



DFT investigation of Ni(II) adsorption onto MA-DTPA/PVDF chelating membrane in the presence of coexistent cations and organic acids

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ABSTRACT

Melamine-diethylenetriaminepentaacetic acid/polyvinylidene fluoride (MA-DTPA/PVDF) chelating membrane bearing polyaminocarboxylate groups was used to remove Ni(II) from nickel plating effluents. Adsorption experiments were conducted to study the adsorption of the membrane towards Ni(II) in Ni(II)–Ca(II), Ni(II)–NH₄⁺, Ni(II)–Fe(III) binary systems, and Ni(II)–lactic acid, Ni(II)–succinic acid and Ni(II)–citric acid complex systems. For the ternary nickel plating processes, the effects of 3d transition metals including Fe(II), Co(II), Cu(II) and Zn(II) on Ni(II) adsorption were evaluated. The influences of the aforementioned coexistent cations and organic acids were elucidated by the continuum solvation model (COSMO)-corrected density functional theory (DFT) method. Geometries and complexation energies were analyzed for metal–MA-DTPA and Ni(II)–organic acid complexes. DFT results accord with the experimental data, indicating that DFT is helpful to evaluate the complexation between the membrane and metal cations. The coexistent Ca(II) tends to form more stable complex with MA-DTPA ligand than NH₄⁺ and Fe(III), and can interfere with the formation of Ni(II)–MA-DTPA complex. The complexing sequence of 3d metals with MA-DTPA ligand is Zn(II) < Co(II) < Ni(II) < Fe(II) < Cu(II). Therefore, both Fe(II) and Cu(II) have the considerable competition with Ni(II). The stabilities of Ni(II)–organic acid complexes follow the order of lactic acid < succinic acid < citric acid, but cannot be comparable to that of Ni(II)–MA-DTPA complex.

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1. Introduction

Contamination of water resource by metal plating industries has been a serious environmental problem. In China, nickel electroless plating and electroplating industries discharge a large amount of wastewater. Therefore, nickel ions and their compounds are ubiquitous in the environment and are thus found frequently in surface water. Toxicity of nickel to living organisms is essentially exerted on enzymes, especially enzymes whose activities depend on sulphydryl and amino groups, because nickel, like other heavy metals, shows high affinity for ligands containing oxygen, nitrogen and sulfur donors [1,2]. Before discharge, wastewater containing nickel should be treated to maintain the legislative standards. According to the published “Emission standard of pollutants for electroplating” (GB 21900–2008, China), emission of the effluents containing Ni(II) has been controlled strictly in China, and the discharged concentration of total nickel should not exceed 0.1 mg/L. In general, the citric, lactic and succinic acids are found to be widely used in the nickel plating processes, and nickel exists in the form of metal–organic complexes rather than the hydrated form. Ca(II),

NH₄⁺ and Fe(III) will be coexistent with Ni(II) in the plating solution. Also, Fe(II), Co(II), Cu(II) and Zn(II) are also existent in Ni–Fe–P, Ni–Co–P, Ni–Cu–P and Ni–Zn–P ternary plating processes. The presence of the coexistent cations and organic acids has posed challenge to the disposal of Ni(II). To our knowledge, there is little information available using the effective and economical techniques to recover nickel from the Ni(II)–organic acid complexes.

The conventional methods used to remove Ni(II) include hydroxide precipitation/neutralization [3], ion exchange [4], adsorption [5,6], solvent extraction [7,8], and membrane techniques [9–11]. Among the techniques above, the membrane technique has become increasingly attractive for the treatment and recycling of Ni(II) in the metal plating industry. For the membrane techniques, UF/RO [12,13], electrodialysis [14,15], liquid membrane extraction [16], and polymer-enhanced ultrafiltration [17] have been applied to remove Ni(II). However, the cost of the aforementioned membrane technologies is higher than that of the conventional adsorption processes.

The chelating membrane functionalized with chelating groups [18,19], like the chelating resins [5,20–22], can be recommended for the treatment of wastewater containing Ni(II). The chelating membrane, loading ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) chelating group for removing Ni(II)–organic complexes, is deserved to be investigated.

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However, there are few investigations in terms of the modification of polyvinylidene fluoride (PVDF) membrane with DTPA. We have performed a primary study of the removal of the hydrated Ni(II) using PVDF-based (MA-DTPA/PVDF) chelating membrane [23]. Further studies, such as the influences of coexistent cations and organic acids on the adsorption performance of the chelating membrane towards Ni(II), should be considered.

Compared with the experimental results, we confirm that the investigation of the complexation characteristics of metal-MA-DTPA complexes using density functional theory (DFT) will provide an insight into the removal nature of heavy metals from wastewater. DFT calculations allow the possibility of modeling the metal complexes, providing the structural and energetic information [24]. With the assistance of theoretical techniques [25–28], the electronic properties of metal complexes can be elucidated. Some DFT investigations about metal complexes of amino polycarboxylic acid sorbents have been reported [29–31]. Although the aforementioned theoretical investigations of the metal-amino polycarboxylic acid interactions have been done, few reports about theoretical calculations of DTPA-based complexes using the solvation effect-corrected DFT methods can be found. In our previous research [32], it has been confirmed that the solvation effect-corrected DFT theoretical calculations are suitable for evaluating the favorable coordination between the chelating adsorbents and metal cations.

The aim of this work is to combine the experimental measurement and DFT simulation to investigate the influences of coexistent cations and organic acids on the adsorption performance of the MA-DTPA/PVDF chelating membrane. Experiments regarding the influences of Ca(II), NH_4^+ , Fe(III), citric acid, lactic acid and succinic acid on the adsorption properties of the membrane have been carried out. The effects of Fe(II), Co(II), Cu(II) and Zn(II) on Ni(II) adsorption of the membrane in Ni-P ternary plating processes were also taken into account. Geometrical optimizations of the coexistent cations with MA-DTPA and Ni(II)-organic acid complexes have been calculated. Moreover, the complexation energies of them were also calculated to obtain the minimum energy configurations. In addition, the Mulliken charge population of the metal-MA-DTPA and Ni(II)-organic acid complexes was analyzed for evaluating the charge transfer. This research will lend some supports to the further treatment of metal plating wastewater.

2. Methods

2.1. Experimental

2.1.1. Materials

Analytical grade of polyvinylidene fluoride (PVDF), polyvinyl pyrrolidone (PVP), dimethylsulfoxide (DMSO), diethylenetriamine-pentaacetic acid (DTPA) and melamine (MA) were used for the preparation of the chelating membrane. The preparation process of the MA-DTPA/PVDF chelating membrane could be found in our previous paper [23]. A stock solution of Ni(II) (1000 mg/L) was prepared and the working solutions were prepared by diluting the stock solution to appropriate volumes. Analytical grade of the reagents including $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, CaCl_2 , NH_4Cl , $\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, lactic acid, succinic acid and citric acid were used as received.

2.1.2. Adsorption experiments

Adsorption experiments of Ni(II) on the chelating membrane were carried out at 298 K for 120 min. The Ni(II)-Ca(II), Ni(II)- NH_4^+ , Ni(II)-Fe(III) binary systems and Ni(II)-lactic acid, Ni(II)-succinic acid, Ni(II)-citric acid organic complex systems were investigated. The adsorption of Ni(II) on the chelating membrane from Ni-Fe-P,

Ni-Co-P, Ni-Cu-P and Ni-Zn-P ternary electroless nickel plating solutions was also considered. All the experiments were conducted in 200 mL solutions containing Ni(II), and the solutions were treated by the chelating membrane with the diameter of 10 cm. pH of the solutions was adjusted to 6.0 using HAc-NaAc buffer solutions. The effects of the coexistent cations including Ca(II), NH_4^+ , Fe(III), and 3d transition metals involving Fe(II), Co(II), Cu(II) and Zn(II) on Ni(II) adsorption were studied by a set of adsorption tests with a step-wise addition in the range of 0–5 mmol/L. The influences of citric, lactic, and succinic acids ranging from 0 to 10 mmol/L, were also considered.

The initial concentration of Ni(II) was 50 mg/L. At different intervals, 1 mL liquor was withdrawn from the solution to measure the residual concentration of Ni(II). The concentrations of Ni(II) and other metals were measured using atomic absorption spectroscopy (AAS, WFX-110 spectrometer). The concentration of NH_4^+ was measured using Nessler's reagent colorimetric method according to the Chinese water quality determination (GB 7479-1987). The amounts of nickel adsorbed on the chelating membrane were calculated according to Eq. (1):

$$q = \frac{(c_0 - c_t)V}{A} \quad (1)$$

where q is the amount of Ni(II) adsorbed onto a unit area of the membrane (mg/cm^2). c_0 and c_t (mg/L) are the concentrations of Ni(II) in the aqueous phase at the initial time and time t , respectively. V is the volume of the aqueous phase (L) and A is the surface area of the membrane (cm^2).

2.2. Computational details

All the calculations are based on density functional theory and were performed with Materials Studio DMol³ from Accelrys (version 4.1) [32]. Double numerical plus polarization functions (DNP) and BLYP approximation nonlocal functionals (GGA-BLYP) were employed. All calculations employed a method based on Pulay's [33] direct inversion of iterative subspace (DIIS) technique to accelerate SCF convergence, where necessary, a small electron thermal smearing value of 0.005 Ha was used.

For the study of metal-organic complexes, the core treatment pattern used for all complexes is effective core potentials (ECP). The geometries of Ca(II), Fe(III), Fe(II), Co(II), Cu(II) and Zn(II) complexed with the polyaminocarboxylate functional groups of the chelating membrane, and that of Ni(II) with lactic, succinic, citric acids were optimized. Convergence criteria for geometry optimizations were the default threshold values. A continuum solvation model (COSMO) was used, taking the solvation effect into account. Frequency calculations and Mulliken population analyses were performed to obtain the geometrical and energetic parameters. Bond lengths and angles were elucidated for the complexes regarding the geometrical deformation. The complexation energies and Gibbs free energies were calculated to illustrate the comparative complexation stability. Complexation energy, $\Delta E(\text{compd.})$, is calculated according to Eq. (2):

$$\Delta E(\text{compd.}) = E(\text{ML}^{2-}) + 6E(\text{H}_2\text{O}) - E(\text{L}^{4-}) - E((\text{M}(\text{H}_2\text{O})_6)^{2+}) \quad (2)$$

where $E(X)$ is the COSMO-corrected total energy of species (X). M and L refer to metal and ligands, respectively. The complexation Gibbs free energies are then determined using Eqs. (3) and (4):

$$\Delta G_{298.15\text{K}} = G(\text{ML}^{2-}) + 6G(\text{H}_2\text{O}) - G(\text{L}^{4-}) - G((\text{M}(\text{H}_2\text{O})_6)^{2+}) \quad (3)$$

$$\Delta G(\text{compd.}) = \Delta E(\text{compd.}) + \Delta G_{298.15\text{K}} \quad (4)$$

where $G(X)$ is the computed temperature-corrected free energy of species (X) at 298.15 K. $\Delta G_{298.15\text{K}}$ is the resulting corrected free

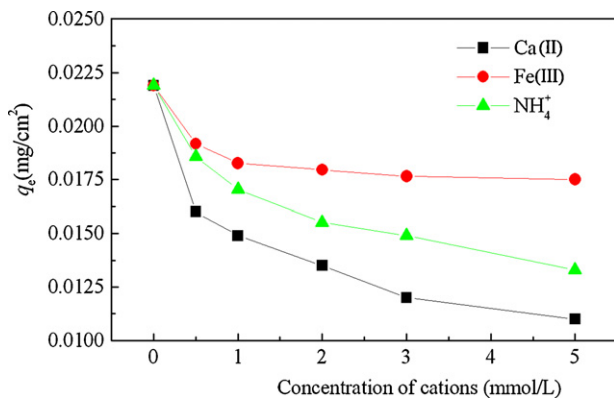


Fig. 1. Effects of the coexistent cations on the adsorption of Ni(II) by the chelating membrane. $C_0(\text{Ni(II)}) = 50 \text{ mg/L}$; $t = 120 \text{ min}$; membrane area: 157 cm^2 ; temperature: 298 K ; pH: 6.0.

energy for the reaction. $\Delta G(\text{compd.})$ is the complexation Gibbs free energy.

3. Results and discussion

3.1. Effect of variables

3.1.1. Effect of the competitive cations

Nickel electroless plating and electroplating processes involve the addition of NH_4^+ , the coexistence of Ca(II) , and the formation of Fe(III) because of the dissolution of the coated alloys containing iron. The polyaminocarboxylate groups of the chelating membrane can bind with these cations, thus interfering with Ni(II) adsorbed onto the membrane. Fig. 1 describes the nickel uptake varying the concentration of competitive cations. As the concentration increases from 0 to 1 mmol/L, the nickel uptake decreases significantly. The existence of Ca(II) , NH_4^+ and Fe(III) at the concentration of 1 mmol/L reduces the nickel uptake by 24%, 15% and 7.7%, respectively. On the basis of this, it is apparent that Ca(II) , NH_4^+ and Fe(III) compete with Ni(II) for the adsorption sites. Nevertheless, the chelating membrane shows more affinity for Ca(II) than NH_4^+ and Fe(III) . It is reasonable to assume that the chelating membrane exhibits higher binding capability for Ca(II) than that for NH_4^+ and Fe(III) . The adsorption of Ca(II) and Fe(III) is due to the formation of metal complexes of M(MA-DTPA) , while the ion exchange plays a role in the NH_4^+ adsorption by means of the electrostatic relationship. Fe(III) exists in the form of Fe(OH)_2^+ rather than the hydrated form, presenting some challenges for its adsorption [34].

With the concentrations of the competitive cations exceeding 1 mmol/L, the influence of the concentration variation is moderate, taking the ionic strength into account. Therefore, nickel adsorption still predominates the adsorption process with the presence of the competitive cations.

3.1.2. Effect of 3d transition metal ions

Ni–P ternary plating processes including Ni–Fe–P, Ni–Co–P, Ni–Cu–P and Ni–Zn–P discharge the spent wastewater, in which Fe(II) , Co(II) , Cu(II) and Zn(II) will coexist with Ni(II) , respectively. These four cations may induce the competitive adsorption with Ni(II) adsorbed onto the chelating membrane. Fig. 2 shows the nickel uptake as a function of the concentration of 3d transition metal cations. It is observed that the nickel uptake variations under these binary mixtures show a similar trend. When the initial concentration ratio of Ni(II) and Fe(II) , Co(II) , Cu(II) or Zn(II) was approximately 1:1, the nickel uptake decreases by 40.3%, 37.3%, 51.5% and 31.8%, respectively. In these binary mixtures, Ni(II) still gets adsorbed and it can be concluded that the membrane shows

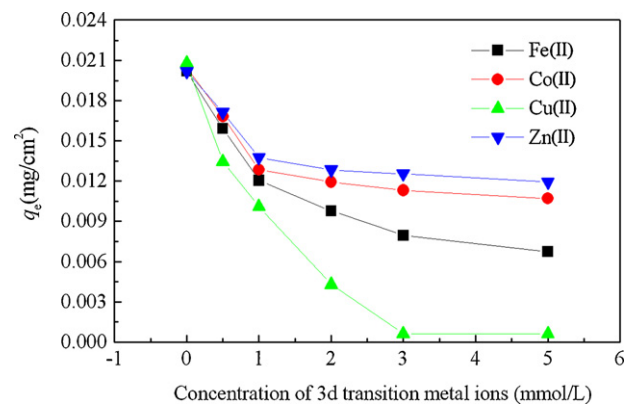


Fig. 2. Effect of 3d transition metal ions on the adsorption of Ni(II) by the chelating membrane. $C_0(\text{Ni(II)}) = 50 \text{ mg/L}$; $t = 120 \text{ min}$; membrane area: 157 cm^2 ; temperature: 298 K ; pH: 6.0.

affinity for Cu(II) , followed by Fe(II) , Co(II) and then Zn(II) . As a consequence, not only could the chelating membrane be used as a potential adsorbent for nickel removal, but also its application for removing other 3d metal cations from Ni–P ternary plating wastewater can be considered.

3.1.3. Effect of the organic acids

In the spent solution of nickel plating, Ni(II) is coordinated by the organic acids and exists in the form of metal–organic complexes. The organic acids were reported that their stabilities may hamper the adsorption process. Fig. 3 depicts the adsorption curves of the chelating membrane towards Ni(II) at different organic acid concentrations. As can be seen in Fig. 3, the complexation of the organic acids at low concentrations (0–2 mmol/L) exerts a significant influence on the nickel uptake. This phenomenon can be attributed to the complete complexation of Ni(II) at higher concentrations of the organic acids, and also the crowding effects of them are not considerable. With the presence of lactic, succinic, and citric acids at the concentration of 1 mmol/L, the nickel uptakes decrease by 6.1%, 11.0% and 12.9%, respectively. This suggests the order of complexing capability associated with the size of the ligands is lactic acid < succinic acid < citric acid.

Of course, other parameters, such as pH, temperature and the concentration of nickel ion, have also influenced the adsorption performance of the chelating membrane. The influences of pH, temperature and the concentration of Ni(II) were elucidated in our previous research [23].

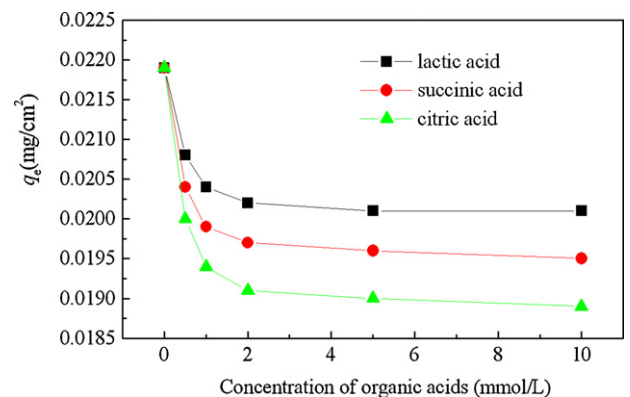


Fig. 3. Effect of the organic acids on the adsorption of Ni(II) by the chelating membrane. $C_0(\text{Ni(II)}) = 50 \text{ mg/L}$; $t = 120 \text{ min}$; membrane area: 157 cm^2 ; temperature: 298 K ; pH: 6.0.

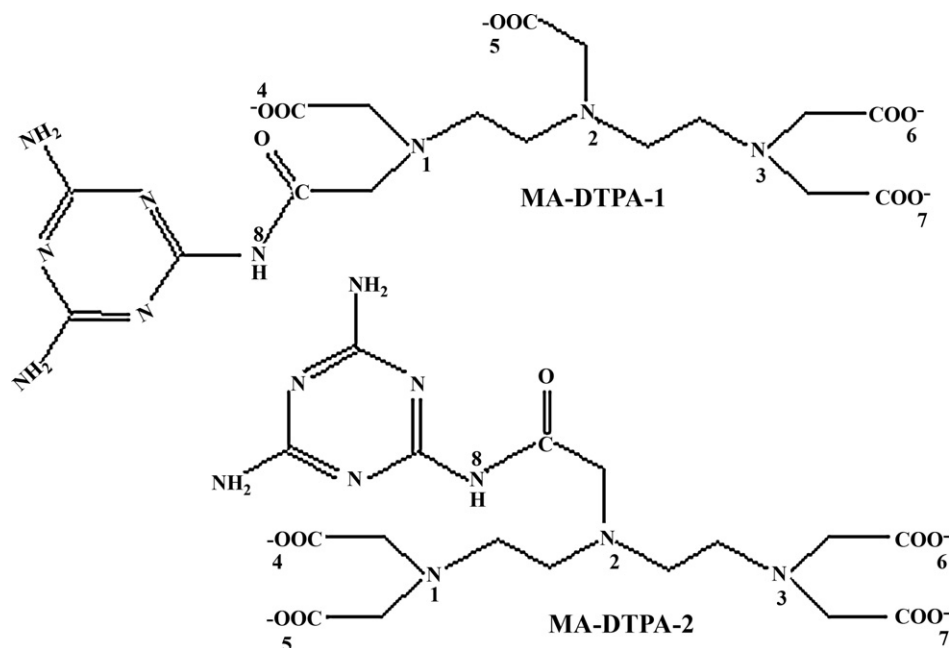


Fig. 4. Computational structures of MA-DTPA chelating ligand.

3.2. DFT simulation of the metal–organic complexes

3.2.1. Geometrical analysis of the metal–organic complexes

Considering the physical combination between PVDF polymer and the polyaminocarboxylate functional compound of the chelating membrane, MA-DTPA-1 and MA-DTPA-2 ligands (Fig. 4) as the two different complexing reaction sites of the chelating membrane, were chosen as the computed geometries in terms of the computational simplification [32].

Heavy metals have a maximum coordination number of six and may adopt octahedral complexing arrangement for MA-DTPA ligand (Fig. 5). The complexation behavior of the polyaminocarboxylate groups with the hydrated Ni(II) and Cu(II) was investigated in our previous work [32]. This section applies the most favorable configuration for Ni(II) to model other cations (Fig. 6). The complexation of Ca(II), Fe(III), Fe(II), Co(II), Cu(II), and Zn(II) with the polyaminocarboxylate groups and that of Ni(II) with

the organic acids (lactic acid, succinic acid, and citric acid) were studied. The configurations of Ni(II)–organic acid complexes are shown in Fig. 7. Then the configurations were optimized and the energies were calculated. The optimized geometrical parameters of $M(\text{MA-DTPA})^{2-}$ are listed in Table 1. The data concerning NH_4^+ are not included because the main interaction between NH_4^+ and MA-DTPA ligand is ion exchange rather than complexation.

The energy level splitting of $d_{x^2-y^2}$ and d_{z^2} orbital states induced by the Jahn–Teller exerts an effect on the bond lengths of metal complexes. The Jahn–Teller distortion leads to an elongated octahedral geometry. As seen in Table 1, it is apparent that the bond length of $M-N_1$ is longer than that of $M-O$ for the same metal complex, which can be attributed to the electronic delocalization interaction between $C=O$ double bond and the complexed COO^- oxygen atom. Furthermore, the bond length for $M-N_1$ of $M(\text{MA-DTPA-1})^{2-}$ complexes increases from 2.154 Å to 2.609 Å, indicating the formation of relatively stable complexes. It is observed that the bond length of $\text{Ca}(\text{MA-DTPA})^{2-}$ is significantly longer compared with that of other $M(\text{MA-DTPA})^{2-}$ complexes, suggesting the weaker complexing ability of Ca(II). This is confirmed by the

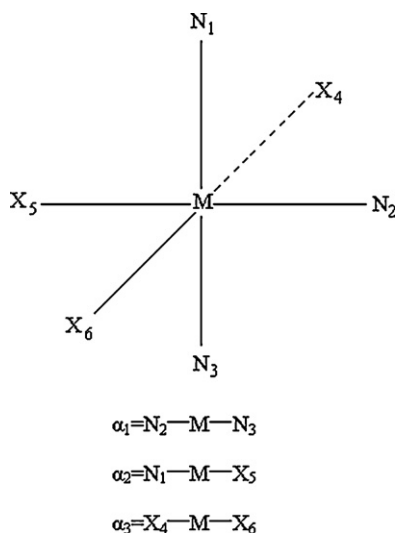


Fig. 5. Atomic numbering and α_i notation for $M(\text{MA-DTPA})^{2-}$ complexes (X represents the coordination atom to be determined for MA-DTPA-1 and MA-DTPA-2).

Table 1

Optimized geometrical parameters of $M(\text{MA-DTPA})^{2-}$ complexes (lengths in Å and angles in degrees).

M	Ni–N ₁	Ni–X ₅	Ni–X ₆	α_1	α_2	α_3
M(MA-DTPA-1) ²⁻ complexes						
Ca(II)	2.609	2.377	2.652	73.037	67.952	163.040
Fe(III)	2.304	2.016	2.038	82.900	78.046	169.036
Fe(II)	2.359	2.092	2.176	80.686	76.007	168.760
Co(II)	2.289	2.112	2.167	83.101	77.907	171.703
Ni(II)	2.220	2.091	2.153	85.731	81.143	175.055
Cu(II)	3.103	2.067	1.983	81.187	66.427	174.976
Zn(II)	2.399	2.107	2.191	83.623	78.238	174.795
M(MA-DTPA-2) ²⁻ complexes						
Ca(II)	2.588	2.361	2.359	68.487	73.913	160.322
Fe(III)	2.289	2.049	2.012	82.011	75.819	160.927
Fe(II)	2.339	2.146	2.106	79.116	75.007	161.099
Co(II)	2.219	2.144	2.092	82.643	78.148	171.375
Ni(II)	2.146	2.107	2.119	81.581	111.182	159.006
Cu(II)	2.199	2.405	2.000	80.715	73.856	176.757
Zn(II)	2.257	2.158	2.139	82.094	77.323	168.310

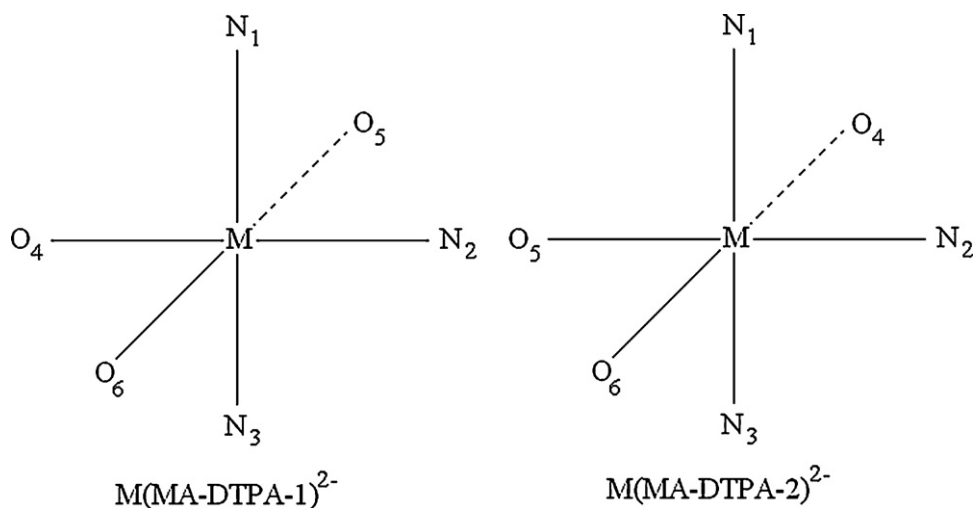


Fig. 6. Illustration of geometries for $M(\text{MA-DTPA})^{2-}$ complexes ($M = \text{Ca(II)}, \text{Fe(III)}, \text{Fe(II)}, \text{Co(II)}, \text{Cu(II)}, \text{Zn(II)}$).

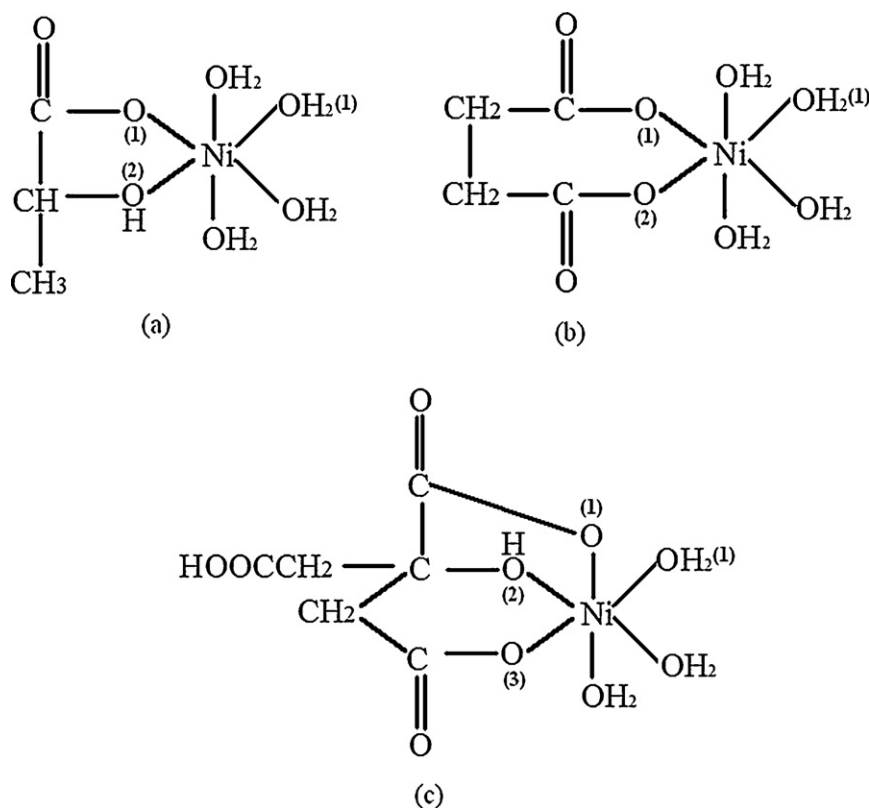


Fig. 7. The configurations of Ni(II)-organic acid complexes: (a) Ni(II)-lactic acid, (b) Ni(II)-succinic acid, (c) Ni(II)-citric acid.

small bond angles of $\text{Ca}(\text{MA-DTPA})^{2-}$ due to the higher distortion magnitude.

Due to the little distortion magnitude of Ni(II)-organic acid complexes, only the bond lengths are given out in Table 2. As seen in Table 2, the bond lengths of Ni(II)-lactic acid, Ni(II)-succinic acid

and Ni(II)-citric acid complexes show no significant changes after optimization. When comparing the bond of Ni-OH₂(1), it can be found that the bond length of Ni-OH₂(1) in the Ni(II)-citric acid complex exceeds 3.6 Å. Therefore, this water molecule tends to separate from Ni(II), and it can be inferred that Ni(II) is not coordinated by H₂O(1) in the Ni(II)-citric acid complex.

Table 2
Optimized geometrical parameters of Ni(II)-organic acid complexes (lengths in Å).

Ni(II)-organic acid complexes	Ni-O ₍₁₎	Ni-O ₍₂₎	Ni-O ₍₃₎	Ni-OH ₂ (1)
Lactic acid	2.003	2.097	-	2.136
Succinic acid	2.126	2.126	-	2.125
Citric acid	2.021	2.099	2.017	3.657

3.2.2. Energetics of the metal-organic complexes

Energetics involving the complexation energies and the Gibbs free energies of the octahedral complexes were assessed. The complexation energy indicates the complexing ability for the metal ion and chelator. The Gibbs free energy reflects the trend of the spontaneous reaction. Tables 3 and 4 summarize the calculated

Table 3
Calculated complexation energies and Gibbs free energies for M(MA-DTPA)²⁻ complexes (in kJ mol⁻¹).

	MA-DTPA-1		MA-DTPA-2	
	$\Delta E(\text{compd.})$	$\Delta G(\text{compd.})$	$\Delta E(\text{compd.})$	$\Delta G(\text{compd.})$
Ni(II)	-350.2635	-575.9716	-337.3494	-560.7097
Cations				
Ca(II)	-273.569	-490.9107	-270.934	-472.733
NH ₄ ⁺	-227.974	-62.8682	-237.989	-67.3854
Fe(III)	-40.060	-230.734	-39.834	-219.119
3d transition metals				
Fe(II)	-361.069	-560.137	-353.953	-561.925
Co(II)	-344.217	-564.07	-327.041	-536.642
Cu(II)	-378.464	-601.651	-381.627	-611.862
Zn(II)	-334.977	-543.344	-332.869	-550.37

Table 4
Calculated complexation energies and Gibbs free energies for Ni-organic acid complexes (in kJ mol⁻¹).

Organic acids	Ni(II)	
	$\Delta E(\text{compd.})$	$\Delta G(\text{compd.})$
Lactic acid	-79.857	-120.4669
Succinic acid	-162.613	-189.0059
Citric acid	-209.496	-292.955

complexation energies and Gibbs free energies of M(MA-DTPA)²⁻ and Ni(II)-organic acid complexes, respectively.

As seen in Table 3, the sequence of the complexing energies between coexistent cations and MA-DTPA ligand of the membrane (i.e. the complexation stability) is Ca(II) > NH₄⁺ > Fe(III), which is in accordance with the experimental analysis. Fe(III) exists in the form of Fe(OH)₂⁺, determining the lower complexation energy. We have performed the energy calculation of the hydrated Fe(III) and the complexation energy indicates that the hydrated Fe(III) seems to form extremely stable complex with the MA-DTPA ligand. The complexing energies of the 3d transition metals and the MA-DTPA ligand increase gradually in the order of Zn(II) < Co(II) < Ni(II) < Fe(II) < Cu(II), confirming the experimental results (shown in Fig. 2).

The organic acids such as lactic acid, succinic acid and citric acid, are known to form some stable complexes with Ni(II) compared with the hydrated Ni(II). The stability constants of the complexes formed between Ni(II) and lactic, succinic and citric acids are 2.22, 2.36, 6.7, respectively, consistent with the energetic sequence: lactic acid < succinic acid < citric acid (Table 4). As there are no

Table 5
Mulliken atomic charges of MA-DTPA ligand and M(MA-DTPA)²⁻ complexes.

	M(II)	N ₁	N ₂	N ₃	O ₄	O ₅	O ₆	O ₇	N ₈
M(MA-DTPA-1) ²⁻ complexes									
Ca(II)	1.621	-0.578	-0.579	-0.574	-0.696	-0.709	-0.702	-	-
Fe(III)	0.873	-0.527	-0.522	-0.525	-0.565	-0.572	-0.576	-	-
Fe(II)	0.790	-0.519	-0.513	-0.526	-0.597	-0.596	-0.592	-	-
Co(II)	0.628	-0.500	-0.486	-0.504	-0.585	-0.576	-0.574	-	-
Ni(II)	0.620	-0.502	-0.489	-0.500	-0.583	-0.580	-0.581	-	-
Cu(II)	0.487	-0.457	-0.471	-0.468	-0.539	-0.520	-0.525	-	-
Zn(II)	0.655	-0.513	-0.500	-0.510	-0.579	-0.580	-0.576	-	-
M(MA-DTPA-2) ²⁻ complexes									
Ca(II)	1.614	-0.564	-0.583	-0.584	-0.696	-0.695	-0.708	-	-
Fe(III)	0.885	-0.511	-0.534	-0.519	-0.567	-0.555	-0.570	-	-
Fe(II)	0.795	-0.497	-0.519	-0.513	-0.585	-0.596	-0.603	-	-
Co(II)	0.612	-0.416	-0.504	-0.499	-0.567	-0.580	-0.572	-	-
Ni(II)	0.623	-0.479	-0.500	-0.500	-0.574	-0.587	-0.576	-	-
Cu(II)	0.446	-0.457	-0.470	-0.468	-0.522	-0.594	-0.514	-	-
Zn(II)	0.652	-0.483	-0.509	-0.502	-0.572	-0.582	-0.578	-	-
Ligand									
MA-DTPA-1	-	-0.461	-0.480	-0.453	-0.681	-0.720	-0.687	-0.664	-0.353
MA-DTPA-2	-	-0.461	-0.498	-0.463	-0.682	-0.643	-0.718	-0.690	-0.344

Table 6
Mulliken atomic charges of organic acids and Ni-organic acid complexes.

	Ni(II)	O(1)	O(2)	O(3)
Ni(II)-organic acid complexes				
Lactic acid	0.792	-0.573	-0.497	-
Succinic acid	0.777	-0.615	-0.614	-
Citric acid	0.878	-0.619	-0.480	-0.585
Organic acid				
Lactic acid	-	-0.688	-0.555	-
Succinic acid	-	-0.729	-0.730	-
Citric acid	-	-0.710	-0.603	-0.704

experimental energetic data of the stability constants of Ni(II)-MA-DTPA, the reliable DFT results can also provide some information about the complexation stability. The complexing abilities of these three organic acids with Ni(II) cannot be comparable to that of MA-DTPA ligand with Ni(II). This confirms the application of the chelating membrane for the removal of Ni(II) from metal-complex wastewater.

3.2.3. Mulliken population of the metal-organic complexes

To further compare the complex stabilities and understand the complexation behavior of the polyaminocarboxylate groups with different metals and that of the organic acids with Ni(II), the electronic charge population and transfer were evaluated in detail. The Mulliken population data are shown in Tables 5 and 6. The metal charges do not agree with their formal charges due to the chelator's screening effect. For M(MA-DTPA)²⁻ complexes, the charges of Ca(II), Fe(III), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) decrease by 19.0%, 70.9%, 60.5%, 68.6%, 69%, 75.7% and 67.3%, respectively, in comparison to the free cations. This result accords with the energetic data, except Fe(II); thus, the charge analysis can be only used for quantitative analysis. Metal complexation basically induces an increase of electron population at nitrogen atoms and a decrease at carboxylic oxygen atoms. This change is reasonable as the carboxylic oxygen atoms show high electro-negativity while nitrogen atoms show weak donor nature, and the electrostatic inductive effect plays a role in the electron density increases. The charge population of Ni(II)-organic acid complexes also confirms the geometrical data. Compared with the free Ni(II), the charge of Ni(II) decreases by 60.4%, 61.2% and 56.1% in Ni(II)-lactic acid, Ni(II)-succinic acid and Ni(II)-citric acid complexes, respectively. Among the aforementioned Ni(II)-organic acid complexes (Table 6), the Mulliken charge of Ni(II) in citric acid complex is larger than that of Ni(II)-lactic acid and Ni(II)-succinic acid complexes. The higher Mulliken charge

of Ni(II) in the Ni(II)–citric acid complex can be attributed to the dissociation of H₂O(1) water molecule.

Summarizing the discussions above, based on DFT theoretical calculations, the influences of the coexistent cations and organic acids on the adsorption performance of MA-DTPA/PVDF chelating membrane are confirmed. However, some issues should be considered, such as the effects of Ni(OH)⁺, Ni(OH)₃[−] and Ni(OH)₄^{2−} forms existing at different pH on the performance of the membrane, and the rejection performance of the chelating membrane in the continuous adsorption process. These issues will be investigated in the further research.

4. Conclusions

The MA-DTPA/PVDF chelating membrane bearing polyaminocarboxylate groups was synthesized to remove Ni(II) from nickel electroless plating and electroplating effluents. Adsorption experiments and DFT calculations were combined together to study the adsorption properties of the membrane towards Ni(II) in Ni(II)–Ca(II), Ni(II)–NH₄⁺ and Ni(II)–Fe(III) binary systems, and Ni(II)–lactic acid, Ni(II)–succinic acid and Ni(II)–citric acid organic complexes. For the ternary electroless nickel plating solutions, the effects of Fe(II), Co(II), Cu(II) and Zn(II) on Ni(II) sorption were also taken into consideration. The conclusions are listed below.

(1) The results of DFT calculations are in accordance with the experimental data, and it can be inferred that DFT molecular simulation is suitable for evaluating the favorable coordination between MA-DTPA/PVDF chelating membrane and metal cations.

(2) The coexistent cations and 3d transition metals interfere with Ni(II) adsorption to different degrees, and it can be inferred that the affinity of the chelating membrane for the aforementioned cations is responsible. Ni(II) adsorption of the chelating membrane was not significantly affected by the complexation of the organic acids, allowing the potential application of the chelating membrane to nickel plating wastewater.

(3) The distortion magnitude of the geometries for metal complexes indicates the stability and can provide reliable initial configurations for the energy calculation. The coexistent Ca(II) tends to form more stable complex with MA-DTPA ligand than NH₄⁺ and Fe(III). The sequence of the complexing energies for the 3d transition metals and the MA-DTPA ligand of the chelating membrane is in the order of Zn(II) < Co(II) < Ni(II) < Fe(II) < Cu(II). As a consequence, 3d transition metals existing in Ni–P ternary plating solutions will have considerable competition with Ni(II).

(4) The stabilities of Ni(II)–organic acid complexes follow the order of lactic acid < succinic acid < citric acid. However, the complexing abilities of lactic acid, succinic acid and citric acid with Ni(II) can not be comparable to that of MA-DTPA chelating ligand. Thus the complexation of the organic acids will not hamper the removal of Ni(II) from the organic acid complexes.

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