



Mixed matrix membranes for efficient adsorption of copper ions from aqueous solutions

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ABSTRACT

This work presents adsorption of copper (Cu^{2+}) ions from aqueous solutions using mixed matrix membrane (MMM) and its elution afterwards. The developed flat sheet MMM, comprises of chitosan beads incorporated in Ethylene vinyl alcohol (EVAL) polymer porous matrix and exhibits static Cu^{2+} ion adsorption capacity of 410.5 mg Cu^{2+} ions per g chitosan bead, which is higher than earlier studies reported on chitosan as adsorbent (beads, membranes and hydrogel). Dynamic adsorption of Cu^{2+} ions from aqueous solution with MMM is similar to static adsorption but it is achieved much faster (15 min versus 60 min). Attempts to desorb Cu^{2+} ions from chitosan beads in packed bed column resulted in bead aggregation, restriction of Cu^{2+} ion desorption and reusability of the column. Under similar experimental conditions, Cu^{2+} ions desorbed successfully from the MMM without loss of beads from the membrane structure and the MMM was reusable. Overall, the MMM developed in this study shows superiority over packed bed columns in terms of low pressure drop, high adsorption capacity, successful desorption of Cu^{2+} ions and reusability for few cycles.

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1. Introduction

Waste aqueous process streams generated from industry such as mining, metal plating, surface treatment industry, and electric device manufacturing contain various heavy metals e.g. copper, lead, mercury, etc. that are difficult to remove [1]. These heavy metals are not biodegradable and are a major concern for our environment due to their toxicity, which has adverse effects on living organisms. Removal of such metal ions from contaminated aqueous process streams is carried out by various traditional techniques e.g. chemical precipitation, solvent extraction, adsorption etc. Adsorption has in fact the ability to remove even trace quantities of metal ions [2]. Although various materials e.g. yeast, algae, agricultural wastes, etc. have been evaluated, chitosan with its high ability for metal adsorption caught the attention of researchers [3–9]. Chitosan, a β -(1-4)-linked polysaccharide and the third most abundant polymer after cellulose and chitin, comprises of hydroxyl and amine groups [10,11]. The adsorption of metal ions to chitosan is due to the lone pair of electrons on nitrogen atoms that have strong tendency to form chelation complex with metal ions [12]. The number of amine groups that bound to copper ions can vary depending on pH of the solution. At pH 6–8, there is also a possibility of hydroxyl groups forming chelation complex with metal ions. Due to its chemical and physical properties, chitosan can be

prepared in different forms like chitosan beads [8,13–16], membranes [3,5,10,17–19] etc. For metal ion adsorption, either chitosan bead packed bed columns or chitosan membranes are employed. However both packed bed columns and membranes have certain limitations like e.g. high pressure build-up and low mass-transfer due to lack of convective flow for packed bed columns and low surface area for membranes. So there is a clear need of new technology that could circumvent those issues and achieve high removal of metal ions.

The last decade witnessed the introduction of polymer mixed matrix membranes (MMMs) as an alternative technology for packed bed columns and membranes in the field of biomolecule separations [20–25]. A typical MMM consists of a functional porous or non-porous bead incorporated in a porous membrane. The advantages of MMM are high surface area and high adsorption capacity of beads; easy scale-up, high mass transfer and low pressure drop of the membrane while tightly holding the beads in its porous structure and attaining the efficient adsorption capacity of incorporated beads. Ladhe et al. recently developed thiol functionalized MMM (silica beads as sorbent material) for silver removal from aqueous solutions [26]. This MMM however has the limitation of employing thiol molecules which are toxic to environment and removes metal ions that have specific affinity towards thiol molecules. An alternative approach with no toxic effect to environment, straight forward chemistry and with wider metal ion adsorption capacity is using chitosan beads [27].

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In this work, we report for the first time the development of an MMM containing chitosan bead (20–40 μm size) for efficient adsorption of metal ions from aqueous solutions. For this study, copper ions (Cu^{2+}) are chosen as a model target molecule and EVAL is chosen as polymer material. Taking into account the above mentioned advantages of MMM compared to beads, the MMM prepared in this study is evaluated in terms of adsorption capacity (in comparison with chitosan beads alone), accessibility of chitosan beads, and its reusability. Also the efficiency of MMM against packed bed column in terms of pressure drop and adsorption capacity is validated for the first time.

2. Experimental

2.1. Materials

Chitosan (Molecular weight of ~ 150 KDa), dimethyl sulfoxide (DMSO), 1-octanol, EVAL (a random copolymer of ethylene and vinyl alcohol) with an average ethylene content of 44 mol%), acetic acid, ethanol, sodium hydroxide, Ethylene diamine tetraacetic acid (EDTA) and copper sulfate were all purchased from Sigma Aldrich, The Netherlands. Fresh MilliQ water was used in preparation of all solutions.

2.2. Preparation of chitosan bead

Chitosan beads were prepared with slight modification of a protocol reported elsewhere [28]. Briefly, chitosan (20 g) was dissolved in 5 wt% acetic acid aqueous solution (800 mL) by overnight stirring. The obtained clear solution was taken in a storage tank containing array of syringe needles and placed at a height of 20–25 cm from the coagulation bath containing 650 mL 1 N NaOH solution and 250 mL ethanol. The chitosan solution was added in a drop wise manner from the storage tank to the coagulation bath using syringe needles that resulted in chitosan beads. The formed beads were left overnight in the coagulation bath and later washed with MilliQ water until the pH became neutral. Afterwards, the beads were dried in vacuum for 7 days. To improve the active surface area, provide a better embedding and reduce the diffusive path, the chitosan beads were grinded and fractionated to 20–40 μm size class using a Fritsch analysette shaker stacked with 20 μm and 40 μm sieves.

2.3. Preparation of mixed matrix membrane

EVAL flat sheet MMMs of 400 μm thickness was prepared according to earlier research [20,22,23] as follows: A polymer dope solution comprising 10 wt% EVAL, 80 wt% DMSO and 10 wt% 1-octanol was stirred overnight at 45 $^{\circ}\text{C}$. To this solution, 55 wt% chitosan beads (20–40 μm) (relative to EVAL polymer weight) were added and the solution was stirred for another 24 h at 45 $^{\circ}\text{C}$ to homogenize the solution. After 24 h, the dope solution was left for degassing and subsequently, the MMM's were cast on a glass plate using a 400 μm casting knife and immersed in a coagulation bath containing water as non-solvent at 45 $^{\circ}\text{C}$ until the membrane was obtained. Finally, the membranes were washed with MilliQ water for another 72 h to remove the solvent traces. The bead loading to prepare this MMM was calculated using equation:

$$\text{Loading (\%)} = \frac{W_R}{W_R + W_P} \times 100 \quad (1)$$

where W_R is dry weight of chitosan bead and W_P is dry weight of EVAL polymer.

2.4. Membrane characterization

2.4.1. Scanning electron microscope (SEM)

The membrane structures were investigated by viewing cross sectional area and both the top and bottom surface of the MMM. The membrane was cut into pieces after freeze drying in liquid nitrogen, placed in holders and dried in vacuum. The membranes were gold coated using Balzers Union SCD 040 coater and investigated using Jeol JSM-5600 LV scanning electron microscope.

2.4.2. Membrane permeance

The pure water permeance (P) of MMM was determined using the equation:

$$J = P \cdot \Delta p \quad (2)$$

For this, MilliQ water was pressurized at different transmembrane pressures (0.2, 0.5 and 1 bar) using nitrogen gas through a stack of five MMM in a AMICON dead-end filtration cell. In Eq. (2), J is the clean water flux of the membrane (in $\text{l/m}^2/\text{h}$) and Δp is the transmembrane pressure.

2.5. Non-specific and specific adsorption of copper ions

A EVAL membrane (45 mg), chitosan bead (55 mg) and MMM (100 mg) were suspended in 25 mL of copper solution (3 mg/mL) for 24 h at room temperature on a shaker. After 24 h, the amount of Cu^{2+} ions adsorbed non-specifically on the EVAL membrane (without chitosan bead) and specifically on chitosan bead and MMM were studied using UV–VIS spectrophotometer at a wavelength of 740 nm (the visible region). Our protocol was slightly modified in comparison to earlier reported protocols [18,29] and was as follows: 1 mL of sample solution was mixed with 1 mL of 50 mM EDTA solution and measured with a Varian Cary 300 UV–VIS spectrophotometer at a wavelength of 740 nm. The scan spectrum of EDTA, Cu^{2+} ion, Cu^{2+} –EDTA complex can be found in [supplementary information \(Fig. S1\)](#).

2.6. Adsorption capacity

The adsorption isotherm of Cu^{2+} ions was determined by suspending 55 mg chitosan bead and 100 mg of MMM for 24 h at room temperature on a shaker in 25 mL freshly prepared Cu^{2+} ion solutions with concentrations in the range 0.1–5 mg/mL. After 24 h, the amount of Cu^{2+} ions adsorbed on chitosan beads and MMM were measured with Varian Cary 300 UV–VIS spectrophotometer at a wavelength of 740 nm. The amount (q , mg/g) of Cu^{2+} ions adsorbed on MMM was calculated using the equation:

$$q = \frac{(C_i - C_{eq})V}{W} \quad (3)$$

C_i is initial concentration of Cu^{2+} ions (mg/mL); C_{eq} is concentration of Cu^{2+} ions at equilibrium (mg/mL); V is the volume of sample (mL) and w is weight of the MMM or chitosan bead (g). The kinetics of Cu^{2+} adsorption on MMM was also studied using a solution of Cu^{2+} ions (3 mg/mL). All the experiments were carried out in triplicate and an average of this data (standard deviation is <3%) is presented.

2.7. Desorption of Cu^{2+} ions

The adsorbed Cu^{2+} ions on MMM were desorbed by suspending the membranes in different EDTA concentrations (0.1 mM, 1 mM, 10 mM, 25 mM and 50 mM) on a shaker for 24 h at room temperature. The amount of Cu^{2+} ions desorbed was calculated by dividing the amount of desorbed Cu^{2+} ions with the amount of adsorbed Cu^{2+} ions and is reported in terms of percent (%) eluted.

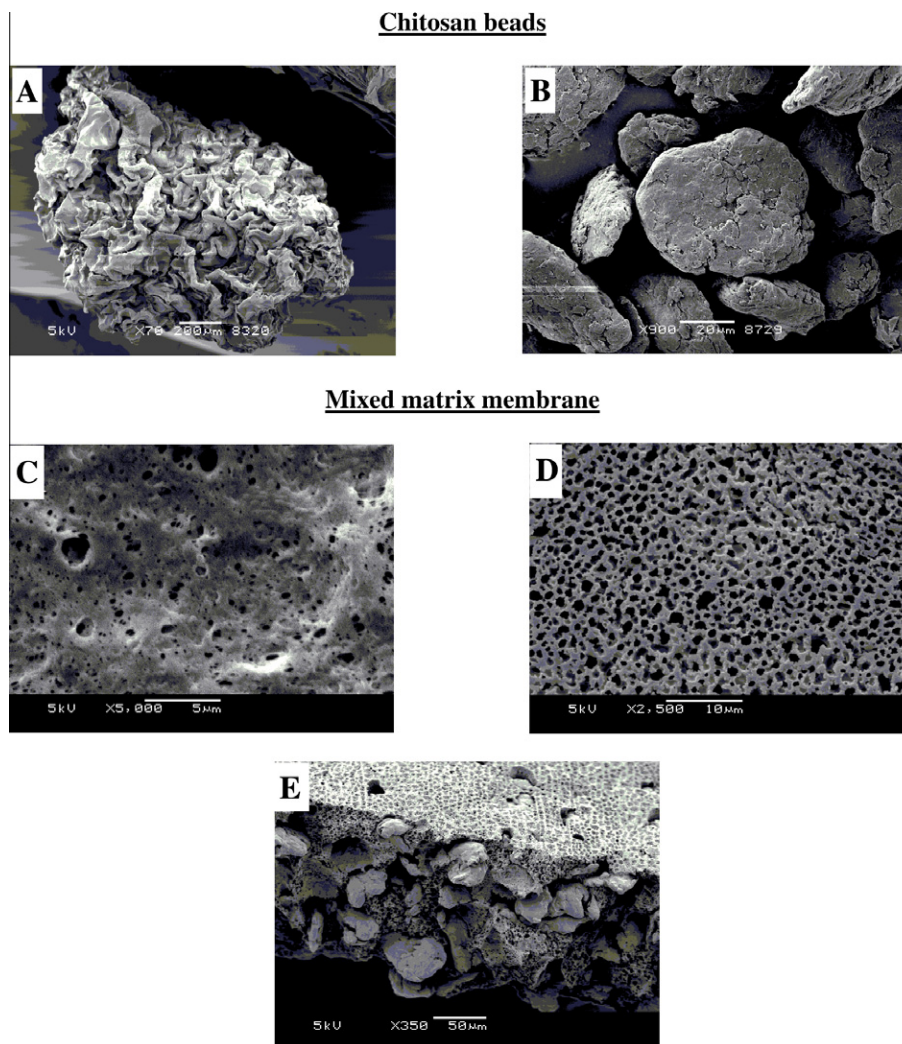


Fig. 1. SEM images of (A) chitosan beads before grinding; (B) chitosan beads after sieved to 20–40 μm (B); (C) top layer of MMM with a magnification of 5000 \times , size bar 5 μm ; (D) bottom layer of MMM with a magnification of 2500 \times , size bar 10 μm ; (E) cross section of MMM with a magnification of 350 \times , size bar 50 μm .

2.8. Pressure drop of MMM vs packed bed

The pressure drop of both packed bed column and MMM was studied by constantly pumping Cu^{2+} ions (3 mg/mL) solution via an HPLC pump through a stack of 10 MMMs (23 mm effective diameter per membrane) or 168 mg chitosan bead (20–40 μm) packed Omnifit column (6.6 mm \times 11 mm) at different flow rates between 0.5 mL/min and 4 mL/min.

2.9. Dynamic adsorption of Cu^{2+} ions on packed bed and MMM

The adsorption capacity of Cu^{2+} ions on chitosan bead (20–40 μm) packed column and MMMs was carried out as follows: A 40 mL solution containing Cu^{2+} ions (3 mg/mL) was recirculated via an HPLC pump through a stack of 10 MMMs (23 mm effective diameter per membrane) or 168 mg chitosan bead (20–40 μm) packed Omnifit column (6.6 mm \times 11 mm) at a flow rate of 2 mL/min. The amount of Cu^{2+} ions adsorbed over a period of time (15, 30, 45, 60 and 90 min) was monitored using offline UV–VIS spectrophotometer at a wavelength of 740 nm (EDTA–copper complex) as mentioned in Section 2.5. The amount of Cu^{2+} ions adsorbed on MMM and packed bed column was eluted using 10 mM EDTA solution. The regeneration and reusability of MMM was studied for up to three consecutive cycles.

3. Results and discussion

3.1. Preparation and characterization of MMM

Chitosan beads of ~ 2000 μm in diameter were first successfully prepared, dried and then they were grinded and sieved to a bead size of 20–40 μm . Fig. 1 depicts the SEM images of chitosan beads before (Fig. 1A) and after sieving (Fig. 1B). These chitosan beads were then embedded in the membrane network with a 55 wt% loading relative to EVAL polymer weight. Higher loading (>55 wt%) of chitosan beads resulted in MMM that were fragile and difficult to handle. Therefore only MMM with loading of 55 wt% were used for further studies. The water permeance for a stack of five such MMMs was 495.2 $\text{L}/\text{m}^2/\text{h}$ at a transmembrane pressure of 1 bar. SEM was employed to visualize the membrane structure (top and bottom surface; Fig. 1C,D) and the distribution of chitosan beads incorporated in the membrane matrix (Fig. 1E, membrane cross sectional area). From the images, it is clear that these membrane possess highly interconnected pores with no macrovoids. The high pore interconnectivity of the membrane is expected to provide good accessibility to the beads in the matrix. Besides, the chitosan beads were tightly embedded and well distributed in the EVAL matrix and no particle loss was observed.

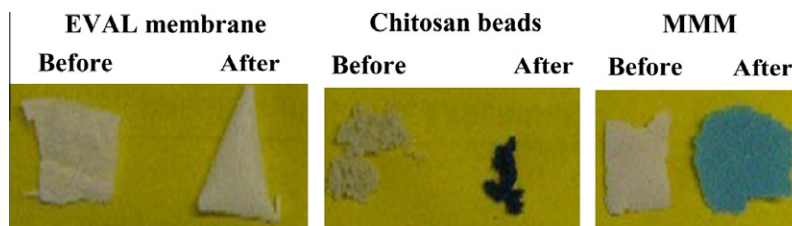


Fig. 2. Photos of EVAL membranes, chitosan beads and MMM before and after Cu^{2+} ion treatment.

Table 1

Non-specific and specific adsorption of Cu^{2+} ions (Initial Cu^{2+} ion concentration was 3 mg/mL).

| Material | Adsorbed Cu^{2+} ions (mg/g adsorbent) |
|--------------------------------------|---|
| EVAL membrane | 0 |
| Chitosan bead (20–40 μm) | 415 |
| MMM | 225 (409.1 mg/g bead) |

3.2. Non-specific and specific adsorption of Cu^{2+} ions

To determine the specific adsorption of Cu^{2+} ions towards MMM, first it is important to determine the non-specific adsorption of Cu^{2+} ions on EVAL membrane alone. Fig. 2 depicts pictures of EVAL membrane, chitosan beads and MMM before and after treatment in Cu^{2+} ion solution. The EVAL membrane alone is white indicating that in the absence of chitosan beads Cu^{2+} ions do not interact with the membrane itself. For the chitosan beads and

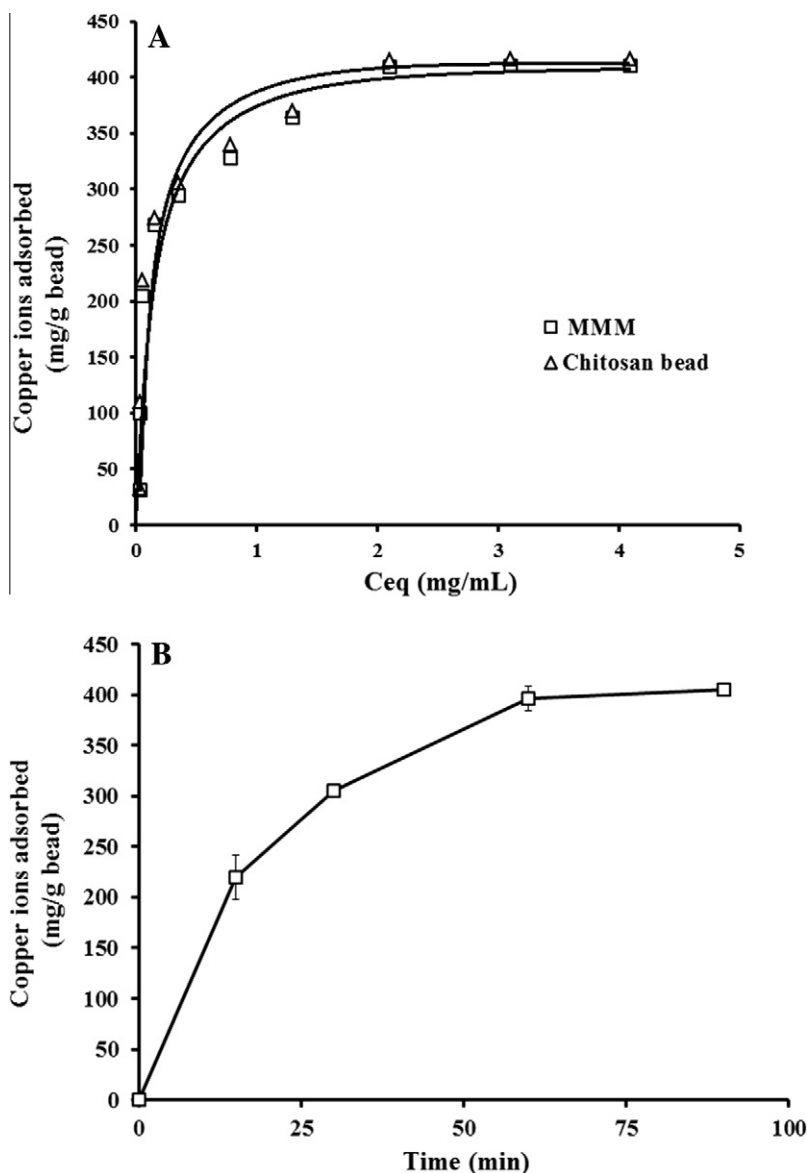


Fig. 3. (A) Adsorption isotherm of Cu^{2+} ions (Cu^{2+} concentration: 0.1–5 mg/mL) after 24 h at room temperature. (B) Adsorption kinetics of Cu^{2+} ions (Cu^{2+} ions concentration was 3 mg/mL) on MMM at room temperature.

Table 2

Comparison of the static maximum adsorption capacity of MMM to maximum adsorption capacity of various chitosan adsorbents reported in literature.

| Adsorbent type | Adsorbed Cu ²⁺ ions (mg/g adsorbent) |
|--|---|
| <i>Beads/flakes</i> | |
| Chitosan (Plain) [32] | 45.2 |
| Chitosan flakes [33] | 20.92 |
| Chitosan bead (<250 μm) [8] | 80.7 |
| Chitosan coated bentonite bead [34] | 12.21 |
| Chitosan coated PVC beads [30] | 87.9 |
| Cross-linked chitosan bead [35] | 130.72 |
| <i>Other forms</i> | |
| Chitosan nanofiber mat [31] | 485.44 |
| Carboxymethyl-chitosan with Cu ²⁺ template [36] | 383.1 |
| Chitosan-cellulose hydrogel [37] | 53.2 |
| <i>Membranes</i> | |
| Chitosan membrane [17] | 5.9 |
| Chitosan coated nylon membrane [18] | 10.79 |
| Chitosan-alumina membrane [38] | 200 |
| Chitosan-cellulose membrane [39] | 35.3–48.2 |
| MMM (this study) | 225.7 (410.5 mg/g bead) |

MMM, a very striking bright blue color is obtained after treatment with copper solution indicating the adsorption of Cu²⁺ ions to both chitosan beads and MMM is successful.

Table 1 presents the quantitative results of Cu²⁺ adsorbed to EVAL membrane alone, chitosan beads and MMM. EVAL membranes have no non-specific adsorption of Cu²⁺ ions (0 mg/g membrane). Chitosan beads adsorb 415 mg/g of Cu²⁺ ions, whereas MMM adsorbed 225 mg/g of Cu²⁺ ions. To compare the MMM capacity with free chitosan beads, the obtained value should be normalized, because the MMM comprises of 55% chitosan beads only and the rest 45% is EVAL polymer that provides the porous network for MMM. The obtained normalized value for MMM is 409.1 mg of Cu²⁺ ions per gram chitosan beads similar to the beads alone implying that chitosan beads in the MMM are equally accessible. The reported values are an average of 3 data points and the standard deviation is <2%.

3.3. Adsorption isotherm and adsorption kinetics

To study the maximum adsorption capacity of MMM, adsorption isotherm and adsorption kinetic experiments were performed using chitosan beads alone and MMM. The adsorption isotherm on both chitosan beads and MMM were carried out in varying Cu²⁺ ion concentrations (0.1–5 mg/mL) for 24 h. The obtained results are plotted as amount of Cu²⁺ ions adsorbed (mg/g bead) versus con-

centration at equilibrium (C_{eq}) in Fig. 3A. The adsorption capacity of the beads in the MMM at different Cu²⁺ ion concentrations is similar as chitosan beads alone indicating that the incorporated chitosan beads are equally accessible in the MMM. The maximum adsorption capacity of MMM is 410.5 mg/g bead. The adsorption isotherm curves appear to be of Langmuir type, suggesting that a monolayer of Cu²⁺ is adsorbed on the non-porous bead surface. It is interesting to see how many Cu²⁺ atoms are adsorbed per N atoms present in chitosan. Taking the content (7.33%) of N atoms in chitosan and deducting ~15% acetylated N atoms, $\sim 2.9 \times 10^{21}$ N atoms are estimated to be present per gram chitosan. From the adsorption isotherm data, $\sim 1.4 \times 10^{21}$ Cu²⁺ atoms were adsorbed per gram chitosan (bead alone or in MMM) indicating that ~2 N atoms in the chitosan are involved to chelate with 1 Cu²⁺ atom at pH 5–5.5, which is in very good agreement with the literature [12].

Fig. 3B depicts the adsorption kinetics curve of Cu²⁺ ions (3 mg/mL concentration) on MMM. The maximum adsorption of Cu²⁺ ions is achieved in 60 min, which is 3–8 folds faster than chitosan beads (<250 μm bead size) [8], chitosan coated PVC beads [30], chitosan nanofiber [31], etc. The adsorption of Cu²⁺ ions onto chitosan beads in the MMM is rapid due to abundant and readily available amino groups in smaller beads (20–40 μm). The possibility of hydroxyl groups forming chelation complex with Cu²⁺ ions can be ruled out because Cu²⁺ ion solution pH is in the range of 5–5.5.

Table 2 compares the maximum Cu²⁺ ion adsorption capacity of our MMM to various other chitosan based adsorbents (beads, membranes, and hydrogels). The MMM has very high Cu²⁺ ion adsorption compared to for e.g. chitosan beads of <250 μm size, chitosan coated on beads, chitosan blended membranes, chitosan-cellulose hydrogels and chitosan membrane itself. This high adsorption capacity of MMM can be attributed to abundant available binding sites of smaller chitosan bead (20–40 μm). Only the electrospun chitosan nanofiber has higher Cu²⁺ adsorption than the MMM, which is possibly due to more open porous structure of the nanofiber mat. However, an important point worth mentioning is that the adsorption of Cu²⁺ to the MMM is much faster (60 min) in comparison to the chitosan nanofiber (8 h [31]).

3.4. Desorption of Cu²⁺ ions and reusability of MMM

Desorption of target molecule and regeneration of the matrix to reuse with maximum adsorption capacity is an important issue. In this study, the desorption of adsorbed Cu²⁺ ions from MMM was carried using various concentrations of EDTA (0.1 mM, 1 mM, 10 mM, 25 mM and 50 mM). The obtained results are shown in Fig. 4. At 0.1 mM and 1 mM concentration only 2.9% and 14.1% of Cu²⁺ ions

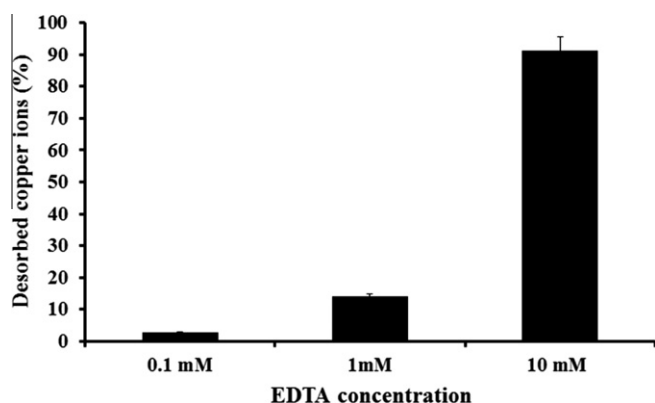


Fig. 4. Desorption of Cu²⁺ ions from MMM using various concentrations of EDTA (0.1 mM, 1 mM and 10 mM).

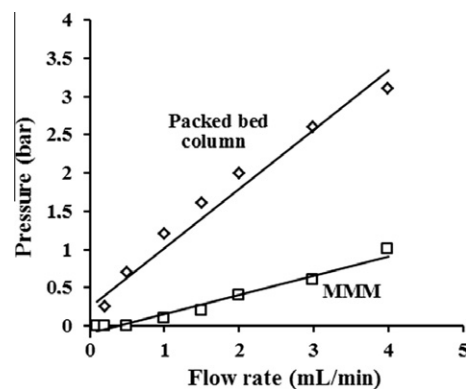


Fig. 5. Pressure drop at different flow rate during dynamic adsorption experiments for packed bed column (column length: 1.3 cm; 6.6 mm × 11 mm) and MMM (10 sheets; 23 mm effective diameter per membrane).

Table 3

Comparison of Cu²⁺ ions adsorbed on chitosan bead in MMM and packed bed column (initial Cu²⁺ ion concentration was 3 mg/mL).

| Material | Amount adsorbed (mg/g bead) | | Recovery (%) |
|-------------------------|-----------------------------|---------|--------------|
| | Static | Dynamic | |
| MMM ^a | 409.1 ^c | 399.4 | 92.2 |
| MMM ^a | | 397.3 | 91.7 |
| MMM ^a | | 396.1 | 91.4 |
| Packed bed ^b | 415 ^d | 330.1 | – |

^a 10 sheet MMM (23 mm effective diameter per membrane, 344.17 mg) was used in membrane holder.

^b Chitosan bead (20–40 μm) was packed in Omnifit column (6.6 mm × 11 mm, 168 mg), effective Column length: 1.3 cm; column volume: 3.7 mL; flow rate: 2 mL/min.

^{c,d} Static adsorption value from adsorption isotherms (Fig. 3A).

were desorbed whereas at 10 mM EDTA, 91.1% of Cu²⁺ ions were eluted from MMM without loss of chitosan beads from the MMM (see [supplementary information](#)). At higher EDTA concentrations (25 and 50 mM) although a high elution of Cu²⁺ ions can be obtained (94.2% and 95.5%), the membrane is damaged resulting in leakage of chitosan beads. These results suggest that 10 mM EDTA is the best concentration to elute Cu²⁺ ions from the MMM.

3.5. Adsorption of Cu²⁺ ions using MMM and packed bed column

The characteristic that shows the superiority of the MMM over packed bed columns is the efficiency in adsorbing target molecules at low pressure drop. To evaluate this, a known concentration of copper solution (3 mg/mL, 40 mL) was recirculated over a stack of 10 MMM (23 mm diameter effective diameter per membrane) and chitosan bead packed bed column (1.3 cm long, 6.6 mm × 11 mm, 3.7 mL column volume) at a fixed flow rate of 2 mL/min [30]. At this flow rate, the packed bed column generates a pressure drop of 2 bar, whereas for MMM it is only 0.4 bar (see Fig. 5).

Table 3 compares the adsorption, desorption and reuse of the MMM and packed bed column. MMM has higher Cu²⁺ ion adsorption (399.4 mg/g chitosan bead) than packed bed column (330.1 mg/g chitosan bead) and almost similar to static adsorption value. The decrease in packed bed column capacity is probably due to limitations in mass transfer, non-convective flow and plugging of packed bed systems. The maximum adsorption of Cu²⁺ ions for both MMM and packed bed column is completed in 15 min, which is three times faster than the static adsorption (60 min). The attempts to desorb Cu²⁺ ions from packed bed column with EDTA failed due to dramatic pressure increase (>20 bar) and leaking of EDTA solution from the column. In fact during elution, the chitosan beads in the column were pressurized and aggregated resulting into a hard “block” material (see images in [supplementary information](#), Fig. S2), which restricted complete desorption process and further reuse of the column. In case of MMM, the Cu²⁺ ions were successfully desorbed with 92.2% recovery. The MMM was tested further for reusability and showed no problems during 3 repeated adsorption and desorption cycles. In fact, the adsorption and desorption of Cu²⁺ ions was similar for all the three cycles (see [supplementary information](#) Fig. S3 for images representing the Cu²⁺ ions adsorption with packed bed column and MMM). All the above results clearly indicate the clear edge of MMM technology over packed bed columns for the adsorption and removal of Cu²⁺ ions from aqueous solutions.

4. Conclusions

In this work, MMM was developed and investigated for adsorption of copper ions from aqueous solutions. In comparison to most existing studies with chitosan sorbents, our MMM has faster

adsorption rate and higher adsorption capacity. Furthermore, the main advantages of our MMM over packed bed column are: faster adsorption and low pressure drop, no aggregation of beads under desorption conditions, successful regeneration and reusability without losing adsorption capacity.

Since chitosan has also the ability to adsorb other metal ions like silver, lead, iron, cadmium, zinc, and chromium [7,27], perhaps our MMM can be used to efficiently adsorb these metals, too. This could be the target of a future work.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2012.11.022>.

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