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Multiamine modified chitosan for removal metal ions from their aqueoussolution

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ABSTRACT

Chitosan was chemically modified with glycidylmethacrylate and ethylenediamine or diethylenetriaminein 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, ^{13}C-NMR, XRD, SEM and employed for barium, manganese, cobalt, nickel, copper, zinc and cadmiumbiosorption. Elemental analysis data based on nitrogen atom content gave an incorporation oforganic pendant groups to the modified chitosan. ^{13}C-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 chitosandue to the increment of basic centers attached to the pendant chains. The experimental data were adjusted toLangmuir, 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.

KEYWORDS

Chemically modified chitosan;
Multiamine;
Sorbtion;
Metal ion;
Kinitic and isotherm model.

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 andcadmium are listed in the toxicitylist[1]. Metal ions accumulate and their amountsare increased dueto their non-biodegradability properties. Owing to the toxic effects, the industries are advised that thewaste waters be treated systematically toremove/minimize themetal contents in their wastes.

Many methods are already used forthis purpose. Metal adsorption by activated carbon is the most efficientclassical way as it removes more than 99% of certain metal ionsbut the cost of its production is prohibitive and it cannot be regenerated and re-

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cycled. Many other treatments like ion exchange, evaporation, precipitation, coagulation and membrane separation etc. are tooexpensive 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 isdefined as passive, not involving metabolically mediated processes,with the property to bind metals by living or dead biomass[2].

Considerableattention has been paid to the recovery and removal ofvaluable heavy metal ions from industrial and municipal wastewaterby using various biosubstances or natural products, particularlybecause of the low cost and high availability of these materials,without needing arduous regeneration process for reuse, beingcapable of binding heavy metals by sorption, chelation and ionexchange processes[3, 4]. These low-cost abundant natural materialssuch as chitin, chitosan, alginate, cellulose, peat and biomassrequire little processing and are abundant in nature, mainly whenobtained 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 animportant natural biopolymer due to its biocompatibility andbiodegradability, with broad applications in wastewater treatmentin chemical, biomedical and pharmaceutical applications and inagriculture 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 usedto 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 zincnitrate ($Zn(NO_3)_2$) were all of analytical grade.

Synthesis

Modification of chitosan with glycidylmethacrylate(Chito-gly)

In the step, in a 250 ml three neckedflask 4 g of chitosanwas 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 stirringover 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 neckedflask 4 g of Chito-gly

was suspended in 150 ml of ethanol with stirring at 60°C, followed by slow additionof 1.67 ml of diethylenetriamine (DETA)or ethylenediamine (EDA) in the presence of 1 ml oftriethylamine as a catalyst, this suspension was maintained underreflux with mechanical stirring for 72 h. the new composite (Chito-DETA and Chito-EDA) was filtered, washed withethanol and deionized water and then dried under vacuum at 45°C for 6 h. This new compositesare very stable for severalmonths at room temperature, without presenting anydecomposition.

Characterization

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

$$\mathbf{Lo} = \frac{\mathbf{Element\ \%} \times \mathbf{10}}{\mathbf{Atomic\ mass\ of\ element}}$$

The FT-IR tester of Nicolet Magna-IR 560 spectrometer was used to analyse the spectrum of the untreated and treated samples. KBrwas 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}.

^{13C}NMRspectra of the samples were obtained on a Bruker AC 300/Pspectrometer, using the CP–MAS technique, with pulse repetitionsof 5 s and contact times of 1ms, at 75.47MHz and with magic anglespinning of 4 kHz.

TheXRDpattern was recorded using (Empyrean, pixcel^{3D}, Amedipixz collaboration, PANALYTICAL Netherland) with Cu- Kα radiation (γ = 0.15406 nm) in the 2θ range from 5 to 50 at the scanning rate of 2°perminute. The driedpowderswereloadedonglassand subjected to X-Ray and the diffracted pattern was recorded.

Thermal behaviourwasinvestigated usingathermo gravimetricanalyser (TGA)ShimadzuTGA 50 apparatus. The samples were heated at therate of 10°C perminfrom room temperatureto600°C in nitrogen atmosphere.

The amountof cationsorbed was determined using a Cary100 UV-visspectrophoto-meter, considering the difference between the initialconcentration in the aqueous solution and that found in thesupernatant 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 λmax 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 1g-modified chitosan (Chito-EDA or Chito-DETA) intoa series of flasks containing metal salt solution in deionized waternear neutral pHat a liquor ratio 1:20. The concentration of metal salt solution ranging from0.2 – 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 λmax 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 it back into the treatment solution for keeping the concentration constant.

Isotherm models

Equilibrium isotherm equations are used to describe theexperimental sorption data. Equilibrium models and their equation parameters often provide some sorptionmechanisms 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-

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ematical forms. The most common isotherms model for describing solid/liquidsorption systems are the Langmuir, the Freundlich[13-16] and the Temkinisotherms[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,$N_s$andbare the Langmuir constants related tothe 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 monolayercoverage of sorbent species with sorbate andbrepresents theenergy of sorption[16, 18, 20]. The feasibility of the Langmuir isothermcan be given by a dimensionless constant separation factor or theequilibrium parameterR_L, defined as

$$R_L = \frac{1}{(1 + (C)_s b)}$$

Wherebis the Langmuir constant and$C_s$the initial concentrationof cation (mmol dm^{-3}). $R_L$correlates with the shape as well as thefeasibility 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 selectivityfor biosorption of certain metal ions by some specific biosorbent[21]

Freundlich isotherm model

The Freundlich isotherm was originally empirical in nature, buthas 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 bythe sorbate molecules, then by weaker binding sites in thenext step, consequently, the degree of site occupation increaseswith the decreasing binding strength[22]and to obtain the sorptionparameters, following equation was applied:

$$LogN_f = LogK_F + \frac{1}{n} LogC_s$$

Where$K_F$andnare constants and related to the sorption capacityof the biosorbent and the sorption intensity. The plot of log$N_f$vs. log$C_s$for the biosorption was employed to generate$K_F$andnfromthe 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 onsorption isotherms. It was deduced in these interactions that theheat of sorption of all the molecules in the layer would decrease linearly rather than logarithmic sorption oc-

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)

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

curs[17] and the isothermcan be given by the following form:

$$N_f = n_T LnK_T + n_T LnC_s$$

A plot of lnC_s versus N_f enables determination of K_T, n_T and bvalues. The constantbis related to the heat of sorption, which canbe calculated using the following equation:

$$n_T = \frac{R_T}{b}$$

For comparing models three statistical tools have been used. It is the correlation coefficient (r) obtained by means of linear regression of each equation, with a scaling factor derived by the division of each individual deviation with the standard deviation of the corresponding variable.

RESULT AND DISCUSSION

Charachtrisation of modified chitosan

Elemental analysis

Chitosan and their chemically modified (Chito-GMA, Chito-EDA and Chito-DETA) were analyzed for carbon and nitrogen contents. The amount of both elements were calculated, C/N relationship as well as the general amounts of each element (Lo) attached in the pendant chains and listed in TABLE 1.

The nitrogen content in the chemicallymodified chitosanChito-GMA, 4.02mmol.g^{-1}, decreased when comparedto the chitosan, 5.11 mmol.g^{-1}, reflecting thechemical incorporation of the organic moiety GMA,which is covalently bonded to the available amino groups ofthe chitosan structure. In the next step, the Chito-GMAwasfurther chemically modified with EDA and DETA,whose molecule contains two and three available nitrogen atoms respectively, causinga proportional increase in this element in the chemicallymodified chitosanChito-EDA and Chito-DETA, resulting in an increased amountof 4.42 and 4.76mmol.g^{-1}. These values are in agreement with the incorporationof EDA and DETA molecule as pendant chains in thechitosan backbone.

Infrared spectroscopy

FT-IR spectrum of the chitosan in Figure 1 is present a series of characteristic bands: (i) a broad one at3410cm^{-1}attributed to amino stretching band which overlapswith OH stretching in the same region, ii) due to incomplete deacetylationof 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 associatedwith the pyranosidic ring, reflecting C–O–C and β-glycosidiclinkage as well as the C–O related to primary and secondary alcohols. The FT-

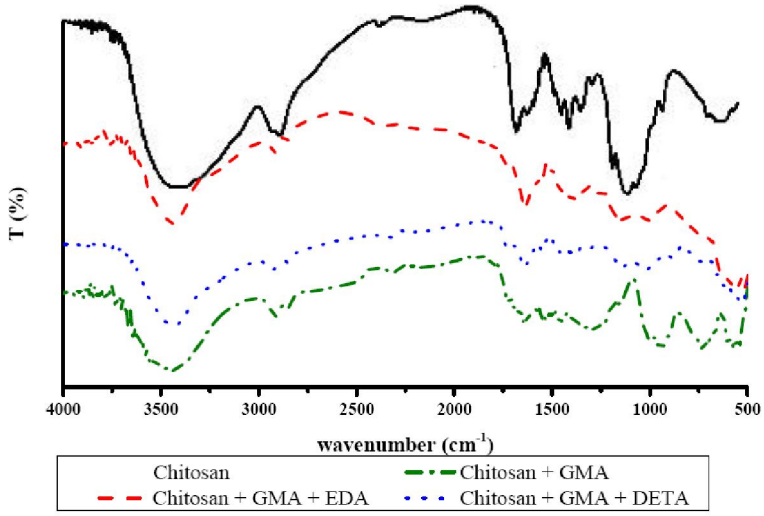

Figure 1: FT-IR spectra of chitosan and chemically modified chitosan (Chito-EDA and Chito DETA)

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IR spectra of chemically modified chitosan demonstrated some changes when compared to theoriginal chitosan, as observed in Figure 1.

For the Chito-GMA spectrum,the band at 1709 cm^{-1}clearly showed the presence of thecarbonyl group of GMA in the chemically modifiedchitosan. Evidence of the success of this incorporation isassociated with the appearance of a band at 1630 cm^{-1}, which attributed to the double bond[23] of GMA moiety.

Due to reactioninvolving 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 1726cm^{-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, $C_{c\text{-}e}$ and C_a carbons, respectively. The methyl and carbonyl groups from the original chitin signalsat 23 and 175ppm are associated with incomplete deacetylation,as indicated by the labeled carbon atoms in the inserted skeletonstructure of the biopolymer in Figure 2. As expected, chemicallymodified chitosan Chito-EDA and Chito-DETA presented peaks at 137 and 128ppmthat corresponds to vinyl group carbons of GMA. Inaddition, there are two signals at 19 and 169ppm are attributed to methyland carbonyl from ester functionality associated with GMA. When the intermediate product Chito-GMA was further modifiedwith 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[24, 25]. However, for the final chemically modified chitosan the peakscorresponding to the vinyl group carbons of GMA are absent. This confirmed the successful chemicalmodification of the chitosan.

X-ray diffraction

The original chitosan contains intra- and intermolecular hydrogenbonds that drive the related crystallinity toward the ability tomaintain the polymeric chains[26, 27]. The chemically modified chitosan incorporating GMA and subsequently EDA and DETA in the chitosan disrupt these sets ofhydrogen bonds in all polymeric chains and the bulkier substitution on it, during the course of the reaction. The newchemically modified chitosans decreases in crystallinity in comparisonwith the chitosan[28].

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

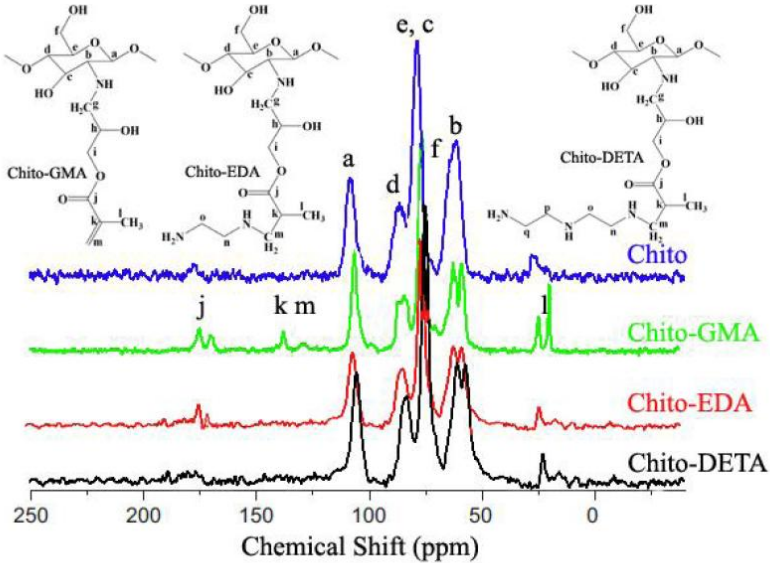

Figure 2: ^{13}C NMR spectra of chitosan Chito and chemically modified chitosans Chito-GMA Chito-EDA and Chito-DETA

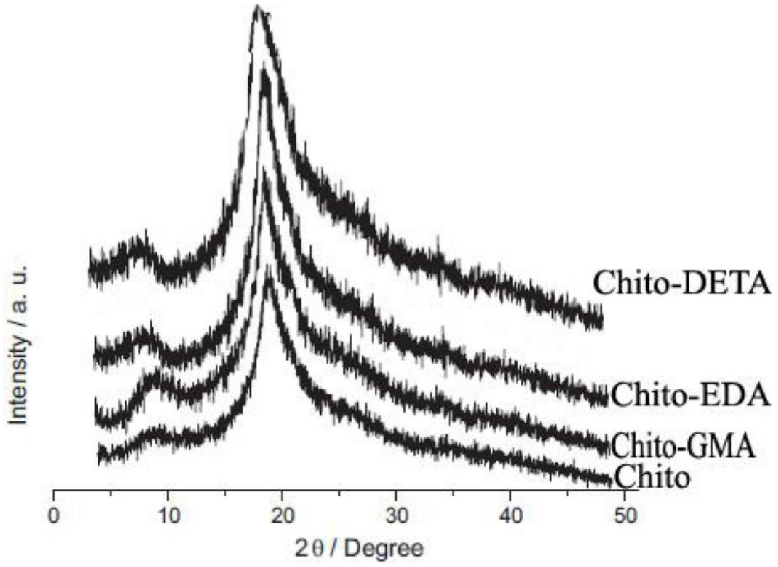

Figure 3: X-ray diftractogram patterns for chitosan (Chito) and chemically modified chitosans (Chito-GMA Chito-EDA and Chito-DETA)

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

	2θ°	FWHM	Calculated particles size (µm)
Chitosan	18.0	0.331	6.34384
Chito-GMA	17.4	0.335	34.2219
Chito-EDA	17.4	0.301	38.0875
Chito-DETA	17.4	0.2805	40.8711

Figure 3. Chitosanpresents a diffraction pattern that indicates poor crystallinity, ascan be seen through the two characteristic broad peaks at 2θ = 9.0and 18.0°. The chemically modified chitosan, incorporating GMA, EDA and DETA, (Chito-EDA andChito-DETA)showed further decreases in the crystalline nature. For chemicallymodified chitosan, the first peakwas shifted to lower values andappears at 8.4 and 17.4°, 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[29],

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

whered is size of the chitosan particles (µm), λ is X-ray wavelength, β is FWHM of the diffraction line, θ 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 poly crystalline in nature[29].

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 thebiosorption process to extract divalent metal (barium, manganese, cobalt, nickel, copper, zinc and cadmiumcations) 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 specificsorbent for a constant temperature have been

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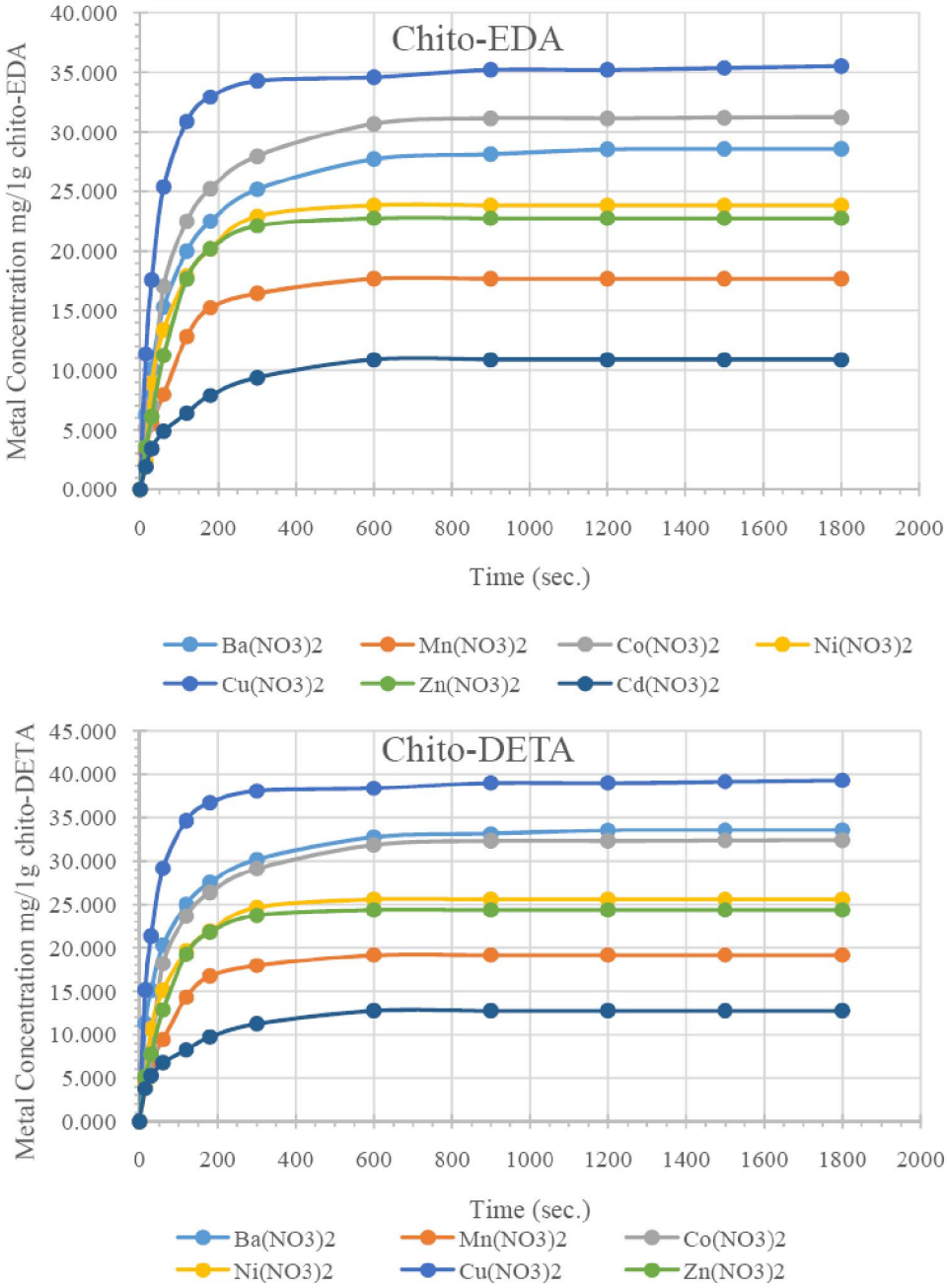

Figure 4: Metal ionconcentration adsorbed on chemically modified chitosans (Chito-EDA and Chito-DETA)

inferred.

The relationship between cation uptake and time were plotted in Figure 4 for Chito-EDA and Chito-DETA, with higher metaluptake 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

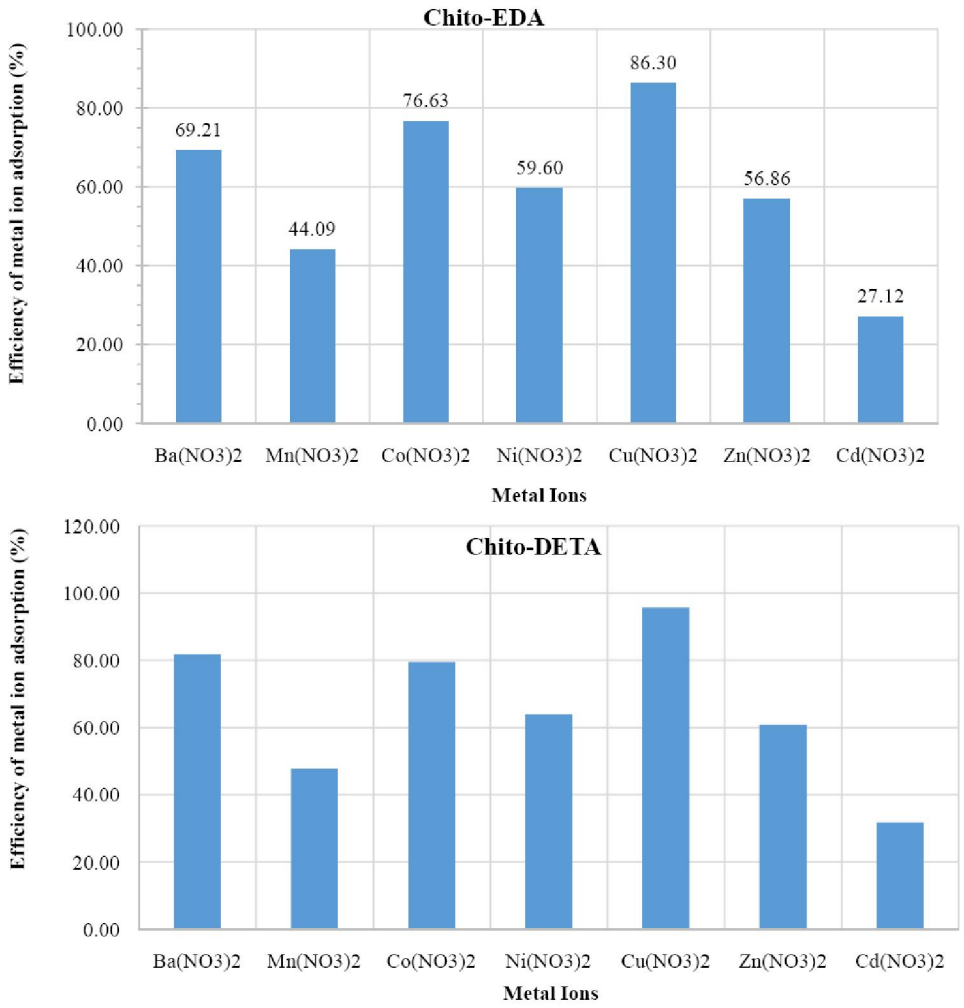

Figure 5: Efficiency of metal ion adsorption (%)onchemically modified chitosans (Chito-EDA and Chito-DETA)

sorption constant and C_{max}were calculated. Furthermore, second model is Freundlichmodel, and the Freundlichparameters were determined. In addition, third model is Temkin model, 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 workhave reports a modificationof chitosan with glycidylmethacrylatefollowed bydiethylenetriamineorethylenediamine underenvironmental friendly conditions. The chemically modified chitosan were characterized and approved. In addition, the presence ofpendant chains containing attached basic nitrogen and oxygen cen-

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

Metal ion	Modified chitosan	Langmuir isotherm			Freundlich isotherm			Temkin isotherm			
		K	C_{max} (mg/g)	R^2	K	1/n	R^2	K	n	b	R^2
Ba (II)	Chito-EDA	24.71	11.24	0.991	13.08	0.281	0.964	0.0595	22.16	0.142	0.975
	Chito-DETA	11.72	10.64	0.993	32.07	0.158	0.963	0.958	13.87	0.226	0.970
Mn (II)	Chito-EDA	174.00	25.00	0.972	1.119	0.658	0.947	0.008	39.82	0.079	0.974
	Chito-DETA	117.96	20.00	0.976	1.456	0.589	0.950	0.009	37.34	0.084	0.973
Co (II)	Chito-EDA	17.28	10.99	0.999	21.06	0.217	0.975	0.1667	18.42	0.170	0.982
	Chito-DETA	14.64	10.87	0.998	25.56	0.191	0.976	0.316	16.56	0.190	0.983
Ni (II)	Chito-EDA	47.04	13.16	0.981	5.116	0.415	0.952	0.0191	30.05	0.105	0.969
	Chito-DETA	36.65	12.35	0.983	7.547	0.361	0.952	0.027	27.26	0.115	0.968
Cu (II)	Chito-EDA	8.985	10.53	0.999	37.24	0.141	0.995	2.231	12.72	0.247	0.996
	Chito-DETA	3.456	10.42	0.996	67.16	0.059	0.999	2.869	5.801	0.541	0.999
Zn (II)	Chito-EDA	58.40	14.08	0.993	2.862	0.501	0.981	0.014	33.83	0.093	0.989
	Chito-DETA	44.84	12.987	0.994	4.461	0.438	0.982	0.018	30.93	0.102	0.990
Cd (II)	Chito-EDA	125.58	16.949	0.987	0.009	1.339	0.961	0.004	58.64	0.053	0.989
	Chito-DETA	97.27	15.15	0.988	0.032	1.155	0.965	0.004	55.26	0.057	0.989

ters helping incation removal. Seven divalent metal ion, which they used in textile dyeing processes, were chosenforused during this study, namely cupper, chromium and manganese.

The final chemically modified chitosan contains nitrogen and hard oxygen basic centers that favor to bonding borderline metal.

The performance of biosorption of chemically modified chitosan (Chito-EDA and Chito-DETA) havehigher metal uptake obtained for copper > cobalt > barium > Nickel > Zinc > Manganese > cadmium from aqueous solution for both modified chitosan.

The Langmuir isotherm model provided the best fit of experimental sorption data for all these ions as compared to the Freundlich and the Temkin models.

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REFERENCES

[1] B.Volesky; FEMS Microbiol Rev, **14**, 291-302 **(1994)**.
[2] N.A.Negm, H.E.Ali; Engineering in Life Sciences, **10**, 218-224 **(2010)**.
[3] K.Kaikake, K.Hoaki, H.Sunada, R.P.Dhakal, Y.Baba; Bioresour Technol, **98**, 2787-91 **(2007)**.
[4] J.C.Ng, W.H.Cheung, G.McKay; Chemosphere, **52**, 1021-30 **(2003)**.
[5] C.Gérente, P.Couespel du Mesnil, Y.Andrès, J.F.Thibault, P.Le Cloirec; Reactive and Functional Polymers, **46**, 135-144 **(2000)**.
[6] W.S.Ngah, S.Fatinathan; J Environ.Manage, **91**, 958-69 **(2010)**.
[7] A.T.Paulino, M.R.Guilherme, A.V.Reis, E.B.Tambourgi, J.Nozaki, E.C.Muniz; Journal of Hazardous Materials, **147**, 139-147 **(2007)**.
[8] E.Guibal, J.Roussy; Reactive and Functional Polymers, **67**, 33-42 **(2007)**.
[9] A.R.Cestari, E.F.S.Vieira, I.A.de Oliveira, R.E.Bruns; Journal of Hazardous Materials, **143**, 8-16 **(2007)**.
[10] K.Azlan, W.N.Wan Saime, L.Lai Ken; Journal of Environmental Sciences, **21**, 296-302 **(2009)**.
[11] V.A.Vasnev, A.I.Tarasov, G.D.Markova, S.V.Vinogradova, O.G.Garkusha; Carbohydrate Polymers, **64**, 184-189 **(2006)**.
[12] A.Khan, S.Badshah, C.Airoldi; Chemical Engineering Journal, **171**, 159-166 **(2011)**.
[13] S.Chakraborty, S.De, S.DasGupta, J.K.Basu; Chemosphere, **58**, 1079-1086 **(2005)**.
[14] V.Gökmen, A.Serpen; Journal of Food Engineering, **53**, 221-227 **(2002)**.

[15] O.Nitzsche, H.Vereecken; Mine Water and the Environment, **21**, 15-23 **(2002)**.
[16] A.G.Hassabo, A.Mendrek, C.Popescu, H.Keul, M.Möller; RJTA, **18**, 36-49 **(2014)**.
[17] Y.Liu, Y.-J.Liu; Separation and Purification Technology, **61**, 229-242 **(2008)**.
[18] M.Er-Rafik, A.L.Mohamed, M.Möller, K.Spyropoulos, R.Wagner; Melliand Inter., **5**, 3157 **(2012)**.
[19] S.Oh, M.Y.Kwak, W.S.Shin; Chem.Eng.J, **152**, 376-388 **(2009)**.
[20] S.Badshah, C.Airoldi; Chem.Eng.J, **166**, 420-427 **(2011)**.
[21] S.J.Allen, G.McKay, J.F.Porter; J Colloid Interface Sci, **280**, 322-33 **(2004)**.
[22] K.Y.Foo, B.H.Hameed; Chemical Engineering Journal, **156**, 2-10 **(2010)**.
[23] S.T.Chang, H.T.Chang; Polymer Degradation and Stability, **71**, 261-266 **(2001)**.
[24] A.Zhu, Y.Pan, T.Liao, F.Zhao, T.Chen; Journal of biomedical materials research part B: Applied biomaterials, **85B**, 489-495 **(2008)**.
[25] E.C.N.Lopes, K.S.Sousa, C.Airoldi; Thermochimica Acta, **483**, 21-28 **(2009)**.
[26] K.S.Sousa, E.C.Silva Filho, C.Airoldi; Carbohyd.Res., **344**, 1716-1723 **(2009)**.
[27] M.O.Machado, E.C.N.Lopes, K.S.Sousa, C.Airoldi; Carbohydrate Polymers, **77**, 760-766 **(2009)**.
[28] L.Qi, Z.Xu; Colloids and Surfaces A: Physicochemical and Engineering Aspects, **251**, 183-190 **(2004)**.
[29] A.G.Hassabo, A.A.Nada, H.M.Ibrahim, N.Y.Abou-Zeid; Carbohydrate Polymers, **122**, 343-350 **(2015)**.