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Iminodisuccinic acid as a new complexing agent for removal of heavy metal ions from industrial effluents

Dorota Kołodyńska*

Department of Inorganic Chemistry, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 2, 20-031 Lublin, Poland

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ABSTRACT

The sorption parameters of Cu(II), Co(II), Ni(II) as well as Fe(III) in the presence of a complexing agent of a new generation to the anion exchangers of different basicity of functional groups were investigated. A series of experiments were conducted to optimise the method for the their removal from industrial effluents. It was found that the sorption efficiency of strongly, medium as well as weakly basic anion exchangers varied depending on metal ions concentration, pH, contact time, agitation, temperature and properties of anion exchangers such as their form. From the determined breakthrough curves the distribution coefficients (D_g) and (D_v), the ion exchange capacities (C_w, C_t) and the time required for the moving the exchange zone (t_z) as well as the total time required for the formation of exchange zone (t_T) were calculated. The largest percentages of heavy metal complexes with IDS removal were found for the strongly basic anion exchanger (up to 98% for Cu(II), 82% for Fe(III), 67% for Ni(II) and 55% for Co(II)). Satisfactory results were also obtained for medium and weakly basic anion exchangers. Besides, a kinetic procedure was developed to study the kinetics of anion exchange. Two different kinetic behaviours were tested for the investigated systems.

1. Introduction

Industrial development has lead to a drastic increase of heavy metal concentrations in the environment. Except for heavy metal ions, synthetic organic metal-sequestering ligands such as aminopolycarboxylic acids (mainly ethylenediaminetetraacetic acid, EDTA and nitrilotriacetic acid, NTA) are also present in various wastewaters. Their presence is associated, among others, with their application in pulp and paper, textile, metallurgical, food, cosmetics, pharmaceutical and agricultural industries. The complexones such as EDTA, NTA, Quadrol (N,N,N′,N′-tetrakis(2-hydroxopropyl)-ethylenediamine) (Fig. 1) are extensively used in electroless copper plating in manufacture of printed circuit boards. Aminopolycarboxylates have also been reported as the most common substitutes for sodiumtriphosphate (STPP) in detergents. By forming complexes with calcium and magnesium ions they increase the cleaning action of soaps and detergents. They are also extensively used as stabilizing agents in food industry, in wastewater treatment plants they dissolve $CaCO_3$ scale deposit from hard water without the use of corrosive acids, they act as an anticoagulant for stored blood as well as in the decontamination of radioactive effluents from nuclear industry. Radioactive wastewaters contain both complexing agents (for example, EDTA concentration up to 30 mM) and radioactive metals like ^{60}Co, ^{239}Pu and ^{240}Pu. They are also used in the separation of rare earth elements from each other [1–5].

In the aminopolycarboxylates group, EDTA and DTPA have proven to be practically non-biodegradable in standard tests. The available data suggest that EDTA and its salts are not generally removed during wastewater treatment [6–8]. Under anaerobic conditions, no degradation could be found for any of the EDTA complexes and in the case of EDTA its degradation rate strongly depends on the type of microorganisms [9]. On the other hand, elimination of EDTA of up to 70–80% was found in wastewater treatment plants with facilities for chemical phosphate precipitation.

In the case of effluents containing heavy metal ions together with complexing agents, typical chemical precipitation methods in the presence of strong chelating agents such as EDTA, NTA, citrate, and tartarate may make the precipitation process ineffective, even when treating effluents of high metal concentration, because most metal ions are complexed with organic ligands over the entire pH range [9–11]. Therefore, more advanced techniques are required for the cleanup of such contaminants and retardation of heavy metal ions mobility.

Generally, the treatment methods can be grouped into three categories: chemical, physical and electrochemical. The chemical methods include substitution, reduction of the metal ion, oxidation of complexing agent and ion exchange. The physical methods include, among others, reverse osmosis. The electrochemical methods are, for example, electrowinning and electrochemical displacement. In the electrochemical reduction processes metal

* Tel.: +48 81 537 57 36; fax: +48 81 533 33 48.
E-mail address: kolodyn@poczta.onet.pl.

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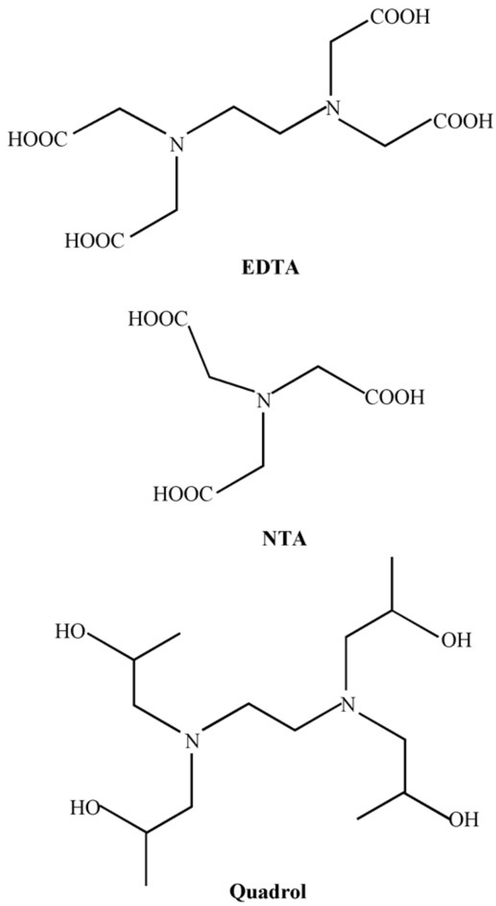

Fig. 1. The structure of EDTA, NTA and Quadrol.

ions from the effluents are removed and then deposit as elemental metals on the cathodic plate to enable the complexing agent to be recovered for reuse from power plants. However, they are affected by several operating problems, e.g. membrane fouling and degradation [12,13]. One possible solution is carrying out biodegradation process resulting in the liberation of metal ions, having lower mobility under neutral conditions. To this end, studies on application of advanced oxidation processes (AOP) or advanced oxidation techniques (AOT) including some processes with such reactives like ozone, hydrogen peroxide, iron ions or UV irradiation as well as with such catalysts as TiO_2 are carried out [14–18]. Ozone has been found to degrade EDTA and the rate of destruction is influenced by coordination. It has been demonstrated that photocatalysis is a promising technology applicable for efficient removal of metal–EDTA complexes from, for example, radioactive wastewater containing Fe(III), Cu(II), Co(II) and Ni(II) [19,20]. Moreover, dissolved transition metal ions in aqueous solutions affect the rate and efficiency of photocatalytic oxidation of organic compounds. One of the recycling methods also investigated was the application of electrolysis in conjunction with a cation-exchange membrane for the recovery of metals in a solution of metal–EDTA complexes. With the current interest in remediation technologies, the electrolysis method has been extended for recycling of wastewater from soil washing [21].

Increasing concern about the direct or indirect potential effects of the presence of the above mentioned complexones in the environment, that is:

1. mobilization of contaminant metal ions adsorbed in sediments;
2. solubilization of radioactive metal ions and increase of their environmental mobility;
3. contribution to eutrophication water processes (e.g. the EDTA molecule contains approximately 10% of nitrogen that could eventually be available to the aquatic microbiota and redissolves calcium and ferrium phosphates, releasing phosphorous);
4. the ligand–metal complexes may significantly increase the bioavailability of extremely dangerous heavy metals, for example, Cu(II)–EDTA and Cd(II)–EDTA complexes which are more toxic than their respective free metals

cause, that these complexons are nowadays replaced by modern agents sufficiently biodegradable or eliminable. There is a number of alternative products on market which are claimed to be as effective as EDTA and NTA but most of them have also their restrictions. For example, organophosphonates were found to be not readily biodegradable. Others are readily biodegradable, such as citrates and gluconates, but do not have a sufficiently strong chelating power compared to NTA or EDTA. A series of new diethanolamine derivatives such as complexing agents have been designed by the Kemira Oyj Espoo Research Centre (Finland): N-bis[2-(carboxymethoxy)ethyl]glycine (BCA3), N-bis[2-(methyl-carboxymethoxy)ethyl]glycine (MBCA3), N-bis[2-(1,2-dicarboxyethoxy)ethyl]glycine (BCA5) and N-bis[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid (BCA6). However, being of technical quality these new alternative complexing agents of low nitrogen content proved to be not readily biodegradable compounds. BCA6 was found to be the most sensitive to photodegradation, whereas BCA3 was quite photostable [22–24]. More recently, tetrasodium salt of L-asparaginic-N,N-diacetic acid (ASDA), 1,3-propylenediaminetetraacetic acid (1,3-PDTA), N-2(-hydroxyethyl)iminodiacetic acid (HEIDA), β-alaninediacetic acid (β-ADA) and methylglycinediacetic acid (MGDA) were introduced [25–29]. Particularly, MGDA is readily biodegradable in compliance with the OECD standards and is used for enhancing the cleaning efficiency of laundry and dishwashing detergents as well as industrial and all-purpose cleaners. Also such chelating agents as EGTA (ethylenedioxydiethylenediaminetetraacetic acid) and HEDTA (N-hydroxyethylethylenediaminetriacetic acid), EDDS (N,N′-ethylenediaminedisuccinic acid), IDS (N-(1,2-dicarboxyethyl)-D,L-aspartic acid also known as iminodisuccinic acid) and DS (polyaspartic acid) have also been proposed [30–37]. According to recent investigations, especially S,S′-EDDS is a viable replacement ligand in pulp and paper industry, in cosmetics, etc. and also IDS is comparable to EDTA. β-ADA is also a potential alternative. The structural formulae of the above-mentioned complexones are presented in Table 1

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The aim of this study was to explain the influence of chemical conditions on the ion exchange capacity and on the kinetics of copper(II), cobalt(II), nickel(II) and iron(III) in the presence of the complexing agent of a new generation that is sodium salt of N-(1,2-dicarboxyethyl)-D,L-aspartic, which has the commercial name Baypure CX 100. In the studies there was applied the ion exchange which is a method used in water treatment and wastewater purification. This method is suitable for removal of all contaminants in the ionic form also including heavy metal ions in the presence of complexing agents from different systems. The results obtained under different experimental conditions will be presented and discussed in this paper.

2. Materials and methods

2.1. Resins

The following medium and weakly basic anion exchangers Lewatit MonoPlus MP 64, Lewatit MP 62 produced by the Bayer