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Valorisation of acid mine drainage through effective recovery of selected rare earth elements using cationic resins

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Acid mine drainage (AMD) presents a challenge to the environment if not well managed, but it also presents an opportunity for the recovery of economically valuable products, including rare earth elements (REEs), which are critical for the development of advanced, and green technologies. REE concentrations in AMD samples from coal and gold mines were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) and their sorption by different cationic resins (CHT4083, CHP4502 and CHP00712) was evaluated. Optimum conditions for the sorption of the REEs by these resins were determined through batch experiments and desorption of the REEs from the resins using different concentrations of sulphuric acid (H_2SO_4) solutions. Coal mine drainage (CMD), with a low pH of 2.37, had higher amounts of REEs (ΣREE 226.3732 mg/L) than AMD from the gold mines (ΣREE 4.9705 mg/L), with a pH of 3.21. A REE sorption efficiency of up to 98% was obtained with CHP4502 and CHP00712 resins and further optimisation of CHP00712 revealed that a resin volume of 250 mL and a contact time of 10 min were required to successfully remove REEs from 500 mL AMD. The sorption capacities of the resin for the selected REEs were 3.88 mg/g, 0.88 mg/g, 1.37 mg/g, 3.18 mg/g, 0.67 mg/g, 0.01 mg/g and 0.27mg/g for Pr, Gd, Nd, Ce, Sm, Eu and Y, respectively. Elution of the resin with a 0.5 N solution of sulphuric acid desorbed the REEs. AMD from coal mines could be an alternate source of REEs and cationic resins can be used to recover these REEs from the CMD. Further investigations, including impregnation of resin to improve its sorption capacity, and temperature effects on the sorption process, are recommended.

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INTRODUCTION

Industrial development has led to an increase in demand for various minerals with a consequent increase in mining, and generation of huge amounts of acid mine drainage (AMD) that require treatment prior to disposal. South Africa is one of the most industrialised countries in Africa and has various types of mines, including gold and coal mines (Masindi et al., 2018), some of which have been closed. Coal is a major source of energy and revenue for South Africa. About 90% of South Africa's electricity needs are met by coal-fired power stations (Beidari et al., 2017). Massive amounts of coal are mined and processed in the country, leading to the generation of huge volumes of acidic effluents known as coal mine drainage (CMD) (Mhlongo and Amponsah-Dacosta, 2015). Gold minerals were once an important source of revenue and job creation in South Africa. However, some of these gold mines have been closed due to the depletion of gold-containing minerals but AMD generated in these mines is still a source of concern (Naicker et al., 2003; Neingo and Tholana, 2016).

Several methods have been developed to treat industrial effluents, including AMD and CMD, with various advantages and disadvantages. Some of the methods are costly, depending on the intended goal of treatment, and quality and quantity of AMD to be treated (Hermassi et al., 2021). The quality of AMD is influenced by its composition, which in turn is influenced by the orebody from which the mineral is extracted, source of water, microclimate and group of microorganisms present (Rambabu et al., 2020). It could contain numerous elements, including rare earth elements (REEs), at different concentration levels (Mwewa et al., 2022). Due to the challenges associated with its treatment, some industries have resorted to storing AMD in ponds or dams while waiting for an affordable treatment solution. Storing this kind of untreated waste for a long period could result in leakages and eventual deterioration of the surrounding environment. Thus, the need exists for an effective treatment process and recovering some of the components in the waste, including commercial metals such as REEs which have been associated with various coal minerals (Zhang et al., 2020). Recovery can only be encouraged to reduce their dispersal in the environment. This study therefore focused on the occurrence of REEs in CMD.

Rare earth elements refer to a group of 17 elements, which include cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), yttrium (Y), scandium (Sc) and lanthanium (La)) (Neves et al., 2022; Wang et al., 2022). Based on their atomic numbers, REEs are subdivided into light rare earth element (LREEs), which include La, Ce, Pr, Nd, and Pm, middle rare earth elements (MREEs) with Sm, Eu and Gd, and heavy rare earth elements (HREEs) made of Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y (Lefticariu et al., 2020; Mwewa et al., 2022). These elements are crucial in the development of modern technologies (Neves et al., 2022; Wang et al., 2022) and their utilization is projected to increase from 62% to 92% in the coming decade to meet supply needs for their application in emerging renewable energy and low-carbon transportation technologies (Felipe et al., 2020; Strzelecki et al., 2022). Some REEs (Nd, Eu, Tb, Dy and Y) considered as critical are already in high demand (Mancheri, 2016; Lefticariu et al., 2020). Not only are REEs of paramount importance to green technology, but they are also known to be toxic and could harm the environment when disposed of carelessly (Elbashier et al., 2021). Therefore, their removal or recovery from waste streams prior to disposal is necessary to minimize the negative impacts on the environment. Recovering REEs from waste materials is beneficial because the cost and excessive pollution associated with open-pit mining and disintegration of natural raw material to recover REEs directly are eliminated (Rychkov et al., 2018).

Though several efforts have been invested in the development of treatment processes such as chemical crystallisation, precipitation, ion exchange, adsorption, coagulation, and solvent extraction that could help recover REEs from industrial effluents (Felipe et al., 2020; Soyol-Erdene et al., 2018; Hassas et al., 2020), most of these methods have been limited to synthetic AMD, or have been carried out at pilot or laboratory scale (Wu et al., 2018). In addition, the costs of these methods, the total REE content in the effluent, and the quality (presence of other metals) of the AMD or industrial effluent to be treated (Elbashier et al., 2021), are other factors which affect the use of these methods. Ion exchange comprising a simple ion exchange system is one of the preferred techniques to recover REEs from aqueous solutions (Grawunder et al., 2014; Felipe et al., 2020).

Cationic exchange or acid resins have been extensively used to recover REEs from different media (Felipe et al., 2020; Kurkinen et al., 2021). A REE recovery efficiency of 83% was achieved by José and Ladeira (2021) using Lewatit 200H to recover REEs from AMD, and they also found that it was possible to elute the REEs from the resin using 0.02 mol/L NH_4EDTA solution. Hermassi et al. (2021) succeeded in separating REEs from acid mine water using ion exchange (IX) resins at a pH range of 0.2 to 2.0. Felipe et al. (2020) reported on the ability of some resins to better adsorb LREES than HREEs. Thus, ion exchange on both weak acid (-COOH) and strong acid ($-SO_3H$) resins, according to Reynier et al. (2022) is one of the methods available to separate the two groups of REEs. Efforts have also been made to separate REEs from transition metals using resins (Hermassi et al., 2021). The development of methods that can be used to recover REEs from AMD is still very rudimentary, yet REE concentrations in AMD could provide an additional source that could reduce the scale of mining required to meet the imminent demand for these metals, while reducing the cost and environmental impact associated with their mining. The search for different cationic resins in the recovery of REEs from AMD is therefore necessary as this could make a huge difference in the recovery processes for these very important elements.

This study therefore investigated the presence of REEs in AMD collected from gold and coal mines in South Africa and the efficiency of three cationic resins in recovering them from the AMD.

MATERIALS AND METHODS

Description of the study area

The AMD samples used in this study were collected from the Randfontein and Roodepoort mining areas in Gauteng, and eMalahleni in Mpumalanga. Randfontein and Roodepoort are urban centres that grew because of the discovery of gold and the development of mines. Randfontein is located in western Gauteng, 40 km west of Johannesburg. Gold mining was the main source of employment and the backbone of the economy in this area. The gold-bearing reefs in this region contain gold, uranium oxide, and sulphide-bearing minerals (Lusilao-Makiese et al., 2014). REEs are often associated with uranium- and thorium-bearing minerals (Whitty-Léveillé et al., 2018) and they are thus expected to be contained in the waste originating from the mining and processing of gold. Roodepoort is a region of Johannesburg where gold was first discovered at the beginning of the year 1880 (Nhlengetwa and Hein, 2015). The geology of the area includes a thick sequence of sediment overlain by Achaean sedimentary rocks. Hard dolomitic rocks occur at a range of 0 to 50 m below the ground (Njinga et al., 2016). Roodepoort is part of the Witwatersrand Mining Basin where mining of gold has happened for more than 100 years. Wastes generated from this activity are known to contain various types of elements and pose environmental impacts even after the closure of the mine. Industrial mining of gold has ceased in both the Randfontein and Roodepoort areas, and efforts are underway to neutralise AMD generated in these areas with lime.

eMalahleni (formerly Witbank), situated on the highveld of Mpumalanga, is one of the richest coal areas in South Africa, with more than half of South Africa's coal production occurring around the town (Pone et al., 2007). Its coal field is located on the northern margin of the Karroo Basin, south of the town, at approximately 144 km north-east of Johannesburg. Coal mining in the area dates back to 1908 (Pone et al., 2007). In this area, coal processing is still in operation and some CMD are being treated and others are kept in ponds without any treatment.

AMD sampling and description of samples

Acid mine drainage samples were collected in 25 L high density polyethylene (HDPE) plastic containers from sampling sites in the different study areas. At the Randfontein area, 5 AMD samples were collected from the water treatment plant of Sibanye Gold: Pora Dam (PD), Portugiese Dam (POD), 18 Winze under the grid (18WUTG), Q1-Sump Pump 1 (Q1SP1) and Q2-Sump Pump 2 (Q2SP2). Two samples of AMD were also collected from the central basin dams, Basin Dam 1 (BD1) and Basin Dam 2 (BD2) in Roodepoort. One composite CMD sample was collected from various dams at a coal-washing plant (CWP) in eMalahleni. These various sampling sites were chosen because they were either the source or the outlet points of the treatment plants, and tunnels in the mines. Samples were collected at the designated sampling points using a sampling device comprised of pipes, a pump and a generator. The pH of the samples was measured on-site before transportation to the laboratory, where samples destined for REE analysis were acidified with 65% supra-pure nitric acid, passed through a 0.45 µm syringe filter and kept in a refrigerator at 4°C until analysis. All chemicals used were of analytical grade unless stated otherwise.

Characterisation of AMD samples

The AMD samples were characterized for their pH, electrical conductivity (EC), and sulphate content. The pH analysis was conducted using a Systronics Digital pH meter 335 with a combined glass and calomel electrode. Electrical conductivity was measured using a conductivity meter (HI98192, Hanna Instrument, Romania). Sulphate, phosphate, carbonate and hydroxide ions play an important role in the stability of REEs in solution, according to Wood (1990), because they form strong and stable complexes with each other. Amongst the above-mentioned anions, sulphate is usually the most frequently encountered in AMD and so its concentration in the AMD samples was determined as described by Kolmer et al. (2000). Following this procedure, 5 mL of a conditioning reagent was added to 2 mL of filtered sample. The conditioning reagent was prepared by mixing 30 mL of concentrated HCl, 300 mL of distilled water, 100 mL 95% ethanol or isopropyl alcohol, 75 g NaCl, and 50 mL (63 g) glycerol, and making the volume up to 1 L in a container.

The sample and conditioning reagent mixture was then diluted to 100 mL with deionised water. Nephelometric turbidity unit (NTU) readings for the mixture were taken using a Thermo Scientific, AQUAfast, Turbidity Meter previously calibrated using solutions of known concentration (0, 5, 10, 25, 50, 100 mg/L) of sulphate.

Characterisation of REEs in AMD samples

The concentrations of REEs in the samples were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Arcos, Kleve, Germany) with argon plasma source (6 000–14 000 K). The ICP-OES was calibrated prior to analysis using REE standard solutions prepared from a 50 mg/L stock solution purchased from a local supplier. A 25 mL aliquot of each AMD sample was filtered using filter paper (MN 1640 m, Germany) and analysed directly for REE content. Dilution was applied where necessary using deionised water. Wherever no response was obtained from the ICP-OES, the element was considered as not detectable (nd) and consequently below the method detection limit. The AMD with the highest amounts of REEs was then used for the recovery of REEs.

Resin specification and pre-treatment

Three types of resins, namely, the Lewatit MDS TP 208 (CHP00712) which is a chelating macroporous resin with chelating iminodiacetic acid group (Lanxes 2022a), and the Lewatit MDS 1268 (CHT4083) and Lewatit MDS 200H (CHP4502) resins which are both strongly acidic gel type cation exchangers (Lanxes 2022b), were bought and tested for their efficiency in removing REEs from AMD.

Batch experiments

A batch experiment which comprised mixing 200 mL of each resin with 500 mL of AMD sample in a 1 000 mL beaker at room temperature and homogenising the mixture at a constant rate of 500 rotations per minute (r/min) with an overheard stirrer for 60 min was set up. The time of 60 min was used as this was determined to be the average contact time for the sorption of REEs from AMD based on studies by Khawassek et al. (2019) and Junior et al. (2021), among others. A batch experiment was chosen as the best operation mode for this study, after obtaining non-satisfactory outcomes with a column experiment. A portion of the solution was filtered after 60 min, and the filtrate analysed for REE concentrations. The concentrations of the REEs in the filtrate from all three resins were compared to identify the most effective of the three resins in removing REEs from AMD after 60 min.

Optimization of resin sorption conditions

The resin with the highest REE recovery from AMD was further optimised to determine its optimum volume and the contact time required for the removal of the REEs. The optimum resin volume was identified by testing 50, 100 and 250 mL of resin, separately, with 500 mL of each AMD type for 60 min at a constant mixing rate of 500 r/min under ambient temperature conditions. At the end of 60 min the mixture was filtered and the filtrate analysed for REE content. The volume of resin that reduced the concentration of REEs in AMD was noted as the best volume to be used in the removal of REEs. The optimum contact time between the resin and AMD for efficient removal of REE from the AMD samples by the best resin was determined by mixing the optimum resin volume and 500 mL AMD at 500 r/min for 10, 30, 60 and 120 min. At the end of each of these times, the mixtures were filtered and the filtrates analysed for REE content. The optimum reaction time was the one after which no further removal of REEs from the AMD was noticed. The percentage REE removal and the adsorption capacity (qe) in mg/g of REE from AMD were calculated as shown in Eqs 1 and 2 (Carvalho et al., 2016; Özer and Imamoğlu, 2024).

$$\% \text{ Adsorption} = [(C_o - C_e)/C_o] \text{ x } 100 \quad (1)$$

$$\text{qe} = (C_o - C_e) \text{ x } V/m \quad (2)$$

where: C_o = initial REE concentration (mg/L) in the AMD and C_e = REE concentration (mg/L) in the supernatant at equilibrium; V = volume (L) of AMD used, m = mass (g) of resin used.

Elution of REEs from resins

Elution experiments were also conducted in a batch mode using different concentrations (0.5, 0.5 and 1 M) of sulphuric acid solutions for 10, 20 and 30 min at ambient temperature, to determine whether the sorbed REEs can be desorbed from the resin. After using the resin to recover REEs from the CMD, the resin was mixed with 500 mL of the eluting solution in a 1 000 mL beaker under constant stirring (500 r/min) throughout the duration of the experiment. Upon completion, the resins were filtered, and the filtrate was analysed for both REEs. Selected base metals, including Fe, Mn, Mg, Ca and Na, were also analysed in the filtrate after desorption. Although these metals were not determined in the AMD initially, their presence in AMD and CMD has been widely reported in other studies (Petrik et al., 2003; Akinwekomi et al., 2020). They were therefore determined in the filtrate in an endeavour to determine at what eluting solution concentration the REEs could be recovered from the resin with minimal contamination by base metals.

Quality control and assurance

Prior to sampling, the HPDE sample containers were washed and soaked in 10% nitric acid for 24 h, after which they were rinsed thrice with deionised water and dried in the laboratory at room temperature (Ntumba et al., 2018). At the sampling sites, pre-cleaned containers were rinsed thrice with the sample prior to collection and thereafter filled with the respective AMD samples and tightly closed. Method validation was achieved though the spike-recovery method as presented by Nsaka et al. (2023). A 2.5 mg/L multi-element REE standard solution was prepared and analysed using the developed analytical method on the ICP-OES and the percentage recoveries of the different elements determined.

RESULTS AND DISCUSSION

Electrical conductivity, pH, and sulphate content of AMD samples

The analysed CMD sample was found to have a lower pH value (2.37) than the AMD from gold mines, with pH values ranging from 3.01 to 5.53, as reported in Table 1. The CMD sample was therefore more acidic than those from Malan and Sitai coal mines in Shanxi Province, China (2.99–7.82) (Sun et al., 2012). The high pH values for samples from gold mines (Table 1) could be

Table 1. Concentration of sulphate, pH, and electrical conductivity of collected AMD

Sample name	Sulphate (mg/L)	pH	EC (mS/cm)
POD	3 230	3.33	3.05
18WUTG	3 820	5.14	3.87
Q1SP1	4 800	3.21	3.81
Q2SP2	3 730	3.01	3.86
CMD	8 020	2.37	8.58
BD1	5 840	3.19	6.80
BD2	5 540	5.53	6.80

justified by the neutralisation processes that are initiated at the mine as remedial action to reduce the acidity of the AMD prior to disposal. The AMD is neutralised with lime to a targeted pH of 7. This might affect the concentrations of REEs in the AMD as they precipitate within a pH range of 3.3–9.3, depending on the alkali used and the specific REE (Khawassek et al., 2015).

The EC was higher in the AMD from eMalahleni, followed by samples from BD1 and BD2. This shows that there are free ions in these samples, as compared to samples from POD, 18WUTG, Q1SP1 and Q2SP2 collected from Randfontein where remediation actions were underway. This is important since it has been reported by Mihajlovic et al. (2017) that low pH increases REE mobility, which makes it available for sulphates to form stable complexes with. This might be one of the reasons, besides the composition of the ore and process followed, why AMD from eMalahleni may contain more REEs.

The highest concentration of sulphate was found in the CMD (Table 1). This is not unexpected as studies by Wu et al. (2022) have shown that coal streams are usually rich in sulphur. In addition, the sulphate forms a complex with REEs, inhibiting the sorption and stabilization of the REEs in solutions of $pH < 5$, whereas at $pH > 5$, the concentrations of REEs decrease (Mwewa et al., 2022). This may explain the high concentrations of sulphur in the CMD relative to the AMD from the gold mines.

Concentrations of REEs in AMD samples

The percentage recoveries and results obtained during the validation of the analytical method and characterisation of REEs in AMD samples are shown in Table 2. The overall percentage recoveries ranged between 93 and 99.8%. The highest percentage recovery was that of Ce (99.8%), whereas the lowest was obtained with Y (93.0%). The recoveries indicate that the analytical method was suitable for the analysis of samples. Amongst all the samples, CMD was found to contain more REEs than the AMD from the gold mine. The enhancement of REEs in coal and coal by-products has been confirmed by several other studies (Peiravi et al., 2017; Eterigho-Ikelegbe et al., 2021). As can be seen in Table 2, BD1 and BD2 AMD samples had very low amounts of only a few REEs (Pr, Gd and Y), the rest being undetectable. This could be due to poor enrichment of REEs in AMD during treatment and the fact that mining activities in this area have been suspended and AMD remediation action (neutralisation) is currently ongoing at this mine, which may have affected the concentration of the REEs. REE complexation with the neutralising agent used (carbonate) could also have taken place, leading to their deposition in the sediment. It could also be that the geology of the mined deposit had low amounts of LREEs, as also found by Echeverry-Vargas et al. (2023) in alluvial-gold-mining waste. However, the few REEs that were detected could indicate that REEs were previously present in the samples. In the POD and Q2SP2 samples, limited concentrations of Ce, Nd, Sm, Er and La were found, while in the 18WUTG and Q1SP1 samples, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb and La were present, indicating that the region was dominated by LREEs rather than HREEs. The low concentrations of REEs found in the AMD samples are restrictive to recovery actions.

The CMD sample, however, contained higher amounts of REEs than the AMD samples (Table 2). This could be attributed to the fact that the CMD sample was not subjected to any treatment and it is possible that enrichment of REEs throughout the processing of the coal could have occurred. The CMD also had a lower pH than the AMDs, which explains why more REE ions are still present, since most of the REEs would have been leached out of the mine waste into the CMD. Reports by other researchers (e.g. Hedin et al., 2019; Lefticariu et al., 2020) have shown that a variation of the pH of CMD from strongly acidic to alkaline can markedly affect the presence of REEs in solution. A study conducted by Hedin et al. (2019) revealed higher amounts of total REEs in CMD than in other effluents as well as in solids formed from CMD treatment. CMD, therefore, seems to be a potential secondary source of REEs.

LREEs occurred at higher concentrations than HREEs in the samples, with the main elements being Ce, Pr, Nd, Sm and Gd. The link between REEs and coal minerals has long been established through previous studies (Zhao et al., 2007; Zhang et al., 2007; Lin et al., 2017; Lefticariu et al., 2020). In some cases, the levels of REEs in coal ash and/or rocks adjacent to coal deposits seems to be equal to or even higher than those found in REE ores (Dai et al., 2017).

Table 2. Percentage recoveries and concentrations (µg/L) of REEs in collected samples

REE	Percentage recovery	Randfontein				Roodepoort		Witbank
		POD	18 WUTG	Q1SP1	Q2SP2	BD1	BD2	CMD
La	95.6	64.2	143	342	200	nd	nd	2 310
Ce	99.8	646	795	1 180	1360	nd	nd	80 890
Pr	92.9	nd	643	676	nd	312	2910	67 270
Nd	98.6	841	1 120	1 480	1270	nd	nd	33 540
Sm	96.0	177	226	349	374	nd	nd	19 360
Eu	98.0	nd	Nd	nd	nd	nd	nd	180.2
Gd	98.4	nd	119	224	nd	0.421	357	13 500
Dy	94.3	210	200	634	581	nd	nd	2 630
Ho	96.7	nd	Nd	nd	nd	nd	nd	269
Er	94.0	32.8	53.8	72.1	68.1	nd	nd	306
Tm	95.9	nd	Nd	nd	nd	nd	nd	20.0
Yb	97.3	nd	6.40	13.4	4.92	nd	nd	229
Lu	98.7	nd	Nd	nd	nd	nd	nd	317
Sc	94.6	nd	Nd	nd	nd	nd	nd	152
Y	93.0	nd	Nd	nd	nd	18.7	25.4	5 420
ΣREE		1 971.0	3 306.2	4 970.5	3 858.0	331.1	3 292.4	226 373.2

nd = not detected

These metals are further leached out into the effluent during coal processing or washing. Hence, the occurrence of both LREEs and HREEs in the CMD is possible. Q1SP1 was second in total REE content but had fewer HREEs than LREEs. BD1 had the lowest amount of REEs of all the samples. The total concentration of REEs in the CMD used in this study (226 373.2 µg/L) was above the 559.9 µg/L and 9 879 µg/L reported in CMD from Shanxi Province in China and Illinois in the USA, respectively (Sun et al., 2012; Lefticariu et al., 2020). For further investigations, therefore, only the CMD which had relatively high amounts of REEs was utilised, whereas the AMD samples were disregarded because of the low amounts of REEs detected in them.

Efficiency of REE removal from AMD by resins

An attempt to recover 3 identified HREEs (Nd, Eu and Y) and 4 most abundant LREEs (Ce, Pr, Sm and Gd) in the CMD samples was carried out. A reduction in the concentrations of REEs in the CMD sample was observed after mixing it with CHP4502 and CHP00712 resins but not after mixing with CHT4083, as shown in Fig. 1. This indicates that CHP4502 and CHP00712 sorbed the REEs much better than CHT4083.

The calculated percentage removal of all REEs after using the three cationic resins is presented in Fig. 1. The CHT4083 resin removed only about 57.1 to 77.7 mg/L of Pr and 8.39 to 15.7 mg/L of Gd. The rest of the REEs had concentrations similar to those in the initial CMD sample, indicating the poor efficiency of this resin in the recovery of the REE under the experimental conditions (Fig. 2). The highest pH values, of 2.35 and 2.21, were found in solutions obtained after reaction of the CMD sample at pH 2.37 with CHP4502 and CHT4083, respectively, whereas the pH value obtained after reacting the same sample with CHP00712 separately was 2.08. This could simply indicate that CHP00712 is a stronger acid cation exchange resin, followed by CHP4502 and then CHT4083. Page et al. (2017) reported that strong acid cation exchange resins have a stronger affinity for trivalent REEs over base metal impurities. Both CHP4502 and CHP00712 produced approximately 99% removal for all tested REEs (Fig. 2), but the latter was randomly chosen for further optimisation of reaction time and resin volume.

Optimum resin volume and sorption time

It was of paramount importance to know the volume of resin to be used for effective sorption of REEs, to avoid unnecessary usage of large volumes that could increase the cost of treatment, or of low volumes that would not effectively remove the REEs from the AMD samples. The results obtained (Fig. 3) proved that 100 mL resin volume was sufficient to effectively remove the majority of REEs from a 500 mL sample.

Thus, 100 mL resin volume is the optimal resin volume to be used in this circumstance. It was also noted that by using 100 mL as resin volume, Pr could only be reduced to 6 mg/L. The other REEs were completely removed. To substantially remove Pr from 500 mL of CMD, a 250 mL resin volume was required (Fig. 3). The sorption capacities (mg/g) obtained for the selected REEs after reacting 500 mL of CMD with 250 mL of CHP00712 were 3.88 mg/g; 0.88 mg/g; 1.37 mg/g; 3.18 mg/g; 0.67 mg/g; 0.01 mg/g and 0.27 mg/g, respectively, for Pr, Gd, Nd, Ce, Sm, Eu, and Y. This shows that the used resin had higher sorption capacity for Pr, followed by Ce, as compared to the rest of the REEs.

It was also observed that 10 min was sufficient contact time to remove most of the REEs from 500 mL of CMD using CHP00712 resin (Fig. 4). After 10 min, there was no noticeable change in the concentration of the REEs in the CMD samples.

Desorption of REEs from sorbed resin

Based on the difference between the concentration adsorbed and found in the eluate, it is possibility to state that there was elution. The effect of eluting time and concentration of eluting

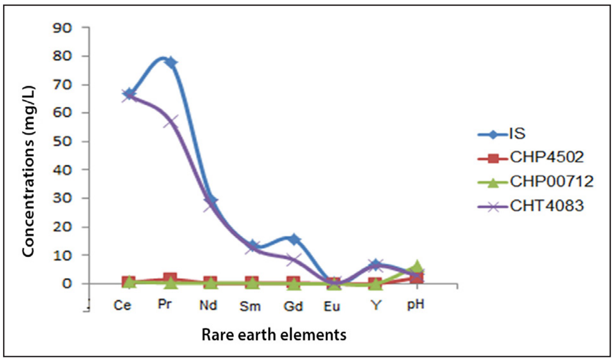

Figure 1. Sorption of REEs on different resins (IS = initial sample)

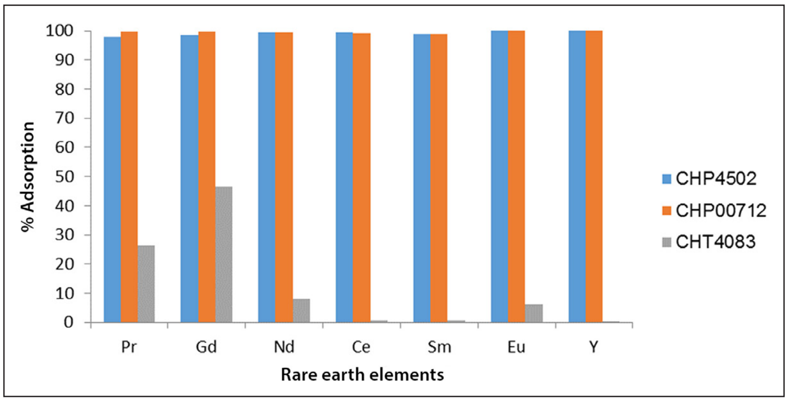

Figure 2. Removal efficiencies (%) for REEs by resins (at pH = 2.37, S/L= 2/5, contact time = 60 min, speed of mixing, = 500 r/min)

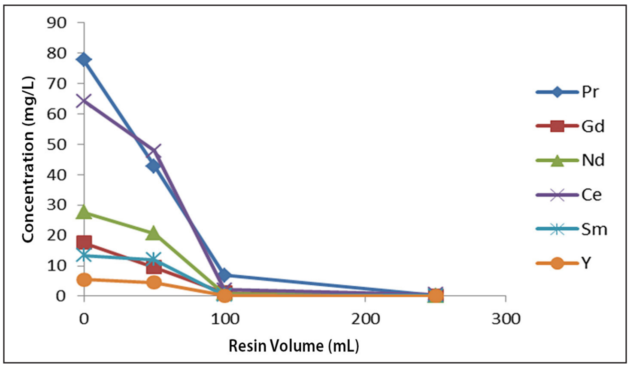

Figure 3. Optimisation of resin volume for the removal of REEs

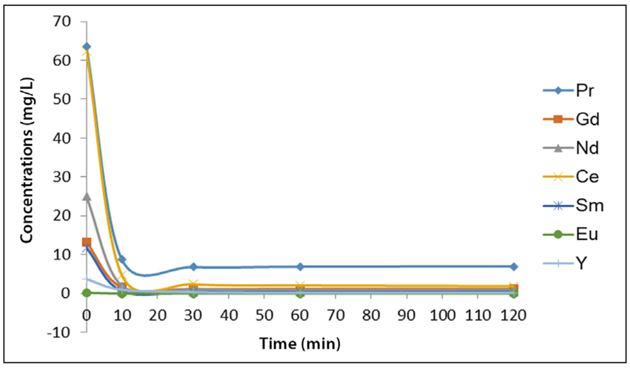

Figure 4. Effect of time on the removal of REEs with CHP00712 resin

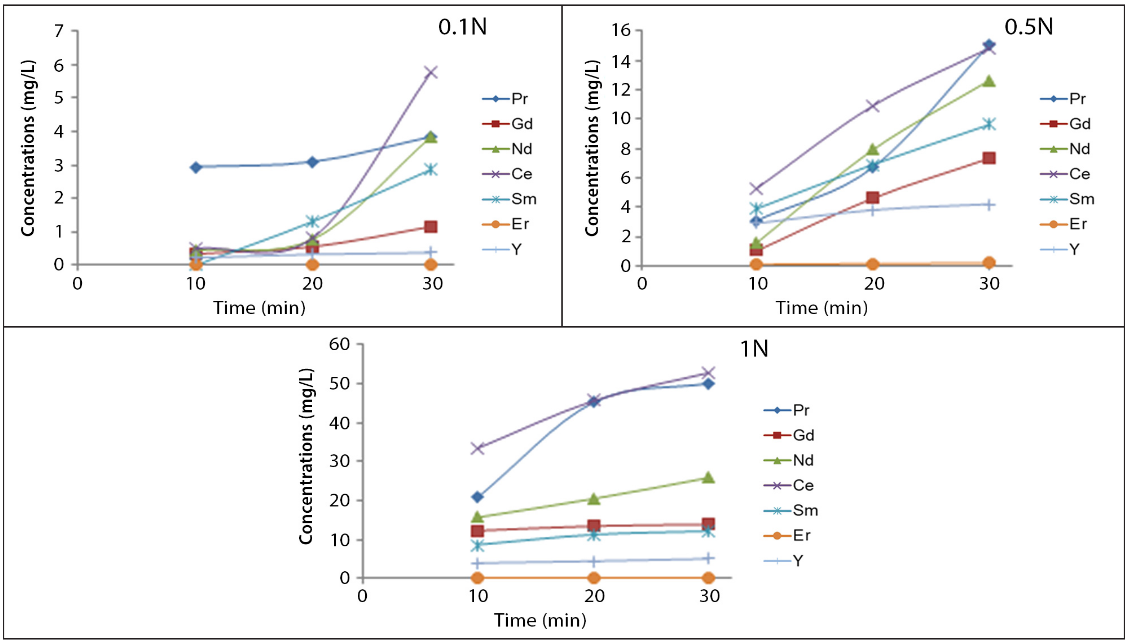

Figure 5. Elution of REEs from sorbed resin with solution of sulphuric acid (0.1, 0.5 and 1 N) for 10, 20 and 30 min

solution were determined to identify the optimal condition for REE recovery from the resins. Eluting time had an effect on the amount of the REEs released from the sorbed resin, irrespective of the concentration of the eluting solution. The longer the eluting time, the higher the amount of REEs released. The results obtained during elution experiments are presented in Fig. 5. Good bulk elution was obtained.

REEs and base metals were found in the eluting solution. Factors that influenced the elution of REEs were seen to be the concentration of REEs sorbed on the resin, the concentration of the eluting solution, and the eluting time. With a high concentration of the eluting solution, it was unnecessary to elute for a longer time. Given the amount of Pr that was sorbed on the resin, a greater eluting time was required to desorb these REEs from the resin (Fig. 5). When increasing the concentration of eluting solution, it is quite important to consider the amount of base metals (Fe, Mn, Mg, Ca and Na) that are released concurrently with the REEs during elution. The concentrations of the base metals eluted from the resin positively correlated with the concentration of sulphuric acid solution used (Fig. 6).

From Fig. 6, it was noted that the elution of base metals trapped on the resin increased with increase in the concentration of sulphuric acid. The idea is to have the concentration of the eluting solution within a range where all REEs are recovered and impurities are kept at a minimum level. Thus, using low concentrations (0.5 N) of sulphuric acid as eluting solution is recommended.

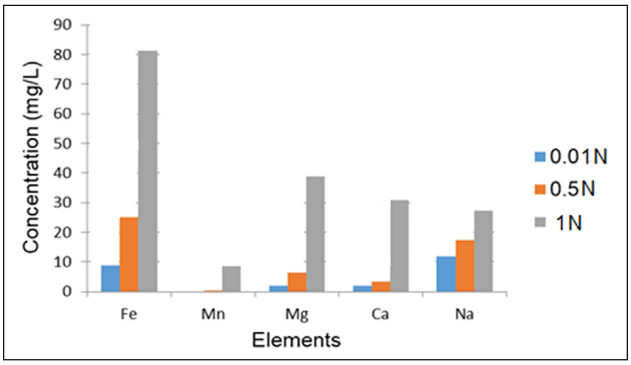

Figure 6. Concentrations of Fe, Mn, Mg, Ca and Na eluted from the resin using different concentrations of sulphuric acid

The findings of this study have shown that AMD from coal mining could be considered as an additional source of REEs. Amongst the used cationic resins, two showed strong removal efficiencies and could potentially be used in recovering REEs from real AMD. To avoid excess usage of resins and time, which could render the whole process expensive, it was found that 10 min of reaction time and a solid/liquid ratio of 2/5 are the optimum conditions to remove REEs from AMD at room temperature and a mixing rate of 500 r/min. The sorbed resins could be cleaned up using a 0.5 N sulphuric acid. However, further optimisation is required to determine the elution efficiency and re-usability of the resin.

CONCLUSIONS

Coal mine drainage contains relatively higher amount of REEs (ΣREE = 226 373.2 µg/L) than AMD from gold mines, indicating that coal mine drainage could be a potential secondary source of REEs. The REEs could potentially be successfully recovered from the CMD using resins. Evaluation of REE removal efficiency by three different resins showed up to 98% efficiency for two of these (CHP4502 and CHP00712). 100 mL and 10 min were found to be the optimum volume and contact time when CHP00712 Lewatit cationic resin is used to recover REE from CMD at room temperature. The REE with the highest percentage recovery was Pr, whereas Eu had the lowest recovery among the REEs investigated with the specific resin. Elution experiments revealed that there is a need to strike a balance between the concentration of eluting solution and contact time, as a high concentration of eluting solution, though requiring a shorter recovery time, may result in co-desorption of high amounts of base metals. A 0.5 N solution of sulphuric acid was found to be able to elute REEs with a relatively minimal amount of base metals co-desorbed. Further assessment of the CMD and optimisation of these resins should be considered to maximise their efficiency, selectivity, and utilization as a potential source and effective method for REE recovery.

AUTHOR CONTRIBUTIONS

Nsaka Christophe Ntumba and Jannie Philippus Maree conceived the project and collected samples, Jannie Philippus Maree provided research supervision, Nsaka Christophe Ntumba ran the experiment and wrote the first draft, and Jannie Philippus Maree and Veronica Ngole-Jeme commented on the draft.

DECLARATION OF COMPETING INTEREST

All authors declare that there is no conflict of interest.

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