Multiamine modified chitosan for removal metal ions from their aqueous solution

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ABSTRACT

Chitosan was chemically modified with glycidylmethacrylate and ethylenediamine or diethylenetriamine in a two-step reaction. Firstly, opening of the three-ring of glycidylmethacrylate, leaving a double a bond for further reaction. Finally, produced product was reacted through the free glycidylmethacrylate double bond with ethylenediamine or diethylenetriamine. The chemically modified chitosan were characterized by elemental analysis, IR, 13C-NMR, XRD, SEM and employed for barium, manganese, cobalt, nickel, copper, zinc and cadmium biosorption. Elemental analysis data based on nitrogen atom content gave an incorporation of organic pendant groups to the modified chitosan. 13C-NMR and FT-IR results are in agreement with the success of the proposed chemical modification. The metal sorption capability of the final chelating material was higher than chitosan due to the increment of basic centers attached to the pendant chains. The experimental data were adjusted to Langmuir, Freundlich and Temkin sorption isotherm models. The behavior suggested that this new modified biopolymer could be employed as a promising sorbent for cation removal from polluted dye bath.

INTRODUCTION

Heavy metal ions have lethal effects on all forms of life and these enter the food chain through the disposal of wastes in water channels. From among various metal ions, barium, manganese, cobalt, nickel, copper, zinc and cadmium are listed in the toxicity list[1]. Metal ions accumulate and their amounts are increased due to their non-biodegradable properties. Owing to the toxic effects, the industries are advised that the waste waters be treated systematically to remove/minimize the metal contents in their wastes.

Many methods are already used for this purpose. Metal adsorption by activated carbon is the most efficient classical way as it removes more than 99% of certain metal ions but the cost of its production is prohibitive and it cannot be regenerated and re-
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Many other treatments like ion exchange, evaporation, precipitation, coagulation and membrane separation etc. are too expensive to treat low levels of heavy metal in wastewater. In addition, some of these methods which they used for removal metal ions from aqueous solution and produce concentrated and further toxic wastes, creating yet another disposal problem.

Nowadays, biosorption is a strongly explored technique; it is defined as passive, not involving metabolically mediated processes, with the property to bind metals by living or dead biomass[2]. Considerable attention has been paid to the recovery and removal of valuable heavy metal ions from industrial and municipal wastewater by using various biosubstances or natural products, particularly because of the low cost and high availability of these materials, without needing arduous regeneration process for reuse, being capable of binding heavy metals by sorption, chelation and ion exchange processes[3, 4]. These low-cost abundant natural materials such as chitin, chitosan, alginate, cellulose, peat and biomass require little processing and are abundant in nature, mainly when obtained as by-products and waste from industry[5].

Due to its high nitrogen atom contents, chitosan is one of the most reported biosorbents and has also been investigated by many research groups for heavy metal recovery from aqueous solution. Since both amine and hydroxyl groups act as chelating sites for metal ions[6], so, chitosan allows uptake of several metal ions through various mechanisms such as electrostatic attraction, ion-exchange or chelation. Chitosan, a partially N-deacetylated product of chitin, is an important natural biopolymer due to its biocompatibility and biodegradability, with broad applications in wastewater treatment in chemical, biomedical and pharmaceutical applications and in agriculture and biotechnology[7].

The physicochemical properties are closely related to solubility and cationicity properties, and the presence of the amine function, that make it very efficient for binding cations in solutions[8]. In addition, the sorption efficiency depends on its source, its deacetylation degree, the pH of the solution and the nature of the cation[9]. Therefore, modifications of chitosan are important to increase its potential applications. Presence of amino and two hydroxyl groups on each glucosamine repeating unit can act as reactive sites for chemical modification. Many methods have been used to modify raw chitosan, in order to improve its sorption capacity, pore size, mechanical strength, chemical stability, hydrophilicity and biocompatibility[10-12].

The present research is aimed to modification of chitosan with two different multiamine compounds after pre-modification with glycidylmethacrylate (GMA). After that, both modified chitosan were used to remove the metal ions from their aqueous solution. Adsorption and kinetics studies were take place onto both modified chitosan with different six metal ion (divalent) with same anion (to neglect the effect of anion for all metal).

EXPERIMENTAL

Materials

Chitosan high molecular weight, with a 78% degree of deacetylation, supplied by Sigma-Aldrich, diethylenetriamine, ethylenediamine, glycidylmethacrylate, and ethanol were supplied in analytical grade from (Aldrich). Barium nitrate (Ba(NO$_3$)$_2$), manganese nitrate (Mn(NO$_3$)$_2$), cobalt nitrate (Co(NO$_3$)$_2$), nickel nitrate (Ni(NO$_3$)$_2$), copper nitrate (Cu(NO$_3$)$_2$) and zinc nitrate (Zn(NO$_3$)$_2$) were all of analytical grade.

Synthesis

Modification of chitosan with glycidylmethacrylate (Chito-gly)

In the step, in a 250 ml three necked flask 4 g of chitosan was suspended in 200 ml of distilled water by stirring for 15 min at 80°C. 2.65 ml of glycidylmethacrylate was slowly added to this suspension under mechanical stirring over 2 h. This product was filtered, washed with water, ethanol and dried under vacuum at 45°C for 6 h.

Modification of (Chito-gly) with multiamine compounds

In a 250 ml three necked flask 4 g of Chito-gly
was suspended in 150 ml of ethanol with stirring at 60°C, followed by slow addition of 1.67 ml of diethylenetriamine (DETA) or ethylenediamine (EDA) in the presence of 1 ml of triethylamine as a catalyst, this suspension was maintained under reflux with mechanical stirring for 72 h. The new composite (Chito-DETA and Chito-EDA) was filtered, washed with ethanol and deionized water and then dried under vacuum at 45°C for 6 h. This new composite is very stable for several months at room temperature, without presenting any decomposition.

**Characterization**

The carbon and nitrogen contents of the precursor chitosan and of the chemically modified chitosan were determined through elemental analysis on a Perkin Elmer elemental analyser. The general amounts of each element (Lo) attached in the pendant chains are calculated using the following equation:

\[
Lo = \frac{\text{Element} \times 10}{\text{Atomic mass of element}}
\]

The FT-IR tester of Nicolet Magna-IR 560 spectrometer was used to analyse the spectrum of the untreated and treated samples. KBr was used to prepare the thin film together with the samples. The tester collected transmittance of the infrared in the film between 400 and 4000 cm\(^{-1}\).

\(^{13}\)C NMR spectra of the samples were obtained on a Bruker AC 300/P spectrometer, using the CP–MAS technique, with pulse repetitions of 5 s and contact times of 1 ms, at 75.47 MHz and with magic angle spinning of 4 kHz.

The XRD pattern was recorded using (Empyrean, pixcel3D, Amedipixz collaboration, PANANTICAL Netherlands) with Cu–K\(\alpha\) radiation (\(\gamma = 0.15406\) nm) in the 2\(\theta\) range from 5 to 50 at the scanning rate of 2° per minute.

The dried powders were loaded on glass and subjected to X-Ray and the diffracted pattern was recorded.

Thermal behaviour was investigated using a thermo gravimetric analyser (TGA) Shimadzu TGA 50 apparatus. The samples were heated at a rate of 10°C per minute from room temperature to 600°C in nitrogen atmosphere.

The amount of cations sorbed was determined using a Cary100 UV–vis spectrophotometer, considering the difference between the initial concentration in the aqueous solution and that found in the supernatant after the sorption process.

**Sorption experiments**

Five known concentrations for each metal salt compound (Ba(NO\(_3\))\(_2\), Mn(NO\(_3\))\(_2\), Co(NO\(_3\))\(_2\), Ni(NO\(_3\))\(_2\), Cu(NO\(_3\))\(_2\), Zn(NO\(_3\))\(_2\), and Cd(NO\(_3\))\(_2\)) were prepared and measured by using a UV–vis spectrophotometer (model Cary 100) (at suitable \(\lambda_{max}\) for each metal) to making the calibration standard curve. This allows us to convert the measured absorbance into the equivalent concentration in order to monitor the amount of metal salt absorbed onto the modified chitosan.

For each experimental treatment run, isotherm studies, sorption assays were carried out by adding 1 g of modified chitosan (Chito-EDA or Chito-DETA) into a series of flasks containing metal salt solution in deionized water. At neutral pH, a liquor ratio of 1:20. The concentration of metal salt solution ranging from 0.2 – 1 mg/ml. The flask was agitated in a shaking water bath at a constant speed of 100 rpm for 30 min.

The residual solutions were analysed for the residual metal salt concentration by measuring absorbance at \(\lambda_{max}\) for each metal salt using UV–vis spectrophotometer.

For kinetic studies, same process was done but the measuring for the residual concentration of the metal salt solution were occurred at 0, 30, 60, 90... 1800 seconds. 1 ml of the metal salt solution was measured for the residual concentration of metal salt using a UV-vis spectrophotometer. Then it was put back into the treatment solution for keeping the concentration constant.

**Isotherm models**

Equilibrium isotherm equations are used to describe the experimental sorption data. Equilibrium models and their equation parameters often provide some sorption mechanisms and the surface properties and affinities of the sorbent. Adsorption isotherms describe how adsorbates interact with adsorbents and are crucial in optimizing the use of adsorbents. Adsorption isotherms are described in many math-
emathematical forms. The most common isotherms model for describing solid/liquidsorption systems are the Langmuir, the Freundlich\(^{[13-16]}\) and the Temkin isotherms\(^{[17]}\).

**Langmuir isotherm model**

The Langmuir isotherm has been widely used to describe single-solute systems\(^{[13, 15, 18]}\). Langmuir isotherm theory assumes monolayer coverage of sorbate over a homogenous sorbent surface. Therefore, at equilibrium a saturation point is reached where no further sorption can occur, which means that sorption takes place at the specific homogeneous sites within the sorbent. Once a cation occupies a site, no further sorption can use the same place\(^{[18, 19]}\).

This isotherm assumes that intermolecular forces decrease rapidly with distance and consequently it can predict monolayer coverage of the adsorbate on the outer surface of the adsorbent. Further assumption is that adsorption occurs at specific homogeneous sites within the adsorbent and there is no significant interaction among adsorbed species. The Langmuir isotherm is given by the following equation:

\[
\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b}
\]

Where\(N_f\) is the sorption capacity at equilibrium, \(C_s\) is the equilibrium concentration, \(N_s\) and \(b\) are the Langmuir constants related to the maximum sorption capacity and the sorption energy, respectively. The plot of \((C_s/N_f)\) versus \((C_s)\) gives a straight line with the slope of \((1/N_s)\) and the intercept of \((1/N_s b)\). Maximum sorption capacity \(N_s\) represents the monolayer coverage of sorbent species with sorbate and \(b\) represents the energy of sorption\(^{[16, 18, 20]}\). The feasibility of the Langmuir isotherm can be given by a dimensionless constant separation factor or the equilibrium parameter \(R_L\), defined as

\[
R_L = \frac{1}{1 + (C_s/b)}
\]

Where \(b\) is the Langmuir constant and \(C_s\) the initial concentration of cation (mmol dm\(^{-3}\)). \(R_L\) correlates with the shape as well as the feasibility of sorption and indicates if the isotherm is unfavourable \((R_L > 1)\), linear \((R_L = 1)\), irreversible \((R_L = 0)\) or favourable \((0 > R_L > 1)\). In addition, \(R_L\) values can give the order of preference or selectivity for biosorption of certain metal ions by some specific biosorbent\(^{[21]}\).

**Freundlich isotherm model**

The Freundlich isotherm was originally empirical in nature, but has had intense use to interpret sorption processes on heterogeneous surfaces or on surfaces supporting sites of varied affinities\(^{[16, 18]}\). Stronger binding sites from this model are first occupied by the sorbate molecules, then by weaker binding sites in the next step, consequently, the degree of site occupation increases with the decreasing binding strength\(^{[22]}\) and to obtain the sorption parameters, following equation was applied:

\[
\log N_f = \log K_F + \frac{1}{n} \log C_s
\]

Where \(K_F\) and \(n\) are constants and related to the sorption capacity of the biosorbent and the sorption intensity. The plot of \(\log N_f\) vs. \(\log C_s\) for the biosorption was employed to generate \(K_F\) and \(n\) from the intercept and the slope values, respectively.

**Temkin isotherm model**

This model was developed by Tempkin and Pyzhev to understand the effects of some indirect sorbate-sorbent interactions on sorption isotherms. It was deduced in these interactions that the heat of sorption of all the molecules in the layer would decrease linearly rather than logarithmic sorption occurence.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>N (%)</th>
<th>C (mmol.g(^{-1}))</th>
<th>N (mmol.g(^{-1}))</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td>39.35</td>
<td>7.16</td>
<td>32.79</td>
<td>5.11</td>
<td>6.41</td>
</tr>
<tr>
<td>Chito-GMA</td>
<td>42.04</td>
<td>5.62</td>
<td>35.03</td>
<td>4.02</td>
<td>8.72</td>
</tr>
<tr>
<td>Chito-EDA</td>
<td>41.21</td>
<td>6.19</td>
<td>34.34</td>
<td>4.42</td>
<td>7.77</td>
</tr>
<tr>
<td>Chito DETA</td>
<td>39.75</td>
<td>6.67</td>
<td>33.13</td>
<td>4.76</td>
<td>6.96</td>
</tr>
</tbody>
</table>

**TABLE 1:** Carbon (C) and nitrogen (N) percentage, number of moles for chitosan and chemically modified chitosan (Chito-GMA, Chito-EDA and Chito DETA) and the corresponding molar ratio (C/N)
The nitrogen content in the chemically modified chitosan Chito-EDA and Chito-DETA, resulting in an increased amount of 4.42 and 4.76 mmol.g⁻¹. These values are in agreement with the incorporation of EDA and DETA molecule as pendant chains in the chitosan backbone.

Infrared spectroscopy

FT-IR spectrum of the chitosan in Figure 1 is present a series of characteristic bands: (i) a broad one at 3410 cm⁻¹ attributed to amino stretching band which overlaps with OH stretching in the same region, (ii) due to incomplete deacetylation of chitin, their is absorption at 1650 and 1373 cm⁻¹ assigned to CO and C–H deformation of acetamide group, (iii) typical C–H stretching vibrations at 2916 and 2877 cm⁻¹ and (iv) bands in the 1200–800 cm⁻¹ region associated with the pyranosidic ring, reflecting C–O–C and β-glycosidic linkage as well as the C–O related to primary and secondary alcohols. The FT-
IR spectra of chemically modified chitosan demonstrated some changes when compared to the original chitosan, as observed in Figure 1.

For the Chito-GMA spectrum, the band at 1709 cm\(^{-1}\) clearly showed the presence of the carbonyl group of GMA in the chemically modified chitosan. Evidence of the success of this incorporation is associated with the appearance of a band at 1630 cm\(^{-1}\), which attributed to the double bond of GMA moiety.

Due to reaction involving the double bond of the GMA moiety, the characteristic band at 1635 cm\(^{-1}\) is disappeared. In addition, the band assigned to the CO group shifted to a highervalue and appears as a shoulder at 1726 cm\(^{-1}\) in final modified chitosan (Chito-EDA and Chito-DETA). Finally, these changes confirmed the proposed chemical modification.

Nuclear magnetic resonance spectroscopy

\(^{13}\)C NMR spectra of the chitosan and its derivatives are shown in Figure 2. The characteristic chemical shifts for chitosan are exist at 62, 84, 58, 75 and 105 ppm and assigned to C\(_f\), C\(_d\), C\(_b\), C\(_c\)-e and C\(_a\) carbons, respectively. The methyl and carbonyl groups from the original chitin signals at 23 and 175 ppm are associated with incomplete deacetylation, as indicated by the labeled carbon atoms in the inserted skeleton structure of the biopolymer in Figure 2. As expected, chemically modified chitosan Chito-EDA and Chito-DETA presented peaks at 137 and 128 ppm that corresponds to vinyl group carbons of GMA. In addition, there are two signals at 19 and 169 ppm are attributed to methyland carbonyl from ester functionality associated with GMA. When the intermediate product Chito-GMA was further modified with EDA and/or DETA, the peak for C\(_b\) and C\(_f\) at 58 and 62 ppm presented separated due to the increased number of carbon-nitrogen bonds. However, for the final chemically modified chitosan the peaks corresponding to the vinyl group carbons of GMA are absent. This confirmed the successful chemical modification of the chitosan.

X-ray diffraction

The original chitosan contains intra- and intermolecular hydrogen bonds that drive the related crystallinity toward the ability to maintain the polymeric chains. The chemically modified chitosan incorporating GMA and subsequently EDA and DETA in the chitosan disrupt these sets of hydrogen bonds in all polymeric chains and the bulkier substitution on it, during the course of the reaction. The new chemically modified chitosans decreases in crystallinity in comparison with the chitosan.

X-ray diffraction patterns of chitosan and its modified presented two common peaks as shown in

![Figure 2: \(^{13}\)C NMR spectra of chitosan Chito and chemically modified chitosans Chito-GMA Chito-EDA and Chito-DETA](image)
Ahmed G.Hassabo and Amina L.Mohamed

Figure 3: X-ray diffractogram patterns for chitosan (Chito) and chemically modified chitosans (Chito-GMA Chito-EDA and Chito-DETA)

TABLE 2 : Particle size of chitosan and its modified calculated from XRD analysis

<table>
<thead>
<tr>
<th></th>
<th>$2\theta^{\circ}$</th>
<th>FWHM</th>
<th>Calculated particles size ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td>18.0</td>
<td>0.331</td>
<td>6.34384</td>
</tr>
<tr>
<td>Chito-GMA</td>
<td>17.4</td>
<td>0.335</td>
<td>34.2219</td>
</tr>
<tr>
<td>Chito-EDA</td>
<td>17.4</td>
<td>0.301</td>
<td>38.0875</td>
</tr>
<tr>
<td>Chito-DETA</td>
<td>17.4</td>
<td>0.2805</td>
<td>40.8711</td>
</tr>
</tbody>
</table>

Figure 3. Chitosan presents a diffraction pattern that indicates poor crystallinity, as can be seen through the two characteristic broad peaks at $2\theta = 9.0^{\circ}$ and $18.0^{\circ}$. The chemically modified chitosan, incorporating GMA, EDA and DETA, (Chito-EDA and Chito-DETA) showed further decreases in the crystalline nature. For chemically modified chitosan, the first peak was shifted to lower values and appears at 8.4 and $17.4^{\circ}$, when compared to the chitosan.

Crystallite size of the chitosan and its modified were calculated using full width at half maximum (FWHM) of the 100% of characteristic peak and the Scherrer’s formula:

$$d = \frac{K \times \lambda}{\beta \times \cos \theta}$$

where $d$ is size of the chitosan particles ($\mu$m), $\lambda$ is X-ray wavelength, $\beta$ is FWHM of the diffraction line, $\theta$ is diffraction angle, and $K$ is constant, generally assumed as 0.9. Calculated average crystallite sizes are illustrated in TABLE 2, and it is show that, the particle size of Chito-GMA is higher than chitosan itself, and that is indication of the chemically interaction of chitosan with GMA. Furthermore, the particle size was increased via increasing the molecular weight of amine compounds. Therefore, the particle size of chitosan and their modified are arranged as Chito-DETA > Chito-EDA > Chito-GMA > Chitosan. In addition, chitosan and their modified are in microform and it is polycrystalline in nature.

Sorption studies

In order to explore the Lewis basic properties of the nitrogen and oxygen centres attached to the pendant organic chains, both chemically modified chitosan (Chito-EDA and Chito-DETA) were employed for the biosorption process to extract divalent metal (barium, manganese, cobalt, nickel, copper, zinc and cadmium cations) from dilute aqueous solutions.

Langmuir, the Freundlich and the Temkin models have been used for each sorbent with all metal ion solution and the amount of metal sorbed on a specific sorbent for a constant temperature have been...
The relationship between cation uptake and time were plotted in Figure 4 for Chito-EDA and Chito-DETA, with higher metal uptake obtained for copper > cobalt > barium > nickel > zinc > manganese > cadmium for both modified chitosan, but with higher concentration for Chito-DETA than Chito-EDA and it is also confirmed in Figure 5. This behaviour is associated with metal ion interactions with nitrogen and hard oxygen basic centres attached to the chitosan chains. As the final concentration of cations increased the metal uptake increased until reaching a plateau at higher cations concentrations. Furthermore, Chito-DETA have higher metal uptake than Chito-EDA for each metal ion, and that may be because Chito-DETA have three nitrogen centres (more than Chito-EDA) attached to the pendant organic chains.

Three isothermal model have been applied for the absorption of all metal cation with both modified chitosan. First model is Langmuir model, the parameters $K$ that corresponds to the equilibrium
Figure 5: Efficiency of metal ion adsorption (%) on chemically modified chitosans (Chito-EDA and Chito-DETA)

The sorption constant and $C_{max}$ were calculated. Furthermore, the second model is the Freundlich model, and the Freundlich parameters were determined. In addition, the third model is the Temkin model, and the Temkin parameters were also calculated to give the results for all cations, and these data for all the cations are listed in TABLE 3.

For the Langmuir model, high values of $K$ indicate the desirable high affinity. In spite of the performance of cationsorption, the best desirable condition for the chemically modified chitosan is related to both high $C_{max}$ and high $K$ values. In addition, as $R$ values lie between 0 and 1, indicating that the sorption process is favourable.

For the Freundlich model, both $K$ and $1/n$ reached their corresponding maximum values, this implies that the binding capacity reaches the highest value and show that the affinity between the biopolymer and cations was also high. The Temkin constants confirming that, the Temkin model is able to describe the data.

Finally, comparing the data for all three models applied, found that, Langmuir model is the best isothermal model to describe the absorption of cations (copper, cobalt, barium, nickel, zinc, manganese, cadmium) on both modified chitosan.

CONCLUSION

The present work have reports a modification of chitosan with glycidylmethacrylate followed by diethylenetriamine or ethylenediamine under environmental friendly conditions. The chemically modified chitosan were characterized and approved. In addition, the presence of pendant chains containing attached basic nitrogen and oxygen cen-
Multiamine modified chitosan for removal metal ions from their aqueous solution

FULL PAPER

TABLE 3: adsorption parameters of three isotherm model for the interaction of divalent metals with chemically modified chitosan at 25±1°C

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Modified chitosan</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>Temkin isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>Cmax (mg/g)</td>
<td>R²</td>
<td>K</td>
</tr>
<tr>
<td>Ba (II)</td>
<td>Chito-EDA 24.71</td>
<td>11.24</td>
<td>0.991</td>
<td>13.08</td>
</tr>
<tr>
<td></td>
<td>Chito-DETA 11.72</td>
<td>10.64</td>
<td>0.993</td>
<td>32.07</td>
</tr>
<tr>
<td>Mn (II)</td>
<td>Chito-EDA 174.00</td>
<td>25.00</td>
<td>0.972</td>
<td>1.119</td>
</tr>
<tr>
<td></td>
<td>Chito-DETA 117.96</td>
<td>20.00</td>
<td>0.976</td>
<td>1.456</td>
</tr>
<tr>
<td>Co (II)</td>
<td>Chito-EDA 17.28</td>
<td>10.99</td>
<td>0.999</td>
<td>21.06</td>
</tr>
<tr>
<td></td>
<td>Chito-DETA 14.64</td>
<td>10.87</td>
<td>0.998</td>
<td>25.56</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>Chito-EDA 47.04</td>
<td>13.16</td>
<td>0.981</td>
<td>5.116</td>
</tr>
<tr>
<td></td>
<td>Chito-DETA 36.65</td>
<td>12.35</td>
<td>0.983</td>
<td>7.547</td>
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<tr>
<td>Cu (II)</td>
<td>Chito-EDA 8.985</td>
<td>10.53</td>
<td>0.999</td>
<td>37.24</td>
</tr>
<tr>
<td></td>
<td>Chito-DETA 3.456</td>
<td>10.42</td>
<td>0.996</td>
<td>67.16</td>
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<tr>
<td>Zn (II)</td>
<td>Chito-EDA 58.40</td>
<td>14.08</td>
<td>0.993</td>
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<td></td>
<td>Chito-DETA 44.84</td>
<td>12.987</td>
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<td>4.461</td>
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<tr>
<td>Cd (II)</td>
<td>Chito-EDA 125.58</td>
<td>16.949</td>
<td>0.987</td>
<td>0.009</td>
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<tr>
<td></td>
<td>Chito-DETA 97.27</td>
<td>15.15</td>
<td>0.988</td>
<td>0.032</td>
</tr>
</tbody>
</table>

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REFERENCES