. Du, X. Xie, Z. Pan, J. Zhou, L. Li, Application of amine-functionalized MCM-41 modified ultrafiltration membrane to remove chromium (VI) and copper (II), *Chem. Eng. J.* 281 (2015) 460–467.
- [28] C. Liu, R. Bai, Adsorptive removal of copper ions with highly porous chitosan/cellulose acetate blend hollow fiber membranes, *J. Membr. Sci.* 284 (2006) 313–322.
- [29] C. Magnenet, F.E. Jurin, S. Lakard, C.C. Buron, B. Lakard, Polyelectrolyte modification of ultrafiltration membrane for removal of copper ions, *Colloids and Surfaces A: Physicoch. Eng. Aspects* 435 (2013) 170–177.
- [30] E. Salehi, S.S. Madaeni, L. Rajabi, A.A. Derakhshan, S. Daraei, V. Vatanpour, Static and dynamic adsorption of copper ions on chitosan/polyvinyl alcohol thin adsorptive

membranes: Combined effect of polyethylene glycol and aminated multi-walled carbon nanotubes, Chem. Eng. J. 215–216 (2013) 791–801.

ACCEPTED MANUSCRIPT

Scheme 1. Reaction route for preparation of PVT-co-PAN from PAN via a [3+2] cycloaddition reaction at 60°C.

Table 1. Values of the parameters associated with the Langmuir and Freundlich models for membranes.

Membrane	Langmuir model			Freundlich model		
	q_m (mg g ⁻¹)	K_L (ml mg ⁻¹)	R^2	K_F (mg g ⁻¹)	n	R^2
M1	58.47	0.187	0.9287	12.1	2.21	0.9434
M2	56.48	0.248	0.9256	23.2	3.05	0.9898
M3	53.45	0.979	0.972	44.3	4.97	0.978

Table 2. Comparison of adsorption capacity of the fabricated membrane for Cu with reported membranes in the literature.

Membrane	Cu(II) ions adsorption capacity (mg g ⁻¹)	Ref. No.
Chitosan	5.9	[2]
Novel chitosan-PVA	11.1	[13]
Activated Nylon	10.3	[25]
Chemically modified chitosan	18.2	[26]
PVDF-aminated MCM-41	3.7	[27]
PVT-co-PAN	44.2	This work

Fig. 1. Water contact angle and the surface free energy values for PVT-co-PAN derived membranes.

Fig. 2. The top surface SEM images for membrane: (A) M0; (B) M1; (C) M2 and (D) M3.

Fig. 3. The adsorption of Cu(II) and Pb(II) ions by the membranes at pH = 5 (initial concentration: 10 ppm; contact time: 24 h and temperature: 23°C).

Fig. 4. Schematic presentation for adsorption of Cu(II) ions by the membranes from aqueous solution at pH = 5.

Fig. 5. Effect of contact time on the adsorption capacity of membranes for Cu(II) ions (Initial concentration: 10 ppm; pH = 5 and temperature: 23°C).

Fig. 6. (A) Adsorption of Cu(II) ions by the membranes at varied concentration (ppm) (contact time: 24 h; pH =5 and temperature: 23°C) and (B) the desorption efficiency of HCl and EDTA to remove the adsorbed Cu(II) ions from membranes.

Fig. 7. The water permeability and binding capacity of membranes (mg g^{-1}) for Cu(II) ions at 1 bar feed pressure (Initial concentration: 10 ppm; pH = 5 and temperature: 23°C).

Fig. 8. The cross-section (A and B) and the surface SEM images for hollow fiber membrane at varied magnifications.

Fig. 9. The permeability and binding capacity of hollow fiber membrane for Pb(II) and Cu(II) ions (Initial concentration: 10 ppm; pH = 5; filtration time: 8 h and feed pressure: 0.6 bar).

Graphical Abstract

Novel adsorptive ultrafiltration membranes based on polyvinyltetrazole-co-polyacrylonitrile polymer were manufactured for an efficient copper removal.

Highlights

- Polyvinyltetrazole (PVT)–co–PAN based ultrafiltration membranes were fabricated.
- PVT segment played a significant role for copper adsorption.
- The binding capacity of PVT-PAN membranes for Cu(II) ions exceeded 130 mg g^{-1} .
- Copper loaded membranes could be regenerated with 0.25 mM EDTA solution.