REMOVAL OF COPPER(II) IONS FROM AQUEOUS EFFLUENT USING MELAMINE-FORMALDEHYDE-DTPA RESIN IN A FIXED-BED UP-FLOW COLUMN

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ABSTRACT
Melamine-Formaldehyde- diethylenetriaminepentaacetic acid (MF-DTPA) resin was prepared as a new adsorbent for removing heavy metals from wastewater effluents. In the synthesis process, the chelating agent diethylenetriaminepentaacetic acid (DTPA) anchored to melamine via amide covalent bond during melamine-formaldehyde condensation reaction in aqueous acidic medium. Resin characterisation using FT-IR, elemental analysis and N$_2$ gas adsorption (BET) were carried out to determine DTPA functionality and porosity. Water regain factor was also determined to find out hydrophilic character of the resin. Removal of Cu(II), as a representative of heavy metals, from synthetic wastewater using fixed-bed column packed with MF-DTPA grains was studied considering bed height, influent concentration and influent flow rate as controlling factors. The Thomas model was used to fit the adsorption data and its constants were evaluated. The Bed Depth Service Time (BDST) model was conducted to predict the service time of columns operated at different influent concentration and influent flow rates. It was found that DTPA successfully anchored to MF during resin matrix formation. The produced resin is hydrophilic (water regain 72%) and its surface area is 162 m$^2$ g$^{-1}$ with neglected micro-porosity. DTPA is suggested to be present as 0.93 mmole per gram solid resin. The removal of Cu(II) ion using fixed-bed mode column packed with MF-DTPA grains kinetically follows Thomas model. BDST model was found to fit the results and applicable for scaling up the system with dynamic capacity, $N_c$=7232 mg ml$^{-1}$ and active zone, $Z_0$=2.2 cm.

The MF-DTPA resin has a potential for removal of heavy metals from wastewater effluents.

KEY WORDS
Heavy metals; copper(II) ion removal, adsorption; MF-DTPA resin; Thomas model; BDST model.

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NOMENCLATURE

\( C_b \) Break through concentration (mg \( g^{-1} \)).
\( C_t \) Effluent metal ion concentration (mg l \( ^{-1} \)) at time \( t \).
\( C_\circ \) Influent metal ion concentration (mg l \( ^{-1} \)).
\( I \) Intercept of BDST model.
\( I' \) New intercept of BDST model.
\( k_{\text{ad}} \) Adsorption rate constant (l mg \( ^{-1} \) min \( ^{-1} \)) of BDST model.
\( k_{\text{Th}} \) Thomas rate constant (l mg \( ^{-1} \) min \( ^{-1} \)).
\( m \) Mass (g) of adsorbent in the column.
\( N_\circ \) Dynamic bed capacity (mg l \( ^{-1} \)) of BDST model.
\( Q \) Capacity (mg g \( ^{-1} \)) of the adsorbent according to Thomas model.
\( q_m \) Mass of Cu\( ^{2+} \) ion (mg) adsorbed by one gram of the resin.
\( q_{\text{ma}} \) Capacity (mg g \( ^{-1} \)) for the time period where concentration of effluent is zero.
\( q_{\text{mb}} \) Capacity (mg g \( ^{-1} \)) in the time period begins once concentration starts to increase till \( C_t/C_\circ = 1 \).
\( S \) Slope of BDST model.
\( S' \) New slope of BDST model.
\( T_s \) Column service time (min.).
\( V_{\text{eff}} \) Effluent volume (ml).
\( Z \) Bed height (cm).
\( Z_\circ \) Minimum column height (cm) necessary to give the effluent of concentration \( C_b \).
\( \nu \) Linear flow rate (cm min \( ^{-1} \)) of solution through the bed.
\( \nu' \) New linear flow rate (cm min \( ^{-1} \)).

INTRODUCTION

The discharge of heavy metal ions into ecosystem has shown rapid increase due to increase of industrial activities such as electroplating, paper production, electronic industries, etc. The need to remove heavy metals from wastewater effluents originate from its high toxicity. Developing cost-effective and highly efficient material able to reduce the heavy metal concentrations in wastewater effluents to acceptable regulation standards is of great importance. Synthetic resin can contribute in the heavy metal remediation by introducing efficient adsorbents. This efficiency means simply, cheap, high capacity and reusability of the resin which has to be employed with reliable technique. Packed-column operation is the most practical and economical way to remove contaminants, including heavy metals, from wastewater effluents. There were many studies concerned with heavy-metal adsorption using fixed-bed column system and most of this used biosorbing materials, different types of active carbon, and different inorganic sorbents [1-6]. In this work, melamin-formaldehyde-diethylenetriaminepentaacetic acid (MF-DTPA) chelating resin was synthesised via anchoring DTPA to melamine by the reaction of carboxyl group of DTPA with a primary amine group of melamine forming covalent amide bond during MF matrix formation. The granular form of the formed resin was used in column mode for removal of Cu\( ^{2+} \) ion from flowing synthetic wastewater.
THEORY

Resin Preparation and Characterization
Melamine, formaldehyde and DTPA were mixed in pre-acidified water. By heating the mixture, methylolation reaction takes place, catalyzed by acid, where −NH₂ groups of melamine react with formaldehyde to give methylol (−NH−CH₂OH) groups. The methylol groups condense upon further heating and form methylene and ether bridges [7]. Anchoring of DTPA to the forming MF resin matrix occurs by reaction of carboxylic groups of DTPA with amine groups of melamine where amide covalent bonds are formed [8-11]. MF resin sample was prepared under same conditions as a reference for MF-DTPA. Characterization of MF-DTPA resin was carried out using IR spectrometry, CHNO elemental analysis for MF-DTPA and MF resins and BET method analysis for MF-DTPA resin.

Column Adsorption Studies
(Analyses and Modelling of Column Adsorption Process)
Adsorption within a packed bed column is a continuous process where mass transfer of the solute (Cu²⁺) occurs from the mobile phase (Cu²⁺ solution) to the solid phase (the MF-DTPA resin bed). The experimental capacity q_m is the mass of Cu²⁺ ion in mg adsorbed by one gram of the resin and can be calculated using the following equation:

\[ q_m = q_{ma} + q_{mb} \]  \hspace{1cm} (1)

where \( q_{ma} \) is the capacity (mg g⁻¹) for the time period where concentration of effluent is zero and can be calculated using the following equation:

\[ q_{ma} = \frac{V_{eff} C_o}{1000 m} \]  \hspace{1cm} (2)

where \( V_{eff} \) the effluent volume (ml), \( C_o \) is the influent metal ion concentration (mg l⁻¹) and \( m \) is the mass of adsorbent in the column (g). \( q_{mb} \) is the capacity (mg g⁻¹) in the time period begins once concentration starts to increase till \( C_t/C_o = 1 \) and can be calculated by considering the area above the breakthrough curve.

The data collected in continuous mode studies was used to determine the kinetic parameters using Thomas model which is widely used for column studies [2,5]. Thomas model has the following linearized expression:

\[ \ln \left( \frac{C_o}{C_t} - 1 \right) = \frac{1000 k_{Th} Q m}{\nu} - \frac{k_{Th} C_o V_{eff}}{\nu} \]  \hspace{1cm} (3)

where \( C_t \) (mg l⁻¹) is the effluent metal ion concentration at time \( t \). \( k_{Th} \) is the Thomas rate constant (l mg⁻¹ min⁻¹); \( Q \) (mg g⁻¹) is the capacity of the adsorbent, \( m \) (g) is the mass of adsorbent in the column, \( \nu \) (ml min⁻¹) is the linear flow rate. The model constants, \( Q \) and \( k_{Th} \), can be determined from the plot of \( \ln(C_o/C_t - 1) \) versus time \( t \), \( t=V_{eff}/\nu \), by calculating slope and intercept.
Practical full-scale adsorption column can be designed based on results obtained from laboratory-scale adsorption column when appropriate mathematical model adequately verifies these results. The Bed Depth Service Time (BDST) model proposed by Bohart and Adams[12] and linearized by Hutchins [13] and McKay and Bino[14] is the simplest and rapid approach to describe column adsorption process. This model ignores the intra-particle mass transfer and external film resistances and considers, only, the solute reaction to the adsorbent vacant sites to control the adsorption process [3,4]. The model relates column service time, $T_s$ (min.), and bed depth, $Z$ (cm):

$$T_s = \frac{N_o Z}{C_o \upsilon} - \frac{1}{k_{ad} C_o} \ln \left( \frac{C_o}{C_b} - 1 \right)$$

(4)

The slope and intercept of equation (4) are as follows:

$$\text{slope} = S = \frac{N_o}{C_o \upsilon}$$

(5)

$$\text{intercept} = I = \frac{1}{k_{ad} C_o} \ln \left( \frac{C_o}{C_b} - 1 \right)$$

(6)

where $N_o$ (mg l$^{-1}$) is the dynamic bed capacity, $C_o$ (mg g$^{-1}$) is solute initial concentration, $\upsilon$ (cm min$^{-1}$) is the linear flow rate of solution through the bed, $C_b$ (mg g$^{-1}$) is the pre-specified break through concentration, and $k_{ad}$ (l mg$^{-1}$ min$^{-1}$) is the adsorption rate constant. Hence, this equation can be used to calculate the adsorption service time, $T_s$, of a column of bed height $Z$, given the parameters $N_o$, and $k_{ad}$ which must be determined from laboratory experiments.

Three bed heights at the same flow rate and influent concentration are sufficient to be experimentally carried out to establish BDST equation for column adsorbing system [15]. Setting $T_s=0$ and solving Eq (4) for $Z$ gives

$$Z_o = \frac{\upsilon}{N_o k_{ad}} \ln \left( \frac{C_o}{C_b} - 1 \right)$$

(7)

where $Z_o$ (cm) is the minimum column height necessary to give the effluent of concentration $C_b$.

From equation (4), prediction of service time, $T_s$, for different flow rates, $\upsilon$, can be conducted by modifying the slope according to the next relation [15,16]:

$$S' = S \frac{\upsilon}{\upsilon'}$$

(8)
where $S'$ and $\nu'$ are the new slope and new flow rate respectively. The intercept part of equation (4) need not to be modified as $k_{ad}$ is not affected by changing flow rates. Also, prediction of service time, $T_s$, for different influent concentration, $C_\circ$, can be conducted by modifying the slope and intercept according to the next relations respectively [15,16]:

\[
S' = S \frac{C'_\circ}{C_\circ}
\]

\[
I' = I \left( \frac{C'_\circ}{C_b} \right) \ln \left( \frac{C'_\circ}{C_b} - 1 \right)
\]

where $C'_\circ$ and $I'$ are the new influent concentration and new intercept respectively.

**Column Regeneration Study**

Efficient regeneration and reuse of an adsorbent is an important criterion to reduce the cost of removal process. For successful regeneration process, eluting agent should not deteriorate the adsorbent so much. In this work regeneration was carried out using EDTA solution as this agent is strong chelating agent and can elute Cu$^{2+}$ forming a stable soluble Cu(II)-EDTA complex.

**EXPERIMENTAL**

**Preparation of Resin**

Analytical grade of Melamine 99% (Aldrich), formaldehyde 38% (BDH), DTPA and EDTA (Sigma) were used in this work. For all solution preparation deionised water was used. The MF-DTPA resin was prepared as follows; 0.01 mole Melamine (1.26 g), Formaldehyde (2 ml), and 0.003 mole DTPA (1.31 g) were added into 5 ml acidified water (pH 1.5). The vial containing the mixture was vigorously agitated to guarantee complete homogeneity of slurry formed. The tightly closed vial then was put in preheated oven at 120 °C. Under this condition, a monolith solid gel was formed within about 20 minutes. The product was left for extra 30 minutes at the same temperature for more curing. The vial then removed and left on bench over night. The solid monolith resin then was ground and sieved. The grains (size=710:355 µm) were washed in 100 ml deionised water 5 times at ambient temperature using shaker at 150 rpm, each wash process lasted for 30 minutes. These washing processes were for removing acidity and any other remaining reactants (melamine, DTPA, and Formaldehyde).

**Resin Characterization**

**IR and Elemental Analysis Measurements**

For the IR analysis, Perkin-Elmer Spectrum one FT-IR spectrometer was used for IR spectra analysis using KBr discs with a suitable amount of MF and MF-DTPA resins. Analysis was made in the range 400 to 4000 cm$^{-1}$. Perkin-Elmer Series II CHNS/O Analyser model 2400 was used for elemental analysis of dried MF and MF-DTPA samples.
Porosity

Micromeritics ASAP 2405N adsorption analyzer was used for conducting nitrogen adsorption/desorption isotherms at 77.4 K to determine porosity characteristics of the MF-DTPA resin. An MF-DTPA Sample was freeze dried to remove all gelling water without distorting the pores or shrinkage of the matrix. The porosity parameters were derived by BET analysis method.

Metal Ion Continuous Adsorption

Metal Ions Solutions

Chloride salt was used for Cu$^{2+}$ ion, CuCl$_2$.2H$_2$O (May & Baker Ltd). Cu$^{2+}$ standard stock solution of 1000 ppm (1% HCl) was prepared where standard diluents were freshly prepared from it for adsorption experiments and pH was adjusted to 5 – 5.5 using concentrated and diluted HCl.

Column Studies

A Perkin-Elmer atomic absorption spectrometer 3100 with multi-element hollow cathode lamp and an air-acetylene burner was used for determining the effluent Cu$^{2+}$ ion concentrations. The wave-length, 324.8 nm, applied was that recommended by the manufacturer. Hanna Instrument pH model H18519 was used for Cu$^{2+}$ solution pH measurement. The continuous removal system is composed of influent solution reservoir, resin-packed bed glass column; effluent solution reservoir and peristaltic pump as shown in Fig.1. The height and internal diameter of the glass column was 1.4 and 25 cm respectively. During packing the column with MF-DTPA resin, care was taken to avoid air entrapment to avoid channelling. Experiments were conducted varying fixed-bed height (5, 7 and 9 cm), flow rate (3.2, 5.5 and 8.1 ml min$^{-1}$) and metal ion influent concentration (20, 30 and 40 mg l$^{-1}$). The metal solution was up-flow pumped through the fixed-bed using peristaltic pump at room temperature.

Column Regeneration and Reuse

Disposal of exhausted adsorbent loaded with heavy metal ions with out treatment causes another problem due to probable leach of these ions back into environment. This problem can be avoided by using one of elimination techniques such as elution, incineration and pyrolysis. The elution technique is the most preferred and so common allowing both recoveries of heavy metals at higher concentration and recycling of the adsorbent for subsequent use [5]. The recycling process is always accompanied by degradation of the adsorbent because of the deterioration phenomenon of active sites[6].

Cu$^{2+}$ loaded MF-DTPA resin (under conditions: Z = 7 cm, C$_o$ = 30 mg g$^{-1}$ and $\nu$ = 5.5 ml min$^{-1}$) was eluted using EDTA solution (0.01 M) with $\nu$ = 5.5 ml min$^{-1}$. Before elution, the resin was washed with 500 ml distilled water to remove all Cu$^{2+}$ solution may still present in the resin pores. After elution, the resin was washed again by 500 ml distilled water to remove all EDTA solution may still present in the resin pores. To examine the reuse, the same resin mass was used for second adsorption process under the same original adsorption conditions. The washing processes were carried out under the same flow conditions.
RESULTS AND DISCUSSION

General
The produced resin is hydrophilic (water regain 72%) and after grinding and sieving, 63.4% of original mass was found to be in the size range needed (710:355 µm).

IR Spectra and Elemental Analysis
The difference between the spectra of MF and MF-DTPA resins (not shown) implied the anchoring of DTPA to MF matrix such that peak at 1636 cm \(^{-1}\) is due to amide (carboxylic) carbonyl C=O stretch, 690 cm \(^{-1}\) is due to amide N–H out of plane and peak at 1390 cm \(^{-1}\) is due to Carboxylic In plane O–H bend. From elemental analysis result, 36.7% of the resin mass is DTPA (0.93 mmole DTPA per gram of solid resin). Fig.2. gives a suggested structure of the MF-DTPA resin.

Porosity (BET Characterization)
Basic porosity parameters of MF-DTPA resin were found to be: BET surface area=162 m\(^{2}\)/g, micropore area \(\approx\) 0 m\(^{2}\)/g and average pore diameter=95 Å. \(\text{N}_2\) adsorption /desorption hysteresis loop ranges from 0.7 to 1 (\(P/P_0\)) indicating open pore structure [17].

Adsorption Process (Column Studies)
Initially in the up-flow mode, when Cu\(^{2+}\) solution was introduced into the virgin resin bed, almost all Cu\(^{2+}\) ions were bonded to the chelating sites of the bottom layer of the resin, which can be imagined as a slice of the resin and can be recognised as adsorption-zone. As operation continued, this slice became saturated by Cu\(^{2+}\) ions and so the adsorption-zone moved up-word for the next slice. This ascending process is smooth and slices are merging not discrete. The process continued till reaching the top of the resin bed where the last slice became saturated and concentration of Cu\(^{2+}\) started to increase in the effluent till equalled initial influent concentration.

Effect of Bed Height on Adsorption
The breakthrough curves (\(C_t/C_0\) versus time) for Cu\(^{2+}\) ions adsorption on MF-DTPA resin packed column for bed heights 5, 7 and 9 cm at Cu\(^{2+}\) solution flow rate of 5.5 ml min\(^{-1}\) and initial concentration of 30 mg l\(^{-1}\) are shown in Fig.3. From curves we can notice that break-point, \(T_b\) (\(C_t/C_0=0.1\)) and exhaustion time (\(C_t/C_0=1\)) increased as bed height increased which means an increase in column service time. The Cu\(^{2+}\) ion experimental adsorption capacity of MF-DTPA, \(q_m\), significantly increased with height increase (27.6, 32.3 and 33.4 mg/g for heights 5, 7 and 9 cm respectively) and the solution volume treated, \(V_{\text{eff}}\), increased in the same manner (1072, 1788 and 2530 ml for heights 5, 7 and 9 cm respectively) (Table 4). This behaviour is attributed to increase of the amount of resin (more chelating sites become available for adsorption).

Effect of Initial Concentration on Adsorption
The effect of influent concentration (20, 30 and 40 mg l\(^{-1}\)) on breakthrough curves for bed height 7 cm and flow rate 5.5 ml min\(^{-1}\) is shown in Fig.4. It can be noticed from the curves that as influent concentration increases, the break-point \(T_b\) (\(C_t/C_0=0.1\)) and exhaustion time (\(C_t/C_0=1\)) were reached earlier. The results demonstrated that the increase in concentration is accompanied by increase in experimental adsorption.
capacity, \( q_m \), (29.2, 32.3 and 33.3 for influent concentrations 20, 30 and 40 mg l\(^{-1}\) respectively) whereas the solution volume treated, \( V_{\text{eff}} \), shows a decrease (2475, 1788 and 1403 ml for influent concentrations 20, 30 and 40 mg l\(^{-1}\) respectively) (Table 4). This can be explained by considering that a higher influent concentration may saturate the MF-DTPA resin more quickly. The larger the influent concentration, the steeper the breakthrough curve due to increase of saturation rate, Fig.4. Hence, as influent concentration increases, \( \text{Cu}^{2+} \) ions loading rate increases so does the driving force for mass transfer (i.e. diffusion process is concentration dependent).

**Effect of Flow Rate on Adsorption**

As the sectional area of the column is uniform, the linear flow rate (which is considered in this work) is directly proportional to volumetric flow rate. The effect of different flow rates (3.2, 5.5, 8.1 ml min\(^{-1}\)) on breakthrough curves for bed height of 7 cm and influent concentration 30 mg g\(^{-1}\) is shown in Fig.5. It can be noticed from the curves that as flow rate increases, the break-point, \( T_b \), (\( C_t/C_\circ = 0.1 \)) and exhaustion time (\( C_t/C_\circ = 1 \)) were reached earlier. The \( \text{Cu}^{2+} \) ion experimental adsorption capacity of MF-DTPA, \( q_m \), changed with flow rate (48.5, 32.3 and 19.25 mg/g for flow rates 3.2, 5.5 and 8.1 ml min\(^{-1}\) respectively). Also, treated volume, \( V_{\text{eff}} \), increased as flow rate decreased (2212, 1788 and 1296 ml for flow rates 3.2, 5.5 and 8.1 ml min\(^{-1}\) respectively) (Table 4). This behaviour may be attributed to predominance of axial dispersion over horizontal dispersion at higher flow rates which causes less time for \( \text{Cu}^{2+} \) ions to diffuse into the resin pores and this strongly supported by noting less steepness in breakthrough curve for the higher flow rate, Fig.5 [16].

<table>
<thead>
<tr>
<th>( Z(\text{cm}) )</th>
<th>( C_\circ ) ( (\text{mg l}^{-1}) )</th>
<th>( \nu ) ( (\text{ml min}^{-1}) )</th>
<th>( V_{\text{eff}} ) ( (\text{ml}) )</th>
<th>( T_b ) ( (\text{min}) )</th>
<th>( q_m ) ( (\text{mg g}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5, 30, 5.5]</td>
<td>1072</td>
<td>195</td>
<td>27.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[7, 30, 5.5]</td>
<td>1788</td>
<td>320</td>
<td>32.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[9, 30, 5.5]</td>
<td>2530</td>
<td>460</td>
<td>33.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[7, 20, 5.5]</td>
<td>2475</td>
<td>450</td>
<td>29.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[7, 40, 5.5]</td>
<td>1403</td>
<td>255</td>
<td>33.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[7, 30, 3.2]</td>
<td>2212</td>
<td>660</td>
<td>48.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[7, 30, 8.1]</td>
<td>1296</td>
<td>160</td>
<td>19.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Thomas Model Analysis**

The Thomas model was applied to experimental results with respect to bed height, influent concentration and influent flow rate. For bed heights 5, 7 and 9 at flow rate of 5.5 ml/min and influent concentration of 30 mg l\(^{-1}\), data showed linearity with Thomas model as shown in Fig.6. Form Table 5 it can be noticed that Thomas rate constant, \( k_{\text{th}} \), and capacity, \( Q \), increased with bed height which means that increasing bed height has positive influence on process.

For \( \text{Cu}^{2+} \) ions influent concentrations 20, 30 and 40 mg l\(^{-1}\) at flow rate of 5.5 ml/min and bed height of 7 cm, data showed linearity with Thomas model as shown in Fig.7. With the increase of influent concentration Thomas rate constant, \( k_{\text{th}} \), did not give a trend but column capacity, \( Q \), showed an increase which is in agreement with experimental capacity (Table 5).
For influent flow rates 3.2, 5.5 and 8.1 ml/min at bed height of 7 cm and influent concentration of 30 mg l⁻¹, data showed linearity with Thomas model as shown in Fig.8. Table 5 summarises corresponding Thomas parameters \( k_{th} \) and \( Q \). Thomas rate constant, \( k_{th} \), increased with flow rate whereas capacity decreased which is in agreement with experimental capacity.

Generally, Thomas rate constant, \( k_{th} \), is in the range of \( 1.3 \times 10^{-3} \) l mg⁻¹ min⁻¹ which is comparable with some other studies [5]. Thomas model estimated capacities, \( Q \), are very comparable with experimental capacities which suggest good representation of the model to adsorption under up-flow conditions for MF-DTPA resin.

Table 5. Parameters predicted from Thomas model considering bed height, influent concentration and influent flow rate

<table>
<thead>
<tr>
<th>([Z(cm), C_0 (mg l^{-1}), \nu (ml min^{-1})])</th>
<th>(k_{th} ) (l mg⁻¹ min⁻¹)</th>
<th>(Q) (mg g⁻¹)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5, 30, 5.5]</td>
<td>(1.17 \times 10^{-3})</td>
<td>21.97</td>
<td>0.9748</td>
</tr>
<tr>
<td>[7, 30, 5.5]</td>
<td>(1.21 \times 10^{-3})</td>
<td>32.30</td>
<td>0.9766</td>
</tr>
<tr>
<td>[9, 30, 5.5]</td>
<td>(1.25 \times 10^{-3})</td>
<td>43.75</td>
<td>0.9800</td>
</tr>
<tr>
<td>[7, 20, 5.5]</td>
<td>(1.50 \times 10^{-3})</td>
<td>29.69</td>
<td>0.9593</td>
</tr>
<tr>
<td>[7, 40, 5.5]</td>
<td>(1.32 \times 10^{-3})</td>
<td>33.16</td>
<td>0.9702</td>
</tr>
<tr>
<td>[7, 30, 3.2]</td>
<td>(9.13 \times 10^{-4})</td>
<td>36.55</td>
<td>0.9923</td>
</tr>
<tr>
<td>[7, 30, 8.1]</td>
<td>(1.42 \times 10^{-3})</td>
<td>26.13</td>
<td>0.9847</td>
</tr>
</tbody>
</table>

Correlation factor, \( R^2 \), is high which means good fit of data with the Thomas model.

BDST Model Analysis

From the breakthrough curves shown in Fig.3, BDST plots were determined for \( C_t/C_0 = 0.033, 0.1, 0.5 \) and 0.9 as shown in Fig.9.

The BDST equations of these lines are as follows:

\[
T_s = 62.5 Z - 144.17 \quad \text{for} \quad C_t/C_0 = 0.033 \quad \text{(}R^2 = 0.9995\text{)}
\]

\[
T_s = 67.5 Z - 149.17 \quad \text{for} \quad C_t/C_0 = 0.1 \quad \text{(}R^2 = 0.9995\text{)}
\]

\[
T_s = 66.3 Z - 65.417 \quad \text{for} \quad C_t/C_0 = 0.5 \quad \text{(}R^2 = 0.9999\text{)}
\]

\[
T_s = 63.75 Z - 1.25 \quad \text{for} \quad C_t/C_0 = 0.9 \quad \text{(}R^2 = 0.9988\text{)}
\]

The slopes are nearly the same for all lines which means, according to equation (3), that \( N_o \) value did not change with bed height indicating that adsorption zone is moving up the column at a constant speed [3]. For \( C_t/C_0 = 0.1, \ k_{ad} \) was calculated using equation (4) and the minimum column height necessary to give effluent of concentration \( C_b = 3 \) mg g⁻¹, \( Z_o \), was also calculated using equation (5). These design parameters were found to be, \( N_o = 7232 \) mg ml⁻¹ (correspond to 25.8 mg per gram of solid resin), \( k_{ad} = 4.91 \times 10^{-4} \) l mg⁻¹ min⁻¹ and \( Z_o = 2.2 \) cm according to BDST model.

Correlation factor, \( R^2 \geq 0.9995 \) which means good fit of data with the BDST model.

Examining BDST Model with Influent Concentration and Flow Rate Conditions

To examine the BDST model for practical application, a comparison of experimental service time and predicted service time according to BDST model with respect to influent concentration (at \( C_t/C_0 = 0.1 \), flow rate 5.5 ml min⁻¹ and bed height of 7 cm) and with respect to influent flow rate (at \( C_t/C_0 = 0.1 \), influent concentration 30 mg g⁻¹ and bed height of 7 cm) are given in Table 6. It is clear from the table the high match
between experimental and predicted service times which suggest using this model for the purpose of scaling-up of the system.

Table 6. BDST model fitting with influent concentration condition and influent flow rate condition

<table>
<thead>
<tr>
<th>[Z(cm), C○ (mg l⁻¹), υ (ml min⁻¹)]</th>
<th>Experimental service time (min)</th>
<th>Tₛ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[7, 20, 5.5]</td>
<td>450</td>
<td>485</td>
</tr>
<tr>
<td>[7, 30, 5.5]</td>
<td>320</td>
<td>324</td>
</tr>
<tr>
<td>[7, 40, 5.5]</td>
<td>252</td>
<td>243</td>
</tr>
<tr>
<td>[7, 30, 3.2]</td>
<td>660</td>
<td>663</td>
</tr>
<tr>
<td>[7, 30, 8.1]</td>
<td>160</td>
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**Column Regeneration and Reuse**

About 1100 ml of EDTA solution was accumulated after completed elution process of Cu²⁺ ion from loaded MF-DTPA dose. Cu²⁺ ion concentration of this solution was 48 mg l⁻¹. This means that removal from the total dose mass of the resin is 52.8 mg(Cu²⁺) which corresponds to 26.94 mg g⁻¹. First adsorption process gave \( q_m = 32.26 \) mg g⁻¹ and by calculation, the elution efficiency is 84%. Fig.10 shows the elution cycle using EDTA solution. From the figure we can consider that most of Cu²⁺ ions were eluted in the fist 100 minutes which corresponds to 9.3 bed volumes. The number of bed volumes is an important parameter from design point of view as it suggests practical amount of eluting solution to be used.

Fig.11 shows first adsorption and second adsorption processes (after elution) with the same conditions (\( Z=7 \) cm, \( C○ =30 \) mg g⁻¹ and \( υ=5.5 \) ml min⁻¹). The second adsorption process has \( T_b=290 \) minutes (at \( C_t/C○ = 0.1 \)) which is less than that of first adsorption process by 30 minutes and \( V_{eff}=1595 \) ml which is less than that of first adsorption process by 165 ml. Adsorption capacity \( q_m \) was calculated and found to be 25.48 mg g⁻¹ which means 79% of the first adsorption capacity. This decrease in performance can be attributed to deterioration of the resin because of loss of active sites which mainly occurred by hydrolysis of DTPA during adsorption process, elution and washing. This deterioration by hydrolysis is strongly suggested as pH of the effluent shows decrease. The deterioration is

**CONCLUSIONS**

Melamine-Formaldehyde-DTPA (MF-DTPA) resin was prepared as a new adsorbent for removing heavy metals from wastewater effluents. The MF-DTPA resin is formed by anchoring DTPA, through the amide bond, with MF matrix. IR and elemental analysis proved the success of anchoring DTPA to the MF matrix and DTPA present in resin was found to be 36.7%. DTPA, as strong chelating agent, can chelate (chemi-sorp) heavy metals present in water effluent. The preparation conditions was pH=1.5, a temperature of 120°C, and a water content of 5 ml with the stated amounts of reactants. The produced resin is hydrophilic (water regain 72 %) with surface area =162 m² g⁻¹ and neglected micro-porosity. DTPA is calculated to be present as 0.93 mmole per gram solid resin. The removal of Cu²⁺ ion, as a representative of heavy metals, from an aqueous solution, by adsorption using up-flow method on fixed-bed
packed column with MF-DTPA grains, was studied kinetically by Thomas model and results were found to fit the model for different bed heights, Cu\(^{2+}\) influent concentration and influent flow rate with correlation factor \(R^2 \geq 0.9593\). The Bed Depth Service Time (BDST) model was found to fit the experimental results as well with correlation factor \(R^2 \geq 0.9988\), hence being a suitable candidate for scaling up the fixed-bed up-flow column system for the purpose of removal of heavy metals using MF-DTPA resin as a packing adsorbent.

REFERENCES

Fig. 1. Experimental fixed-bed up-flow column setup.

Fig. 2. Suggested structure of MF-DTPA resin.

Fig. 3. Breakthrough curves for Cu(II) adsorption on MF-DTPA resin at three different bed heights ($C_0=30$ mg l$^{-1}$ and $\nu=5.5$ ml).
Fig. 4. Breakthrough curves for Cu(II) adsorption on MF-DTPA resin at three different influent concentrations ($Z=7$ cm and $\nu=5.5$ ml).

Fig. 5. Breakthrough curves for Cu(II) adsorption on MF-DTPA resin at three different flow rates ($C_o=30$ mg l$^{-1}$ and $Z=7$ cm).

Fig. 6. Thomas model fitting Cu(II) adsorption on MF-DTPA resin at three different bed heights ($C_o=30$ mg l$^{-1}$ and $\nu=5.5$ ml).
Fig. 7. Thomas model fitting Cu(II) adsorption on MF-DTPA resin at different influent concentrations ($Z=7$ cm and $\nu=5.5$ ml).

Fig. 8. Thomas model fitting Cu(II) adsorption on MF-DTPA resin at different influent flow rates ($C_o=30$ mg l$^{-1}$ and $Z=7$ cm).

Fig. 9. BDST plots at $C_t/C_o = 0.033, 0.1, 0.5$ and $0.9$ ($C_o=30$ mg l$^{-1}$ and $\nu=5.5$ ml).
Fig. 10. Time profile of Cu(II) concentration during elution of the resin with 0.01 M EDTA solution.

Fig. 11. First and second adsorption breakthrough curves.