

Chemical Feasibility of Chlorine Dioxide as an Extractant of Transition Metals from Chelated Complexes in Wastewaters for Recycling and Reuse

Philip Chi-Wah Cheung^{1, *}, Daryl Robert Williams¹, Donald Wilfrid Kirk², James Barker³

¹Department of Chemical Engineering, Imperial College, London, United Kingdom

²Department of Chemical Engineering, University of Toronto, Toronto, Canada

³Department of Chemical and Pharmaceutical Sciences, Kingston University, Kingston-on-Thames, United Kingdom

Email address

philip.cheung@imperial.ac.uk (P. Chi-Wah C.)

*Corresponding author

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Abstract: In this article experimentation to establish the feasibility of a chemical reaction between free radical chlorine dioxide ClO_2 and chelated complexes of Co^{2+} , Ni^{2+} and Cu^{2+} with citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and ethylenediaminetetraacetic acid (EDTA, $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$) as ligands, leading to the stoichiometric recovery of the metallic ions, is described. The procedure is one of empirical observation and discovery in the laboratory. This novel concept of the chemical-induced separation process predicated upon its ability to extract and precipitate metallic ions as insoluble metal oxides and oxyhydroxides, but not as hydroxides which are epitomized by the green hydrophilic gel $\text{Ni}(\text{OH})_2$ and extremely difficult to dewater. Chelation technology has many applications in industry and the wastewaters from these operations also contain a myriad of non-complexing agents such as brighteners used in electroplating. This work explores the option of in-house recovery of valuable resources such as transition metals, recognizing that the most formidable challenge is the separation of metallic ions from the organic ligands that protect them from precipitation in alkaline environments. Simulated wastewaters are used to study this reaction, free from the interference of proprietary additives and imposed operational conditions of the commercial sectors. The near 99% recovery of cobalt, nickel and copper ions is successful. This creates the possibility of scaling up from laboratory glassware to larger reactor vessels such as a semi-batch reactor in a small pilot-plant facility. This present work is not about the production of potable water, but much expertise has been accumulated pertaining to the efficacy of chlorine dioxide as a disinfectant and some of the relevant literature deserves attention here. The “future work” section discusses process development by way of a pilot plant investigation. It must be emphasized that this technology is not developed to be applied in public sewage treatment and no such inference should be made. (75 references from 1963 to 2018).

Keywords: Chlorine Dioxide, Cobalt, Nickel, Copper, Citrate, EDTA, Recycling

1. Introduction

A platform of innovative technologies which enables the recovery and reuse of metals from wastes will be of interest to a wide readership. The skills and knowledge are relevant not only to chemical engineers and practitioners of the circular economy, but also to company directors as sustainability moves up high on the agenda in boardrooms. Ways to integrate green functions into all facets of business

life are much sought after. Companies always take pride when they can demonstrate environmental friendliness, of which minimization of the loss of precious materials by a combination of process optimization and recycling is a concrete example. Ecologists and policy makers alike may approach the present work as a case study of the centrality of scientific knowledge in resource management and pollution control. Henceforth, the authors abide by their professional duty to elaborate, at some length, on the strategy,

technological challenge and fundamental chemistry foundational to this work.

1.1. Wastewater as a Resource Matrix

The United Nations General Assembly has assigned 22nd March of every year as World Water Day to highlight the work of UN-Water, a body which coordinates the efforts of over thirty UN entities and those of international organizations striving towards the enhancement of freshwater and sanitary provisions around the world. UN-Water focuses on a special theme each year to achieve tangible results systematically. This present work reflects the keynote extolled on World Water Day 2017: recognizing wastewater as an “untapped resource” and that recovering any recyclable material is a method to preserve it including, of course, water itself (UNESCO, 2017). Payne (2017) cited many examples in the UN report and argued convincingly that many components in wastewaters can be extracted for recycling [1]. This UN motif parallels the environmental management strategy of “Zero Waste”, which is part of the overarching philosophy of sustainable economies.

The original notion of “Zero Waste” is one of eliminating the formation of materials which will not add economic value to society at the end of their life-cycle and compel incineration, landfilling or encapsulation in solid matrixes as the only options of disposal. Cheung *et al.* (2018) has questioned the value of immobilization of large amounts of metallic wastes to long term sustainability of commercial operations [2]. In industry, the generation of wastes can be mitigated through process optimization of materials and energy consumption, and reusing valuable resources. These practices are best incorporated during the earliest stages of process plant/flowsheet design. This work aims to demonstrate the chemical feasibility of retrieving cobalt, nickel and copper ions from chemically complex wastewaters, for recycling and reuse, within the concept of resource management.

1.2. Technological Challenge Defined

The presence of organic chelating agents such as the conjugate bases (*i.e.*, anions) of citric acid and EDTA, amongst many others, means that metal complexes in waste liquors produced by electroplating and any other manufacturing industry are less amenable to removal by established methods. These methods are dependent upon the formation of insoluble metal hydroxides by addition of alkali. The problem is that metal-sequestering ligands provide formidable steric hindrance to the approach of OH⁻ ions towards the central metal ions to form hydroxides. The EDTA ligand and its metal complexes have long been known to be resistant to a variety of conventional treatment methods in the water industries, both in the production of potable water and during sewage treatment [3]. In fact, most of the full-scale plant data involve the performance of systems that are not specifically designed or operated for removal of certain toxic materials, and urban sewage treatment facilities

are good examples of such systems.

A review of the chemical composition of public wastewaters within the European Union reveals that this situation of non-specificity did not change on entering the 21st century [4]. The general consensus is that, with a few exceptions, none of the practices of adsorption by activated charcoal or biodegradation are effective methods of removal, unless special adsorbents and bacteria are discovered to suit a particular metal-ligand pair. These techniques have their own merits, but seldom do they produce the target material in a physical (*e.g.*, granular) form which can be easily handled, transported and processed for the next step of recycling.

There are scant reliable data for the success of treating specific metal chelated complexes in public treatment plants. It has been alleged that Fe(III)-EDTA is the only EDTA complex of the 1st row transition elements easily photolyzed, but its staunch resistance to raw sewage treatment is beyond doubt [5]. The earliest evidence of long-distance transport of industrial metals with the aid of chelants was provided by the complex Ni(II)-EDTA. The entity was so stable that its influx into San Francisco Bay could be traced back to the sources of wastewater discharges and urban runoff [6].

The authors of this work are developing new methods for the purposeful removal of complexed metal ions, and the subject matter itself has been reviewed by Cheung & Williams (2015) [7]. The present work demonstrates success in extracting nickel, cobalt and copper ions from their chelated complexes by chlorine dioxide.

1.3. Surface Deposition Operations as an Origin of Wastewater with Metal Complexes

The first row transition elements on the Periodic Table from chromium to copper have the ability to form chelated complexes mainly of mole ratio 1:1, with citric acid and its conjugate bases in aqueous solution, as does zinc and its subgroup members, cadmium and mercury. The cations of scandium, titanium and vanadium do form complexes with citrate, but these complexes are not utilised in industry to any significant extent. By the end of the 20th century the use of cadmium had been phased out in many countries. On 21st September 2017, the European Union enacted legislation banning the use of Cr(VI) compounds in “production” (manufacturing and the plating of decorative components). A handful of operations are allowed only by special permits from Brussels [8]. Cobalt, nickel and copper citrates are used extensively in industry, as are their EDTA counterparts. Each of the citrate and EDTA complexes of the three metals has been the main component of both electroless and electroplating; references [9] to [17] are a handful of examples. Many plating bath systems in use are patented. The chemical recipes of these baths are modified continually to cope with 21st century demands in technology and quality.

Deposition of alloys is also very popular amongst plating practitioners. Martins *et al.* (2016) reported co-deposition of Co-Cu-P in a citrate bath [18]. Toda *et al.* (2013) coated surfaces with a Ni-Co-P alloy in the presence of mixed

ligands, namely, citrate, tartrate and ammonia [19]. These multi-component recipes are commonly used today.

The chemical composition of the wastewater generated from plating operation will be very different to that of a freshly prepared solution at the commencement of the operation. The mole fraction of each component varies with time. Operators must replenish the bath with certain chemicals as plating proceeds. In rare instances when products fail to meet quality specifications, the entire bath must be discarded: these are very expensive mistakes. These eventualities demand a wastewater treatment system capable of dealing with them satisfactorily.

The Shipley Company specified the following concentrations for an electroless plating bath [20]. The fresh solution is composed of 0.04 mol dm^{-3} CuSO_4 (3 g dm^{-3} of copper) and 0.13 mol dm^{-3} Na_2EDTA (40 g dm^{-3} with respect to the EDTA ligand alone). The mole ratio of metal-to-ligand is 0.04 to 0.013, or 1:3, *i.e.*, EDTA is in excess. To study the hypothetical situation of evaporation of bath water leading to an increase in concentration of copper in the solution, the stock solution prepared for the experiments in this work was made up to a concentration 50% higher than 0.04 mol dm^{-3} , to 0.06 mol dm^{-3} . Fundamentally, this work focuses on the reactivity of the 1:1 complex and therefore the concentration of Na_2EDTA was also set at 0.06 mol dm^{-3} in the stock solutions.

The mole ratio of metal-to-ligand in all stock solutions of simulated wastewaters in this work was 1:1. The concentration of a complex in a stock solution was 0.06 mol dm^{-3} .

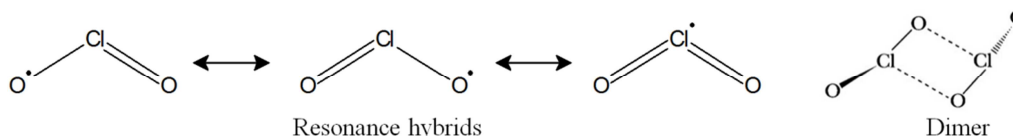


Figure 1. The three resonant structures of ClO_2 , and formation of a weak dimer.

The O-Cl-O bond angle is 117.4° , and the Cl-O bond length is 1.475 \AA . The radical $[\text{ClO}_2]^\bullet$ does not dimerize in the gaseous and liquid states, probably due to the electrostatic repulsion between non-bonding pairs of electrons on Cl, and also to the dislocation of the unpaired electron over the whole molecule, to the effect that, even in the crystalline state, the molecules only associate loosely in pairs. Similarly, the pK_a of chlorous acid HClO_2 is 1.8, a low value [26], which is advantageous to the synthesis of ClO_2 .

It has long been established that, despite having a chlorine atom in the molecule, reactions of organic compounds with ClO_2 do not generate by-products such as trihalomethanes to the extent found in sodium hypochlorite solution [27]. Many environmentalists have embraced the use of ClO_2 as a disinfectant for water due to this reason [28]. The World Health Organization (2018) has addressed the chronic and undesirable problem of the formation of chloramines by the chemical reaction between hypochlorite and ammonia [29]. The advantage of using ClO_2 as an oxidant of EDTA is that ClO_2 is not known to react with NH_3 to form chloramines. In

1.4. Structure and Bonding of the Chlorine Dioxide Radical

The electrically neutral ClO_2 molecule is a free radical. It contains an odd number of valence electrons; there are 19 such electrons with two sets of 6 electrons from oxygen atoms, and 7 electrons from the chlorine atom. This radical is paramagnetic at room temperature and is often written as $[\text{ClO}_2]^\bullet$. The radical is not to be confused with the ions ClO_2^- or ClO_2^+ and can be obtained by the ionization $\text{ClO}_2^- \rightarrow \text{ClO}_2 + e^-$, the ionization energy being 2.1408 eV [21]. Listed in Appendix 1 are the many chlorine and oxygenated-chlorine species frequently encountered in literature, together with their most popular names, including the ones which are the subject of this work.

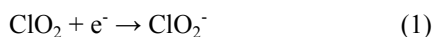
Free radicals have the tendency to dimerize but in the case of ClO_2 , only a weakly bonded dimer exists at a low temperature of -150°C , written as $\text{OCl}(\mu\text{-O})_2\text{ClO}$ in the *trans* configuration, and it is diamagnetic below -84°C . This temperature was observed to be below the melting point of solid ClO_2 at -59.5°C [22]. The radical $[\text{ClO}_2]^\bullet$ is a bent molecule of C_{2v} symmetry when in the ground electronic state. At room temperature, $[\text{ClO}_2]^\bullet$ exhibits a chlorine-oxygen bond length of 1.475 \AA which is notably shorter than the 1.693 \AA single bonds in Cl_2O , but longer than the 1.408 \AA double bonds of ClO_2^+ [23]. The O-Cl-O bond angle in $[\text{ClO}_2]^\bullet$ was assigned a value of 117.4° [24]. Three resonant structures for this radical and the aforementioned dimer are illustrated in Figure 1 [24, 25].

this case, the final product of continuous dehydrogenation of NH_3 is likely to be N_2 . Different reaction pathways between ClO_2 and HOCl have been proposed for target substrates [30].

Chlorine dioxide is a versatile oxidant. Lately, Wang *et al.* (2015) successfully destroyed the pharmaceutical "diclofenac" (a steroid) in wastewaters [31]; Van Haute *et al.* (2017) eliminated *E. coli* during the washing of fresh lettuces using ClO_2 [32]. As a powerful oxidant, ClO_2 has the intrinsic ability to oxidize many organic and inorganic compounds [33, 34].

1.5. Significant Properties of ClO_2 for Process Plant Operation

An attack on a metal chelate by sustained abstractions of its electrons and hydrogen atoms may dismantle it to the extent that ligands lose their sequestration ability. The metallic ion becomes free once again to form hydrated ions of the type $[\text{M}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$. The one-electron reduction of ClO_2 is:



The potential for the half equation relative to a standard hydrogen electrode (SHE) is +0.954 V [35].

ClO_2 is highly soluble in water, particularly ice-chilled water. Unlike Cl_2 , the free radical ClO_2 hydrolyzes up to 10^7 times slower than Cl_2 [36], and therefore ClO_2 remains as molecules [37]. ClO_2 is about ten times more soluble in water than Cl_2 , but can be removed easily from water with gentle aeration. Above 11°C and at atmospheric pressure, ClO_2 is a greenish yellow gas floating above the surface of water, but it can be swept away by bubbling a stream of argon into the solution when extraction reactions are completed. This gaseous mixture can be made to pass through a second vessel containing Na_2SO_3 (aq) for reducing ClO_2 . Disproportionation in alkaline solution is another chemical property of ClO_2 that will render it harmless. (See “Materials and Methods” section below)

2. Literature Survey

In a comprehensive review paper comprised of 263 references, Cheung & Williams (2015) [38], the co-authors of this article, addressed the technical difficulties presented to engineers treating liquid wastes containing chelated complexes of metal ions, of which nickel citrate in electrodeless plating, copper EDTA in electronic chip board manufacturing, and radioactive nuclides sequestered by a host of organic ligands are but three examples. It has become apparent that organic chelating agents have great tendencies to behave in the following ways:

- (i) Attenuate or inhibit precipitation of metallic ions by alkali and sulfide (NaOH and Na_2S), *e.g.*, in one case, the presence of just 1 ppm of EDTA hindered the sulfide precipitation of Ni^{2+} and Zn^{2+} ions considerably.
- (ii) Render cation exchange resins ineffective because the electric charge of the chelated moiety has become the same as that of the exchangeable ion on the resin. A cation exchange resin will not adsorb metallic ions M^{n+} which are trapped in a negatively charged complex.
- (iii) Render other non-exchanging sorbents ineffective because of the same mismatch between species and surface charges, otherwise they would have worked for unbound M^{n+} ions.
- (iv) Cause poor growth and flocculation of nuclei, resulting in no sedimentation of solids.
- (v) Form recalcitrant complexes which respond to treatment poorly, *e.g.*, the reaction between Cu(II) -EDTA and NaOCl is sluggish to the point of cessation, without retrieval of copper.

Cheung & Williams (2015) identified 18 techniques for the treatment of wastewaters containing metal chelated complexes, the organic ligands of which are chelating agents. These methods include direct oxidation of the complexes by O_3 , H_2O_2 , NaOCl , KMnO_4 and Fenton reactions [38]. Aramyan & Moussavi (2017) discussed the limitations of

Fenton systems in their applications to combat environmental pollutants [39]. Lin *et al.* (2015) co-precipitated Ni^{2+} and Cu^{2+} from their EDTA complexes by microwaving a Fenton treatment system followed by hydroxide precipitation, but EDTA did not degrade under these conditions [40]. Zhao *et al.* (2017) named EDTA as a decontaminating agent applied in a nuclear installation for radioactive dose reduction, and their research focused on the subsequent degradation of “EDTA” by electro-oxidation carried out in an electrolysis cell with a platinum electrode supported on an activated carbon fiber matrix [41]. However, in any decontamination exercise in the nuclear industry including processing equipment, the focus is on the removal and isolation of radioactive nuclides for safe disposal. Therefore, it is pertinent to clarify whether Zhao *et al.* (2017) [41] actually meant “the chelated complexes formed by radioactive isotopes and EDTA moieties in aqueous solutions”, or whether a massive overdose of EDTA was applied, with the result that the washwater to be treated contained both metal-EDTA complexes and a preponderance of free ligands. It would also be important to monitor of the fate of the isotopes.

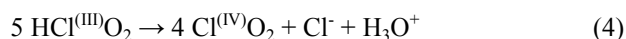
There has been no publication on the deployment of ClO_2 on a large scale for the extraction of transition elements on the Periodic Table, from any kind of industrial waste in bulk, for the sole purpose of recycling and reusing these metallic elements in any commercial sector. The present work is a first step in filling this gap by demonstrating that stoichiometric separation of cobalt, nickel and copper ions from their chelated complexes in aqueous solutions can be reasonably achieved.

3. Materials and Methods

This section is divided into two parts. Part A is the *in situ* synthesis of ClO_2 and its reactions with metal complexes, in the same reaction vessel, which leads to the recovery of metallic ions eventually. Part B consists of two control experiments to validate the efficacy of ClO_2 as an oxidant-extractant.

Part A *In situ* generation of ClO_2 and oxidation of metal complexes

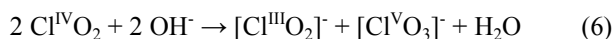
Aqueous solutions of a 1:1 metal citrate or EDTA chelated complexes were prepared using analytical grades of metal sulfates, trisodium citrate, or tetrasodium EDTA hydrate (Sigma-Aldrich). Technical grade sodium chlorite NaClO_2 was purified by recrystallization three times, and reacted with 37 wt.% HCl to give acidic solutions of ClO_2 , the desired oxidant. Dissolving NaClO_2 in HCl gave chlorous acid, HClO_2 , an unstable intermediate. It then disproportionates to give ClO_2 . Therefore:



The overall stoichiometric equation for the preparation of ClO_2 is:

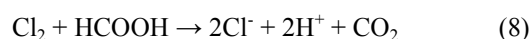


Oxidation of transition metals complexes must occur in acidic media, because ClO_2 itself disproportionates rapidly in alkaline solutions:



This laboratory preparation was carried out according to the method outlined by Occidental Chemical Corporation (OxyChem) [42], a company with considerable experience in advanced oxidation processes. The method was adapted and modified into a batch reactor system here (Figure 2). Recommended volumes of vessels and accessories were strictly followed for health and safety reasons, since ClO_2 is explosive at concentrations $>10\%$ by volume in air. The

disproportionation reaction ($2\text{Cl}^{\text{IV}} \rightarrow \text{Cl}^{\text{III}} + \text{Cl}^{\text{V}}$) represented by equation (6) was not expected to proceed in highly acidic media, and the addition of HCOO^-Na^+ to the reaction solution was a precaution to eliminate any inadvertent formation of Cl_2 as a by-product [43]. Therefore, even if Cl_2 is produced by equation (7), it is reduced to harmless Cl^- ions by equation (8):



The procedure for synthesizing ClO_2 and its reactions is now described.

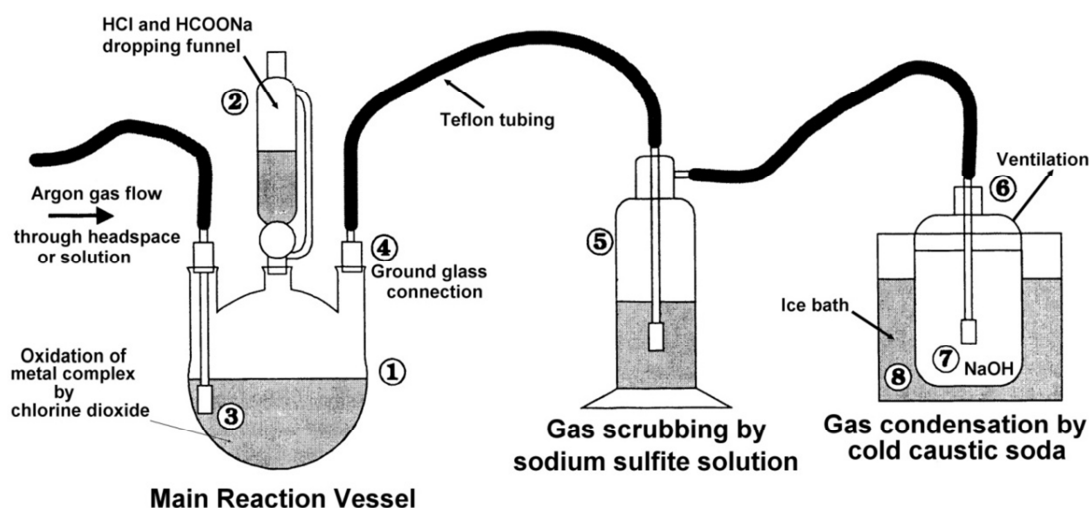


Figure 2. Apparatus set-up for the generation, reaction and removal of ClO_2 . The bold and bracketed numbers from (1) to (8) are the labels for the reaction vessels and/or activities described in the text.

The vessels displayed on Figure 2 were set up in a fume cupboard with an air-tight assembly: the round-bottomed flask, vessel (1), was immersed in a water bath at 10°C . The concentration of HCOO^-Na^+ in vessel (2) was 0.05 mol dm^{-3} . The gas-sparger is labelled (3). The ground-glass connection is labelled (4). Vessel (5) contained a saturated solution of Na_2SO_3 which acted as a reducing agent for ClO_2 . Ventilation piping was labelled (6). Vessel (7) contained an ice cold solution of NaOH of concentration 1 mol dm^{-3} into which residual ClO_2 in the continuous argon stream could dissolve and disproportionate according to equation (6). Vessel (8) was an ice-bath.

A volume of 50 cm^3 of a 0.06 mol dm^{-3} solution of the metal complex of interest was prepared from a stock solution of 1 dm^3 . 5 g of recrystallized NaClO_2 was then dissolved in this solution and introduced into vessel (1) followed by 200 cm^3 of water. In a separate beaker 50 cm^3 of water was added, followed by 11 cm^3 of 37 wt.% HCl in 1 cm^3 aliquots, while continually cooling the beaker. 1 g of sodium formate was dissolved and then transferred to dropping funnel (2). The dropping funnel can be replaced by a thermometer, in the

same position, for the measurement of temperature as the reaction proceeds. The sparger (3) in vessel (1) was situated immediately above the gas-liquid interface. The argon flow into the reactors was turned on until bubbles just appeared in the vessels (5) and (6). It was not planned to remove ClO_2 in solution while the redox reactions were proceeding because ClO_2 is a main reactant itself.

The acid/sodium formate solution in vessel (2) was now released into vessel (1), in 10 cm^3 aliquots, with 5-minute intervals between additions to avoid sudden excessive pressures of ClO_2 as well temperature surges. After the HCl solution addition, $\sim 1 \text{ cm}$ layer of the yellowish green gas ClO_2 was seen floating on the liquid surface and was swept away by the argon stream. The reaction solution is a clear/homogeneous golden-yellowish green coloration. In initial stages of the reaction the intensity of the golden yellow coloration decreased as the reaction between ClO_2 and metal complex proceeded. No yellowish gas was seen to enter the headspace of vessel (1) an hour after HCl was added. At this point, the argon gas stream was switched off, but was switched on again for 5 minutes every 30 minutes to purge

the headspace of ClO_2 . Three hours after the addition of HCl, reaction solutions became very faintly colored, scarcely detectable by the human eye. This observation was shared by White [44], "It is perhaps significant to note that as the chlorine dioxide leaves the solution, the yellowish green color of the solution fades, and it finally becomes colorless. The remaining solution will contain negligible amounts of chloric acid (HClO_3), indicating a very weak acid reaction with water". This is a convenient point to regenerate ClO_2 to complete the reaction with the metal complexes.

The reactants NaClO_2 (5 g) and HCOONa^+ (1 g) were introduced into vessel (1), *via* the dropping funnel vessel (2), under continuous stirring. Then vessel (2) was inserted into the port opening again and 11 cm^3 of 37 wt.% HCl was added dropwise into vessel (1) with argon purging. Three 3-hour regeneration cycles were run. One last ClO_2 generation ensured that there was sufficient ClO_2 for precipitation of metal oxides and oxyhydroxides when these solutions were rendered alkaline by NaOH. The final liquid volume in vessel (1) was 350 cm^3 ; the original solution was diluted 7 times. 50 cm^3 of the final liquor from vessel (1) was withdrawn and then added, under cooling, to 50 cm^3 of 2M NaOH in a 250 cm^3 Pyrex glass beaker, resulting in the precipitation of black metal oxides and oxyhydroxides. The final solution pH was adjusted to 10.0, which ensured precipitation.

This final liquor was filtered through cellulose membranes of pore size 0.45 μm , supplied by the manufacturer of laboratory equipment, Whatman[®]. These filters are highly resistant to chemical attack. The colourless filtrate was analyzed by the instrumental method known as ICP-OES (Induced Coupled Plasma – Optical Emission Spectrometry). The machine model was "Horiba Jobin Yvon, Ultima 2CE", and its lower limits of detections are as follows: Co, 0.2 ppb; Ni, 0.3 ppb; Cu, 0.8 ppb [45].

Each filtrate sample was analyzed thrice for its metallic content. The black precipitates obtained were washed, dried and stored. Filtered solutions were returned to vessel (1). Vessel (3) was then lowered to below the air/water interface and argon was bubbled through vessels (1), (5) and (6) for 20 minutes to drive out residual ClO_2 from the reaction liquor. In vessel (5), ClO_2 will be reduced to Cl^- , and SO_3^{2-} is oxidized to SO_4^{2-} . In vessel (6), ClO_2 will disproportionate in caustic soda according to equation (6), and HCl gas will be neutralized.

Part B Control experiments

Control experiment 1

Subsequent to the completion of the chief experiments in Part A, aqueous solutions of the six metal-ligand pairs of volume 50 cm^3 each were drawn from their respective stock solutions and pipetted into Pyrex[®] glass beakers (of 600 cm^3 size), and made up to 350 cm^3 by de-ionized water; this is the same volume as the final reaction solution. The solutions were rendered alkaline to pH = 10 by adding NaOH (1 mol dm^{-3}) dropwise by a burette. This is the pH value which affected the precipitation of metallic oxides and oxyhydroxides in the main experiments. Had sequestration of metallic ions not taken place by citrate and EDTA, then

precipitation of hydroxides is immediate, but no such precipitation occurred.

The beakers were then placed in a chamber modified from a transparent Perspex[®] plastic container and magnetically stirred. The chamber was filled with argon from a gas cylinder (to exclude air). This inert argon atmosphere eliminates the possibility of absorption of CO_2 from air by alkali, which would have lowered the pH of the solution. Carbonates of the transition metals are largely insoluble and their formation may interfere with the interpretation of the outcomes of the control experiments. Recall that within the confines of the reaction system depicted in Figure 2, air is practically absent because of the continuous sweep of argon. Since the metal-complex solutions were subjected to 9 hours of processing time, the beakers were magnetically stirred for the same amount of time. No ClO_2 was applied to the solutions during the control experiment. At the end of the nine hours, the aqueous solutions remained homogeneous, colored, clear and transparent. There was no precipitate of any sort. Rendering an aqueous solution alkaline by addition of NaOH will result in precipitation of free (hydrated) metallic ions. For example, in the case of copper sulfate solutions, formation of the light glue gel is immediate, therefore: $\text{Cu}^{2+} + 2 \text{OH}^- \rightarrow \text{Cu}(\text{OH})_2 (\text{s}) \downarrow$, but in the presence of EDTA this does not happen. The observed single-phase homogeneity did not change with time.

Control experiment 2

By definition, the "formation constant" K_f of a metal complex is identical to that of the equilibrium constant K_{eqm} of the chelation reaction, so that:

$$K_f = K_{eqm} = [\text{Complex}]/([\text{M}^{2+}] \times [\text{EDTA}^{n-}]) \quad (9)$$

The numerical value of K_f is a positive function of pH. The higher the pH, the higher the degree of ionization of a Brønsted-Lowry acid (one which furnishes protons) will be, and the higher the concentration of anionic conjugate bases which can attract and chelate metallic cations. Conversely, the degree of protonation of the chelating acidic groups such as carboxylic and amino depends on $[\text{H}^+]_{aq}$. The more acidic the solution, the more replete the protonation, and the smaller the numerical value of K_f becomes. However, it is important to note that freeing the metallic ions from sequestration cannot be achieved by acidification alone. A good example is that of Cu(II)-EDTA. The effective $\log_{10} K_f$ values are: 18.4 at pH = 12, and -4.1 at pH = 0, *i.e.*, even a drop of 12 – 0 = 12 units of pH will not detach Cu^{2+} from the organic EDTA moiety completely. In another word, at pH = 0, $K_f \neq 0$, although the mole fraction of free (*i.e.*, non-sequestered) Cu^{2+} ions can be approximated to $(1 - K_f) = (1 - 10^{-4.1}) = 0.999$, over 99%, but will drop rapidly as pH increases. The entire set of effective formation constants for the complex has been reported [46]. In fact, multi-equilibria are set up between unbound metallic ions, free ligands and the chelated metal complexes, even in acidic conditions. The population of a metal complex system at a particular pH is constituted of several distinct species with a characteristic relative abundance. This distribution is represented graphically in

Figure 3, generated by a software package called "MINEQL+" (see Appendix 2 for a qualitative introduction).

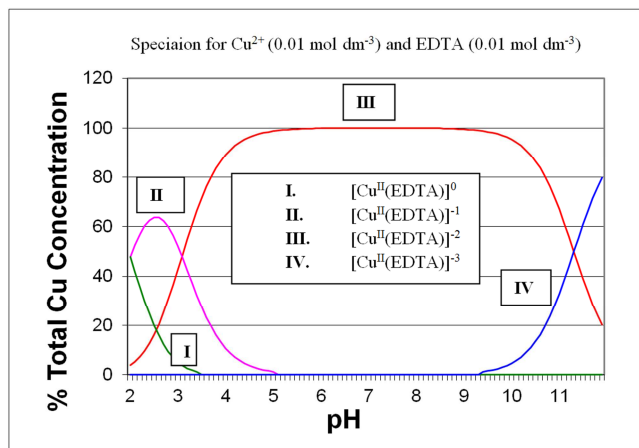


Figure 3. Relative abundance of Cu(II)-EDTA species vs. pH, generated by "MINEQL+".

The EDTA molecular ion has six protonable sites (4 carboxylic and 2 amino acid groups) and is often denoted as $[H_6Y]^{2+}$ when fully protonated. At $pH < 2$, the predominant species are $[H_6Y]^{2+}$ and $[H_5Y]^+$ but they will hardly bind Cu^{2+} ions due to electrostatic repulsion between like charges. Moreover, with $pK_3 = 2.00$ and $pK_4 = 2.69$ [46], half of the EDTA population will be electrically neutral at $pH = 2$ as $[H_4Y]^0$, and precipitates as a white powder. This phase change renders the study of complexes at $pH \sim 2$ problematic. For many metal-EDTA complexes, the "MINEQL+" database only includes species in solutions of $pH > 2$. However, it can be inferred from Figure 3 that species I complex has begun to form in true aqueous solution, at pH just above 2, as EDTA ionizes further. In fact, the curves representing species I and II coincides at $pH = 2$, denoting equimolarity at 48%, while species III is in a minority of 4%. At all values of $pH \geq 2$, calculations performed by "MINEQL+" showed that the concentration of unbound Cu^{2+} ions are "zero". Between $pH = 2.5$ and 2.6, species II dominates at 64%, while species I and III are equimolar at 18%. At $pH = 3.1$, species II and III are equimolar at 48%, while species I comprises only 4% of the populace. At $pH = 3.5$, species I ceases to exist. At $pH = 5.5$, species III is the only significant species. Nowhere in the region $2 \leq pH \leq 7$ are unbound Cu^{2+} ions the predominant species.

Recall that the concentration of metal complexes in the stock solutions prepared for the main experiments was a nominal 0.06 mol dm^{-3} , diluted 7-fold, in the reaction vessel, close to $0.008 \text{ mol dm}^{-3}$. This is a concentration in proximity of 0.01 mol dm^{-3} , and was chosen for the computer modelling exercise.

Another good example is the speciation of copper citrate, portrayed in Figure 4. To be sure, in the very acidic condition at $pH = 0$, hydrated Cu^{2+} ions as a single species constitute 0.92 of the copper population (*i.e.*, 92% but not 100%), and 0.08 (8%) is un-ionized $CuSO_4(aq)$. The population profile diversifies dramatically as pH is raised beyond 2 [13]. In the range $3.5 \leq pH \leq 4.5$, multi-equilibria exists between

monomeric and dimeric species: $[Cu(C_6H_6O_7)]^0$, $[Cu_2(C_6H_5O_7)_2]^{2-}$, $[Cu_2(C_6H_5O_7)(C_6H_4O_7)]^{3-}$ and $[Cu_2(C_6H_4O_7)_2]^{4-}$ (note that the 1:1 mole ratio of metal-to-ligand is preserved in dimeric complexes). In the range $3.7 \leq pH \leq 5.0$, $[Cu^{2+}]$ does not exceed 40% at any time. In fact, as the pH reading nears 4.5, the concentration of Cu^{2+} ions rapidly approaches zero.

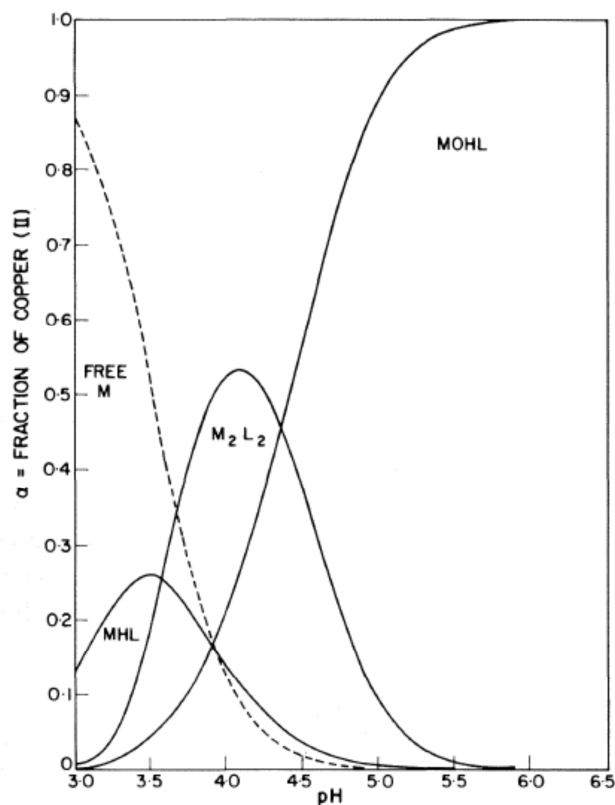


Figure 4. Relative abundance of Cu(II)-citrate species in acidic conditions vs. pH [13].

In the laboratory, every attempt to acidify a solution of Co(II), Ni(II) or Cu(II)-EDTA, and then render it alkaline again by NaOH with the intention of precipitating the metallic ions as hydroxides, had failed. This is not unexpected. Furthermore, addition of EDTA in the stoichiometric mole ratio of 1:1 to a two-phase alkaline mixture containing H_2O and the hydrophilic metal hydroxide gels solubilise the metallic ions with ease, and single-phase homogeneous solutions result.

Continuing with control experiments, in the case of Co(II) citrate, an injection of NaOH into an acidic solution of the metal complex resulted in an opaque, dark purple colloidal solution. As inorganic ligands, OH^- ions from the caustic soda may have competed for Co^{2+} ions successfully over citrate moieties, or formed mixed-ligand Co(II) complexes with them. However, this liquid mixture, which contained very fine colloidal "particles", did not settle after 72 hours of standing in a funnel (for observation). Therefore, sedimentation by gravity (which is preferred over the more elaborate nano-filtration in the first instance) is not an option for a separation process. With Ni(II) citrate, a green gel phase was formed which also

refused to settle, and citrate may well be an intrinsic part of this gel phase. In an aqueous solution of NiSO₄ with no citrate present, any bright grass-green gel formed by addition of NaOH will settle rapidly. Unfortunately, dewatering this gel is notoriously difficult. Lastly, the blue gel formed in the Cu(II) solution on addition of NaOH did not dehydrate to give the pitch black CuO precipitate on boiling, unlike the situation when citrate is absent.

On acidifying a metal-complex solution, it is foreseeable that some, but not all, bare metal ions adsorb onto ion-exchange resins. The metal contents of electroplating wastewaters are high in a NiSO₄/NiCl₂ electroplating bath with no citrate present (*e.g.*, in the traditional “Watts” bath, still in use). Djaenudin *et al.* (2017) encountered a wastewater with a nickel concentration of 2200 ppm which required substantial reduction [47]. Earlier successful work was performed by the Eco-Tech Ltd. in the town of Pickering, Ontario, Canada. The Ni concentration in rinse water (part of an electroplating operation) was as high as 3950 ppm, which was reduced to 1 ppm by ion-exchange [48] (*c.f.*, the metal concentration in the stock solutions prepared for this work is in the vicinity of ~3500 ppm, see “Results and Discussions” below). However, as already mentioned in the “Literature Survey” section, the presence of organic chelating agents in wastewaters does not facilitate their treatment.

Nonetheless, the present work advocates the search for chemical technology which will recover useful and valuable materials from wastes. The question to ask is this: How can the metallic ion population from the wash-water for the regeneration of an ion-exchange column be extracted into a physical form which can be easily handled, unlike the hydrophilic gels mentioned above? If other non-exchange adsorbents are used, what is the manner of disposal of these adsorbents which have become “hazardous” wastes themselves by virtue of the adsorption of metals? Will this chain of events end in a landfill site?

In summation, there is strong indication that the organic ligands such as citrate and EDTA protected the metallic ions from forming insoluble hydroxide gels. Precipitation of black metallic oxides in the main experiments was possible solely from redox reactions between ClO₂ and the metal complexes. It may be inferred that citrate and EDTA ligands were fragmented by ClO₂, followed by oxidation of Co(II) and Ni(II) to higher oxidation states. No binary compound (*i.e.*, one which contains two elements only) called copper (III) oxide with empirical formula Cu₂O₃ has ever been synthesized, unlike Co₂O₃ and Ni₂O₃. Had any oxidation state higher than +II existed, albeit transiently, the species was probably unstable and reverted back to the Cu(II) state. See equation (16) for the formation of the insoluble black Cu^{II}O in the next section, namely, “Results and Discussions”.

4. Results and Discussions

4.1. Data and Calculations

Each of the cobalt, nickel and copper sulfate salts (and the

sodium salts of citrate and EDTA) was weighed separately and precisely. Each stock solution of 1 dm³ (*i.e.*, 1000 cm³) containing a particular transition metal-ligand pair was prepared using these weights, to make a 1:1 metal-ligand aqueous solution. The weighing balance displays 4 decimal places down to 0.0001 g, and the last decimal place is only relevant in so far as it indicates that any error that may incur will be in the last digit. (The last decimal place has no significance in the development of arguments here)

The formula mass of CoSO₄·7H₂O (crystals) = 281.094, and theoretically, in a 1 dm³ solution of concentration 0.06 mol dm⁻³ there will be 0.06 x 281.094 = 16.8656 g dissolved. This number was used to benchmark the actual weighing for all cobalt solutions so that this was not exceeded (while nickel and copper solutions have their own unique bench markers). The actual weight of cobalt sulfate crystals used was 16.863(1) g (note that the last digit displayed by the weighing balance happened to be “1” in this case, and is bracketed to show that readings are accurate to three decimal places). This is equivalent to 16.863/281.094 = 0.059 mol; each 50 cm³ aliquot contained 0.059 x (50/1000) = 2.95 x 10⁻³ mol Co²⁺ ions, equivalent to (2.95 x 10⁻³) x 58.93 (atomic mass of Co) = 0.174 g, before the commencement of treatment by ClO₂. This is the 1st entry in Table 1. The metallic contents of every other solution was worked out and tabulated accordingly. (Atomic mass of Ni = 58.69, formula mass of NiSO₄·6H₂O = 262.839; atomic mass of Cu = 63.54, formula mass of CuSO₄·5H₂O = 249.68).

Standard volumetric equipment in the laboratory such as a calibrated pipette is sufficiently accurate for the delivery of 50 cm³ for the purpose of this exercise, and the actual mass of metallic ions calculated accordingly. It is not necessary to determine the concentration of transition metals in the reaction solutions by ICP-OES down to sub-ppb accuracies in the standardized stock solutions, despite the fact that the instrumentation can. For example, the mass concentration of the Co ions in solution described in the last paragraph is already at (10⁶ x 0.174)/50 = 3480 ppm. Interpretation of numerical data in the context of “orders of magnitude” is intrinsic to this work. The mass of the metallic ions applied in reaction solutions of volume 50 cm³ each are listed in Table 1.

Table 1. Applied mass of transition metallic ions in each 50 cm³ reaction solution.

Metal ions (aq)	Citrate solutions (g)	EDTA solutions (g)
Co ²⁺	0.174	0.176
Ni ²⁺	0.176	0.168
Cu ²⁺	0.159	0.154

The following is a sample calculation for metal recovery used to compile Tables 2 and 3. The example is that of the cobalt citrate reaction solution, the data of which occupies the 1st row in Table 2. Since every reaction was conducted thrice, Sets 1 to 3 are the three ICP-OES determinations of vestigial cobalt ions in the filtrates of the final reaction solutions. The average of the 3 determinations is: (4.1 + 4.3 + 4.2)/3 = 4.2 ppm (in the 5th column). For the purpose of

preliminary estimation, the specific gravity of the clarified liquid (of volume 350 cm³) is approximated to be that of water, *i.e.*, unity. The mass of cobalt which remained in the final solution after clarification is: $(4.2 \times 350)/10^6 = 1.47 \times 10^{-3}$ g (on the 6th column). From Table 1, the applied mass of

cobalt was 0.174 g, and of this the remaining fraction is simply given by: $1.47 \times 10^{-3}/0.174 = 0.0084$ (7th column). The overall recovery of cobalt ions from aqueous solution is then calculated to be: $(1 - 0.0084) \times 100\% = 99.16\%$ (last column).

Table 2. Analysis of residual transition metallic ions by ICP-OES in citrate reaction solutions.

Metal ions (aq)	Set 1 (ppm)	Set 2 (ppm)	Set 3 (ppm)	Average (ppm)	Mass in filtrate (g)	f, fraction of the original applied mass	Recovery, (1 - f) x 100%
Co ^{III}	4.1	4.3	4.2	4.2	1.47×10^{-3}	0.0084	99.16%
Ni ^{III}	4.5	4.9	4.6	4.7	1.65×10^{-3}	0.0093	99.07%
Cu ^{II}	3.5	3.1	3.4	3.3	1.16×10^{-3}	0.0073	99.27%

Table 3. Analysis of residual transition metallic ions by ICP-OES in EDTA reaction solutions.

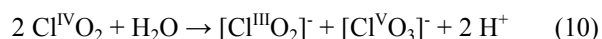
Metal ions (aq)	Set 1 (ppm)	Set 2 (ppm)	Set 3 (ppm)	Average (ppm)	Mass in filtrate (g)	f, fraction of the original applied mass	Recovery, (1 - f) x 100%
Co ^{III}	5.2	5.3	5.9	5.5	1.93×10^{-3}	0.0109	98.90%
Ni ^{III}	4.0	3.8	4.2	4.0	1.40×10^{-3}	0.0083	99.17%
Cu ^{II}	3.8	3.3	3.6	3.6	1.26×10^{-3}	0.0082	99.18%

4.2. Visual Observations

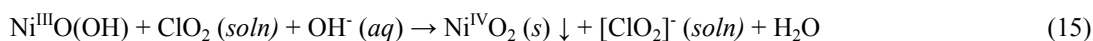
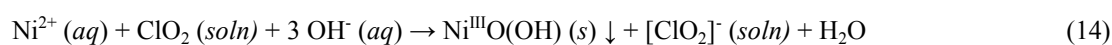
The visual appearances of all treated liquors were clear, transparent and colorless. All precipitates formed pitch black filter cakes. After being oven-dried, the filter cakes were observed to contain amorphous particles between 1 and 3 mm in size, and are amenable to fluidization and pneumatic transport, ideal for industrial handling. The precipitated compounds are most likely to be Co^{III}O(OH) and/or Co^{IV}O₂, Ni^{III}O(OH) and/or Ni^{IV}O₂, and Cu^{II}O. The elemental composition, oxidation states of the precipitated metals, particle size distribution, and compressibility of the filter cakes can be further investigated by instrumental analysis.

4.3. Management of ClO₂ as an Industrial Inventory

Unlike Cl₂, the inherent instability of the ClO₂ free radical prohibits storage for any length of time, and demands that it be generated on-site as an aqueous solution. ClO₂ has been generated *in-situ* by reacting NaClO₂ and HCl in this work. Neither is the long-term storage of aqueous solutions of ClO₂ recommended, as it will react with water to form chlorite and chlorate, albeit slowly:



In near-neutral and acidic conditions, equation (10) is actually a re-iteration of equation (6), the only difference is that the disproportionation is much slower. While the concept of using ClO₂ as an oxidant to extract metallic ions from their chelated complexes has been demonstrated here, it is ideal to minimize the requirement for ClO₂ generation. (See "Further



The black precipitate obtained in these experiments may contain both the Ni(III) and Ni(IV) solids. Note that Ni^{IV}O₂ is

Work" section below).

4.4. Inklings of Reaction Pathways

Free radicals are highly reactive chemical species that can oxidize in two ways, namely, abstraction of electrons or hydrogen atoms, or both. It is likely that a parent metal complex which is subjected to such modes of sustained dismantling will collapse at some juncture, regardless of the mechanistic pathway, with irreversible loss of sequestration ability on the part of the organic fragments. As a result, the freed central metal ion can be retrieved. Complete oxidation of citrate to CO₂ and H₂O (and in the case of EDTA, to N₂ and perhaps NO₂⁻ and NO₃⁻) may not be necessary, as long as the modified molecular structures can no longer protect the metallic ion from oxidation by ClO₂ to an insoluble product.

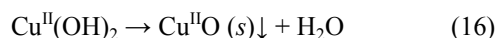
There are many single-electron transfer reactions in which ClO₂ acts as the oxidant. Here are a few examples involving elemental ions in aqueous solutions:



In these reactions, ClO₂ itself is often reduced to the chlorite ion [ClO₂]⁻, with the corresponding electron-transfer reactions comparable to those occurring when singlet oxygen is the oxidant [49]. Here, the accompanying oxidation transitions Ni(II) → Ni(III) → Ni(IV) in alkali can be represented by:

the solid phase present in a nickel battery when it is over-charged. The oxidation transitions Co(II) → Co(III) →

Co(IV) may result in a solid mixture of Co_2O_3 , $\text{CoO}(\text{OH})$ and CoO_2 . For copper, boiling the copper solution in an open vessel will dehydrate $\text{Cu}(\text{OH})_2$ to give black copper oxide [28], and is not a redox reaction:



It must be emphasized that, although mechanisms of oxidative decarboxylation of free ligands such as the β -keto-carboxylic acids have been proposed, oxidation of the metal chelate itself cannot really be treated as though the chemistry is a combination of decarboxylation of the free ligand and oxidation of un-complexed metal ions, proceeding independently of each other. The authors of the present work

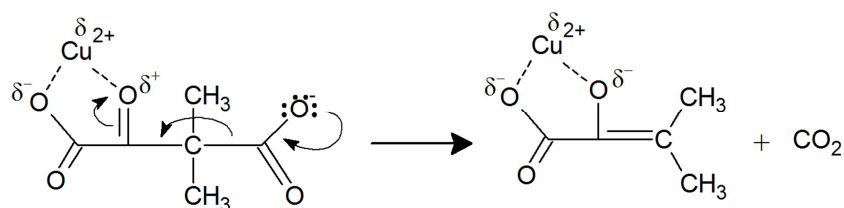


Figure 5. Proposed mechanism of metal-catalyzed decarboxylation [50].

Is prolonged thermal action likely to promote further degradation of the modified complex leading to the release of Cu^{2+} ions? From the point of view of transforming this knowledge into a separation process in chemical engineering, it is a possibility worth exploring. Manganous and nickelous ions (Mn^{2+} and Ni^{2+}) are also known to catalyze the decarboxylation of dimethyloxaloacetate as above, *via* chelate formation, but the free ions are regenerated subsequent to decarboxylation, of which chelation is one intervening step [51]. Semi-empirical arguments have been proposed for the separation of metallic ions from their ligands by H_2O_2 and much doubt has been casted on the proposed mechanisms of Fenton reactions [52].

In the absence of the multi-dentate ligands citrate and EDTA, oxidation of the bare metal ion by ClO_2 can be observed when NaOH is added to the reaction solution, rendering it alkaline and resulting in immediate formation of black colloidal particles. We shall call the rate of this redox reaction R_1 . The rate of dismantling of the metal complex leading to the release of the metal ion shall be R_2 , and the disproportionation reaction of ClO_2 , which is insignificant in very acidic solution such as the reaction solution in this experiment, shall be R_3 . It is not unreasonable to assume that $R_1 \gg R_2 \gg R_3$. The reaction with rate R_2 is the overall rate controlling reaction for the release of metallic ions.

Tracking the progress of the sequential reactions between ClO_2 and the metal complex in acidic media is possible by cyclic voltammetry. The method is employed to study electrical charge transfer processes between electrodes and chemical species in aqueous solutions. The chemical species that will participate in electrode processes are said to be “electroactive” (*e.g.*, Cu^{2+} ions are said to be electroactive when they can be reduced to Cu^0 and deposited on stainless steel surfaces in an electroplating bath).

Cyclic voltammetry is also well known for elucidating the

have identified a mechanism involving a series of intra-molecular electron transfers in literature [50] in which the decarboxylation of dimethyloxaloacetate is “catalyzed” by the Cu^{2+} ion at elevated temperatures (a thermal degradation), Figure 5. On inspection, the moiety undergoing degradation is in fact a copper complex in which the Cu^{2+} ion forms covalent bonds with two oxygen atoms as electron donors. It is suspected that complexation enhances the rate of decarboxylation by rendering “the carbonyl group more susceptible to receiving the electrons left behind when CO_2 is eliminated [50]”, but note that the $\text{Cu}(\text{II})$ ion is now chelated by a new ligand.

mechanisms and rates of chemical reactions between species that occur in various liquid media. The amount of time allocated for the extraction process was 9 hours, although it is possible that the kinetics to completion are more rapid and that treatment time can be shortened. With cyclic voltammetry, the time taken for a particular peak on a voltammogram to appear (which denotes a redox event) can be noted. Moreover, during a repetition of the experiment, samples can be taken at the instances just before and after the peak appearance. The contents of these samples can be analyzed by gas chromatography and mass spectrometry (GC-MS), which reveals the type and nature of chemical reactions and the time taken to reach important landmarks. The rate-determining steps can be identified.

It would be interesting to know whether the central metal ion “flips” its oxidation states back-and-forth while still in a state of complexation, similar to the $\text{Fe}^{\text{II}} \leftrightarrow \text{Fe}^{\text{III}}$ sequential redoxes within the porphyrin ring during the catabolism of human haemoglobin, leading to the incorporation of Fe^{2+} into ferritin for storage. The unwanted scenario is one in which an electron is removed from a complex, leaving its overall structure intact, but the reaction stops after this first redox step. An example is the case of the oxidation, by ClO_2 , of the $\text{Co}(\text{II})$ complex with 2,2':6'2"-terpyridine (“terpy”) as a ligand [53], the organic moiety being a π -acceptor which stabilizes transition metals in their lower oxidation states:



The experience of Kurion Technology Ltd. illustrates why treatment of wastewaters containing metal complexes sometimes fails [54]. When the ore processing technology of electrowinning is used to reclaim copper, the molecular structure of the chelates either remain intact, or change electrochemically to chelates of a different identity, *i.e.*, Cu^{2+} ions remain sequestered by organic moieties in the aqueous

phase. The chelant EDTA has become other homologues formed by electrolysis. In the end, not all the chelated complexes are decomposed which means that copper ions are not recovered exhaustively.

In combination, these activities and debates may suggest plausible reaction pathway(s) but a narrative pertaining to detailed planning of these experiments is beyond the scope of this “Short Communication”. They will, nonetheless, be the focus of forthcoming publications.

5. Future Work

Having established the chemical feasibility of extracting metallic ions from aqueous solution by ClO_2 , it may be possible to extend these preliminary findings to further process development and engineering by designing a small-scale experimental pilot facility to treat 0.05 m^3 (50 litres) of solutions. Pilot plants can provide important information on the best ways to handle the transport and mixing of reactants, intermediates, products, and waste streams; on heat transfer; on the most suitable choice of separation processes; on operating procedures; and on risk assessments such as HAZOP and HAZAN fundamental to any engineering exercise. Although fully integrated pilot plants which include all systems, unit operations and electronic controls such as those operating in a commercial facility can be expensive, it is often not necessary to demonstrate all unit operations in a process.

For full commercial scale processes, “conceptual designs”

are always a first step. Mitsos (2018) defined the term “conceptual design” succinctly: “The main task in conceptual process design is to develop the best process flow sheet and to find an optimal operating point”, and that “a hierarchical strategy in which the overall functionality of the process” has to be mapped out in detail “in a stepwise fashion in order to design alternative flow sheets [55]”. When redox chemical reactions are the critical feature, flowsheeting during the conceptual design of industrial wastewater treatment facilities implies the selection and sequencing of chemical reactors and unit operations in order to obtain a set of practicable treatment options, all achieving the proposed treatment goals. These design activities will rely heavily on the experience and insight gained from pilot plant operations. The following issues should be considered in any conceptualization of the process, in the earliest stages of discovery.

Type of reactor.

When chemical reaction is the cardinal feature, the first consideration for a process plant design is the type of reactor. An option for the extraction of transition metals from the aqueous phase can be performed in a “semi-batch” mode. This *modus operandi* is one in which a homogeneous liquid-phase reaction of the simplified type “ $A + B \rightarrow \text{Products}$ ” is carried out. In general, reactant A is initially deposited in the reaction vessel and reactant B is injected at a prescribed rate as reaction proceeds. In this case, reactant A is the metal complex and reactant B is ClO_2 .

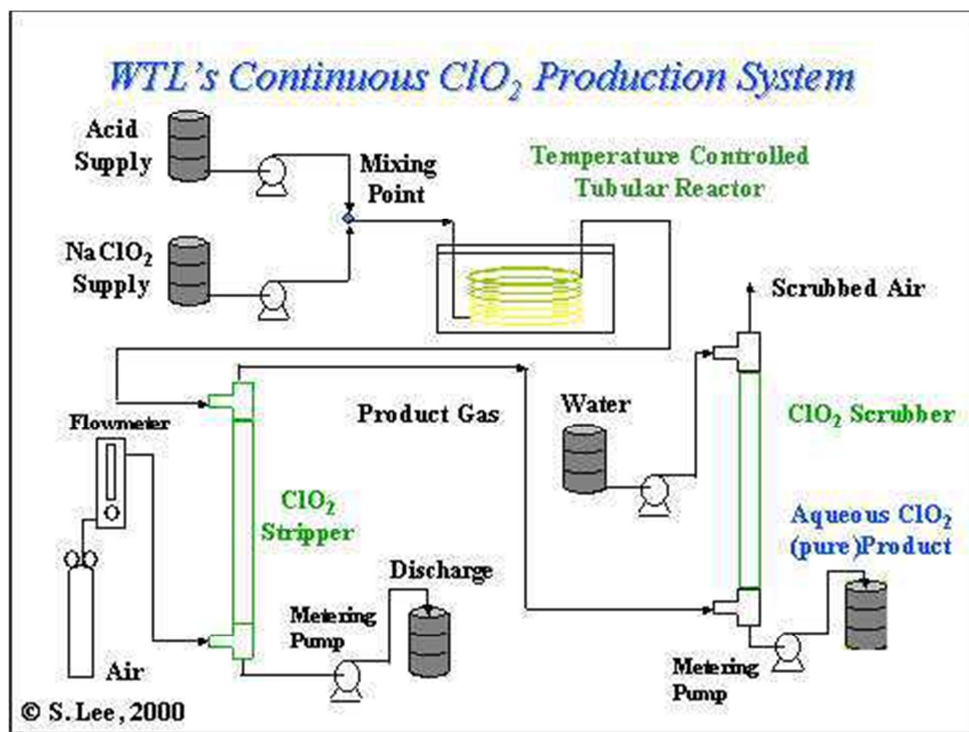


Figure 6. WTL's ClO_2 generator. The system is equipped with a scrubbing system to remove ClO_2 in air streams [56].

As this work has shown, reactant B must to be generated *in situ* by the reaction between NaClO_2 and HCl . An alternative arrangement is the generation of ClO_2 externally and

introduced periodically into the reactor, a delivery system akin to that of the Water Technologies Ltd. (WTL), Figure 6 [56]. This leaves the metal complex to be the only limiting

reagent in a semi-batch reactor.

a. *Cooling requirements.*

A semi-batch operation has an advantage over its batch counterpart because the former may result in tighter control of temperature fluctuations, especially for exothermic reactions. In the initial phases of a reaction, the rate of reaction may be very high because the concentration of the limiting reactant A (the metal complex) will be highest at time = 0, just before reaction begins, although the concentration of A will decrease with time, *i.e.*, $d[A]/dt < 0$. The ignition temperature of ClO_2 is 130°C [57] and temperature control of exothermic reactions by heat-exchange equipment such as cooling jackets or coils is essential. To avoid uncontrollable temperature increases and gas evolutions is paramount. Calorimetric data is required to estimate the rates of heat transfer demanded.

Preliminary investigations prior to performing the bench-scale experiments described in this work show that the amounts of reactant material are so small relative to the large volume of water in which they are dissolved that heat evolution is insignificant. In any case, ClO_2 was only added intermittently to ensure that reaction proceeded relatively slowly and the temperature never rose above 35°C . This can be measured by a thermometer, which can replace the dropping funnel, vessel (2) in Figure 2. The equipment set-up was cooled by air current which ventilated into the fume cupboard; this was found to be adequate.

b. *Dose rate.*

In theory, the concentration of ClO_2 can be kept relatively low (introduced intermittently and externally) or high (heavy loading initially), depending on which mode of injection results in the suppression of side reactions, thereby improving product yield. Identification of undesirable reactions is possible through mechanism elucidation. The dosing rate also affects the rate of exothermicity and continuous monitoring of temperature changes in the reaction solution is vital. This is linked to the issue of cooling requirements.

c. *Operational research with a view to optimization.*

Health-and-safety issues require the minimization of the use of ClO_2 . Minimization of ClO_2 usage commences with determining its stoichiometric requirement for a particular wastewater treatment. The difference between the total amount of ClO_2 synthesized and absorbed by Na_2SO_3 solution (SO_3^{2-} is oxidized to SO_4^{2-} by ClO_2) equals the amount consumed in reactions between ClO_2 and metal complex. Ideally, when no ClO_2 is wasted, the amount absorbed by any “gas scrubber” will be zero.

A pilot plant will provide the opportunity to explore minimizing the use of ClO_2 , *e.g.*, by recirculation into the reactor instead of its destruction, as carried out in vessels (5) and (7) in Figure 2. Lowering the pH necessary for precipitation and therefore minimizing the use of caustic soda can be investigated. Moreover, it may be possible to run one 3-hour operation instead of the three sequential cycles described earlier in the text, and to discover whether this makes a difference to the recovery of metals. Samples from

the reactor can be collected and the point whereby precipitation occurs on adding NaOH can be pinpointed. (Recall that after one cycle, the reaction solution was rendered nearly colorless from the characteristic blue colouration of aqueous copper species. At this point, Cu^{2+} ions might have been freed from their organic ligands, but this can only be ascertained by addition of NaOH to a sample drawn from the reactor).

d. *Integrated waste management.*

It is plausible that, freed from sequestration, the vestigial remnants of the metallic populace (of concentration ~ 5 ppm determined by ICP-OES in this work) in alkali is constituted of the following cationic species reported by Brown & Ekberg (2016): $[\text{Co}^{\text{II}}(\text{OH})]^+$, $[\text{Co}^{\text{III}}(\text{OH})]^{2+}$, $[\text{Ni}(\text{OH})]^+$, $[\text{Ni}_2(\text{OH})]^{3+}$, $[\text{Ni}_4(\text{OH})_4]^{4+}$, $[\text{Cu}(\text{OH})]^+$, $[\text{Cu}_2(\text{OH})_2]^{2+}$ and $[\text{Cu}_3(\text{OH})_4]^{2+}$. These species establish multi-equilibria, in miniscule amounts [58]. Tan *et al.* (2017) reduced the concentration of Ni^{2+} and Cu^{2+} ions from 100 ppm each, to 0.43 ppm and 0.39 ppm respectively, by the ion-exchange resin called “D001” [59]. This ion-exchange method is expected to work for the treated liquor in this work on acidification, since the nominal 5 ppm concentration is well within the reported upper limit of 100 ppm [59], and further bench-scale tests should be conducted to include a study on aqueous cobalt species. It would be interesting to discover whether the same success can be achieved for an alkaline solution containing ions of the type $[\text{M}_x(\text{OH})_y]^{n+}$ listed in this paragraph, as this would save the effort of acidification before ion-exchange.

Collivignarelli *et al.* (2018) reviewed the environmental impact of utilizing ClO_2 as a treatment agent and noted that ClO_2^- and ClO_3^- are present in treated waters, but concluded that “degradation of the residual chlorine dioxide and other final reaction products is faster than that observed in the case of chlorine and therefore these compounds should not represent a hazard to the aquatic environment [60].” In fact, with careful dosing and mixing, the applied $\text{Na}^+\text{ClO}_2^-$ can be consumed stoichiometrically to produce ClO_2 , leaving none to waste. In the case of ClO_3^- ions, they can be reduced to Cl^- with ease *via* equations (7) and (8). Those process plants that witness a high concentration of ClO_3^- in their effluents should attempt to implement this redox, as in this work.

The application of the powerful oxidizing agent ClO_2 is expected to reduce the overall Chemical Oxygen Demand (COD) and Biochemical Oxygen (BOD) of water substantially. It has been known for over three decades that the production of minute amounts of CHCl_3 by the reaction between HOCl and citric acid can be inhibited when HOCl is replaced by ClO_2 [30]. A pilot plant study showed that total trihalomethane concentrations were well below the Promulgated Maximum Contaminant Level (PMCL) of 0 – 0.1 ppm when ClO_2 was used [61]. As of 2017, the position taken by public health scientists and officials in U.S.A. (and many other countries) is that treatment of drinking water by ClO_2 will result in much less chlorinated organic compounds [62, 63].

Furthermore, keen interest to use activated charcoal as an

adsorbent of halogenated organic compounds and potential pollutants has not waned. Jiang *et al.* (2017) reported the advantage of adsorbing aromatic intermediates during chlorination of water rather than before [64]. This “new” approach could be a confirmation of an earlier pilot plant study of an Advanced Oxidation Process (AOP) utilizing ClO_2 , in which granulated activated carbon removed up to 80% of the precursors of trihalomethanes, thereby reducing the production of these haloalkanes substantially [65]. In a very interesting symposium, Dickenson (2018) introduced his work on ozone treatment and adsorption by biological and granular activated carbons on a pilot-plant scale. The main theme of the symposium was the concept of “potable reuse”: treating water from households and businesses from urban settings to a quality sufficient for human consumption, in order to diversify and enhance the portfolio of water sources required to meet future demands [66]. Shimizu *et al.* (2018) compared the molecular sieving of naturally occurring organic matter to adsorption by activated carbon and carbon nano-tubes, and discovered that selective adsorption was affected by the nature of the adsorbent, pore size and porosity [67].

The treated water in this work will be analyzed instrumentally for its organic compounds and COD/BOD determinations will also be done. Post-precipitation, the main inorganic ions in the alkaline filtrate will be non-toxic Na^+ , Cl^- and SO_4^{2-} [68]. In some electroless plating baths, hypophosphite H_2PO_3^- is used as a reductant and the resulting species is phosphite HPO_3^{2-} , which can be removed through crystallization by addition of CaCl_2 to form crystals of $(\text{CaHPO}_3)_2 \cdot 2\text{H}_2\text{O}$. It may be possible to reuse the water for industrial purposes if contaminants are adequately low, depending on the application. (See [69] for a summary of analytical methods for various DBPs and their minimum detection limits)

The doctoral thesis of Sutton (2017) [70] is the most comprehensive documentation and discussion of the spectroscopic and quantum mechanical properties of ClO_2 to date, and is a resource for research. The role that water plays in changing the intrinsic properties of ClO_2 is emphasized. The ClO_2 radical can be solvated by three water molecules,

with more hypothesized. It is not known whether the degree of solvation will alter the pathway of a redox reaction. However, this speculation will provide an opportunity for collaborative work.

e. Other chemicals for the generation of ClO_2 can be considered.

Many treatment plants utilize NaClO_4 as the starting material and CH_3OH or H_2O_2 as the reductant. Also, ferrous and thiosulfate ions are known to be effective in nullifying residual oxidants in treated waters. It is important to identify the process with the least chemical impact to aquatic environments.

6. Conclusions

The transition metal ions Co(II) , Ni(II) and Cu(II) were stoichiometrically recovered (99%) from their chelated complexes in aqueous solutions. The organic ligands were citrate and EDTA. The oxidant used was chlorine dioxide, prepared *in situ*. The reactions were carried out in batch mode in the same vessel for the laboratory synthesis of the oxidant. The desired products were the metal oxides/oxyhydroxides, which precipitated, and constituted the last step of this chemical-induced separation process. Important issues in the conceptualization of a pilot process were discussed. A commercial separation process for the extraction of these transition metals for recycling and reuse using ClO_2 is envisaged.

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Appendix

Appendix 1

Formal oxidation states of some chlorine and oxygenated-chlorine species

Table 4. Nomenclature of the twelve known oxidation states of chlorine.

Frequently used names	Species formulae	Chemical status	Oxidation states
chloride	Cl^-	anion	-1
chlorine	Cl , Cl_2	atom, molecule	0
chlorine (●), IUPAC	Cl^\bullet	free radical	0
dichloride (●1-), IUPAC ($\text{Cl}^\bullet + \text{Cl}^- \rightarrow \text{Cl}_2^\bullet$) [71]	$\text{Cl}_2^{\bullet-}$	radical anion	-1/2
dichlorine (●1+), IUPAC [72]	$\text{Cl}_2^{\bullet+}$	radical cation	+1/2
chlorine cation (1 st ionization)	Cl^+	cation	+1
dichlorine monoxide	Cl_2O	molecule	+1
Hypochlorite	ClO^-	anion	+1
“dichlorine dioxide anion” [73]	$[\text{Cl}_2\text{O}_2]^-$	anion	+1 1/2
hypochlorite radical, or oxydichlorine (●), IUPAC	$[\text{ClO}]^\bullet$	free radical	+2
“dichlorine dioxide cation” [74]	$[\text{Cl}_2\text{O}_2]^+$	cation	+2 1/2
chlorite	ClO_2^-	anion	+3
chlorine dioxide (●), IUPAC	$[\text{ClO}_2]^\bullet$	free radical	+4
dioxidochlorine (1+), IUPAC	ClO_2^+	cation	+5
chlorate	ClO_3^-	anion	+5
perchlorate	ClO_4^-	anion	+7

The chemical symbols and notations are now explained. On the 1st column “Frequently used names”, the items labeled “IUPAC” are the officially designated expressions for the particular species. If the moiety happens to be a free radical, then the species name is followed by the bracketed dot (•) to emphasize its propensity to act as a powerful oxidizing agent. Recall from the main text of this article that a free radical can extract an electron or a hydrogen atom from another species very effectively. In the case of dichloride (•1-), it is essentially the reaction product between a chlorine atom and a chloride ion; the chlorine molecule has one unpaired electron thus making it a *free radical*, but also furnishes an overall *single negative* charge. The symbol (•1-) is a combination of the three properties. The same protocol applies to dichlorine (•1+), which symbolizes the molecular state of the chlorine molecule subsequent to the 1st ionization, leaving it to be a cation with one unpaired electron. In literature, the name “hypochlorite radical” is used much more than the full IUPAC name oxydichlorine (•), and to avoid confusion it is best written as [ClO][•] to distinguish it from ClO⁻, the chief ingredient of many household bleaches. Again, “chlorine dioxide” is a much more popular name than its IUPAC version, namely, chlorine dioxide (•). It is difficult to envisage any discussion of chlorine dioxide without elaborating upon its free radical chemistry. Last but not least, nothing beats the clarity of the species formula ClO₂⁺ which, according to many halogen chemists, is the preferred form of expression than dioxidochlorine (1+).

Appendix 2

Speciation diagrams of metal complexes by MINEQL+

MINEQL+ (hereafter called MINEQL) is a computer software system designed for personal computers that models chemical compounds in multiple equilibria in aqueous solution, *i.e.*, it is a speciation program. The system has been described in great detail by Schecher & McAvoy (1992) [74] but has been updated many times up till 2015 [75].

Calculations can be performed on aqueous systems in the low temperature range of 0 - 50°C, and of low-to-moderate ionic strength ($\leq 1.0 \text{ mol dm}^{-3}$). According to its developers, the MINEQL software code requires no additional programming by the end-user. However, colleagues who had used the program reported the need, in certain situations, to modify certain algebraic equations representing multiple equilibria, or equilibria in solutions of higher ionic strength than recommended, in order that the iterated calculations converge.

The code to solve simultaneous linear and non-linear algebraic equations representing multiple equilibria is a modified version of the original MINEQL software developed at Massachusetts Institute of Technology in the mid 1970's. The present MINEQL software system contains the entire thermodynamic MINTQA2 database used by the U.S. Environmental Protection Agency, plus data of chemical components not included by the EPA. The database which contains experimentally verified species is colossal but not exhaustive, and it should be borne in mind that while many new

chemical species in aqueous solutions are being discovered, their formation constants are not always measured or reported.

The company that manages and markets MINEQL is called *Environmental Research Software* (Hallowell, ME 044347, USA). Its corporate website publishes a list of research papers that report the use of MINEQL software.

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