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EDTA – synthesis and selected applications

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1. INTRODUCTION

Ethylenediaminetetraacetic acid {EDTA, *N,N'*-1,2-ethanediylbis-[N-(carboxy-methyl)glycine]}, nitrilotriacetic acid [NTA, *N,N*-bis(carboxymethyl)glycine], and their salts were first synthesized by Austrian chemist Ferdynand Münz in the I.G. Farbenindustrie AG (*Interessen-Gemeinschaft Farbenindustrie Aktiengesellschaft*) laboratories during the 1930s [1-4]. Since that time, EDTA and similar chelating agents (aminopolycarboxylic compounds), and their salts have become important industrial chelating agents. Aminopolycarboxylic acid chelating agents are capable of forming salts with strong acids or bases. In addition, these chelating agents can form strong, water soluble metal complexes with various cations. The major volume usage of aminopolycarboxylic acid chelating agents is in preventing or removing scales and insoluble deposits or precipitates containing Ca, Ba, Fe, and other cations. These agents are also added to many industrial processes [3].

The structures and physical properties of the most important aminopolycarboxylic acid chelating agents (including EDTA) and their salts can be find elsewhere [2]. EDTA, related aminopolycarboxylic acids, and their salts form a water soluble complexes with alkaline earth and heavy metal ions. These metal ions are incorporated into a ring structure called a *chelate*, after the Greek word *chele* or *khele*, which means *claw* (Fig. 1).

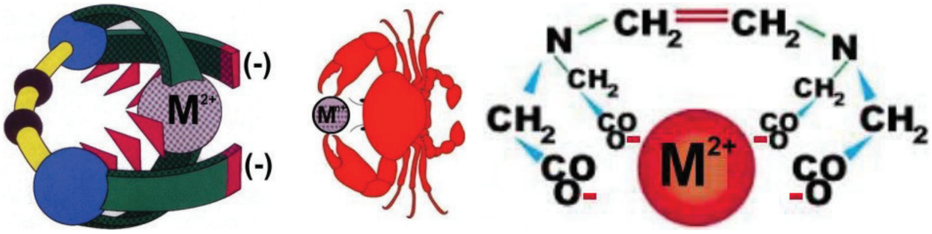


Fig. 1. The structure of the chelated metal ion.

EDTA is a common polydentate ligand. In EDTA, the hydrogen atoms are easily removed in solution to produce anionic EDTA^{4-} (Fig. 2).

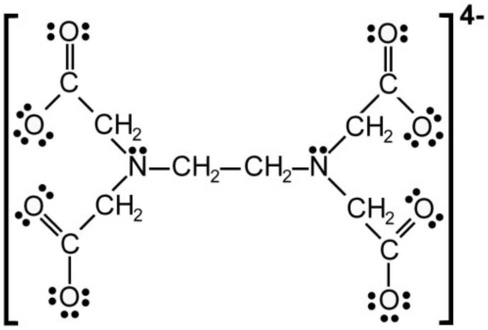


Fig. 2. The structure of ethylene diamine tetra-acetate ion.

In its anionic form EDTA has six binding atoms, two nitrogen and four oxygen as depicted in Figure 3.

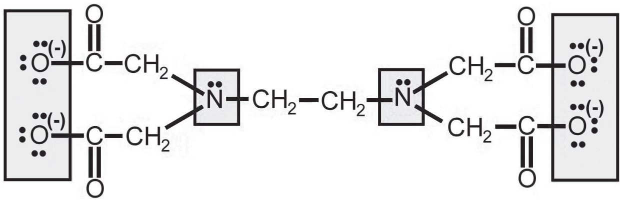


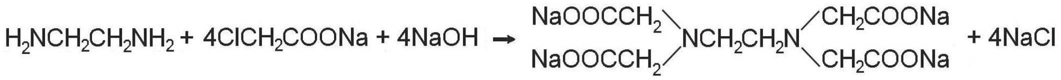
Fig. 3. Potential binding sites in EDTA.

EDTA binds to a metal ion at the six binding sites, wrapping itself around the metal ion, forming a very stable complex. The strong grasp of EDTA on the metal ion is analogous to a crab or lobster clamping down on an object with its claw (Fig. 1), hence the name chelation.

2. INDUSTRIAL SYNTHESES OF EDTA

The first registered trademark for EDTA was „Trilon B" by I.G. Farben and its successor BASF. Other commercial names are sequstrene (Ciba-Geigy), Versene (Dow), Chelest (Chelest, Japan), Rexene (Grace, Sweden) and Hampene (Grace, USA).

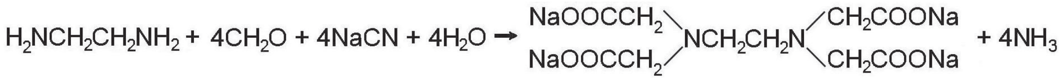
Münz designed and synthesized EDTA as a substitute for citric acid in order to reduce the dependency of the German government on the import of foreign chemicals. He noted that an aminocarboxylic acid worked much better than citric acid as a chelating agent, and therefore reasoned that a polyaminopolycarboxylic acid would have worked even better. The main purpose was to remove calcium ions from water in order to improve the dyeing process on the fabric. His method involved the reaction between hot ethylenediamine with monochloroacetic acid and sodium hydroxide [5]. The final product was, however, contaminated with sodium chloride (Fig. 4). This process, though used in Europe, has never been used in the US [6].



$$H_2NCH_2CH_2NH_2 + 4ClCH_2COONa + 4NaOH \rightarrow \begin{matrix}NaOOCCH_2\diagdown\\NaOOCCH_2\diagup\end{matrix}NCH_2CH_2N\begin{matrix}\diagup CH_2COONa\\\diagdown CH_2COONa\end{matrix} + 4NaCl$$

Fig. 4. Münz's first reaction scheme to produce EDTA.

In 1941 Frederick C. Bersworth synthesized EDTA in the United States using a different and more convenient synthesis. This process is still used today. It is an alkaline cyanomethylation of ethylenediamine: tetrasodium EDTA and ammonia are produced by reacting ethylenediamine with formaldehyde and sodium cyanide (Fig. 5).

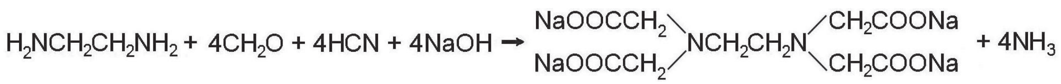


$$H_2NCH_2CH_2NH_2 + 4CH_2O + 4NaCN + 4H_2O \rightarrow \begin{matrix}NaOOCCH_2\diagdown\\NaOOCCH_2\diagup\end{matrix}NCH_2CH_2N\begin{matrix}\diagup CH_2COONa\\\diagdown CH_2COONa\end{matrix} + 4NH_3$$

Fig. 5. Bersworth's one-step cyanomethylation to produce EDTA.

Much of the NH_3 evaporates, but part of it reacts with the starting materials to form NTA. To separate and purify the product, the solution needs acidification with sulfuric or hydrochloric acid, which allows the formation of insoluble EDTA and consequently its separation from NTA, which remains in solution.

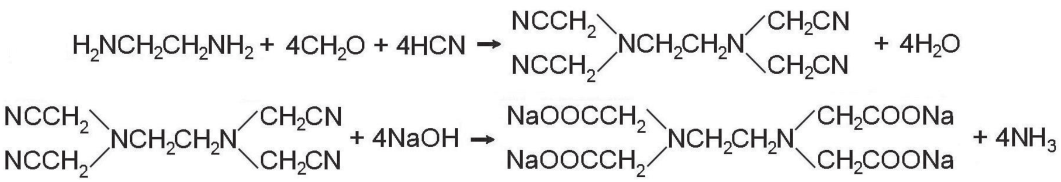
Geigy's process (Fig. 6), like the Bersworth synthesis (Fig. 5), is a one-step cyanomethylation process, but it uses hydrogen cyanide instead of sodium cyanide. The advantage is obvious: it costs less. However, hydrogen cyanide is much trickier to handle.



$$H_2NCH_2CH_2NH_2 + 4CH_2O + 4HCN + 4NaOH \rightarrow \begin{matrix}NaOOCCH_2\\NaOOCCH_2\end{matrix}\!\!\!>\!NCH_2CH_2N\!<\!\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 4NH_3$$

Fig. 6. Geigy's one-step cyanomethylation.

In 1962 a third EDTA synthesis pathway was developed by John Singer and Mark Weisberg, that produces a very pure form of its disodium salt. In this process the cyanomethylation is separated from the hydrolysis (Fig. 7) [7].



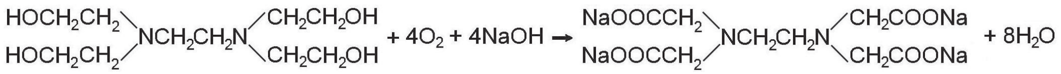
$$H_2NCH_2CH_2NH_2 + 4CH_2O + 4HCN \rightarrow \begin{matrix}NCCH_2\\NCCH_2\end{matrix}\!\!\!>\!NCH_2CH_2N\!<\!\!\!\begin{matrix}CH_2CN\\CH_2CN\end{matrix} + 4H_2O$$

$$\begin{matrix}NCCH_2\\NCCH_2\end{matrix}\!\!\!>\!NCH_2CH_2N\!<\!\!\!\begin{matrix}CH_2CN\\CH_2CN\end{matrix} + 4NaOH \rightarrow \begin{matrix}NaOOCCH_2\\NaOOCCH_2\end{matrix}\!\!\!>\!NCH_2CH_2N\!<\!\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 4NH_3$$

Fig. 7. Two-step cyanomethylation (Singer synthesis).

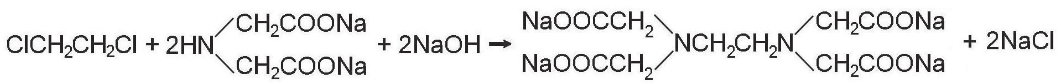
The strategy is to use ethylenediamine, formaldehyde and hydrocyanic acid, to produce EDTN, (ethylenedinitrilo)tetra-acetonitrile which is then separated, washed and hydrolyzed with sodium hydroxide, to form Na_4EDTA and ammonia. By performing this synthesis, the majority of secondary reactions that lead to formation of impurities are removed. The yield is greater than 96%. This method, moreover, is well suited for synthesizing NTA with a high purity grade (and yield).

Other EDTA production processes not commonly used in the commercial field also exist, for example catalytic oxidation of tetra(hydroxyethyl)ethylenediamine (Fig. 8) or reaction between ethylene dichloride and disodium iminodiacetate (Fig. 8) [6].



$$\begin{matrix}HOCH_2CH_2\\HOCH_2CH_2\end{matrix}\!\!\!>\!NCH_2CH_2N\!<\!\!\!\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix} + 4O_2 + 4NaOH \rightarrow \begin{matrix}NaOOCCH_2\\NaOOCCH_2\end{matrix}\!\!\!>\!NCH_2CH_2N\!<\!\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 8H_2O$$

Fig. 8. Catalytic oxidation of tetrahydroxyethylethylenediamine to produce EDTA.



$$ClCH_2CH_2Cl + 2HN\!<\!\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 2NaOH \rightarrow \begin{matrix}NaOOCCH_2\\NaOOCCH_2\end{matrix}\!\!\!>\!NCH_2CH_2N\!<\!\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 2NaCl$$

Fig. 9. Ethylene dichloride and disodium iminodiacetate to produce EDTA.

The scheme of EDTA industrial production is shown in Fig. 10. Full description of the process can be find elsewhere [6].

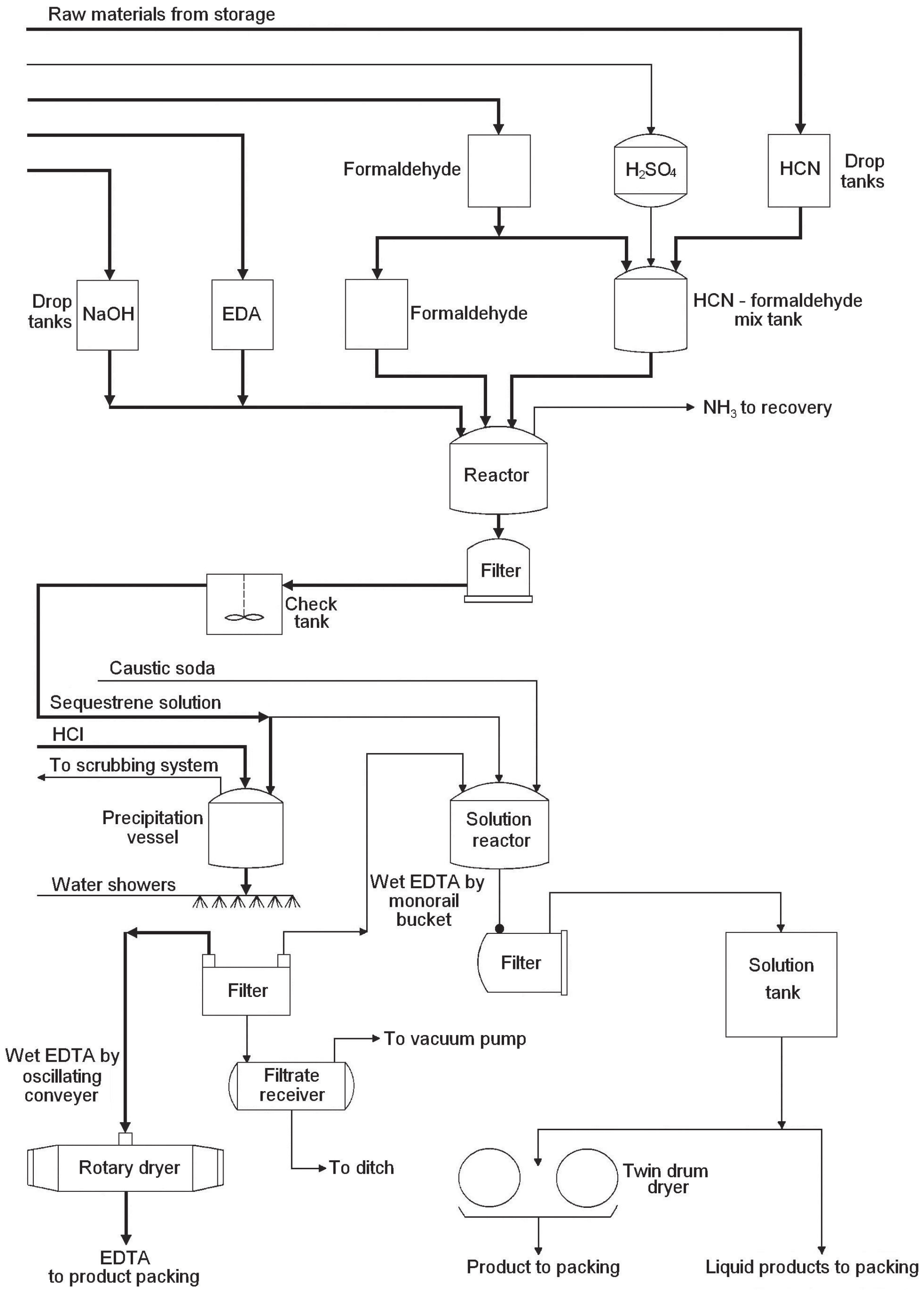


Fig. 10. Flowsheet for the manufacture of EDTA by Geigy Chemical Corporation [5],

3. SELECTED APPLICATIONS OF EDTA

Metals are extensively used by industries in various applications. Nowadays greater pressure has been placed on metal utilization because of population growth coupled with a higher standard of living. Furthermore, industrialization has led to the increasing demand for critical metals, as many of these are required in modern technologies. Industries generate a variety of wastes which contain, among the others, metals. Therefore, there is a need to recycle and recover metals from the environment. In this respect chelating agents can help to solve the above mentioned problem (Fig. 11).

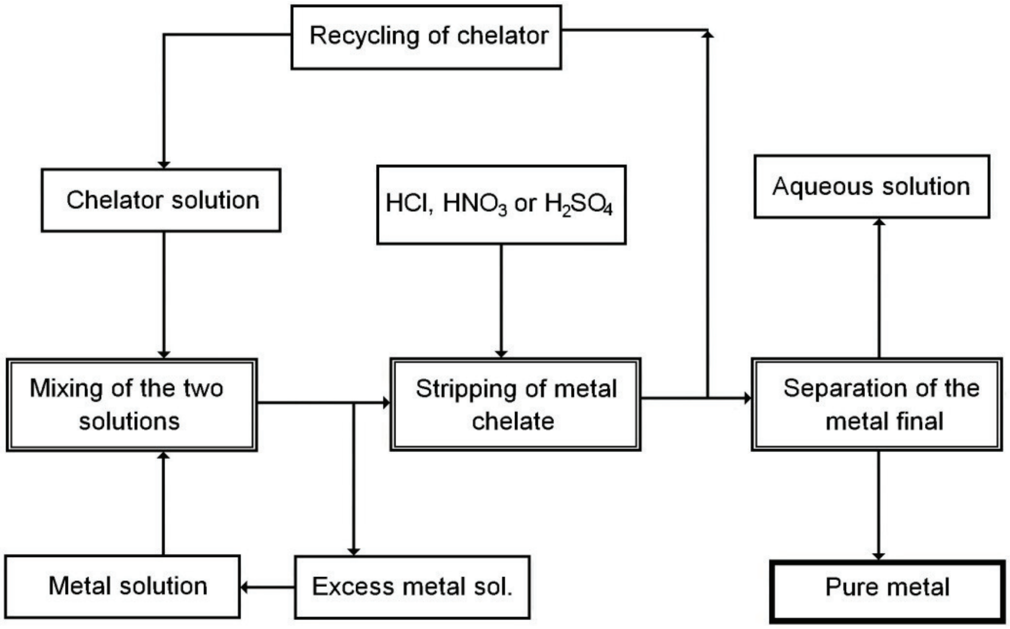


Fig. 11. Flow sheet of recovery of metals using chelating agent [8].

The importance of catalysis to chemical processes is enormous. An estimated 90% of chemical production processes are based on catalytic technologies. In many cases the active phase of those catalysts are metals. One of the major problems related to the use of catalysts in the chemical industry is loss of catalytic activity with time due to loss of surface area, sintering and/or deposition of various compounds. The mentioned changes provoked by the catalyst deactivation play a significant role for a large number of industrial processes. Spent metal catalysts are considered as solid wastes and also the replacement cost with fresh catalyst is significantly high. In many countries spent catalysts have been classified as hazardous wastes. In this respect efforts are being made to recover metals from spent catalysts to an environmentally acceptable safe material for reuse. One of the proposed method for this purpose is the use of chelating agents (Fig. 12) [9-10].

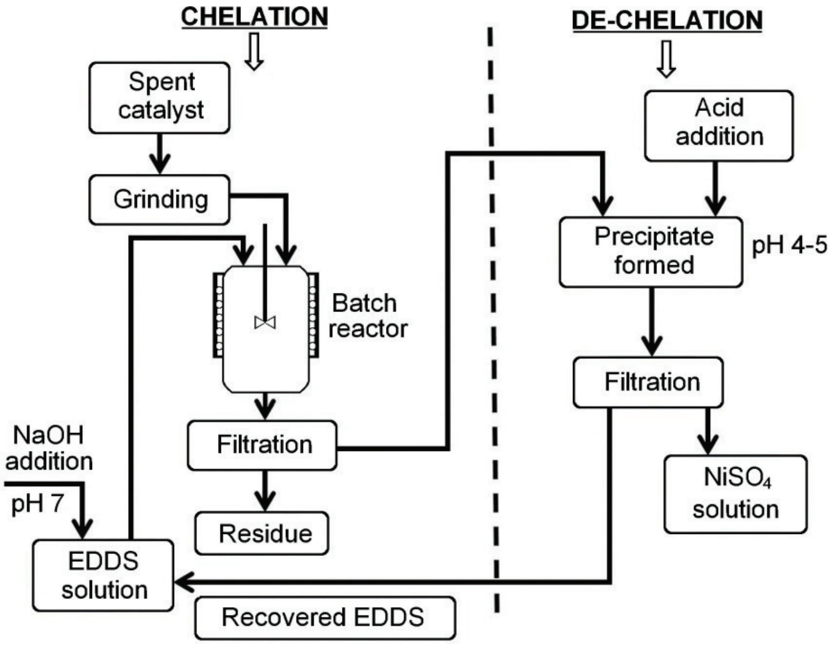


Fig. 12. Process flow chart for solid-liquid extraction and regeneration of chelating agent [10].

Scheme presented above is valid for EDTA [9] as well as for its greener analog, i.e: EDDS – ethylenediamine disuccinic acid [10]. Earlier research in this subject mostly was focused on the traditional chelating agents [11]. Rules of green chemistry and activities connected with sustainable development caused an increase in interest in new chelate compounds that are environmentally friendly due to their biodegradation [12].

CONCLUSION

Classical, well known chelating agents are still used. However, there is an urgent need for new green reagents with the same or similar properties. The tendency to replace traditional EDTA chelates is gradually observed. The future belongs to the biodegradable EDTA analogues.

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