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Removal and recovery of heavy metals from aqueous solution using β-cyclodextrin polymer and optimization of complexation conditions

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ABSTRACT

Removal of heavy metal contaminants from spent streams can be done in many ways using conventional and membrane techniques. Recovering the heavy metal contaminants is very important to prevent recontamination as well as to realize the potential value. Ultrafiltration (UF) has the potential to offer a simple solution in conjunction with size enhancement of the species to be removed referred to as size-enhanced ultrafiltration in literature. The present study focuses on the use of functionalized cyclodextrin, that is, carboxymethyl β-cyclodextrin (CM-β-CD is a derivative of natural material which is easily available) which not only enables the removal of heavy metal contaminants but also amenable for recovering back the contaminant species and the chelating agent for reuse. The experimental studies were conducted using the ultrafiltration system equipped with 50 kDa MWCO (molecular weight cut-off) PES membrane. The design of experiments was done using central composite design of response surface methodology (RSM). The experiments were conducted as per the statistical design to analyze and optimize the process conditions, such as initial pH of the feed, polymer to metal loading rate and initial concentration of the feed solution. The optimization study was done to maximize the rejection, performance index of the membrane (PFI) and recovery of metal. The analysis of variance was performed to examine the developed regression models. Our studies indicated that the CM-β-CD could remove the heavy metal species as well facilitate the recovery of heavy metal species. The experimental values were consistent with the predicted values, which confirm the good validity of the models developed by RSM.

Keywords: Ultrafiltration; Heavy metals; SEUF; Cu(II); Ni(II); Cyclodextrin

1. Introduction

Toxic heavy metals are non-biodegradable and considered to be one of the foremost pollutants that affect man and animals directly [1]. Heavy metals are commonly encountered in effluents from various industries such as electroplating, mining, textile, dye, paint, etc. The major and toxic heavy metals present in wastewater are copper, nickel, chromium, zinc, etc. The effluents must be treated before being discharged into aquatic systems. Through aquatic animals these heavy metal contaminants enter the food chain. Since humans are at the top of the food chain, they receive the higher impact of the contaminants, due to biomagnifications [2]. The excessive intake of copper causes severe health issues such as vomiting, cramps, convulsions or even death. [3,4]. The nickel ingestion exceeding its critical level causes gastrointestinal distress, pulmonary fibrosis, skin dermatitis and also serious lung and kidney problems [3,5]. The maximum permissible limit of copper and nickel in drinking water is

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0.05 and 0.01 mg/L, respectively, as prescribed by World Health Organization [6,7].

In recent years, membrane separation processes particularly reverse osmosis (RO) has been used for industrial effluents for the recovery and recycle of water. However, RO has its drawbacks with reference to percentage recovery and requirement of high pressure. Even though RO could be effective in removing the metal ions, the separation of the metal ion species is more cumbersome and complicated. Ultrafiltration (UF) is slowly emerging as a promising tool in many separations which utilizes size-based separations such as whey protein separation. The sizes of the hydrated metal ion species, no doubt are much smaller compared with pore sizes of UF membranes and as such these species can pass through the UF membranes [3]. However by enhancing the size of these species by chelation they can be separated because of the enhanced size. In recent years, size enhanced ultra-filtration (SEUF) has been used for the removal heavy metal species using polyethylenimine (PEI) as complexing agent. The process can utilize any of the particulate removal mechanisms such as adsorption/ion exchange/complexation, etc., which results in the enhanced size of the species facilitating the removal in conjunction with UF. It appears quite promising because of low-pressure operation, very high recovery, back-washability and requirement of less footprint area [8–11]. The major advantage is the reversal of the size enhancement by altering the operating conditions, enabling the recovery of contaminant species and the recycling of the size enhancing species, high binding capacity, high removal efficiency and back washability [2,3,10–12]. The purpose of the study is to demonstrate the potential of the SEUF in removal and recovery of contaminant species using a simple derivative of a naturally occurring species and also the recycling of the complexing (size enhancing) species. We have chosen copper and nickel species as 'representative species' because of their presence in industrial waste streams, particularly related to electrochemical processes.

A variety of combination of membrane/complexing agents, such as polyethersulfone (PES) (30 kDa)/polyethylenimine (PEI) [13], (10 kDa)/carboxymethyl cellulose (CMC) [10], acrylnitril copolymer (10 kDa)/CMC [14], Iris (10 and 30 kDa)/PEI [15] have been reported for the removal of copper and nickel from aqueous solutions, mostly in the dead-end mode at the laboratories. No doubt, all these studies have established the 'proof of the concept.' For extending the concept from laboratory to field, one may have to look into the aspects economics and sustainability of pollution abatement.

Cyclodextrins (CD) are cyclic oligosaccharides. β-cyclodextrin (β-CD) is the most widely produced cyclodextrin. It has been mainly used in pharmaceuticals, foods, cosmetics and chemical products [16–18]. It is the most accessible, biodegradable compound. The numerous hydroxyl groups available on CD are active sites and capable of forming the number of linkages. It possesses the capability of complex formation. The secondary and primary hydroxyl groups can form a hydrogen bond and are responsible for the solubility of cyclodextrin and their complexes in water [19]. In the past decades, β-CD has proven applications in the removal of heavy metal ions from wastewater as an adsorbent. β-cyclodextrin as a renewable and biodegradable compound can chelate various metal ions and chemical modification can improve this ability through esterification, etherification, oxidation reactions and cross-linking of hydroxyls outside the interior cavity [16]. Though β-CD derivatives have been used in the removal of heavy metals by adsorption, in the recent years the water-soluble derivatives as chelating agent have attracted the attention of many researchers as a better alternative to ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, CMC, PEI for the separation of heavy metal ions. This present work involves the application of carboxymethyl β-cyclodextrin (CM-β-CD). In this context, it is necessary to recover back the contaminants for possible reuse or isolation. Besides, the recycling of the size enhancing agent would also be an advantage. In view of this, it has been decided to undertake studies utilizing carboxymethyl β-cyclodextrin (CM-β-CD) and demonstrate recovery and recycle of metal species (copper and nickel) in aqueous streams.

2. Materials and methods

2.1. Functionalization of β-cyclodextrin

Functionalization of CD was carried out following the procedure outlined in the literature [20–22]. In the present context β-CD in powder form (AR grade, SRL, Mumbai) was dissolved in concentrated sodium hydroxide solution (about 0.6 M) and reacted with 16% of mono-chloroacetic acid at 50°C for 5 h. The pH of the solution was adjusted to 6–7 after cooling to ambient temperature using concentrated hydrochloric acid. CM- β-CD thus formed was precipitated from this solution by adding methanol. The precipitate was filtered and dried in an oven at 50°C. The incorporation of carboxymethyl group was confirmed based on FTIR spectra of β-CD before and after functionalization. The addition of carboxymethyl group is evident from the broadening of peaks as shown in Fig. 1.

2.2. Materials

$CuSO_4.5H_2O$ and $NiSO_4.6H_2O$ (AR grade) were used to prepare stock solutions (1,000 mg/L) of Cu(II), and Ni(II),

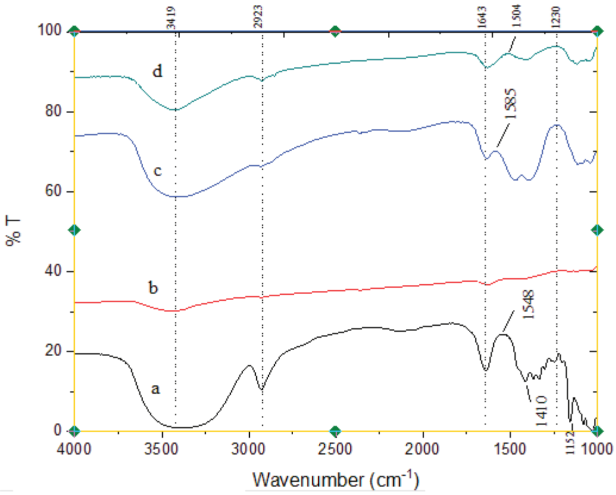

Fig. 1. FTIR analysis of CM-β-CD before and after complexation with Cu(II) and Ni(II). (a) CM-β-CD, (b) β-CD, (c) CM-β-CD – Cu(II) complex and (d) CM-β-CD – Ni(II) complex.

respectively. The solutions were prepared by using water treated through RO and groundwater. The groundwater used did not contain any detectable quantity of heavy metal contaminants. Complexation experiments were carried out with CM-β-CD. The pH adjustment for various experiments was carried out using NaOH or HCl. Cylindrically coated domestic polyethersulfone UF membrane element of MWCO 50 kDa (0.05 m^2) was procured from Rupali Industries, Mumbai. All the chemicals used were of analytical grade.

2.3. Experimental setup

Experiments were carried out with dead-end mode using UF candle type module. The schematic diagram of UF candle is shown in Fig. 2. The UF candle consists of polyethersulphone (PES) coated on a cylindrical surface with diameter 0.054 m, length of 0.27 m and membrane area of 0.05 m^2. Feed flows through the outer surface and permeate is transported to the interior of the hollow portion.

2.4. Experimental procedure

2.4.1. Removal of metal ions

Test solutions with different polymer to metal ratio (P/M) (1:1, 1:2, 1:3 (w/w)) were prepared and taken in the feed tank. The experiments were conducted at pH levels of 4, 6, 8 and 10. The pH levels were adjusted using sodium hydroxide or hydrochloric acid solutions. Feed of desired concentration was mixed with the complexing agent and pumped through the UF module. Permeate was collected continuously. The experiment was stopped, and the candle was opened. The retentate present in the candle was collected. The flow rate of permeate was measured manually using measuring cylinder and stopwatch. The experiments were carried out at a pumping pressure of 2 bar, and the feed flow rate was adjusted by recycling part of the feed stream to provide the desired flow rate to the UF system. The collected samples of permeate and retentate were analyzed using atomic absorption spectrophotometer.

2.4.2. Recovery of metal ions

In the recovery process, the feed sample was the retentate collected from the several experimental runs of complexation process. The feed sample of 5 L was taken, and the pH was altered. The feed sample was passed through the UF candle. The retentate was recycled back to the feed tank to maintain the flow rate. The permeate containing metal ions was collected continuously. The retentate containing polymer was collected from the candle after the run was over. The samples were analyzed.

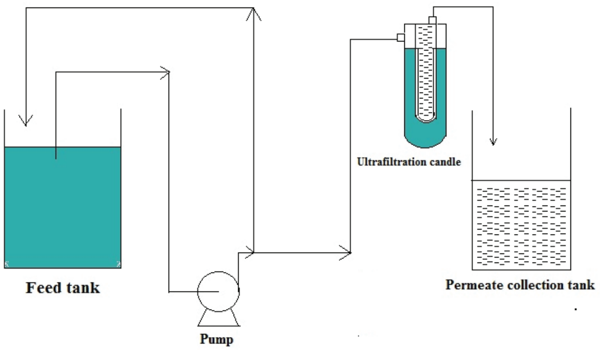

Fig. 2. Schematic diagram of experimental setup. Feed: 5 L, flow-rate: 10 LPH, operating pressure: 2 bar.

The rejection rate R, which measures the membrane's separating capabilities is calculated using Eq. (1).

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\ (\%) \tag{1}$$

The recovery rate A, which measures the recovery of metal after separation is given by Eq. (2).

$$\%A = \left(\frac{C_r}{C_f}\right) \times 100 \tag{2}$$

Loading ratio (L) is calculated as follows (Eq. (3)) to indicate the concentration ratio of polymer to metal ion [13]:

$$L = \left(\frac{C_p}{C_f}\right) \tag{3}$$

where C_f = feed concentration, C_p = permeate concentration, C_r = retentate concentration.

The performance index of the membrane was calculated using the following equation [23,24]:

$$\text{PFI} = R\,J_w \tag{4}$$

where R = rejection rate, J_w = permeate flux.

2.5. Experimental design and optimization of complexation conditions

2.5.1. Response surface methodology

Response surface methodology (RSM) is a collection of a statistical and mathematical tool for the empirical modeling of the process. It explores the relationship between the various independent variables and one or more dependent variables. The objective of RSM is to optimize the dependent variables (response) which are influenced by the various independent variables (input variables) by the proper design of experiments (DoEs). The interaction among the process variables can also be analyzed using RSM. It involves the following steps: DoEs, model fitting, validation of a model and optimization of process conditions [25]. In general, the structure of the relationship between the response and the input variables are unknown. RSM finds the suitable approximation to evaluate the relationship. The prime most important factor in RSM is the DoEs. The proper selection of points to evaluate the response is the objective of DoE. Factorial design approach can be used to examine the several possible combinations of variables to obtain an approximate model to find the interaction among the n design variables. In the 2^n full factorial design, the lower and upper bounds of each of the variables are defined. In RSM design, the central composite designs (CCDs) are widely used to fit a quadratic surface, since it does not require excessive experimental runs [23,25]. The total number of experimental runs (N) required can be calculated by using the following equation:

$$N = 2^n + 2n + \text{No} \quad (5)$$

where n = number of factors analyzed, No = number of center points.

In this study, the following factors were analyzed: (i) the initial pH of the solution, (ii) the polymer to metal ratio and (iii) the initial concentration of the feed. The percentage rejection and the performance index of a membrane were the responses analyzed.

3. Results and discussion

3.1. Characterization of CM-β-CD

The characterization of CM-β-CD before and after complexation with Cu(II) and Ni(II) was done by using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

3.1.1. Surface morphology – SEM

SEM provides the images of the sample by scanning the surface with a focused beam of high energy electrons to generate a variety of signals at the surface of a specimen. It is used to detect the external morphology, chemical composition and crystalline structure. It provides the topography of the surface by scanning the sample and collecting the secondary electrons that are emitted. The morphology of CM-β-CD before and after making the complex with Cu(II) and Ni(II) was analyzed by SEM with field emission operating at 10 kV. The CM-β-CD – Cu(II) complex and CM-β-CD – Ni(II) complex deposited on the surface of PES membrane were collected and dried at room temperature to have the dry sample. The surface morphology of CM-β-CD before and after complexation with Cu(II) and Ni(II) is shown in Fig. 3. The change in the surface morphology of CM-β CD after complexation is evident from Fig. 3. The texture was almost amorphous for CM-β-CD and it got changed into crystalline and plate after the interaction of metal ions with CM-β-CD.

3.1.2. Fourier transform infrared spectroscopy

The functionalization of β-CD, CM-β-CD and complexes was confirmed by using FTIR. The FTIR spectra of the β-CD, CM-β-CD before and after complexation with Cu(II) and Ni(II) are shown in Fig. 1. The vibration broad band at 3,400 cm^{-1} shown in Fig. 1 corresponded to O–H stretching vibration of the hydroxyl groups in the CM-β-CD and the complexes [26]. The vibration band at 2,923 cm^{-1} was due to the CH$_2$ asymmetric stretching vibration. The band corresponded to C–H stretching vibrations in CM-β-CD. The peak observed at 1,643 cm^{-1} was due to the C=O stretching vibration of ester groups and carboxyl groups in β-CD, CM-β-CD and the complexes. The vibration band at 1,410 cm^{-1} observed in Fig. 1(a) corresponded to O–H bending in CM-β-CD. The band at 1,152 cm^{-1} corresponded to C–C–C bending in CM-β-CD [27]. The peaks at 1,643 and 1,410 cm^{-1} corresponded to carboxyl (–COO–) groups of CM-β-CD [27]. The peak observed in Figs. 1(c) and (d) corresponded to C–O–C stretching vibration of ester groups. The peaks observed at 1,100 cm^{-1} and 1,040 cm^{-1} indicated that the structural characteristics of CM-β-CD were maintained. It was evident from the FTIR analysis that the peaks corresponding to C=O has not been altered, but the peaks corresponding to O–H has been modified due to the interaction of metal ions with hydroxyl groups after complexation.

3.2. Studies on the Removal of Contaminant Species

Size-enhanced Ultrafiltration (SEUF) has been studied extensively for the separation of heavy metal ions copper and nickel using a variety of polymers as mentioned earlier. The present study deals with the removal and recovery of Cu(II) and Ni(II) ions by using the water-soluble derivative of β-CD.

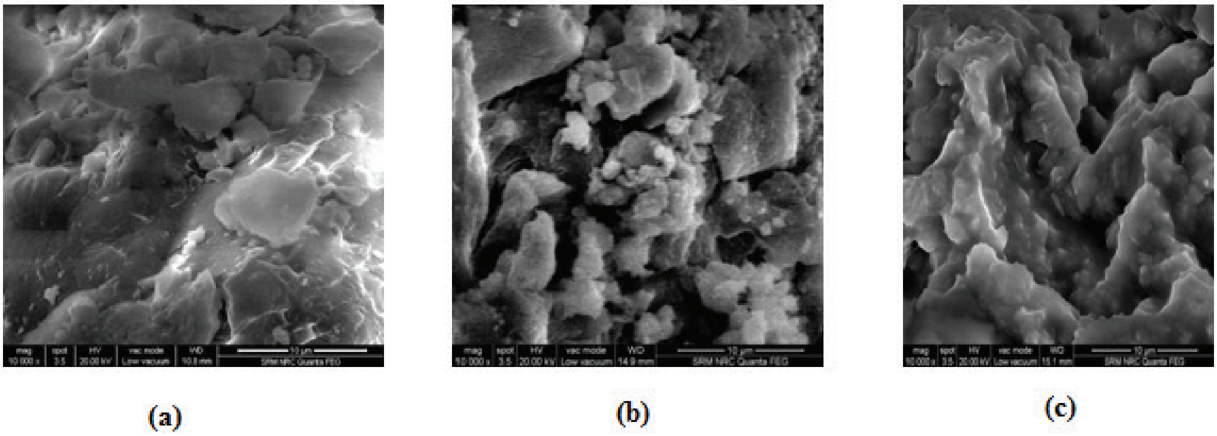

Fig. 3. Scanning electron microscopy (SEM) image of (a) CM-β-CD, (b) CM-β-CD – Cu(II) complex and (c) CM-β-CD – Ni(II) complex.

3.2.1. Design of experiments, development of empirical model and analysis using RSM

The DoEs were carried out by using RSM for the removal of copper and nickel using CM-β-CD by SEUF process. This study was done using Design Expert 10.0.0 statistical software (Stat-Ease, Inc., Minneapolis, USA). The DoE was done by selecting the following three input variables: (i) the initial pH of the solution, (ii) the polymer to metal ratio (w/w) and (iii) the initial concentration of the feed (ppm). The CCD and the experimental response for the SEUF process are shown in Tables 1 and 2. The responses namely percentage rejection (%*R*) and performance index of the membrane (PFI) were determined experimentally and also shown in Tables 1 and 2.

3.2.2. Effect of initial pH of the solution on the removal of the metal ion by SEUF

The interaction between the metal ion and the polymer ligand to a great extent depends on pH. Thus, pH is the most vital factor affecting the removal of heavy metals by SEUF. The stability of the metal complex depends on pH. The pH sensitivities of metal–polymer complex formation vary appreciably from metal to metal [2]. The higher concentration of protons hinders the complexation sites on the polymer ligands at acidic conditions. This behavior reduces the complexation and thus decreases the removal of metal ions. The protons do not hinder the complexation sites on the polymer ligands at basic condition. This behavior increases the removal rate of metal ions due to increase in the complexation. But at higher pH conditions, there is a possibility of precipitation due to the formation of metal hydroxides. Set of experiments were done to confirm that the removal of metal ions was by complexation and not by precipitation. Since the concentration of metal ions was low, there was no precipitation. From the test runs, it was confirmed that the separation was purely by complexation and not because of the precipitation at higher pH. But the pH dependency may vary from metal to metal. This characteristic can be utilized for the selective separation of metal ions.

The effect of pH on the rejection of Cu(II) from aqueous solutions using CM-β-CD is shown in Fig. 4, and the rejection of Ni(II) is shown in Fig. 5. From the results, the rejection of copper and nickel was observed to increase as the pH increases. As the polymer to metal ratio increases, the rejection capacity also increases. At acidic pH, the carboxymethyl end could exist more as $-CH_2-COOH$. But at pH 8 and above, the carboxymethyl end present in CM-β-CD could exist more as $-CH_2-COO^-$ and results in more ionic interaction between the metal ion and CM-β-CD. This characteristic proves the ionic interaction of metal ions with CM-β-CD. The same set of experiments was carried out by using hollow fiber module with different MWCO such as 50 kD and 100 kD. The rejection was almost same as that obtained from the candle module.

Table 1
Central composite design and the experimental response for the removal of Cu(II)

Run	Factor 1 *A*: Initial pH	Factor 2 *B*: P/M w/w	Factor 3 *C*: Initial concentration ppm	Response 1 % Rejection %	Response 2 PFI L/h m^2
1	7	2	30	62.02	131.79
2	10	1	10	97	206.13
3	7	1	30	55.58	118.1
4	4	3	50	65.34	138.85
5	7	2	30	62.02	131.79
6	10	2	30	97.56	207.31
7	7	2	50	80	170
8	4	1	10	25.3	53.76
9	10	3	50	99.9	212.5
10	4	3	10	53.5	113.68
11	4	1	50	35.98	76.46
12	4	2	30	44.23	93.99
13	7	2	30	62.02	131.79
14	10	3	10	97.6	207.4
15	7	2	10	55.76	118.49
16	7	3	30	81.12	172.38
17	10	1	50	99.8	212.23
18	7	2	30	62.02	131.79
19	7	2	30	62.02	131.79
20	7	2	30	62.02	131.79

Table 2
Central composite design and the experimental response for the removal of Ni(II)

Run	Factor 1 *A*: Initial pH	Factor 2 *B*: P/M w/w	Factor 3 *C*: Initial concentration ppm	Response 1 % Rejection %	Response 2 PFI L/h m^2
1	7	2	30	68.9	146.41
2	7	2	50	73.4	155.98
3	10	1	50	98	208.25
4	10	2	30	96	201.88
5	7	2	30	68.9	146.41
6	7	2	30	68.9	146.41
7	4	3	10	58.57	124.46
8	7	2	10	60.14	127.79
9	4	1	10	50.98	108.33
10	7	2	30	68.9	146.41
11	10	3	50	99	210.38
12	10	3	10	96	204
13	7	3	30	74.02	157.29
14	7	2	30	68.9	146.41
15	7	1	30	62	131.75
16	4	1	50	70.46	149.73
17	10	1	10	95	201.88
18	4	2	30	65.32	127.93
19	4	3	50	72.7	154.49
20	7	2	30	68.9	146.41

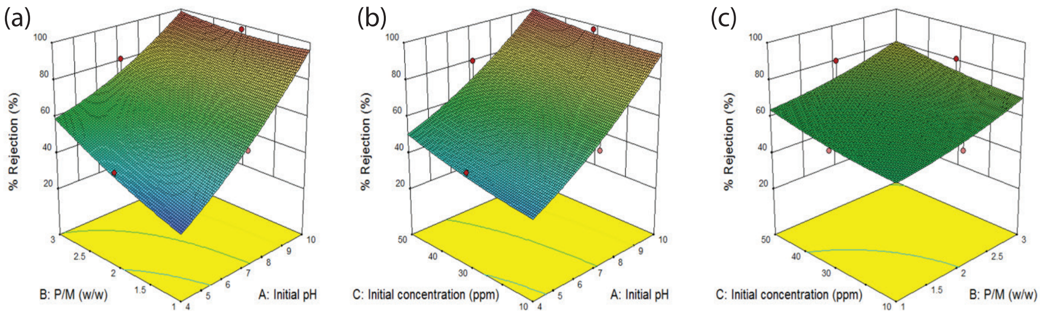

Fig. 4. Interactive effect of input variables on % rejection for the removal of Cu(II). (a) Interaction between P/M and initial pH and its effect on % rejection for the removal of Cu(II). (b) Interaction between initial concentration and initial pH and its effect on % rejection for the removal of Cu(II). (c) Interaction between initial concentration and P/M and its effect on % rejection for the removal of Cu(II).

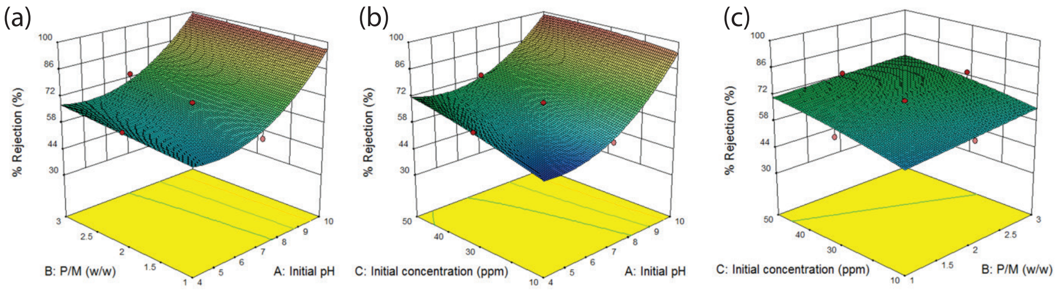

Fig. 5. Interactive effect of input variables on % rejection for the removal of Ni(II). (a) Interaction between P/M and initial pH and its effect on % rejection for the removal of Ni(II). (b) Interaction between initial concentration and initial pH and its effect on % rejection for the removal of Ni(II). (c) Interaction between initial concentration and P/M and its effect on % rejection for the removal of Ni(II).

There were no significant changes in the rejection concerning to MWCO since the separation is due to the metal–polymer complex. For copper and nickel, above pH 8 the rejection rate increased significantly, and it was nearly 100% irrespective of the loading ratio.

3.2.3. *Effect of initial pH of the solution on the performance index of the membrane*

The effect of pH on the performance index of the membrane (PFI) for Cu(II) from aqueous solutions using CM-β-CD is shown in Fig. 6, the PFI of Ni(II) is shown in Fig. 7. From the results, the PFI of copper and nickel was observed to increase as the pH increases. For copper and nickel, above pH 8 the PFI rate increased significantly irrespective of the loading ratio.

3.2.4. *Effect of P/M and initial concentration on the rejection rate and the performance index of the membrane*

The effect of P/M and initial concentration on the percentage rejection and performance index of the membrane (PFI) for Cu(II) from aqueous solutions using CM-β-CD is shown in Figs. 4 and 6, for Ni(II) is shown in Figs. 5 and 7.

3.2.5. *Effect of interaction between the process variables on rejection rate and the performance index of the membrane*

The 3D surface plots representing the polynomial model are represented in Figs. 4–7. These plots can be used to understand the effect of process variables on rejection rate. These plots reveal that increasing the loading ratio (P/M) and initial concentration of the feed solution improves the percentage rejection of metal ions. The interaction effect between initial pH and initial concentration on % rejection of Cu(II) and Ni(II) is represented in Figs. 4(b) and 5(b), respectively. At the higher pH value, the effect of initial concentration on percentage rejection was more than at lower pH. Similarly, the effect of initial pH is more intense at the higher value of initial concentration as shown in Figs. 4(b) and 5(b). At the higher P/M value, the effect of initial concentration on the rejection of Cu(II) and Ni(II) was more as shown in Figs. 4(c) and 5(c), respectively. The effect of P/M is more intense at the higher value of initial concentration. It was observed that increasing the pH from 7 to 8 at constant initial concentration increases the percentage rejection. Further increase in the pH does not show any significant change.

The interaction effect between initial pH and initial concentration on PFI for the removal of Cu(II) and Ni(II) are represented in Figs. 6(b) and 7(b), respectively. At the higher initial pH value, the increase in the initial concentration increases the PFI. The effect of initial pH is more intense at the higher value of initial concentration. The interactive effect of initial concentration and P/M on PFI for the removal of Cu(II) and Ni(II) is shown in Figs. 6(c) and 7(c), respectively. The effect of P/M is more intense at the higher value of initial concentration. It was observed that pH above 8 at constant initial concentration, the PFI increases significantly.

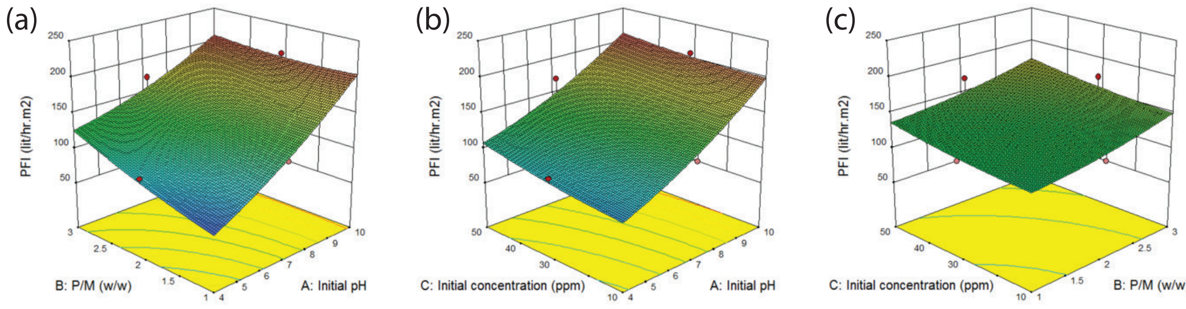

Fig. 6. Interactive effect of input variables on PFI for the removal of Cu(II). (a) Interaction between P/M and initial pH and its effect on PFI for the removal of Cu(II). (b) Interaction between initial concentration and initial pH and its effect on PFI for the removal of Cu(II). (c) Interaction between initial concentration and P/M and its effect on PFI for the removal of Cu(II).

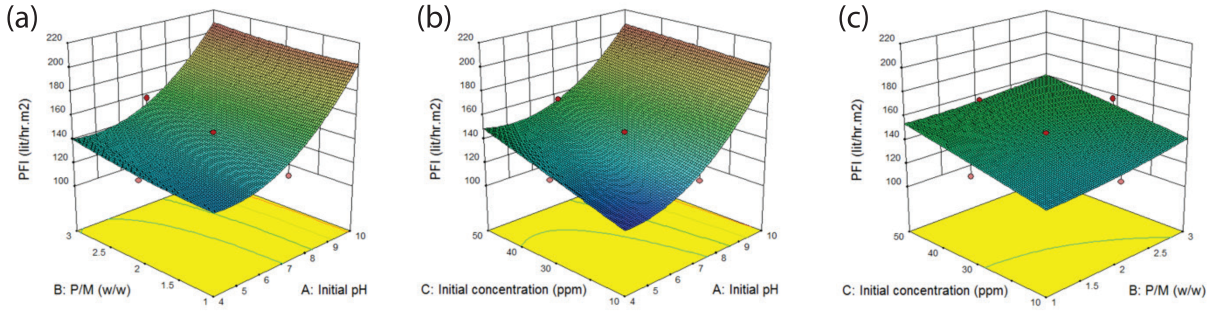

Fig. 7. Interactive effect of input variables on PFI for the removal of Ni(II). (a) Interaction between P/M and initial pH and its effect on PFI for the removal of Ni(II). (b) Interaction between initial concentration and initial pH and its effect on PFI for the removal of Ni(II). (c) Interaction between initial concentration and P/M and its effect on PFI for the removal of Ni(II).

3.2.6. Optimization of complexation conditions and ANOVA using RSM

Based on the CCD, the statistical DoE was done and data were collected for the removal of Cu(II) and Ni(II) using CM-β-CD. A second order polynomial model is developed to fit the experimental data. The final empirical quadratic model developed in terms of coded factors for the process conditions is stated by the following equation:

$$\begin{aligned}\%\ \text{Rejection} = {} & +63.35 + 26.74 * A + 8.37 * B + 5.20 * C \\ & -7.12 * AB - 2.16 * AC + 0.070 * BC \\ & +6.15 * A^2 + 1.79 * B^2 + 1.32 * C^2\end{aligned} \tag{6}$$

The model equation in terms of actual factors is given by the following equation:

$$\begin{aligned}\%\ \text{Rejection} = {} & -21.19737 + 5.48867 * \text{initial pH} \\ & +17.45268 * P/M + 0.29742 * \text{initial concentration} \\ & -2.373633 * \text{initial pH} * P/M \\ & -0.036083 * \text{initial pH} * \text{initial concentration} \\ & +3.50\,E - 0.003 * P/M * \text{initial concentration} \\ & +0.66111 * \text{initial pH}^2 + 1.85641 * P/M^2 \\ & +3.46603\,E - 003 * \text{initial concentration}^2\end{aligned} \tag{7}$$

Similarly, a second order polynomial model is developed to fit the experimental data for the removal of Ni(II) using CM-β-CD. The final empirical quadratic model developed in terms of coded factors and actual factors for the process conditions is stated by the following equations:

$$\begin{aligned}\%\ \text{Rejection} = {} & +68.54 + 16.60 * A + 2.38 * B + 5.29 * C \\ & -0.98 * AB - 3.45 * AC - 0.67 * BC \\ & +12.65 * A^2 + 4..545E - 004 * B^2 - 1.24 * C^2\end{aligned} \tag{8}$$

$$\begin{aligned}\%\ \text{Rejection} = {} & +64.55140 - 11.76803 * \text{initial pH} \\ & +5.67006 * P/M + 0.91980 * \text{initial concentration} \\ & -0.32625 * \text{initial pH} * P/M \\ & -0.057521 * \text{initial pH} * \text{initial concentration} \\ & -0.033437 * P/M * \text{initial concentration} \\ & +1.40561 * \text{initial pH}^2 + 4.54545E - 004 * P/M^2 \\ & -3.09886\,E - 003 * \text{initial concentration}^2\end{aligned} \tag{9}$$

3.2.7. Empirical models for PFI

The empirical equations using coded factors and actual factors for the PFI of the membrane for the removal of Cu(II) are given by the following equations:

$$\begin{aligned}\text{PFI} = {} & +134.62 + 56.84 * A + 17.81 * B + 11.06 * C \\ & -15.10 * AB - 4.58 * AC + 0.18 * BC + 13.08 * A^2 \\ & +3.81 * B^2 + 2.82 * C^2\end{aligned} \tag{10}$$

$$\begin{aligned}\text{PFI} = {} & -44.75378 + 11.62768 * \text{initial pH} + 36.95570 * P/M \\ & +0.62581 * \text{initial concentration} - 5.03208 * \text{initial pH} * P/M \\ & -0.076396 * \text{initial pH} * \text{initial concentration} + 9.18750E - 003 \\ & * P/M * \text{initial concentration} + 1.40550 * \text{initial pH}^2 \\ & +3.95156 * P/M^2 + 7.39141E - 003 * \text{initial concentration}^2\end{aligned} \tag{11}$$

The empirical equations using coded factors and actual factors for the PFI of the membrane for the removal of Ni(II) are given by the following equations:

$$\begin{aligned}\text{PFI} = {} & +144.71 + 36.14 * A + 5.07 * B + 11.24 * C \\ & -2.08 * AB - 7.33 * AC - 1.42 * BC + 22.75 * A^2 \\ & +2.36 * B^2 - 0.27 * C^2\end{aligned} \tag{12}$$

$$\begin{aligned}\text{PFI} = {} & +126.44748 - 18.28568 * \text{initial pH} \\ & +2.59315 * P/M + 1.60017 * \text{initial concentration} \\ & -0.69333 * \text{initial pH} * P/M - 0.12225 \\ & * \text{initial pH} * \text{initial concentration} - 0.071000 \\ & * P/M * \text{initial concentration} + 2.52773 * \text{initial pH}^2 \\ & +2.36455 * P/M^2 - 6.76136E - 004 * \text{initial concentration}^2\end{aligned} \tag{13}$$

To ensure the validity of the model, it was tested with ANOVA. The ANOVA table for the % rejection for the removal of Cu(II) and Ni(II) is shown in Tables 3 and 4. It was observed from ANOVA table for the removal of Cu(II) that the p-value > F value and the R^2 value is 0.98, close to 1. Also the adjusted R^2 value is 0.95. The value of of R^2 is 0.99 and adjusted R^2 value is 0.98 for the removal of Ni(II). The ANOVA table for the PFI for the removal of Cu(II) and Ni(II) is shown in Tables 5 and 6. It was observed from the table for PFI that the value of R^2 is 0.98 and adjusted R^2 value is 0.95 for Cu(II) and for Ni(II), the R^2 value is 0.99 and adjusted R^2 value is 0.97. It could be concluded that the response model is acceptable from the statistical point of view and the model is significant.

3.2.8. Optimum values of input variables

The optimum value for the rejection of Cu(II) by using CM-β-CD was found to be 100% rejection and PFI was found to be 220.189 L/h m^2 at initial pH 10, P/M 3 and initial concentration 50 ppm. The optimum value was found to be 99.13% rejection of Ni(II) and the optimum PFI was found to be 211.167 L/h m^2 at initial pH 10, P/M 3 and initial concentration 50 ppm.

3.3. Recovery of Cu(II) and Ni(II) at optimum operating conditions

The recovery of Cu(II) and Ni(II) was done as explained in the experimental procedure. The complexation runs were done at the optimum values. The decomplexation runs were done by altering the initial pH.

Table 3
Analysis of variance (ANOVA) table for the % rejection for the removal of Cu(II)

Source	Sum of squares	Degree of freedom	Mean square	*F* value	*p*-Value Probability > *F*	SD	R^2	Adjusted R^2
Model	8,861.16	9	984.57	43.90	0.00	4.74	0.9753	0.9531
A-Initial pH	7,156.16	1	7,156.16	319.06	0.00			
B-P/M	702.24	1	702.24	31.31	0.00			
C-Initial concentration	268.95	1	268.95	11.99	0.01			
AB	404.13	1	404.13	18.02	0.00			
AC	37.93	1	37.93	1.69	0.22			
BC	0.05	1	0.05	0.00	0.96			
A^2	62.63	1	62.63	2.79	0.13			
B^2	13.64	1	13.64	0.61	0.45			
C^2	8.49	1	8.49	0.38	0.55			
Residual	224.29	10	22.43					
Lack of fit	224.29	5	44.86					
Pure error	0.00	5	0.00					
Corrected total	9,085.45	19						

Table 4
ANOVA table for PFI of the membrane for the removal Cu(II)

Source	Sum of squares	Degree of freedom	Mean square	*F* value	*p*-Value Probability > *F*	SD	R^2	Adjusted R^2
Model	40,068.47	9.00	4,452.05	44.12	0.00	10.04	0.9754	0.95
A-Initial pH	32,356.76	1.00	32,356.76	320.69	0.00			
B-P/M	3,173.03	1.00	3,173.03	31.45	0.00			
C-Initial concentration	1,222.79	1.00	1,222.79	12.12	0.01			
AB	1,823.17	1.00	1,823.17	18.07	0.00			
AC	168.09	1.00	168.09	1.67	0.23			
BC	0.27	1.00	0.27	0.00	0.96			
A^2	283.79	1.00	283.79	2.81	0.12			
B^2	62.01	1.00	62.01	0.61	0.45			
C^2	38.75	1.00	38.75	0.38	0.55			
Residual	1,008.97	10.00	100.90					
Lack of fit	1,008.97	5.00	201.79					
Pure error	0.00	5.00	0.00					
Corrected total	41,077.45	19.00						

3.3.1. Effect of initial pH of the solution on the recovery of metals using CM-β-CD

The effect of pH on the recovery of Cu(II) and Ni(II) from aqueous solutions using CM-β-CD is shown in Figs. 8 and 9, and Tables 7 and 8. From the results, the recovery of copper and nickel was observed to decrease as the pH increases. For copper and nickel, the optimum pH for the recovery was found to be 2. The maximum recovery of copper and nickel at optimum pH was found to be 82% and 86%, respectively. The same sets of experiments were conducted using hollow fiber module. The recovery was found to be 93%. The recovery of metal ions was observed to be higher in hollow fiber module compared with a candle, since backwashing could be done effectively with hollow fiber module.

Table 5
ANOVA table for the % rejection for the removal of Ni(II)

Source	Sum of squares	Degree of freedom	Mean square	*F* value	*p*-Value Probability > F	SD	R^2	Adjusted R^2
Model	3,911.34	9.00	434.59	91.48	0.00	2.18	0.988	0.98
A-Initial pH	2,754.60	1.00	2,754.60	579.85	0.00			
B-P/M	56.88	1.00	56.88	11.97	0.01			
C-Initial concentration	279.52	1.00	279.52	58.84	0.00			
AB	7.66	1.00	7.66	1.61	0.23			
AC	95.29	1.00	95.29	20.06	0.00			
BC	3.58	1.00	3.58	0.75	0.41			
A^2	440.09	1.00	440.09	92.64	0.00			
B^2	0.00	1.00	0.00	0.00	1.00			
C^2	4.23	1.00	4.23	0.89	0.37			
Residual	47.51	10.00	4.75					
Lack of fit	47.51	5.00	9.50					
Pure error	0.00	5.00	0.00					
Corrected total	3,958.84	19.00						

Table 6
ANOVA table for PFI of the membrane for the removal of Ni(II)

Source	Sum of squares	Degree of freedom	Mean square	*F* value	*p*-Value Probability > *F*	SD	R^2	Adjusted R^2
Model	17,963.35	9.00	1,995.93	81.01	0.00	4.96	0.9865	0.97
A-Initial pH	13,064.61	1.00	13,064.61	530.29	0.00			
B-P/M	256.85	1.00	256.85	10.43	0.01			
C-Initial concentration	1,262.70	1.00	1,262.70	51.25	0.00			
AB	34.61	1.00	34.61	1.40	0.26			
AC	430.42	1.00	430.42	17.47	0.00			
BC	16.13	1.00	16.13	0.65	0.44			
A^2	1,423.24	1.00	1,423.24	57.77	0.00			
B^2	15.38	1.00	15.38	0.62	0.45			
C^2	0.20	1.00	0.20	0.01	0.93			
Residual	246.37	10.00	24.64					
Lack of fit	246.37	5.00	49.27					
Pure error	0.00	5.00	0.00					
Corrected total	18,209.72	19						

4. Conclusions

The present study examined the complexing material CM-β-CD for the removal and recovery of Cu(II) and Ni(II) from aqueous solutions. It was observed from the results that CM-β-CD could be a competent complexing material for the removal and recovery of heavy metals by SEUF. The statistically based DoEs by central composite design of response surface methodology are appropriate for the optimization of SEUF and also for minimizing the number of experiments. The optimum values for the rejection of Cu(II) are as follows: %*R* = 100%, PFI = 220.189 L/h m^2, initial pH = 10, P/M = 3 and initial concentration = 50 ppm. The optimum values for the rejection of Ni(II) are as follows: %*R* = 99.13%, PFI = 211.167 L/h m^2, initial pH = 10, P/M = 3 and initial

Table 7
Recovery of Cu(II) at optimum initial concentration 50 ppm and P/M 3

Initial pH	% Recovery
2	81.95
3	73.01
4	66.59
5	64.42
6	64.16

Table 8
Recovery of Ni(II) at optimum initial concentration 50 ppm and P/M 3

Initial pH	% Recovery
2	85.90
3	77.15
4	69.42
5	69.25
6	67.62

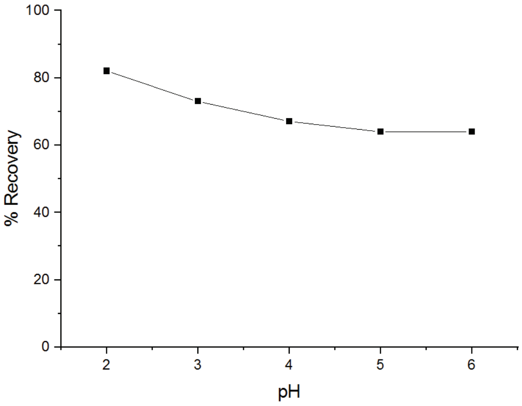

Fig. 8. Recovery of Cu(II) with CM-β-CD at optimum initial concentration 50 ppm and P/M 3.

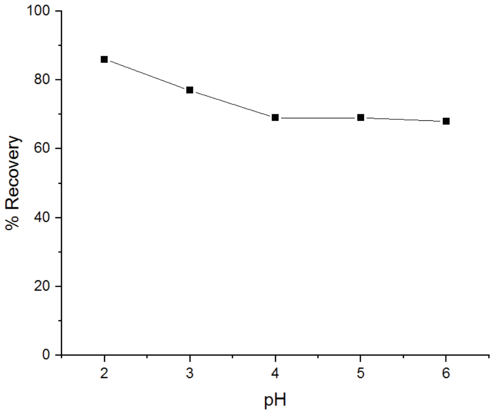

Fig. 9. Recovery of Ni(II) with CM-β-CD at optimum initial concentration 50 ppm and P/M 3.

concentration = 50 ppm. The development of mathematical model and optimization of process parameters using RSM could be a useful technique and tool for predicting and analyzing the interaction between the input variables. The optimized values were compared with the experimental values to ensure the fitness of the model. The experimental values were consistent with the predicted values, which confirm the good validity of the models developed by RSM.

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