NELSON MANDELA

UNIVERSITY

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Prof Zenixole Tshentu
(Faculty of Science)

Title:

Towards mineral beneficiation: from basic chemistry to applications.

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Towards mineral beneficiation: from basic chemistry to applications

Z.R. Tshentu

Abstract

The role of mineral beneficiation in the survival, growth, development and sustainability of a developing economy cannot be overstated. Our development as a human species has always been involvedly linked with the use of mineral resources from the stone, bronze and iron ages through the early modern eras to the present. In the current modern era, characterized by highly technological equipment, fourth industrial revolution (4IR) and new energy technologies, the role of mineral beneficiation has been elevated. Precious metals find use in the fine chemicals and petrochemicals industry, fuel cells, electrical and electronic products, medical and dentistry applications, jewellery, autocatalysts, and glass and ceramics. The markets for precious metals keep growing and the supply does not meet demand. The development of methods for recovery of metal value from feeds of mineral ore solutions, solutions of spent secondary resources and from mining wastewaters remains of great importance. Further beneficiation strategies for utilization of mineral products in other "value-added" applications are also important for the growth of the mineral markets. The usage of platinum, palladium and rhodium in the autocatalyst industry has grown significantly and this has further elevated the importance of platinum group metals (PGMs), but other areas of application of the strategic metals need to be harnessed. The four stages of beneficiation, namely, primary, secondary, tertiary and final stage, provide an opportunity to beneficiate to greater value for domestic or export use. Our own research work is engaged in several of these stages, from hydrometallurgical recovery of base metals and platinum group metals from feeds of primary mining and solutions of waste secondary resources such as spent catalytic converters and e-waste to the use of metals in "value added" products such as metal-based catalysts for the fuel industry and in metallodrugs. Examples of "value added" products include rhodium as a promoter in molybdenum sulfide as a catalyst for hydrodesulfurization of fuel oil, vanadium as a catalyst in oxidative desulfurization of fuel oil, vanadium and palladium as therapeutic agents for diabetes and cancer, respectively. Current and future work involves (i) the development of metal-selective scavengers to recover lost metal value in mining wastewaters, and (ii) the design of metal-based catalytic materials for refinement of bio-based oils to biofuel as well as for production of green LPG through hydroprocessing. Our work centres around both basic and applied chemistry towards mineral beneficiation and with a bias towards greener production.

1. Introduction

Throughout the pre-history, protohistory and recorded history of civilizations up to the modern era, mineral resources have been intricately linked with the development of the human species. Reference can be made to the so-called "Old World", the stone and bronze ages, and the iron age which proceeded those wherein iron and steel tools and weapons began to replace bronze equivalents (Universal History Archive, 2019). The three-age archaeological periods differ in different parts of the world. In Egypt, the bronze age seems to have been sustained over longer periods with minimal involvement into the iron age while evidence of daggers made of steel have been found in archaeological records. The Sahel (Sudan region) and Sub-Saharan Africa are considered outside of the three-age system, there being no Bronze Age, but the term "Iron Age" is sometimes used in reference to early cultures practicing ironworking, such as the Nok culture of Nigeria (National Geographic). But these records require scrutiny considering the omission of African civilizations in recorded history. We have also learnt of the earliest recorded examples of the use of metals in medicine. Chinese used gold in medicine around 2500 BC and the Egyptians used copper to sterilize water around 3000 BC, and a variety of iron

remedies were used in Egypt around 1500 BC; however, the nutritional value of iron was only discovered in the Renaissance era. Around 1500 BC, it was discovered that zinc promoted the healing of wounds (Orvig and Abrams, 1999). If we take a leap to the current situation, which is characterized by highly technological products, 4IR and modern lifestyle, we observe the importance of mineral resources with base metals, precious metals and rare earth elements playing a critical role in advanced materials that drive our everyday work productivity, health and lifestyles.

The demand for precious metals in the fine chemicals and petrochemicals industry, fuel cells, electrical and electronic products, medical and dentistry applications, jewellery, autocatalysts, and glass and ceramics, against the dwindling natural deposits requires improvement of current recovery methods (Matthey, 2022). Given that the supply does not meet demand, a complementary route is to recover the critical metals from end-of-cycle products such as PCs, TVs, laptops, gaming consoles, and mobile phones, and in that way urban mining of metal waste can be advanced to contribute to circular economy (Hagelüken, 2012). Urban mining is becoming more attractive due to the high yields compared with extraction of strategic metals from primary mineral ores. Recycling provides a highly efficient way of reintroducing valuable materials back into the economy, with huge benefits of saving energy and reducing environmental impacts, as opposed to the primary supply (Macaskie *et al.*, 2011). In South Africa, platinum group metals together with gold, silver, nickel, copper and cobalt occur at economic concentrations in the layered reefs associated with the mafic rocks of the Rustenburg layered suite of the Bushveld Complex (Meyer, 1997). South Africa is the largest platinum producing country by far, having produced an estimated 120 metric ton of platinum in 2020. Russia is the second-largest platinum-producing country in the world, with significantly lower production of an estimated 21 metric ton in 2020 (Mordor Intelligence, 2022). In addition, the predominantly nickel ores (laterites and pentlandite) which contain some of the later divalent 3d transition metals are present in the Bushveld Complex albeit in low quantities of the metal. It is therefore not surprising that there are continuous research activities in search for simplified methods for the dissolution of mineral ores, separation and recovery of strategic metals. These critical metals continue to increase the mineral markets in the new areas of fuel cells, hydrogen economy and other that are influenced by 4IR, therefore the drive towards further beneficiation is key for economic growth. A question of whether beneficiation is essential or not should not arise given the opportunities and potential benefits to any developing economy.

However, when we delve into this topic we need not be constrained by a definition of mineral beneficiation as referring to a single concept of extraction and refinery of mineral ores but rather the full scope of beneficiation up to final products. This limits South Africa to be an extractive industry rather than pursue further "value add". The role of beneficiation in the survival, growth, development and sustainability of the South African mining industry cannot be overstated. Beneficiation made significant strides in the 1990s when South Africa transformed from a primary (raw material) commodity exporter to becoming a significant exporter of processed minerals (Hogan Lovells Publications, 2016). This could only be achieved through the commitment to and the implementation of major beneficiation projects and facilities. There are still significant potential benefits to be extracted from the beneficiation process with its various stages of which some, while being part of the beneficiation stages, are not currently considered. The primary mining legislation, the Mineral and Petroleum Resources Development Act 28 of 2002 (MPRDA) (Mineral and Petroleum Resources Development Act 28, 2002), defines beneficiation to include four stages: the primary, secondary, tertiary and final stage. Generally, beneficiation is regarded as the transformation of a mineral (or a combination of minerals) to a higher value product, which can either be consumed locally or exported. Each of the four stages may, therefore, provide an opportunity to beneficiate to greater value, for domestic or export use.

Our own studies look at opportunities for beneficiation of mineral resources from basic hydrometallurgical approaches of metal separation/recovery and studies of the underlying coordination chemistry to application of the strategic metals in making final stage products that are valuable such as

catalysts for the fuel industry and biomedical agents. Some of the basic metal recovery studies that have been undertaken provide an opportunity to produce products such as resins and membranes for application in mining industry feeds and in recovery of precious metals from leachates of spent secondary products such as catalytic converters and e-waste. On the catalysis, we have contributed strategies for beneficiating vanadium as a catalyst for oxidative desulfurization of fuels as well as nickel, cobalt and rhodium as catalyst promoters for hydrodesulfurization of fuels to contribute to responsible use of the unsustainable fossil fuels. We are also proposing production of biofuels by designing hydrodeoxygenation metal-based catalysts to process biocrudes from biomass given the recognition of bioeconomy as a climate change strategy. Other metal-catalysed processes, through the use of precious metals such as palladium, are also being proposed for example for producing green gas from CO_2 as a replacement for the liquefied petroleum gas (LPG) to contribute to the carbon offsetting strategies. In the biomedical field, we have contributed the potential use of vanadium and palladium in therapy of diseases in collaboration with biological scientists as co-investigators.

2. Hydrometallurgy of base metals and platinum group metals

Hydrometallurgical processes involve a leaching stage to dissolve the metal ions followed by further stages to separate the target metal ion from other impurities. Solvent extraction is an important technology that is applied to hydrometallurgical processes of metal separation. Despite the various successes in the industrial processes, solvent extraction retains inherent limitations such as insufficient enrichment efficiency, use of toxic and/or flammable organic solvents, and difficulty in phase separation (Sole, Feather and Cole, 2005). The resin technology presents an attractive alternative for the recovery of low concentrations of metals from solutions of low-grade ores due to the high enrichment efficiency, ease in phase separation and environmental friendliness. Hence, we have explored both solvent extraction and ion exchange in the recovery of important base metals and platinum group metals.

2.1 Ligand design for recovery of base metals

The separation of copper, cobalt and nickel in the presence of other base metal ions has been addressed with the use of organophosphorus extractants (Cyanex reagents) and oxime-type extractants (LIX reagents) (Reddy, Rao and Park, 2009). Some representative extractants in this class such as LIX 64 went to commercialization for the extraction of copper in several plants around the world including USA, England, and Southern Africa [11]. However, Reddy *et al.* (2009) reported that their separation for nickel and cobalt is not satisfactory. Most commercially available extractants like phosphonic and phosphinic acids, hydroxyoximes and β-diketones, cobalt is found extracted preferentially over nickel from the aqueous phase at an equilibrium pH of 4 to 6 in the absence of copper. This relatively high pH range is necessitated by the base properties of these oxygen-donors, and is not effective for recovery of these metals in a highly acidic medium of pH < 4. These commercial O-donor extractants also have high affinity for hard ions such as ferric ions which necessitates for the precipitation of iron(III) ions prior to the extraction of nickel(II) or cobalt(II) ions in these systems (Feather *et al.*, 2002). The N-donor extractants as free bases can readily extract borderline acids such as nickel through inner-sphere complexation in preference to a hard acid such as ferric ions thus reducing cost (Okewole, Magwa and Tshentu, 2012). The basis of metal ion separation could, therefore, be seen as a unique property of the coordination chemistry of the particular metal ion. In the development of a metal ion specific reagent, it is necessary to consider the characteristics of the metal ions from which the desired metal ion must be removed as well as its own. In such studies, the nature of the metal ion, the hydrogen ion concentration, protonation constant(s) of the ligand, the thermodynamics and kinetics of complexation, and the coordinating ability of the anion become important parameters. The denticity, donority and donicity of the binding situation are also key features.

Amines in their neutral form have not been extensively explored as separating agents for metal ions from a basic inner sphere coordination chemistry perspective (Du Preez, 2000). The application of the ammonia derivatives ($R-NH_2$, where R is an alkyl or aryl group) is limited by their high protonation constants which prevent complexation even in weakly acidic solutions thereby resulting in the hydrolysis of metal ions. These strong ligands with σ-donor only character also show lack of relative preference for the metal ions. Aromatic nitrogenous ligands have an apparent relative preference for metal ions which could relate to the possibility of σ and π bonding. Imidazole extractants (Du Preez, 200), show high formation constants with later 3d-transition metals thereby resulting in high extraction efficiencies, and also interact with these metals in slightly acidic media. In one of our studies, we have employed a bidentate ligand, 2,2′-pyridylimidazole (Okewole, Magwa and Tshentu, 2012), that incorporates both the pyridyl and the imidazolyl groups for the selective extraction of nickel(II) from base metals. This is mainly due to the high complex formation offered by the imidazole group and the low protonation constant of the pyridyl group, which allows formation of the complex species in a highly acidic medium. The results are presented in **Figure 2.1**.
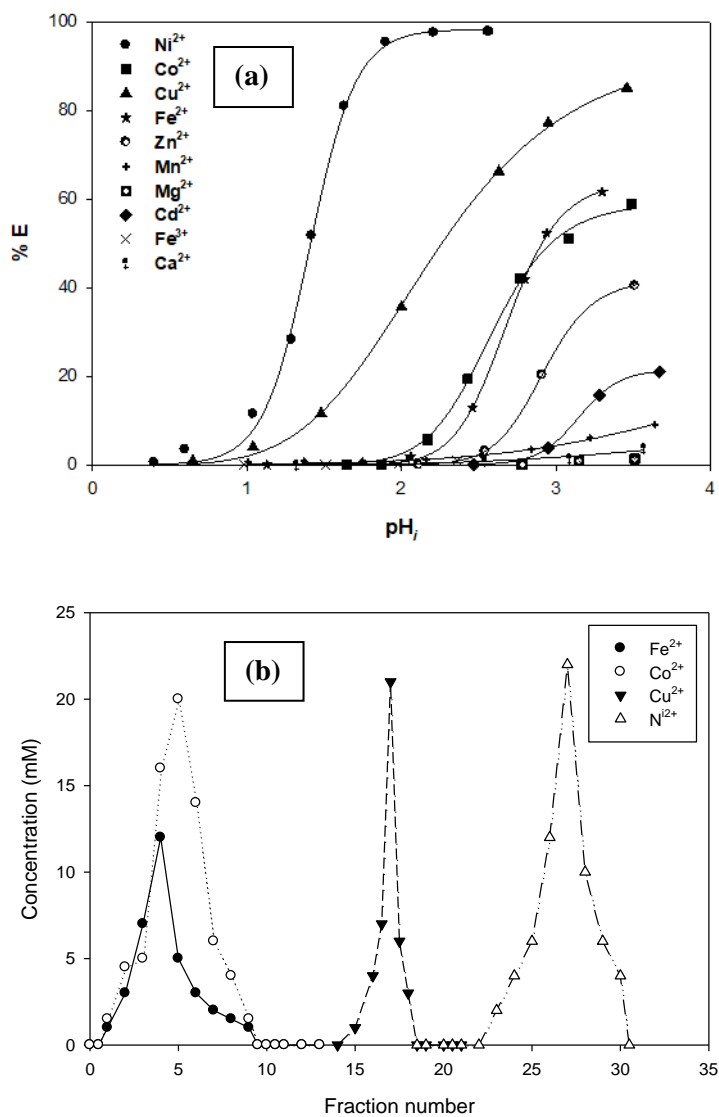

Figure 2.1. (a) Solvent extraction of base metals with a 2,2′-pyridylimidazole-based extractant (Okewole, Magwa and Tshentu, 2012). (b) Chelating ion exchange of base metals with 2,2′-pyridylimidazole-functionalized Merrifield resin (Okewole *et al.*, 2013a).

Extraction was achieved at low pH and selective separation of nickel from cobalt was achieve with a ΔpH_{50} value $\approx$ 1.6, and with copper as the only interfering metal ion (Okewole, Magwa and Tshentu, 2012). This separation was further tested using a chelating resin, where the metal ions were loaded at pH 1.8 followed by scrubbing the copper at pH ~ 8.5 using ammonia/ammonium chloride buffer and then back-extracting the nickel at pH 0.32 (Okewole *et al.*, 2013a). The result of the solvent extraction system and the chelating resin system were complementary and loading capacities for the resin were in the range 65-70 g/kg. The underlying coordination chemistry could be explained based on stability constants and stereochemical "tailor-making" considerations (Okewole, Magwa and Tshentu, 2012 and Du Preez, 2000) where preference to form a certain geometry over another allows for discrimination between the metal ions. Other interesting studies from our group include the use of an imidazole-oxime extractant for selective recovery of copper from other base metals (Okewole *et al*, 2013b). These extractants are now being repurposed for designing new resins and membranes for selectivity towards strategic metals (see **Section 4.1**).

2.2 Receptor design for recovery of chloridometallates of platinum group metals

It is well acknowledged that the fundamental principles of metal-ligand inner sphere coordination design strategies for selective separation are consistent, but the anion counterpart seems be mired with more complexity. This has led to a sub-field of research in the area of supramolecular chemistry called anion coordination chemistry. This describes the chemistry of cations as hosts and anions as guests and this is concerned with outer sphere coordination chemistry (García-España *et al.*, 2006). There are studies that have approached the problem from a structural and solution chemistry perspective which can find themselves in a dichotomy given the low entropy environments in sold state structures vs solution structures resulting in flawed structure-energy relationships (Haj-Zaroubi, Mitzel and Schmidtchen, 2002). Designed anion receptor structures can have an almost unlimited number of possibilities, such as cyclic, multicyclic, acyclic, tripodal frameworks, with rigid or flexible spacers that carry different aromatic and aliphatic linkage groups (Schmidtchen, 2006). Construction of anion hosts for selectivity depends on the kinetic and thermodynamic domains, and more recently the entropic influences in anion host design are emphasized (Schmidtchen, 2006). Given the demands of the task of anion design, computational predictions of the component energies (ΔH and ΔS) of the Gibb's free energy are useful in combination with experimental calorimetry data but in their absence theoretical data calculated at a reliable level of theory including solvation models can be used *a priori*. We have observed such enthalpic and entropic contributions in our own design of hosts for $PtCl_6^{2-}$ (Moyo *et al.*, 2022). In this context, the study seeks to address the anticipated need to design novel and highly selective materials for $PtCl_6^{2-}$ chloridometallate anion binding through outer sphere coordination mechanisms and subsequent extraction from a mixture of Platinum Group Metal (PGM) chlorido species in an ion exchange process. Molecular design features that enhance selectivity for larger and "softer" anions of commercial importance such as chlorido complexes of PGMs are less frequently studied (Busschaert *et al.*, 2015).

In our own attempts, we have used protonated polyamines which have the anion binding NH_n^+ and polarized C_{sp3}-H functional groups to interact with regions of highest electron density of the PGM chlorido complexes. Therefore, building positively charged centers having an appropriate conformation relative to the target anion is the ideal target. Intuitively such a conformation should, preferably, have the cationic centers of the receptors directed towards the regions of highest electron densities of the target anion in HCl medium. Anion receptor design, therefore, requires assessment of the areas of highest electron density of the target anion to enable a strong selective interaction of the two species in the ion-pair complex (Naidoo *et al.*, 2002). In the case of triethylenetetramine (L) (Moyo *et al.*, 2022), we have observed a favourable preorganization of the protonated form $[LH_4]^{4+}$ in its interaction with $PtCl_6^{2-}$ to form the ion-pair complex (**Equation 1**, **Figure 2.2**).

$$[LH_4]^{4+} + 2\ [PtCl_6]^{2-} \rightarrow [LH_4](PtCl_6)_2 \qquad (1)$$
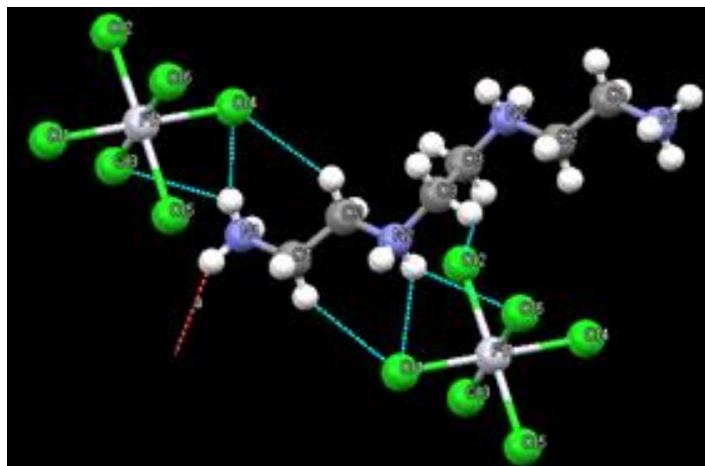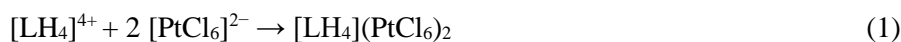
Figure 2.2. An ion-pair complex for the interaction of the protonated triethylenetetramine and $PtCl_6^{2-}$

With regards to $[PtCl_6]^{2-}$ selectivity, molecular modelling studies suggested that $[PtCl_6]^{2-}$ selectivity is only feasible when the protonated triethylenetetramine ($[LH_4]^{4+}$) molecule assumes certain conformations that have more favourable interactions with $[PtCl_6]^{2-}$ relative to $[RhCl_6]^{3-}$ and $[IrCl_6]^{3-}$ chlorido species [21]. The calculated and experimental energies are also in agreement on the selectivity of $[LH_4]^{4+}$ for $[PtCl_6]^{2-}$. We have further derivatized triethylenetetramine to form more preorganized structures by adding benzyl groups (**Figure 2.3**) so as to lower the energetic cost of reorganization in the process of design of the complementarity of the cation host for the anion guest. The screening of all possible structural combinations of the polyammonium receptors to achieve molecular recognition seems unavoidable despite the generalized notion of the use of rigid structures to prevent the energetic cost of reorganization.


Figure 2.3. $[BenzLH_4]^{4+}$ anion receptor binding mode targeting highest electron density areas on the O_h $[PtCl_6]^{2-}$ (Moyo *et al.*, 2022).

We have also contributed to the use of diammonium receptors hosted on polymer nanofiber materials as selective reagents for separation of iridium from rhodium in 6 M HCl with reasonable loading capacities (Majavu and Tshentu, 2017; Majavu *et al.*, 2021). The experimental and theoretical approaches undertaken are useful for the rationalization of the functioning of the diammonium groups with the decamethylenediammonium cation (**Figures 2.3 and 2.4**) being the best performing reagent on kinetic rather than thermodynamic grounds from data derived experimentally and from molecular

modelling (**Table 2.1**) (Majavu *et al.*, 2021). The electronic contribution as evaluated *via* electrostatic potentials was also in line with the thermodynamic trend.
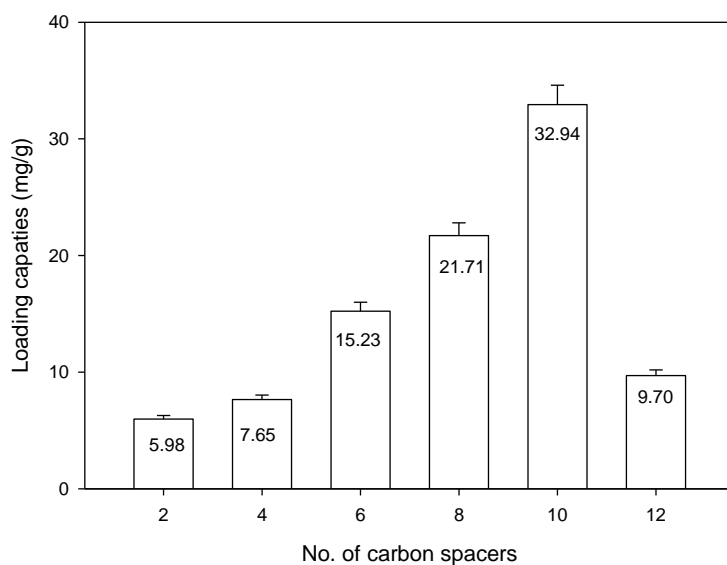
Figure 2.3. Iridium loading capacities calculated from the column study results for F-QUAT EDA (C2), F-QUAT TMDA (C4), F-QUAT HMDA (C6), F-QUAT OMDA (C8), F-QUAT DMDA (C10) and F-QUAT DDMDA (C12) on nanofibers at a flow rate of 0.5 mL/h (Majavu *et al.*, 2021).
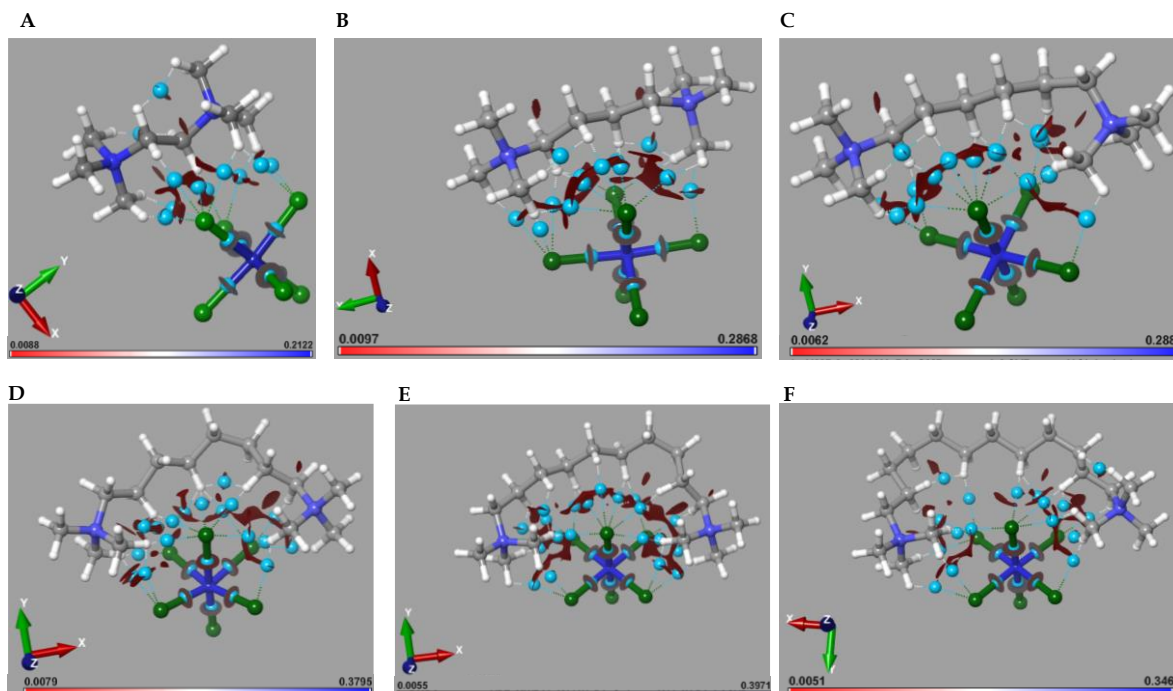
Figure 2.4. Non-Covalent Interaction (NCI) Plots of $Cation^{2+}:IrCl_6^{2-}$ ion-pairs. The red regions contain bond critical points (BCPs) as elucidated using QTAIM theory (Bader, 1998). BCPs are marked with dummy atoms (blue) and the bond paths to the bonded atoms are represented by zero-order bonds (blue lines) (Majavu *et al.*, 2021).

Table 2.1. $\Delta G_{solvation}$ of quaternary diammonium cations and ion-pairs including thermodynamic parameters for the formation of ion-pairs (kcal/mol). The ΔG, ΔH and ΔS values (Table 5) obtained from frequency calculations were calculated according to $\Delta G_{ion-pair} = G_{ion-pair} — (G_{cation} + G_{anion})$ and $\Delta H_{ion-pair} = H_{ion-pair} — (H_{cation} + H_{anion})$.

Complex (ion-pair)	$\Delta G_{solvation}$	ΔG	ΔH	ΔS
[(QUAT EDA)(IrCl$_6$)]	−68,1151	−8,2779	−41,7401	−0,1122
[(QUAT TMDA)(IrCl$_6$)]	−60,0674	−10,6353	−27,7968	−0,0576
[(QUAT HMDA)(IrCl$_6$)]	−55,8732	−12,0131	−21,3314	−0,0313
[(QUAT OMDA)(IrCl$_6$)]	−52,9949	−17,4931	−21,3896	−0,0131
[(QUAT DMDA)(IrCl$_6$)]	−47,7038	−18,5697	−20,2230	−0,0055
[(QUAT DDMDA)(IrCl$_6$)]	−47,2382	−31,0389	−16,3816	0,0492
[(QUAT EDA)(RhCl$_5$(H$_2$O))]	−70,9131	1,0718	−11,0986	−0,0408
[(QUAT TMDA)(RhCl$_5$(H$_2$O))]	−62,8033	1,6378	−11,9834	0,04571
[(QUAT HMDA)(RhCl$_5$(H$_2$O))]	−54,5863	2,5709	−10,6079	−0,0442
[(QUAT OMDA)(RhCl$_5$(H$_2$O))]	−53,2352	1,2500	−12,4866	−0,0461
[(QUAT DMDA)(RhCl$_5$(H$_2$O))]	−45,9606	1,7890	−13,4944	−0,0513
[(QUAT DDMDA)(RhCl$_5$(H$_2$O))]	−43,6018	2,4253	−13,2923	−0,0527

Rationale would therefore suggest that the improvement of molecular recognition of these systems by screening the chemical space with models that consider both the geometrical and electronic properties of the receptor prior to synthesis and evaluation of molecular entities is imminent. In contrast to drug design methodologies, experimental models that allow for the simultaneous optimization of multiple properties are non-existent in anion receptor chemistry. This is an area where we would like to contribute artificial intelligence tools in future to make the receptor design task more efficient. This would allow for rapid development of selective reagents and therefore contribute significantly to the design of resins and scavengers for recovery of strategic metals from mining feed solutions, mining wastewaters and solutions of spent secondary mineral resources.

3. Further metal beneficiation strategies

The Department of Mineral Resources and Energy in South Africa views beneficiation as a means to contribute to a balanced spatial economic paradigm, and intensification of this in the short term is seen as an opportunity for "South Africa Incorporated", i.e., all participants across all organized value chains (Hogan Lovells Publications, 2016). Former Minister of Trade and Industry Rob Davies once commented about 10 years ago as follows, "if we fail to decisively pursue beneficiation, we will relegate the SA economy to a place at the bottom end of the globalisation of labour, with serious consequences for our ability to generate income and employment. We do not have the luxury of debating whether to beneficiate our mineral wealth. We must harness the collective industrial capabilities of SA firms to map how to beneficiate and what enabling policies or support measures are required to ensure this happens successfully and for the benefit of all South Africans" (Hogan Lovells Publications, 2016).

This section presents some attempts to take advantage of mineral resources in the production of "value-added" materials for a variety of applications. It is a summary of the metal application work done during the course of my career as an independent researcher. It varies in terms of scope but with a common theme of beneficiating metal resources, namely, design of catalysts for fuel refinery and use of metals

in biomedical applications. Most noteworthy is the use of vanadium, which is an abundant mineral resource in South Africa, as well as the use of rhodium in catalysis towards fuel refinery applications and the potential use of palladium in nanoradiopharmaceuticals.

3.1 Application in fuel refinery

Reliance on crude oil remains high while the transition to green and renewable sources of fuel remains slow. Therefore, developing and strengthening strategies for reducing sulfur emissions from crude oil is therefore imperative and makes it possible to sustainably meet the more stringent sulfur level legislations (mostly less than 10 ppmS in end-user liquid fuels) (Dembaremba *et al.*, 2022). Fossil fuels constitute about 80% of global energy consumption and contribute about 75% of greenhouse gas emissions. Petroleum fuels are more favourable in most applications due to their liquid form which makes them easier to handle and use. For convenience, coal is also now being converted into liquid fuel (Syncrude). Consumption of crude oil rose from around 70 million barrels per day (Mb/d) in 1995 to 80 and 94.8 Mb/d in 2005 and 2015, respectively (Dembaremba *et al.*, 2022). The 2019 report already shows crude oil consumption to be over 100.9 Mb/d. Demand for petroleum is especially high in motorized transport due to its portability. Most of modern transport relies on petroleum fuels and they are the main consumers of petroleum. It has been difficult to match the use of fossil fuels on a large scale through alternative energy sources, especially renewable energy such as biofuels, sunlight, and wind. Although the use of electricity and hydrogen fuel cell technology are gaining momentum in smaller vehicles and trains, the use of fossil fuel oil will remain for some time to come in larger vehicles such as ships, haulage trucks and aeroplanes. As such, complete replacement of petroleum fuels (e.g. gasoline, diesel, kerosene, jet fuel) is less likely going to happen very quickly due to the rising demand as a result of increasing population (7.9 billion people in 2021).

The fossil fuel is also accompanied by several other elements such as oxygen, sulfur, nitrogen, and metals, which give rise to most of the challenges associated with the handling and use of petroleum. Sulfur and nitrogen pose the biggest challenges (Sami and Hatch 2001). Combustion of fuel oil leads to high local levels of SO_x and NO_x gases which cause several environmental and health concerns. Sulfur oxides and nitrogen oxides react with atmospheric moisture to produce acid rain, which leaves a trail of destruction on infrastructure, vegetation and marine life as well as changing soil composition. The gases react with atmospheric particulates, forming secondary particulate matter (e.g., sulfates) which can cause or increase the severity of respiratory and pulmonary diseases such as asthma and bronchitis. Ambient exposure to sulfur dioxide has been associated with increased morbidity and mortality (Sami and Hatch, 2001). Our approach to desulfurization and denitrogenation of fuel has always been two-fold, namely, (i) oxidative desulfurization using vanadium-based catalysts, and (ii) improve the current hydroprocessing technique to drive towards sustainable use of the fossil fuel. In the latter, we have recently been concerned with the idea of adsorptive denitrogenation using coordination polymers as a precursor to hydrodesulfurization (HDS) (Dembaremba *et al.*, 2022). The inhibition of CoMo and NiMo catalyst by from nitrogen-containing compounds has a serious negative effect on the kinetics of hydrotreatment reactions especially hydrotreatment of sulfur- and nitrogen-containing compounds (**Figure 3.1**). Paraffinic components, *i.e.* aliphatic acyclic sulfides (thioethers), cyclic sulfides (thiolanes), aliphatic amines and anilines can be easily removed by hydrotreatment while sulfur and nitrogen contained in aromatic rings (thiophenes and indoles, and their benzologues) are more resistant to hydrodesulfurization (HDS) and hydrodenitrogenation (HDN).
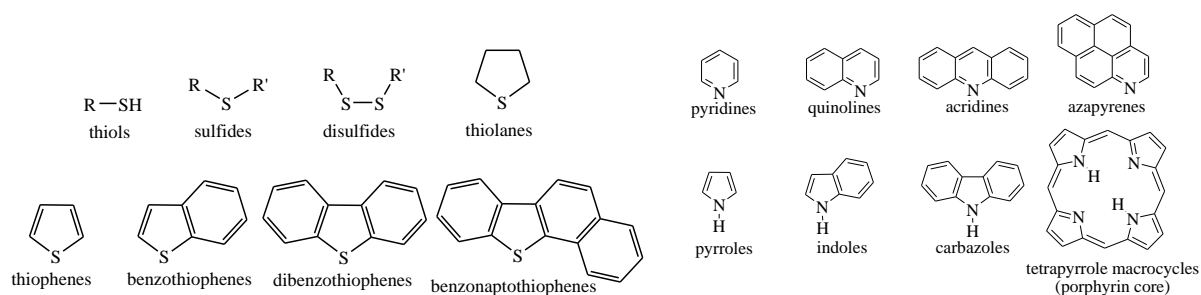
Figure 3.1. Typical families of sulfur- and nitrogen-containing compounds commonly found in crude oil.

Vanadium is a form of vanadium oxides or oxidovanadium(IV) complexes (Dembaremba *et al.*, 2019a; Dembaremba *et al.*, 2019b) has shown excellent performance with > 90% conversion of refractory organosulfur compounds such as benzothiophene and dibenzothiophene and their alkylated derivatives to polar organosulfones which can be extracted from the fuel matrix. We have also studied the mechanistic aspects of this catalyzed reaction (Dembaremba *et al.*, 2019b). The oxidative desulfurization (ODS) process has not gained popularity in the refinery industry and the main inhibiting factor is the additional processing units required to incorporate this technology such as the oxidation unit and a sulfone extraction unit (**Figure 3.2**), which require an initial capital investment. This technology may be considered in future as a complementary technique after mild hydroprocessing given that the sulfur levels remain around 250-500 ppmS without applying harsher conditions of temperature and hydrogen pressure. Harsh conditions are required to lower the sulfur levels, however, such conditions compromise the fuel specification as the aromatic content decreases resulting in additives being required in the final product.
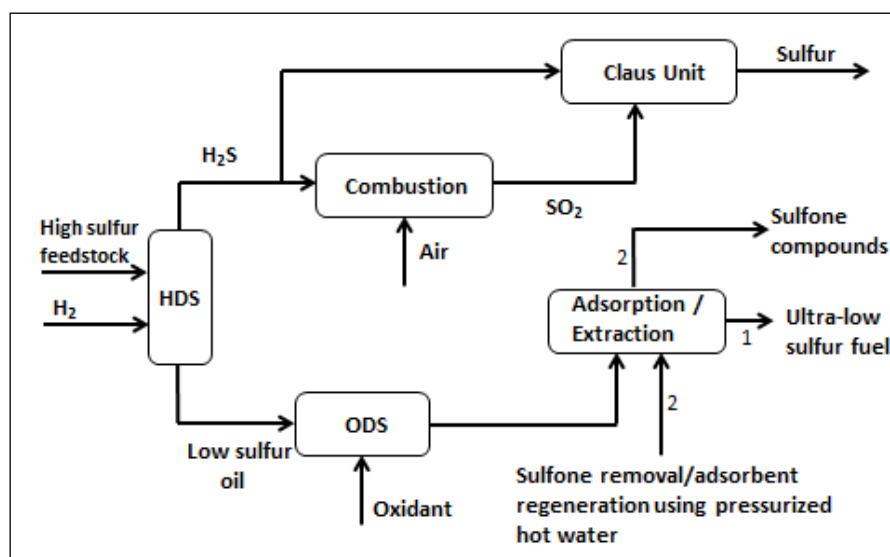

Figure 3.2 Integrated hydrodesulfurization-oxidative desulfurization (HDS-ODS) processes.

Recent studies have given attention to improving catalysts required for the hydrodesulfurization process. We have proposed improvement in catalyst design through the use of platinum group metals such as the highly hydrogenating Rh in RhMo as well as using ligands for improving dispersion of the sulfided MoO_3 sites compared with the less active bulk Co/Ni sulfides (Co_9S_8/Ni_3S_2) in the case of

CoMo and NiMo. The sulfided Mo, preferably type II CoMo-S phase is the active phase for desulfurization of organosulfur compounds (**Figures 3.3 and 3.4**). The following trend was observed for alumina-supported CoMo with and without chelating agents such as ethylenediaminetetraacetic acid (EDTA), acetic acid (AA) and citric acid (CA): CoMo-CA/Al_2O_3 (98%) > CoMo-AA/Al_2O_3 (94%) > CoMo-EDTA/Al_2O_3 (90%) > CoMo/Al_2O_3 (43%). In the case of RhMo, the effect of ligands requires further investigation as a reverse trend, RhMo/Al_2O_3 (88%) > RhMo-AA/Al_2O_3 (73%) > RhMo-CA/Al_2O_3 (72%) > RhMo-EDTA/Al_2O_3 (68%), was observed with RhMo without the use of ligands more active that the rest of the catalysts (Majodina, Tshentu and Ogunlaja, 2021).
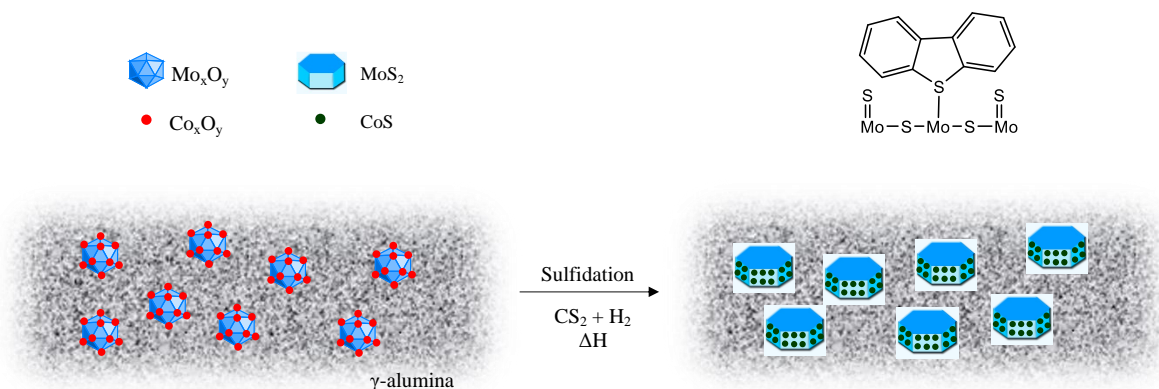

Figure 3.3. Schematic of the sulfidation process for CoMo catalyst showing DBT binding on a coordinatively unsaturated Mo site upon hydroprocessing (Dembaremba *et al.*, 2022).
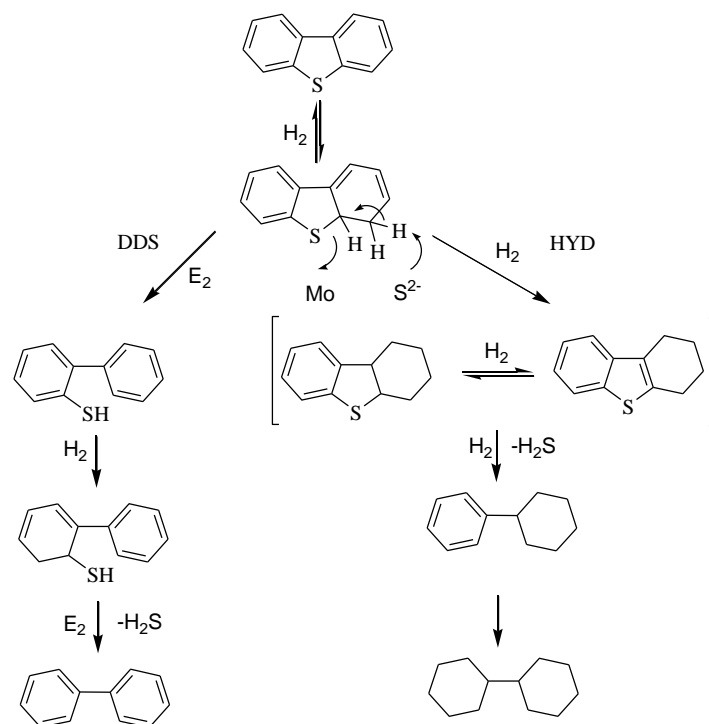
Figure 3.4. Pathways for hydrodesulfurization of aromatic organosulfur compounds.

3.2 Application in medicine

Earlier works of metals in medicine were pursued with the view of beneficiating metals such as vanadium, palladium and gold. The application of vanadium in the treatment of diabetes if driven by their action as phosphatase inhibitors. We have contributed organovanadium(IV) complexes that show glucose lowering effect and in addition they show anti-coagulation effect through prevention of d-dimer formation (**Figures 3.5** and **3.6**) (Gundhla *et al.*, 2015). This is an interesting result given that some diabetic patients suffer from blood clotting. The use of imidazolyl-carboxylate moity as carrier ligands proved useful for the stability of the complexes over a wide pH range since complexes must survive the low pH conditions in the gut and also survive the conditions in the intestines until delivered into the bloodstream. We have also mapped the possible transformation of the complexes under physiological conditions using a range of techniques such as pH-metric speciation using potentiometry, HPLC, LC-MS and EPR.
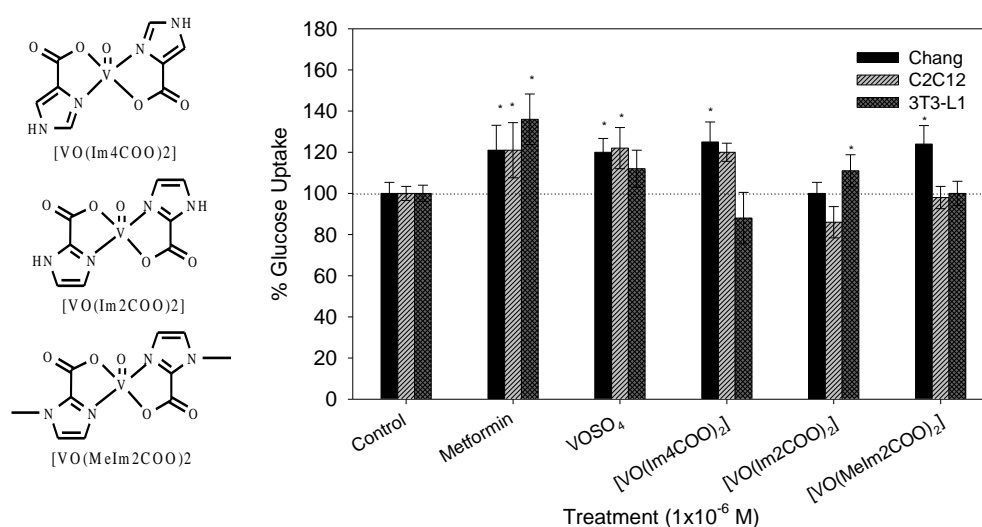

Figure 3.5. The effects of metformin (Met), oxidovanadium(IV) sulfate ($VOSO_4$), [VO(Im4COO)$_2$], [VO(Im2COO)$_2$] and [VO(MeIm2COO)$_2$] (at 1 µM concentration) on Chang, C2C12 and 3T3-L1 glucose uptake. The basal glucose uptake, is represented as 100% (Control). Error bars indicate SEM (n=3), *(p <0.05) relative to the (Con) (Gundhla *et al.*, 2015).

Insulin, a pancreatic signaling hormone, is the principal treatment for type 1 diabetes while type 2 diabetes can often be controlled by oral pharmaceuticals namely; sulphonylureas such as glipizide, biguanides such as metformin, thiazolidinediones such as pioglitazone, and meglitinides such as prandin. However, these available prescription drugs present adverse side effects including hypoglycaemia for sulphonylureas, lactic acidosis for the biguanides, and weight gain for thiazolidinediones. Therefore, there is a need for the development of another class of oral pharmaceuticals that does not present undesirable side effects, and vanadium has shown promise in this regard. In addition to the possibility to use vanadium in type 2 diabetes, we have observed that vanadium complexes can allow for release of endogenous reserves of insulin in case of high glucose levels and this presents a potential application of vanadium in type 1 diabetes but this requires further investigation using an *in vivo* model.
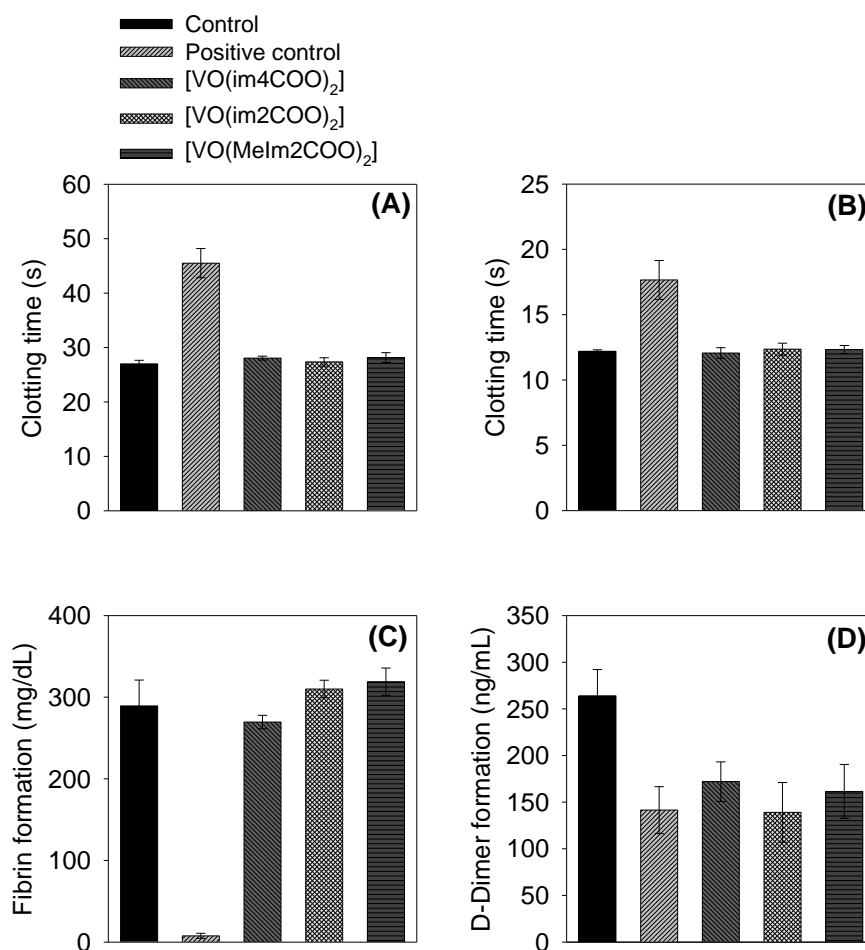
Figure 3.6. The effect of [VO(Im4COO)$_2$], [VO(Im2COO)$_2$] and [VO(MeIm2COO)$_2$] (10 μM) on APTT (A) and PT (B) clotting times, on fibrin formation (C) and D-Dimer formation (D). The control represents untreated sample while the positive control represents the anticoagulant heparin (0.1 U.mL^{-1}) (n = 3) (Gundhla *et al.*, 2015).

The potential use of palladium-109 in radiopharmacy stems from its favourable nuclear properties as a half-life of 13 hours and due to its β-decay process (Gandidzanwa *et al.*, 2022). These properties can be exploited in a nanoradiopharmaceutical design. To the best of our knowledge, a proposal for the use of palladium as a biofunctionalised radionuclide for cancer-specific receptor-mediated targeted endocytosis has not been previously reported. In our study, the folate-conjugated nanoparticles were tailored to accumulate selectively in cancer cells relative to normal cells *via* folate-receptor mediated endocytosis. Folate receptor targeted therapy has excellent prospects for the treatment of breast cancer (Gandidzanwa, 2022). The MDA-MB-231, MDA-MB-468, and MCF-7 breast cancer cell lines, and MCF-10A normal cell line were used in the *in vitro* study. Qualitative and quantitative analysis of the cellular uptake and accumulation of nanoparticles was conducted using transmission electron microscopy (TEM), confocal fluorescence microscopy and inductively coupled plasma-optical emission spectroscopy (ICP-OES). The findings proved that folate-conjugated palladium nanoparticles successfully and selectively accumulated in breast cancer cells. We conclude that folate-conjugated palladium nanoparticles can be used to target breast cancer cells for radiopharmaceutical applications. A similar study was carried out by us using biofunctionalized rhenium oxide nanomaterials due to the favorable properties of Re-188 and Re-186 for radiotherapeutic applications (**Figures 3.7** and **3.8**) (Ntsimango *et al.*, 2022).
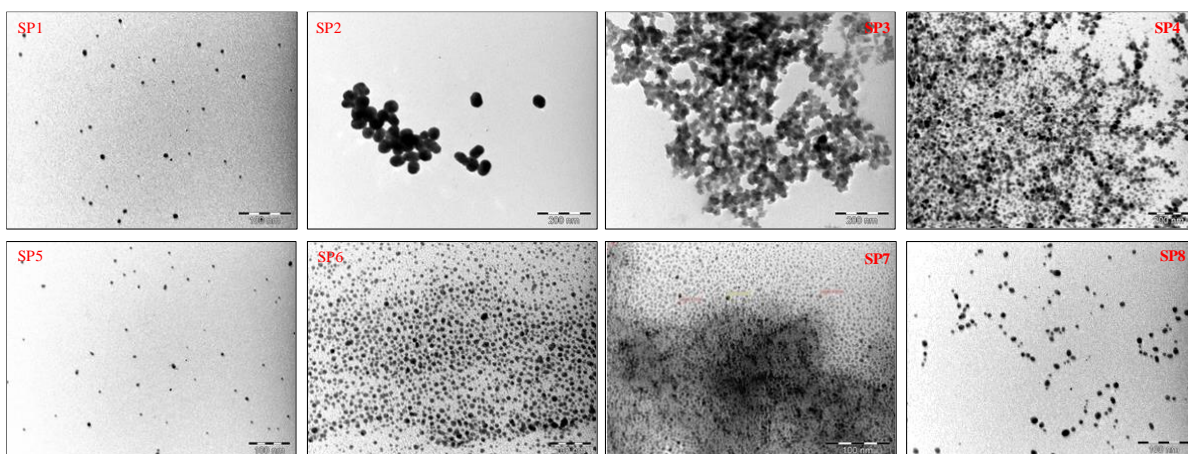
Figure 3.7. TEM micrograms of folate-conjugated tetraaminophthalocyanine (TAPc-FA) capped rhenium nanoparticles by changing reaction conditions in samples SP1-SP8 (Ntsimango *et al.*, 2022).
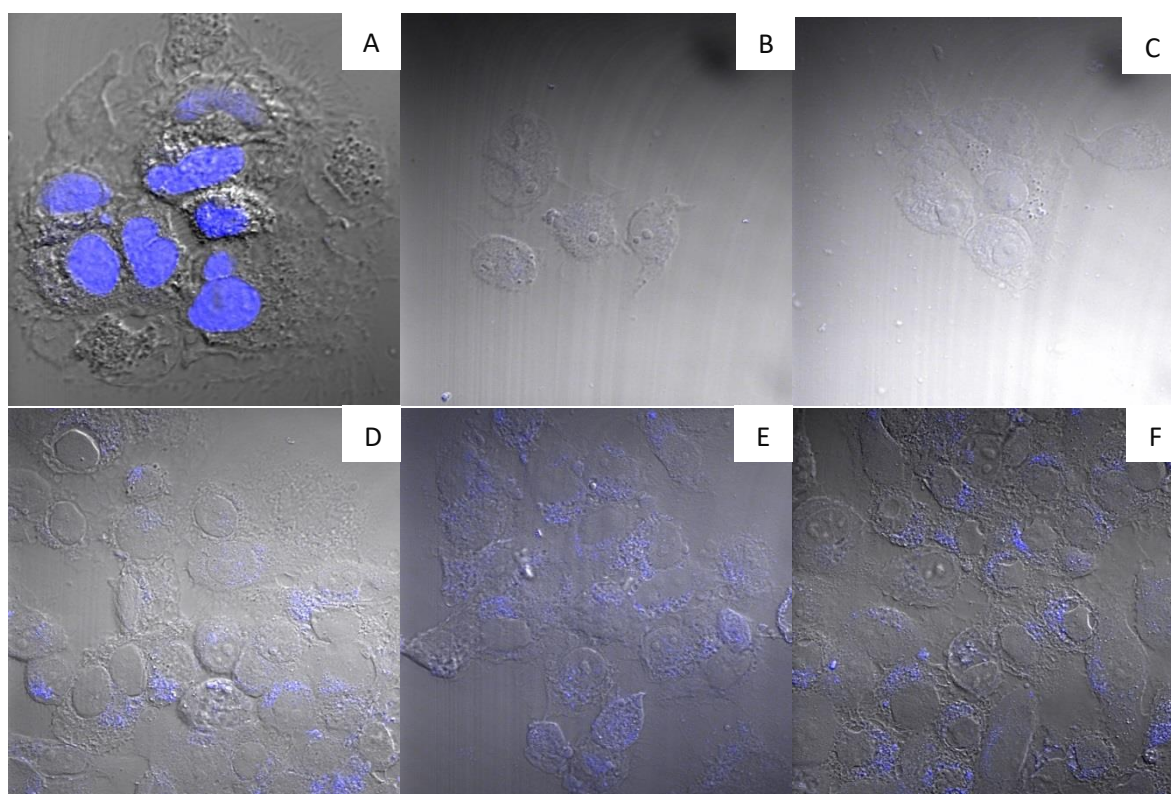
Figure 1: Confocal fluorescence images of HCC1806 cell lines treated with: (A) Hoechst 33324 nuclear stain, (B) Folic acid, (C) Methanol, (D) Uncapped Re_xO_y NPs, (E) 50 nm Re_xO_y NPs and (F) 10 nm Re_xO_y NPs. Blue colour indicates the signal from the treatment, while the cell outline is displayed as differential contrast (Ntsimango *et al.*, 2022).

Several studies in the biomedical field are now beyond the scope of our expertise and require other specialized laboratories that can carry out *in vivo* studies to study the effect of vanadium compounds in diabetic rat models and to study the biodistribution of the radioactive palladium-109 and its tumour irradiation ability in cancer rat models. Only proof of concepts has been undertaken by us using *in vitro* in collaboration with biochemists.

4. Current and future directions

The world is currently focused on strategies towards sustainable habitation on our planet earth and the UN sustainability development goals (SDGs) are the driving instrument for this cause (United Nations, 2008). The emerging trends of circular vs linear economy, climate action, and green and sustainable technologies are attractive to find opportunities for contribution given our expertise in the theoretical and practical aspects of dealing with metals. We have advanced with the concept of "urban mining" which involves recovering critical metals from city treasures such as waste electrical and electronic equipment, batteries, catalytic converters, etc (Xolo *et al.*, 2021). In addition, the recovery of lost precious metals value from mining wastewater is another area of importance to ensure sustainable resource recovery. We also recognise the importance of mineral beneficiation to contribute to energy security and the need to massify the advancement of green and renewable feedstocks as a means to contribute to carbon offsetting and to circular economy strategies.

4.1 Recovery of strategic metals from spent and waste resources

Spent secondary sources or city mines are the new global challenges, as well as the new sources of treasures. Although the world has accepted the importance of these 'wastes', the real challenge lies in the costs of effectively recycling rare and precious elements (Tshentu and Parajuli, 2022; Xolo *et al.*, 2021). It is true that the mass percentage of the platinum group metals in the spent e-waste is more than that in the natural mine, however, the coexistence of several heavy metals and metalloids in a high concentration demands more sophisticated separation protocols. The current recovery rates for precious metals and rare earth elements (REEs) from spent products are low, and there is a need to move towards a closed-loop recycling system.

We have recently undertaken studies on the recovery of precious metals from catalytic converters (**Figure 4.1**) using resin chemistry which we have developed in basic studies undertaken in our hydrometallurgy work (Moleko-Boyce *et al.*, 2022). All the custom-made resins showed selectivity towards palladium. A study has been initiated on the recovery of precious metals from e-waste and it is at early stages, and we have been approached by MT Waste Solutions (Pty) Ltd to assist them with refinery of their e-waste and waste catalyst streams. This gives an opportunity to contribute meaningfully with such studies and a mix of precipitation and resin separation is envisaged for this work.
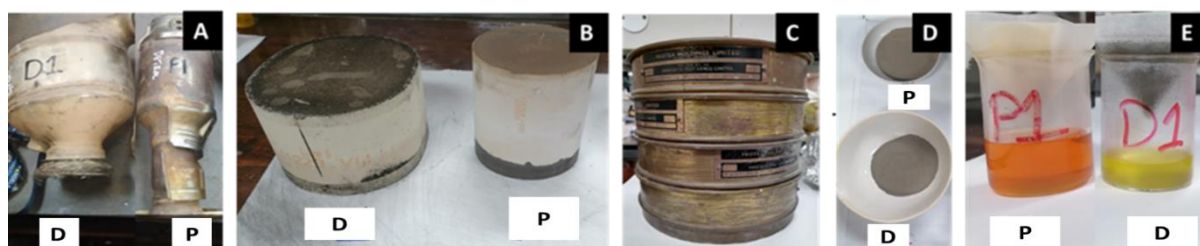
Figure 4.1. Dismantling and leaching process of diesel (D) and petrol (P) spent catalytic converters where (**A**) spent catalytic converters for diesel (D) and petrol (P), (**B**) dismantled catalytic converters, (**C**) Sieving tool used to mesh crushed catalytic converter, (**D**) meshed up to 85 µm particles, and (**E**) leached D and P sample using 3:1 HCl: NHO$_3$ (Moleko-Boyce *et al.*, 2022).

Mining wastewaters have residual heavy metal concentrations in the effluent that are still too high to meet the stringent discharge standards, and in addition there is also a financial loss that is experienced by mining industries due to valuable metals (such as base metals and platinum group metals) ending up

in their effluent streams due to the failure/bleeding of current resins. These mining waste streams are not economical to re-process due to the dilute nature of such steams. This therefore necessitates the use of scavengers to recover such important metals from mining effluent streams. We have proposed use of track-etched PET membranes as composite materials with polymer nanofibers functionalized with selective ligands as devices for recovery of precious metals and toxic base metals from mining wastewater as well as recovery of rare earth elements (REEs). Joint Institute for Nuclear Research (JINR) is Russia has the expertise for fabrication and testing of track-etched membranes (Kristavchuk *et al.*, 2017) while we have expertise in ligand design for metal ions (Okewole *et al.*, 2012; Okewole *et al.*, 2013; Majavu and Tshentu, 2017; Majavu *et al.*, 2021).

4.2 Use of metals for production of green and renewable fuel products

Production of energy from renewable resources is still more costly than the use of fossil fuels. The current attention is on ensuring the sustainable use of fossil fuels by introducing legislation around their use, reducing the carbon footprint, and developing strategies for CO_2 capture and utilization. There has been a major drive in the past decade towards the development of strategies for CO_2 capture, storage and sequestration, a milestone that will ensure the sustainable use of fossil fuels by remaining carbon neutral as we transition to clean energy generation technologies. The world faces a huge problem next to climate change which is the energy problem. There are two main problems associated with the current brown energy, namely, (i) emission of greenhouse gases and (ii) the lack of sufficient energy to millions of people in poor communities. From the time the world became more aware of how the use of fossil fuels for energy is unsustainable, it has become a huge battle to do away with the use of crude oil, natural gas, and coal as main sources of energy. Herein, we propose the use of algae biomass to produce biocrude by the pyrolysis method, and the advantage is that algae uses up CO_2 and grows in all waters. Not only there is an environmental impact of a renewable source, but algae are also predicted to have greater biomass productivity than any other plant crop and have a lower cost per yield. The optimal conditions for the growth of algae (Scenedesmus species) at InnoVenton facilities at Nelson Mandela University have been studied in detail. The pyrolysis (Baloyi and Dugmore, 2019) and processing of pyrolyzed algae biomass oil (biocrude) to remove oxygenates by a process of hydrodeoxygenation (Kim *et al.*, 2019) is proposed. The focus will be on developing metal-based catalysts for hydrodeoxygenation of the biocrude, which is full of oxygen-containing compounds, through hydroprocessing. The biocrude will be hydrotreated using a fixed bed reactor to acceptable fuel properties (cetane index > 52, aromatic content < 15%, density ~ 0.84, Sulfur < 5 ppm, etc). This would be a truly green process of production of biofuel especially if green hydrogen can be employed in future.

The Global Energy Transformation Roadmap to 2050 depicts that a share of power from renewable energy sources shall reach at least 80% by 2050. We have identified the potential to produce green gas as a replacement for liquified petroleum gas (LPG) via a green process in addition to what is known via a bio-based routes. The proposal involves the transformation of CO_2 to propane/butane (LPG) in an integrated multistage process and with each step being fully green. The overall chemical conversion process for $CO_2 + H_2$ -> gLPG (i.e. $4 CO_2 + 13 H_2$ -> butane + $8 H_2O$), literature exits since the 1980's, culminating in two 'processes', viz. that of the Japan Gas Synthesis company (seemingly abandoned some years ago) and more recently, CoolLPG of the Gas Technology Institute (GLPGP Report, 2020), the former using $CO_2 + H_2$ and the latter reformed biogas ($CH_4 + CO_2$) feed – neither have been commercialized. In addition, much literature exists for conventional syngas ($CO + H_2$) as feedstock. Almost all literature reports on a one-pot synthesis covering the full chemical transformation, viz.

1. $4 CO_2 + 4 H_2$ -> $4 CO + 4 H_2O$ RWGS (reverse water-gas shift)   [CuZnAl, FeCrOx]
2. $4 CO + 8 H_2$ -> $4 MeOH$ MeOH synthesis   [CuZnAl, CuZnZrAl]
3. $MeOH$ -> $2 DME + 2 H_2O$ DME synthesis   ['weak' acid]
4. $DME + H_2$ -> butane + $2 H_2O$ LPG (butane) synthesis   [Pd/'strong acid']

for C4 (butane) synthesis and analogously for C3 (propane). In general, the product is a mixture of C1 – C6+, olefins, paraffins and even aromatics. Both water 'poisoning' of the (mostly) final step-4 and 'carbon' laydown result in overall deactivation of the catalytic process. The four catalytic transformations have disparate temperature optima such that one-pot type integration compromises all intermediate steps/catalysts - worsened by the carry-through of all co-reactants and co-products of the preceding steps, e.g. water and CO_x from steps 1 – 3 'poison' step-4 catalysis and convert to undesired methane, respectively (Li *et al.*, 2007). Very little information has been published on a 'clean' step-4 (DME + H_2 -> LPG) and are well outside the optimum conditions (Asami *et al*., 2005). Hence, whereas stage separation, inter-stage recycling and knock-out will resolve much of the current published difficulties, it remains crucial, initially, to determine whether a 'pristine' step-4 synthesis (DME + H_2 alone as feed) will yield an economically viable product with stable catalytic performance. Further, whereas zeolite BEA seems suited to C4 synthesis, CHA structure-types, notably hierarchical materials, are to be synthesized for C3 enhancement. In the DME → hydrocarbons, it is possible that the catalyst would suffer both water 'poisoning' and carbon laydown (coking). However, with adequate hydrogen the feed carbon laydown should not be a problem but the effects of possible co-species will be evaluated. The retarding effect of water will also be dealt with to moderate its influence through increasing catalyst hydrophobicity by increasing the Si/Al ratio in the zeolite structure. Therefore, both catalyst stability and appropriate hydrocarbon product distribution are desirable for the catalyst development aspect of this project.

5. Perspectives

It would be prudent for stakeholders in the mining industry and government to take a critical view on current beneficiation trends in South Africa (SA) to identify potential value that can be unlocked in a sustainable manner. The current progress in mineral beneficiation in SA is not satisfactory and begs the question of lack of competitive advantage from the mineral endowment that SA enjoys. Therefore, mineral endowment on its own is not sufficient. While other areas of science, technology and engineering may have the skills required for beneficiating minerals in South Africa, there may be areas where skills shortage exists such as in cutting and polishing diamond as well as jewellery production. The low pace of growth of mineral markets in South Africa requires a concerted effort to turn the tide given the decline in investor confidence due to several reasons including costs and less access to electricity as well as the lack of necessary infrastructure. The only area where the use of platinum group metals has grown domestically is in the autocatalytic convertor industry that supports the Automotive industry. South Africa also has abundant titanium-bearing mineral reserves and the potential for establishing a thriving titanium industry has been identified in a number of government studies and has featured in various national science and technology strategies (van Vuuren, 2009). Another potential option for South Africa in advancing mineral beneficiation is in the chemicals/materials sector through production of PGM-containing chemical products and catalysts for various industries and end-users, and in the new areas such as fuel cells given the rise in the hydrogen economy. Mineral beneficiation presents the opportunity to contribute to the energy security of South Africa. These efforts require step-by-step approaches otherwise opportunities will be missed. At the level of basic and applied science, we remain committed to improving hydrometallurgical methods for recovery of the critical metals and in their application in emerging fields that are aligned with principles of climate action and circular economy as well as any other applications that can sustain our lives and the environment around us.

Acknowledgements

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