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Green and effective complexation – a comparative study

Introduction

Chelating agents are an essential component of detergent and cleaner formulations. They capture calcium and magnesium ions, reduce water hardness, improve the efficacy of surfactants and facilitate the removal of scale deposits. The complexation of other frequently occurring metal ions, such as copper or iron, is important to avoid the degradation of a product's colour or fragrance and helps to stabilise peroxide bleaches.

Typical common chelating agents include EDTA (ethylenediamine tetraacetic acid), NTA (nitrilotriacetic acid), DTPA (diethylenetriamine pentaacetic acid) and different types of phosphates and phosphonates, such as STPP (sodium tripolyphosphate) and ATMP (aminotris(methylene phosphonic acid)). While these are reasonably efficient, they are of mineral or petrochemical origin, often not readily biodegradable and sometimes dangerous to human health.[1,2,3]

With the overall trend to more sustainable and eco-friendly products, companies are increasingly looking for alternatives. These should be as effective as their traditional counterparts, but of natural origin, readily biodegradable and non-hazardous. Sodium citrate and sodium gluconate – the salts of citric and gluconic acid – fulfil these criteria and have been used on an industrial scale for decades. Both are manufactured on the base of renewable raw materials via fermentation, they are safe to handle, readily biodegradable and with proven chelating performance in food and technical applications. More recently, new alternative chelating agents have been developed, including GLDA (glutamic acid diacetate) and MGDA (methylglycine diacetic acid). These are partially bio-based, offering good biodegradability and low toxicological and ecotoxicological profiles.[4]

Building on previously generated complexation data for sodium citrate (trisodium citrate anhydrous [TSA], the water-free version of trisodium citrate dihydrate [TSC], which contains crystal water), sodium gluconate and EDTA,[5] this article presents and compares recently determined complexation performance data of GLDA and MGDA. Full comparability of data is ensured by applying exactly the same methodology and the same experimental framework as used for the earlier analyses. This enables true benchmarking, helping to provide useful formulation guidelines.

Method for evaluating chelating agents using titration

This study employed a titration method to evaluate the performance of various chelating agents. The titration process was conducted using a precise and reliable titration instrument (Titroline 7000®, Xylem Analytics). Calcium acetate hemihydrate, magnesium sulfate heptahydrate and copper II sulfate pentahydrate were utilised as titration reagents. The sample in the beaker contained the chelating agent along with the counter ion, which in this case were hydroxide and carbonate ions. The pH of the solution was adjusted using sodium hydroxide to ensure optimal conditions for the titration.

During the titration, the ions in the solution interact with the chelating agent, forming complexes. As the titration progresses, the chelating agent gradually complexes the ions until its complexation capacity is exhausted. Once this point is reached, the excess ions begin to interact with the counter ion, resulting in the formation of a precipitate. This precipitation causes turbidity in the solution, which can be detected using a turbidity probe.

The detection of turbidity allows for the assessment of the chelating agent's performance. By monitoring the point at which turbidity begins to form it is possible to determine the capacity and efficiency of the chelating agent in complexing the ions. This method provides a clear and quantifiable measure of the chelating agent's ability to complex ions under controlled conditions.

The study specifically tested MGDA and GLDA. The data for trisodium citrate anhydrous (TSA) and sodium gluconate (SG) were partially derived from studies in 2020.[5] This article consolidates all the data. The study examined various pH ranges from 10 to 13, and different temperature ranges including room temperature (21°C) and elevated temperature (40°C), which is relevant for the homecare sector. The method was not entirely applicable in some matrices. At pH 10 the method was sometimes infeasible because certain hydroxide compounds (for example magnesium hydroxide) are water-soluble in this moderately alkaline milieu and do not precipitate, thus preventing turbidity detection. Furthermore, pH 13 could not be maintained in the 40°C setup. Achieving such a high pH would require adding a large volume of highly concentrated NaOH, leading to a high dilution factor and consequently significant error.

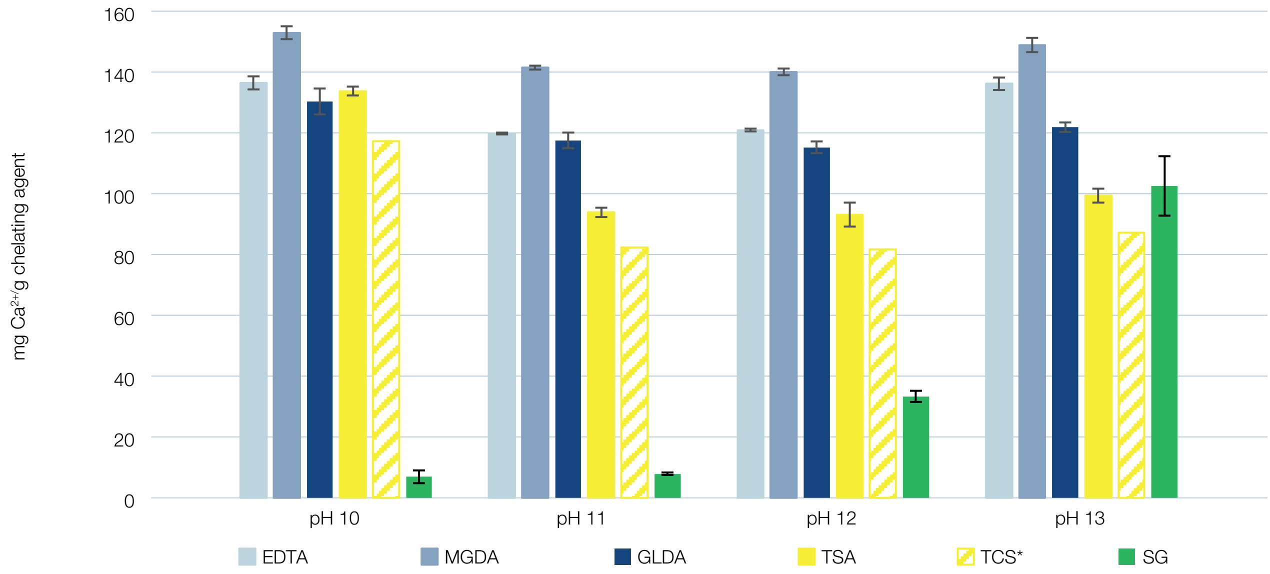
Sustainable and effective solution to chelate Ca^{2+}, Mg^{2+} and Cu^{2+}

1) Results for Ca^{2+}

The performance evaluation of the different complexing agents showed different efficiencies at different pH values and temperatures. The results for Ca^{2+} complexation are shown in figures 1 and 2.

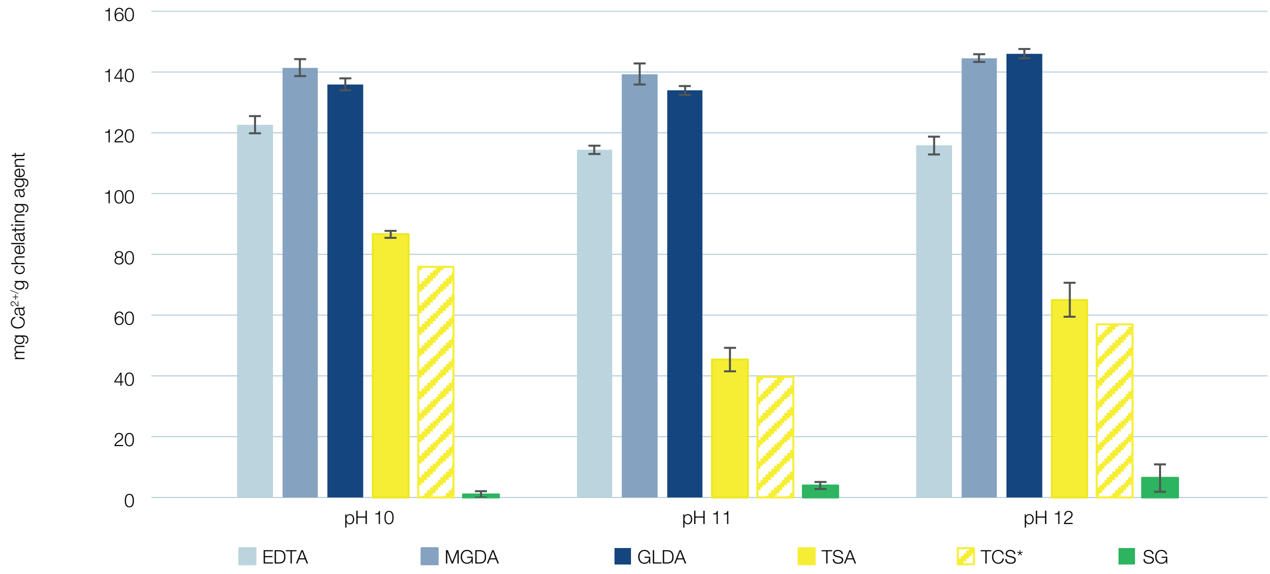
Water hardness is defined by the concentration of Ca^{2+} and Mg^{2+} ions, which is why Ca^{2+} complexation is of particular importance. Above a calcium content of approximately 100 mg/L water is said to be hard. TSA and TSC showed superior complexing performance at pH 10 and room temperature. With 1 g TSA, for example, it is possible to complex around 134 mg Ca^{2+}. Therefore 0.74 g/L chelating agent is sufficient in this case. In this moderately alkaline environment, the citrates showed comparable performance to the petrochemical-based chelating agents. In contrast, SG showed the best performance at pH 13, indicating its optimal functionality under these conditions. Of particular note, EDTA, MGDA and GLDA showed consistent performance at all pH values tested, indicating their versatility and stability as complexing agents. Among these, MGDA was characterised by the best performance in this setup.

However, at elevated temperatures the method proved inapplicable for pH 13. Under these conditions, EDTA, MGDA and GLDA showed the best performance at pH 10, 11 and 12. Conversely, SG showed the poorest performance at these pH values, highlighting its limited effectiveness in moderately alkaline environments under higher temperature conditions. For most agents, the performance decreases at higher temperatures and consequently higher dosing rates are required for sufficient complexation.



*Calculated based on measurement with TSA

Figure 1: **Complexation of Ca^{2+} at room temperature (21°C)**



*Calculated based on measurement with TSA

Figure 2: **Complexation of Ca^{2+} at elevated temperature (40°C)**

2) Results for Mg^{2+}

The performance evaluation of various complexing agents revealed divergent efficiencies across different pH levels and temperatures for magnesium complexation, which is shown in figures 3 and 4. As mentioned above, the method could not be applied at pH 10. At pH 11, TSA and TSC exhibited the best performance, effectively complexing magnesium ions. At pH 11, 1 g TSA can complex 199 mg Mg^{2+}, whereas the same amount of MGDA complexes around 90 mg Mg^{2+}. TSA therefore has a more than 2-fold higher chelating capacity. At pH 13 SG demonstrated the best performance, indicating its optimal functionality under these high alkaline conditions.

A similar pattern was observed at an elevated temperature of 40°C. In moderately alkaline conditions, TSA and TSC performed better, while SG was the most effective at pH 12. MGDA and GLDA exhibited reduced chelating properties across all pH levels at this higher temperature, demonstrating their limited efficacy in magnesium complexation under these conditions.

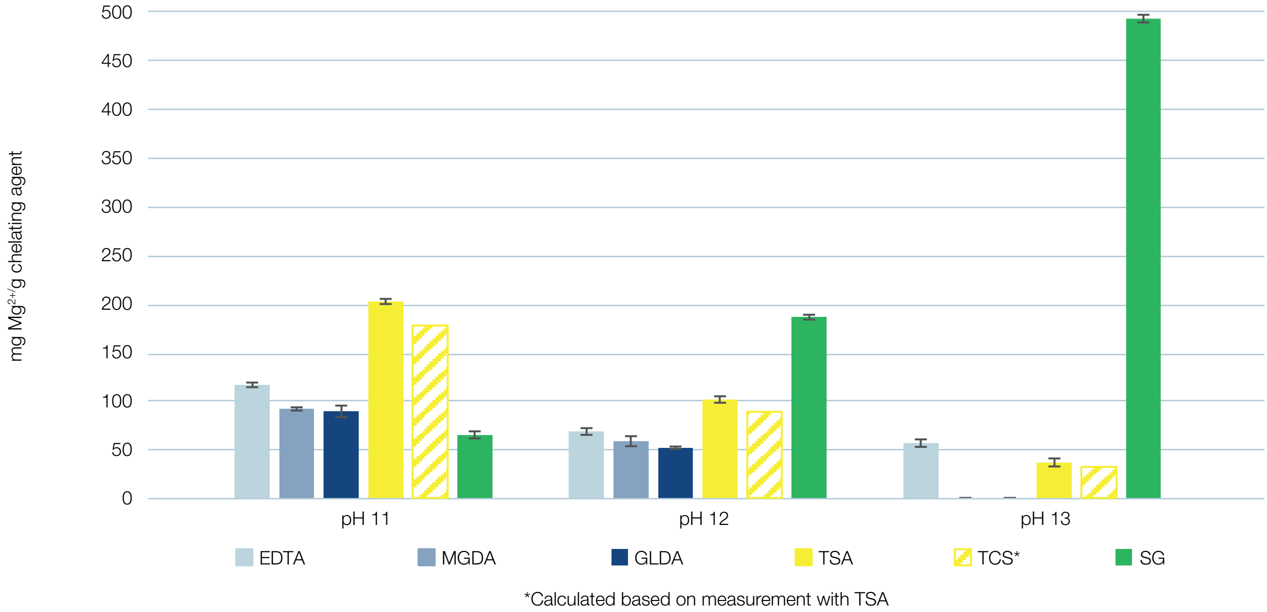


Figure 3: Complexation of Mg^{2+} at room temperature (21°C)

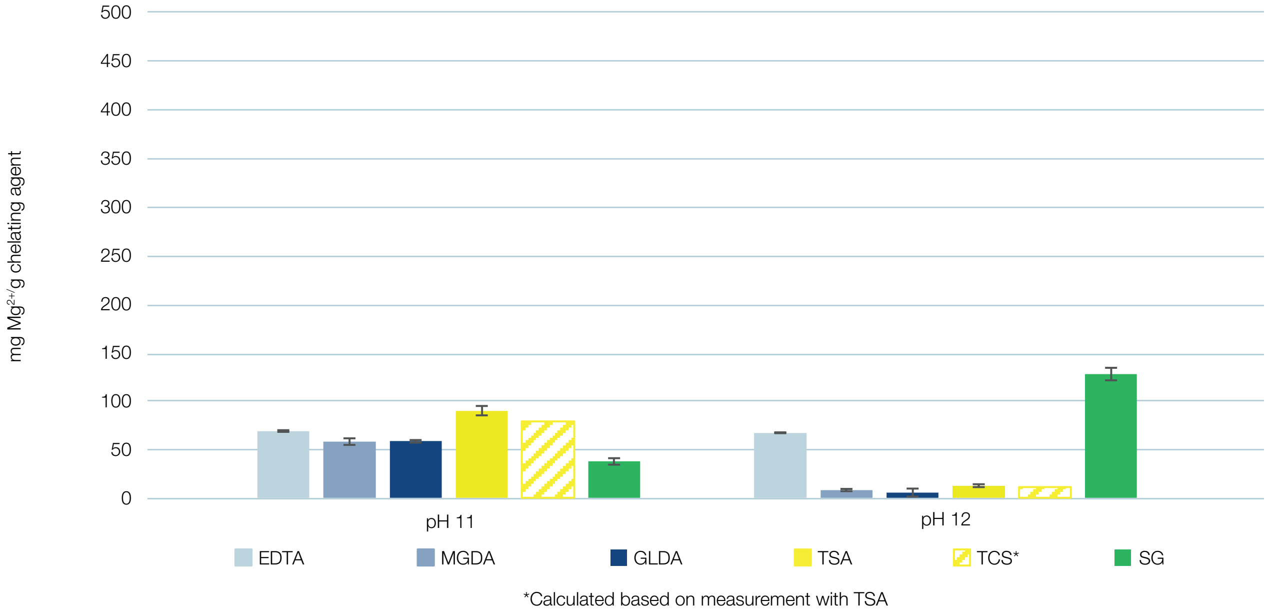
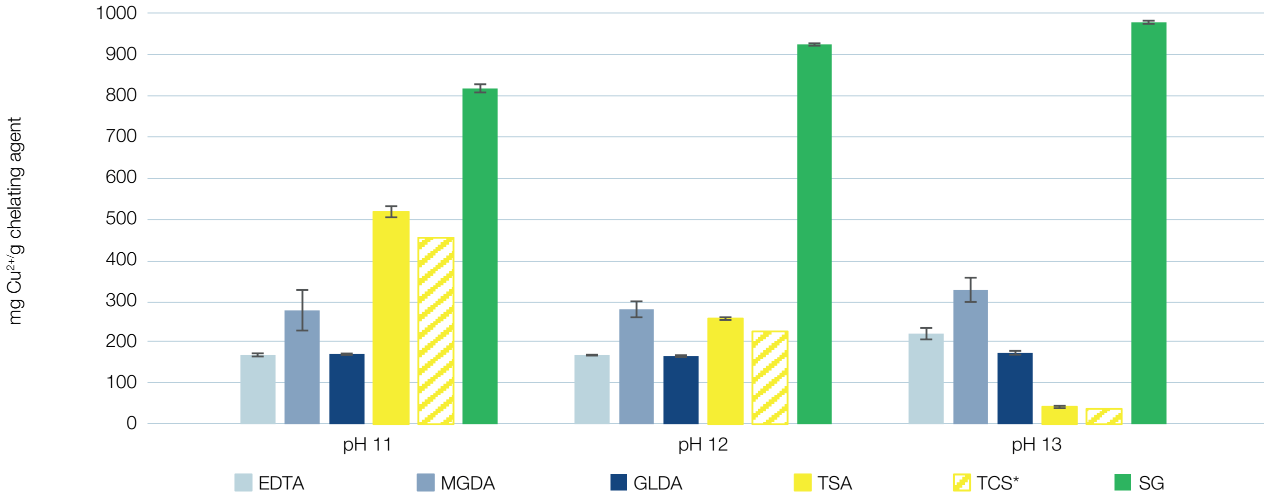


Figure 4: Complexation of Mg^{2+} at elevated temperature (40°C)

3) Results for Cu^{2+}

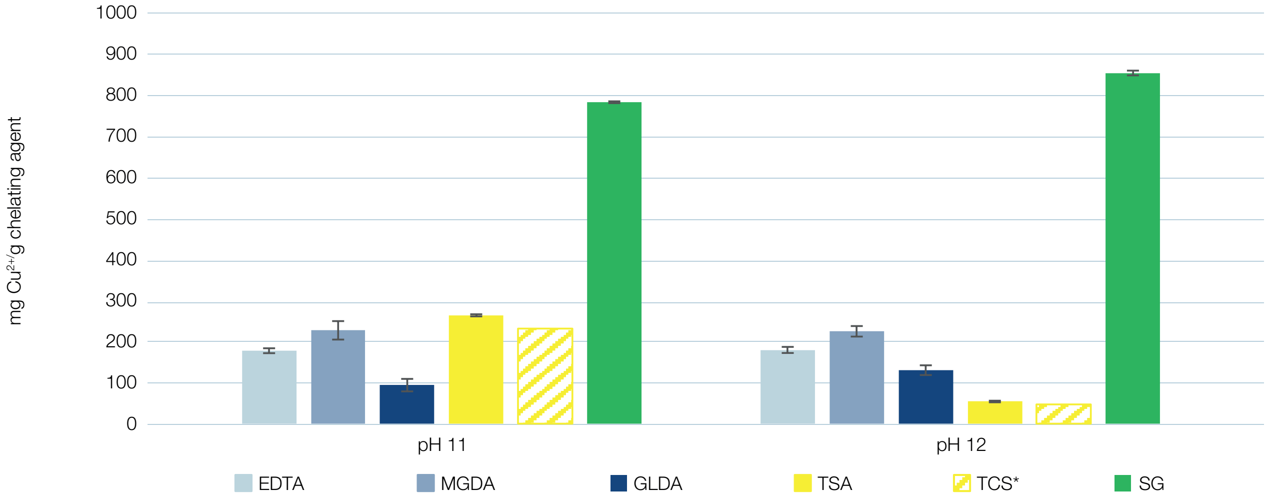
The performance evaluation for copper complexation also revealed divergent results across different pH levels and temperatures. The results for Cu^{2+} complexation at room temperature are shown in figure 5. The method could not be applied at pH 10 due to the water solubility of copper hydroxide in this pH range. SG exhibited the best performance across all pH levels, showcasing its superior ability to complex copper ions. Expressed in figures, this means that 1 g of SG at pH 11 can complex about 815 mg of Cu^{2+}, while the same amount of MGDA complexes 276 mg, which implies that SG has a threefold higher chelating capacity than MGDA. This in turn indicates that the same result can be achieved with much smaller quantities. TSA and TSC also showed good performance at pH 11. In contrast, EDTA, MGDA, and GLDA generally demonstrated poorer performance, with minimal variations across different pH levels.

At 40°C a similar trend was observed, as shown in figure 6. Overall, the performance of most chelating agents was decreased compared to room temperature. SG maintained the best performance across all pH levels. MGDA and GLDA showed reduced or comparable performance across the different pH levels, indicating their limited efficacy in copper complexation at elevated temperatures. At pH 11 and 40°C, for example, SG showed an approximately 3.5-fold higher chelating capacity than MGDA.



*Calculated based on measurement with TSA

Figure 5: Complexation of Cu^{2+} at room temperature (21°C)



*Calculated based on measurement with TSA

Figure 6: Complexation of Cu^{2+} at elevated temperature (40°C)

Conclusion

As shown in this article there is no “one-size-fits-all” solution to the problem of complexation. Chelation capacity strongly depends on the pH value, the temperature and the actual target ion. It is particularly notable that the citrate and gluconate salts, which are of natural origin, generally perform as well as their petrochemical-based counterparts. In many cases, particularly in the case of magnesium and copper, the natural chelating agents performed even better than the benchmarks under the boundary conditions tested. When taking a more holistic view, considering not only origin, performance, and hazard profile, but also ingredient price (cost-in-use), then gluconates and citrates are very valuable alternatives to the other chelating agents tested, even for calcium complexation. Jungbunzlauer offers citrates and gluconates manufactured on the basis of fermentation which act well as chelating agents for various ions.

Overall the data relating to sustainable chelating solutions is very promising and future studies will investigate this topic further, taking into consideration different pH values and other ions.

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About Jungbunzlauer

Jungbunzlauer is one of the world's leading producers of biodegradable ingredients of natural origin. We enable our customers to manufacture healthier, safer, tastier and more sustainable products. Due to continuous investments, state-of-the-art manufacturing processes and comprehensive quality management, we are able to assure outstanding product quality.

Our mission "From nature to ingredients" commits us to the protection of people and their environment.

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