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Recovery of water and valuable metals using low pressure nanofiltration and sequential adsorption from acid mine drainage

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ABSTRACT

Acid mine drainage (AMD) contains an array of valuable resources such as Rare Earth Elements (REE) and Copper (Cu) which can be recovered along with fresh water. Low pressure nanofiltration with NF90 membrane was first studied to recover fresh water from synthetic AMD and concentration of dissolved metals for subsequent efficient selective recovery. Organic matter (OM) present in AMD was found to cause membrane fouling which resulted in significant flux decline. Powdered eggshell was investigated as a low-cost adsorbent for OM removal. The study showed that a 0.2 mg/l dose of powdered eggshell adsorbed 100% of OM and Fe with no significant loss of other dissolved metals. A steady permeate flux of 15.5 ± 0.2 L/m^{2}h (LMH) was achieved for pre-treated AMD with a solute rejection rate of more than 98%.

A chromium-based metal organic framework (MOF) modified with *N*-(phosphonomethyl) iminodiacetic acid (PMIDA) and an amine-grafted mesoporous silica (SBA15) material was synthesized for selective recovery of REE and Cu, respectively. The two adsorbents were used sequentially to selectively adsorb REE (91%) and Cu (90%) from pH adjusted concentrated feed. The formation of coordinating complexes with carboxylate and phosphonic groups on MOF was found to be the primary driving force for selective REE adsorption. Selective uptake of Cu onto amine-grafted SBA15 was due to the formation of strong chelating bonds between Cu and amine ligands. Both adsorbents remained structurally stable over 5 regeneration cycles. The findings here highlight the practical potential of membrane/adsorption hybrid systems for water and valuable metal (REE) recovery from AMD.

1. Introduction

Technological advances in many industries have caused severe environmental pollution and in recent times Acid mine drainage (AMD) has attracted much global attention. AMD is caused by the seepage of water through waste ore piles, exposed cuts and sulphuric rich soils (Ryu et al., 2019). The release of untreated AMD composed of dissolved heavy metals, Rare earth elements (REE), sulphates and high acidity causes contamination of downstream water bodies and poses a severe threat to the functioning of healthy ecosystems. Consumption of water that includes these pollutants can greatly damage the health of people, flora and fauna. Conventional AMD treatment methods such as chemical precipitation

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and wetlands have been found to cause secondary pollution through excessive sludge production (Naidu et al., 2019). The need for sustainable mining practices has increased research interest in recovering resources from waste. Identifying an efficient and cost-effective solution to treat AMD is of paramount importance (Vass et al., 2019).

Membrane processes have been explored to recover fresh water from waste sources and to concentrate valuable metals (Jeppesen et al., 2009; Lopez et al., 2018). The use of membrane technologies has increased in popularity throughout the mining industry for AMD treatment (Agboola, 2019). Most mines are located in arid regions where water is a scarce resource, thus recovering potable water from AMD generates a distinct advantage. The treated water can be reused for mining activities or for drinking with further purification. The major drawback of this technology is its high operational cost and production of reject water which consists of highly concentrated metal ions and sulphates (Saha and Sinha, 2018). Additionally, fouling of membranes due to the presence of organic matter (OM) can increase membrane replacement frequency and cost (Zhong et al., 2007). OM can cause membrane fouling resulting in flux reduction. Studies report that high acidity and sulphates concentrations in AMD increase interaction with OM (Lazareva et al., 2019). Gillmor (2011) found that dissolved organic content in AMD can increase up to 12 mg/l. For this reason, identifying methods to reduce membrane fouling due to dissolved organics is critical for the successful practical application of membrane technology for AMD filtration.

Among membrane fouling mitigation strategies, feed water pre-treatment such as Microfiltration (MF) and Coagulation (Ohno et al., 2010), membrane modification (Bagheripour et al., 2019) and chemical washing (Al-Amoudi and Lovitt, 2007) have proved to be effective. High cost was a limiting factor for membrane modification, while generation of secondary chemical pollutants was an inherent disadvantage of chemical washing (Zhao and Yu, 2015). It is necessary to identify efficient and cost-effective pre-treatment technologies. Among pre-treatment methods, successful application of powdered eggshell for removal of organic pollutants was reported by Zulfikar et al. (2013). Their study found that 95% of humic acid was successfully adsorbed onto powdered eggshell. Furthermore, the experiment was conducted at low pH range (pH 2) similar to that of AMD found near mining sites (Vass et al., 2019). The use of powdered eggshell is a promising low-cost solution for: firstly, reducing organic content in feed water to the NF membrane; and secondly, reducing organic fouling and associated flux reduction.

Nanofiltration is a promising technology investigated for concentrating dissolved metal ions and recovering water from AMD (Mullett et al., 2014; Wadekar et al., 2017; Pino et al., 2020). NF offers advantages such as low operating pressure, high permeate flux over reverse osmosis (RO) leading to lower operational and maintenance costs (Zhao et al., 2018). Wadekar et al. (2017) tested eight commercially available NF membranes for filtration of synthetic and real AMD. NF90 membrane was found to be the most efficient with high ion rejection (> 97%) and stable permeate flux (3 LMH/bar). The study conducted by Pino et al. (2020) compared the performance of NF90 and NF270 for filtration of AMD from an active copper mine. NF90 showed higher metal rejection at low operating pressures, while NF270 was prone to fouling. NF90 is reported as a weakly hydrophilic membrane with positively charged functional groups on the surface (Pino et al., 2020; Jamil et al., 2021). This results in excellent cation rejection enabling valuable trace metals such as REE to be concentrated.

REE are widely used in the production of phosphors, alloys, additives and is a critical raw material for manufacturing smart devices from high resolution colour screens to its circuitry (Wang et al., 2020). The value of REE has risen significantly over the years owing to the scarcity of natural mine deposits and supply risk (Dutta et al., 2016). Cu is another widely used material in the production of electrical devices and pipes (Ryu et al., 2019). The global demand for critical raw materials is rapidly increasing. Recovery of valuable metals from secondary waste sources such as metal ore process residues, acid mine drainage and end of life electronics has been explored extensively in recent years (Borra et al., 2016; Huang et al., 2018; Deshmane et al., 2020; Zhang et al., 2020). Concentrations of REE and other valuable metals such as Cu in AMD can range into trace concentrations depending on the source point (upstream/downstream of the mining area), according to Naidu et al. (2019). In this regard, identifying efficient mechanisms to concentrate valuable metals and selectively recover them in economical quantities is important. Hydrometallurgy (Ambaye et al., 2020), chemical precipitation (Vaziri Hassas et al., 2020), Selective sequential precipitation (Santos et al., 2004; Macingova and Luptakova, 2012) and Ionic liquid (Kilicarslan et al., 2014) are some of the widely tested methods for REE and other valuable metal recovery strategies. Recycling of secondary pollutants emerged as an inherent issue in all these technologies (Kilicarslan et al., 2014; Wu et al., 2014). This highlights why adsorption still remains the most efficient method for selective recovery of valuable metals (Smith et al., 2016).

Modified chromium-based Metal Organic Frameworks (MOF) such as Cr-MIL-PMIDA are regarded as highly efficient adsorbents for the removal of REE from aqueous solutions (Ren et al., 2016; Lee et al., 2018). High stability, large pore area and ability for modification with functional groups make the recovery of REE economically feasible. Mesoporous silica is another adsorbent efficient at removing pollutants from waste streams (Cashin et al., 2018). Mesoporous silica too has a high surface area coupled with stable physical, chemical and thermal characteristics (Liu et al., 2019). Ryu et al. (2019) noted that amine-grafted mesoporous silica selectively adsorbed copper in the presence of competing ions such as Zn, Ni and Mg while maintaining its chemical structure over multiple loading/stripping cycles.

While several studies have been conducted on the recovery of water from AMD, relatively few focused on the optimization of NF/adsorption hybrid system for selective recovery of valuable metals from the concentrated retentate. This study aims to evaluate the efficiency of low-pressure NF in recovering fresh water from AMD while concentrating valuable metals. These will subsequently be selectively adsorbed using metal organic frameworks (MOF) and mesoporous silica materials.

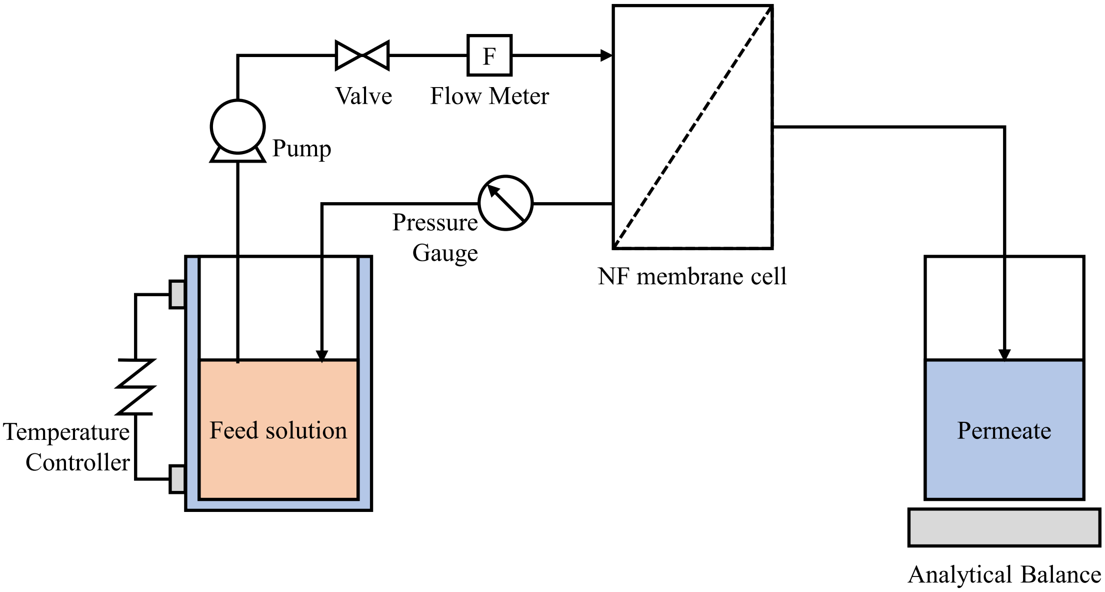

Fig. 1. Schematic diagram of NF setup.

2. Materials and method

2.1. Preparation of AMD solution

Low Pressure NF filtration and adsorption analyses of valuable metals were conducted using synthetic AMD. The composition of AMD prepared for experiments was based on previous studies (Lecomte et al., 2017; Ryu et al., 2020) and is summarized in Table S1. Synthetic AMD was prepared using $Na_2SO_4 \cdot 10H_2O$ (99%), $MgSO_4 \cdot 3H_2O$ (99%), $Al_2(SO_4)_3 \cdot 18H_2O$ (99%), $CaSO_4 \cdot 2H_2O$ (99%), $Fe(SO_4) \cdot 7H_2O$ (99%), $Ni(NO_3)_2 \cdot 6H_2O$ (99%), $CuSO_4 \cdot 5H_2O$ (99%), $ZnSO_4 \cdot 7H_2O$ (99%), $Eu(NO_3)_3 \cdot 5H_2O$ (99.9%) and $Gd(NO_3)_3 \cdot 6H_2O$ (99.9%). Humic acid (HA) (53680, CAS No. 1415-93-6, Sigma-Aldrich) was used to replicate dissolved organic matter (OM) in AMD as previously reported by Holland et al. (2014). All chemical compounds were purchased from Sigma-Aldrich. 2 M H_2SO_4 was used to adjust the initial pH to 2.0 ± 0.2. pH of the solution was measured using HQ40d multimeter, Hach, USA, while the concentrations of dissolved metals were measured using ICP-MS, Agilent 7900, USA.

2.2. NF membrane and operation

The NF membranes used in this experiment were supplied by Sterlitech Corporation, WA, USA. The properties of this membrane are listed in Table S2 and were obtained from Jamil et al. (2021). A feed volume of 2 L and a rectangular cross-flow cell with an area of 54 cm^2 (9 cm × 6 cm) was used for experiments. A schematic diagram of the NF set-up is shown in Fig. 1. Several studies have been conducted at transmembrane pressure of above 10 bar for AMD filtration using NF90 membrane (Wadekar et al., 2017; Pino et al., 2020). Jamil et al. (2021) documented that NF90 demonstrated excellent inorganic salt and dissolved organic rejection at low operational pressure of 2–5.5 bar. Therefore, a low trans-membrane pressure of 3 bar was chosen for this study to analyse performance of NF90 for AMD filtration at a temperature of 25 ± 1 °C. The feed solution was continuously circulated while permeate was collected and its increase in mass measured using analytical balance. Permeate flux and water recovery were calculated based on readings measured from analytical balance at constant intervals. At completion, initial feed, final feed (concentrated feed) and permeate were analysed for metal concentrations, pH and TOC.

The volume concentrating factor (VCF) of the concentrated feed was determined using the following equation:

$$VCF = \frac{V_i}{V_c} \tag{1}$$

Where,
V_i - Initial AMD feed volume (L)
V_c - Final concentrated AMD volume (L)

Permeate flux of the membrane was calculated by measuring the permeate volume collected at 5 min intervals using the following equation:

$$J = \frac{V}{Ax\Delta t} \tag{2}$$

J- Permeate Flux (l/m^2h)
A- Effective filter area of membrane (m^2)
Δt - Time interval (h)

Osmotic pressure (bar) across the membrane was calculated using Van't Hoff equation as reported by Zhang et al. (2020b)

$$\pi = iMRT \tag{3}$$

i - Van't Hoff Factor
M- Molarity of Solute (mol/L^{-1})
R- Universal gas constant (0.08315 L bar mol^{-1} K^{-1})
T- Temperature (K)

Solute rejection was calculated from the concentration of dissolved metals in feed AMD and filtered permeate measured using ICP MS (Agilent 7900, USA):

$$R(\%) = \frac{C_i - C_p}{C_i} \tag{4}$$

R - Solute Rejection (%)
C_i - Initial solute concentration (mg/l)
C_p - Permeate solute concentration (mg/l)

2.3. Preparation of powdered eggshell for TOC removal

Eggshell was examined as a cost-effective solution for selective removal of OM as discussed in the introduction (Zulfikar et al., 2013). The eggshell sample was first washed with detergent and the inner thin membrane under the shell was then removed. The cleaned eggshell was further washed with Milli Q water and air dried for 48 h. The dried eggshell was then ground to a particle size of 75 µm using a mortar and pestle.

2.4. MOF synthesis procedure

Cr-MIL-PMIDA was synthesized using Chromium(III) nitrate nonahydrate, $H_2BDC-NH_2$ and PMIDA as previously reported by Fonseka et al. (2021). The synthesis procedure is described in detail in supplementary text S1.

2.5. SBA15 synthesis procedure

SBA15 was synthesized through hydrothermal reactions and modified with amine ligands following toluene reflux with APTES as previously and recently reported by Ryu et al. (2021). The details of the synthesis are provided in supplementary text S2.

2.6. Characterization of adsorbents

2.6.1. Crystalline structure

Structures of Cr-MIL-NH_2, Cr-MIL-PMIDA, pristine SBA15 and amine-grafted SBA15 were examined using X'Pert PRO Multi-Purpose X-ray Diffractometer (Panalytical, Netherlands) with Cu Kα radiation. The instrument was operated at 0° to 30° range maintaining a 2°/min scan rate at 40 kV and 20 mA.

2.6.2. Physical properties

Physical properties of the adsorbents were established by conducting nitrogen adsorption and desorption studies. Analysis was carried out using Nanoporosity (Mirae SI, South Korea) instrument at 77 K. Brunauer–Emmett–Teller (BET) surface area of samples were calculated using isotherm data obtained in $0 > P/P_0 > 0.5$ range. The Barrett–Joyner–Halenda (BJH) method was implemented to estimate the pore size distribution and pore volume.

2.6.3. Surface morphology

Fourier transform infrared spectroscopy (FTIR) analysis was done using a FTIR-410 (Jasco Co., Japan) spectrometer to identify chemical bonds and vibrations present on the surface of the adsorbent. Field emission transmission electron microscope (FE-TEM) analysis was conducted using a JEM-2100F (JEOL, Japan) instrument to analyse surface morphology. Elemental composition of adsorbent was identified and mapped using an energy dispersive X-ray spectrometer (EDS) in FE-TEM. Scanning electron microscopy (SEM) images were obtained using a Supra 55VP (Zeiss, Germany) field emission instrument operated at 15 kV. Physical and chemical characterization analyses of adsorbents are presented in supplementary text S3.

2.7. REE and Cu selective adsorption experiments

2.7.1. Influence of pH

Concentrated feed solution obtained from the NF filtration was used in this study. Initial pH of concentrated feed was found to be 2.0 ± 0.2. pH was then adjusted to values ranging from pH 2 to 7 using 1 M KOH to: firstly, precipitate competing ions from solution; and secondly, establish the best pH level for the adsorbents to recover REE and Cu. The precipitate was allowed to settle under gravity for 12 h and then the supernatant was filtered using a 0.45 μm syringe filter.

2.7.2. Selective recovery of REE (Gd and Eu)

Optimum pH of 5 was used in these experiments. Cr-MIL-PMIDA adsorbent, ranging from 0.02 g to 0.32 g was used to find the desired adsorbent dosage for selective REE recovery. The adsorbent was mixed with 50 ml of pH adjusted NF concentrated feed solution and then stirred on a flat shaker for 24 h to reach equilibrium. Samples were then filtered and analysed for initial and residual concentration of elements (ICP-MS, Agilent 7900, USA).

2.7.3. Selective recovery of Cu

Residual solution after Cr-MIL-PMIDA adsorption was used in this experiment. Dosages of 0.02 g to 0.32 g of SBA15 were mixed with residual solution and similar experimental conditions to REE adsorption was maintained. Initial and residual concentrations of elements were measured to find the optimum adsorbent dosage (ICP-MS, Agilent 7900, USA). Recovery of elements for both selective adsorption experiments were calculated according to the following equation:

$$\text{Recovery efficiency (\%):} \qquad \frac{C_0 - C_t}{C_0} \times 100 \tag{5}$$

3. Results and discussion

3.1. Performance of low-pressure NF

The performance of bench scale low-pressure NF was analysed using the NF90 membrane supplied by Sterlitech Corporation, WA, USA. Experiments were carried out to evaluate AMD remediation and its ability to produce clean water while increasing the concentration of REE and Cu in the feed. A low feed pressure of 3 bar with a cross-flow velocity of 0.35 m/s (Reynolds Number = 4635) was used in the experiment. The performance of NF was measured using synthetic AMD with and without organic matter.

The results from the experiment show that the NF system achieved steady permeate flux of 15.5 ± 0.2 L/m^2h (LMH) for AMD feed without organic matter. The initial permeate flux for AMD feed with organic matter was 10.2 ± 0.3 L/m^2h (LMH), which is considerably lower compared to the experiment without organic matter. The initial osmotic pressure on the feed side was calculated using Eq. (3) and it was found to be 0.895 bar. Both sets of samples maintained a steady flux up to a volume concentration factor (VCF, Eq. (1)) of 5, recovering 80% of permeate. Solute rejection (Eq. (2)) in both cases were found to be high (> 98%) with the exception of Na. MWCO (molecular weight cut off) value is the molecular weight of the smallest solute of which at least 90% is rejected by the membrane (Drioli et al., 2016). The NF90 membrane consists of positively charged functional groups on its surface. This creates an electrostatic field within the membrane matrix known as the Donnan potential (Mehiguene et al., 1999). This significantly contributes to membrane potential which inhibits transfer of positively charged ions across the membrane. This may be the main reason for the high rejection rates recorded for higher valent cations in AMD. In theory, solutes of lower molecular weights than MWCO should pass on to the permeate side (Franke et al., 2019). According to Franke et al. (2019), when electrostatic repulsion dominates size exclusion, solutes with lower molecular weights were found to be rejected more than expected. This explains the slightly higher rejection rate found for positively charged Na in this study (see Table 1).

The reduction in permeate flux can be attributed to the presence of organic matter which increased pore blocking due to membrane fouling. According to Jamil et al. (2021), NF90 has a contact angle of 79° making it weakly hydrophilic. Studies also found that NF90 is one of the roughest (63 nm) measured using the atomic force microscopic measurement (Xu et al., 2005; Jamil et al., 2021). The rough surface promotes higher deposition of organic matter on the membrane leading to more severe flux decline. Therefore, identifying a cost-effective method to remove organic matter prior to the NF process can significantly increase permeate flux and reduce operation time (see Fig. 2).

3.2. Adsorption of organic matter using powdered eggshell

Coagulation (Callegari et al., 2017), adsorption using activated carbon (Korotta-Gamage and Sathasivan, 2017) and Ultra Filtration (UF) (Brehant et al., 2002) were conventional methods explored for OM removal prior to NF. Coagulation requires the addition of reagents which could increase cost while there is a risk of valuable metals settling out with flocs. Utilizing an UF system could result in higher operational and maintenance costs, while activated carbon has a high affinity to heavy metals which hinders selective recovery of valuable metals (Zhao and Yu, 2015).

Table 1
Permeate quality and solute rejection rates.

Element	Initial Concentration (mg/l)	Permeate quality (mg/l) (AMD with Organic)	Rejection %	Permeate quality (mg/l) (AMD without Organic)	Rejection %
Na	112.92	11.23	90.05	10.56	90.65
Al	101.64	1.33	98.69	1.69	98.34
Ca	168.54	1.92	98.86	1.65	99.02
Cu	107.48	1.52	98.59	1.08	99.00
Fe	302.90	5.20	98.28	2.64	99.13
Mg	300.95	3.65	98.79	3.12	98.96
Ni	6.02	0.08	98.67	0.07	98.84
Zn	101.34	0.95	99.06	0.81	99.20
Gd	0.51	0.0149	97.08	0.0009	99.82
Eu	0.14	0.0034	97.57	0.0042	97.00

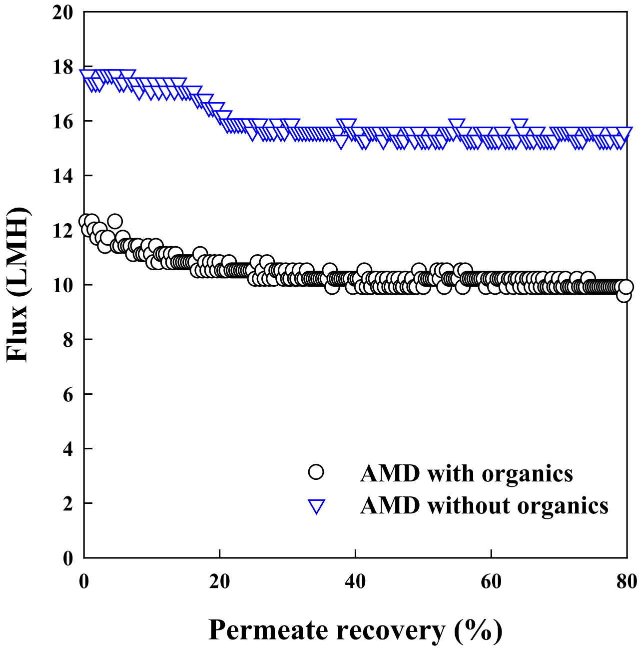

Fig. 2. Permeate flux for AMD with organics and AMD without organics.

Powdered eggshell, which can be easily sourced, was analysed as a low-cost adsorbent for removal of organic matter from synthetic AMD. According to Zulfikar et al. (2013), powdered eggshell has a crystalline structure with a similar morphology to calcite. The point of zero zeta potential for eggshell was found at pH 8.7 ± 0.2, where surface charge becomes positive in acidic conditions (Labidi, 2008). It was also found that close to 50% (initial concentration of 238 mg/l) of organic matter from a solution can be removed in less than 15 min using powdered eggshell (5 g mixed in 50 ml solution). The high initial removal rate is attributed to abundant free sites available for uptake of organic matters. Egg shell reaches equilibrium in about 60 min of contact time (Zulfikar et al., 2013). This contact time was used in our experiment. In their research, Zulfikar et al. (2013) discovered that highest organic removal was recorded at pH 2, which is a similar pH value to synthetic AMD used in our experiment. Here, powdered eggshell could be used without adding chemical reagents for pH correction.

Varying quantities of powdered eggshell were added to 50 ml of AMD solution with organics to assess the removal efficiency and optimum dosage. Adsorbent dosage ranging from 0.1 g/L to 1.6 g/L were used in this experiment to identify the optimum dosage to increase removal of organics with minimum loss of REE and Cu. Fig. 3 shows that an eggshell dosage of 0.2 g/L was optimum. Eggshell adsorbed all organics present in AMD while the loss of REE was relatively minimal. It was discovered that adsorption of REE and Ca leaching significantly increased at higher eggshell doses. The increase in the Ca concentration in AMD was due to eggshell leaching where calcite is rapidly dissolved under acidic conditions. Furthermore, eggshell adsorbed Fe in the solution as illustrated in Fig. 3. Consequently, it was very

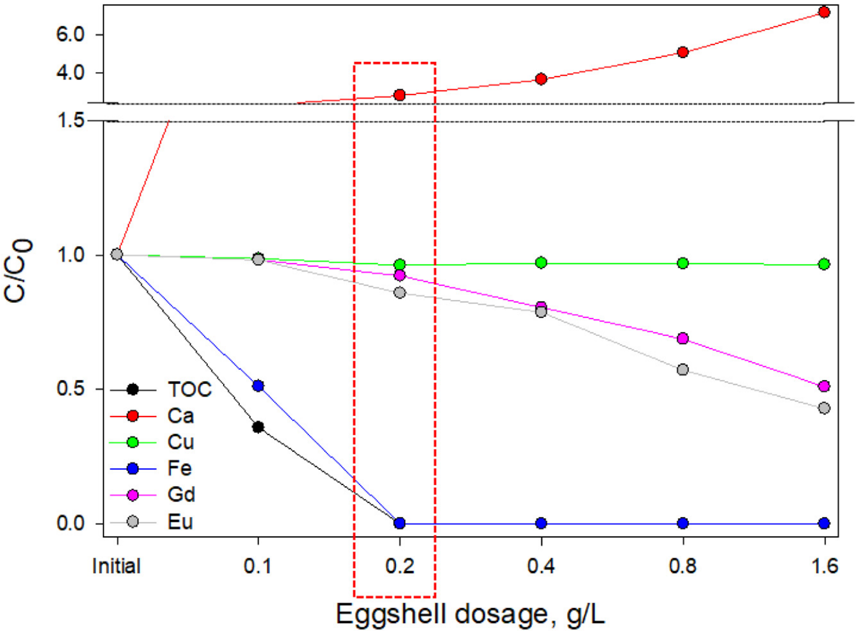

Fig. 3. Adsorption of TOC and dissolved metals onto eggshell (Contact time: 1 h).

evident that eggshell treatment managed to remove two membrane fouling agents (Fe & dissolved OM) without affecting concentrations of targeted valuable metals.

3.3. Influence of pH on adsorption

Adsorption capacity is highly influenced by the pH of the solution. According to Lee et al. (2018), REE forms coordinated bonding between deprotonated phosphonic, carboxyl, carbonyl and ammine groups on the adsorbent surface. Highly acidic conditions would therefore protonate functional groups in the adsorbent resulting in the formation of repulsive force with trivalent REE ions. Subsequently, high pH values are favoured for enhanced binding capacity. Ashour et al. (2017) state that REE can form electrostatic bonds with $-NH_2$-OH^- functional groups at high pH conditions. At pH>7 REE are found to form insoluble $REE(OH)_3$ (Hatanaka et al., 2017; Zhang and Honaker, 2018). Lee et al. (2018) showed that optimum Gd^{3+} adsorption on Cr-MIL-PMIDA was achieved at pH 5–5.5. Zeta potential analysis conducted on Cr-MIL-PMIDA also shows that negative charges on the surface significantly increase at pH >5 (Lee et al., 2018). Prior studies conducted on Cu adsorption onto mesoporous silica found that pH>4 should be maintained to avoid protonation of amine ligands (Shahbazi et al., 2013). In their work, Ryu et al. (2019) found that solution pH in the 5.0–5.5 range yielded the maximum adsorption capacity for Cu uptake onto modified mesoporous silica. Furthermore, the pH of concentrated feed was 2.0 ± 0.3 and it was adjusted to values ranging 2.0–7.0 using 1M KOH. The composition of concentrated feed at different pH levels are tabulated in Table S4.

High concentrations of heavy metals (Ca, Mg, Zn, Cu, Al) were present in the concentrated feed of this experiment along with REE (predominantly Eu). Prior to adsorption, the pH of concentrated feed was increased to analyse solubility of dissolved metals. pH correction experiment for concentrated feed was then performed to identify optimum pH at which Al will be fully precipitated while the targeted valuable metals remained dissolved. Ryu et al. (2019) found that the type of alkaline material used for pH correction influenced adsorption capacity. It was reported that using NaOH can reduce adsorption capacity since Na ions which have a small ionic radius and higher electronegativity interact with active sites of the adsorbent, competing with targeted metals (Reed, 2002; Ryu et al., 2019). Therefore, 1 M KOH was used to raise the solution's pH and the sample was left undisturbed for 2 h to allow precipitates to settle.

Figure S5 shows Fe and Al were completely precipitated at pH 5, while 70% of REE and Cu still remained dissolved. At pH 6, the majority of REE had precipitated which made recovery inefficient. Therefore, pH 5 appears to be the optimum condition for concentrated feed where a majority of targeted metals remain dissolved while all competing trivalent cations are precipitated. The study conducted by Balintova and Petrilakova (2011) found that 97% of Fe is precipitated at pH 4, while 93% of Al is precipitated at pH 5. Furthermore, the study conducted by Ryu et al. (2020) reported both Fe and Al completely precipitates at pH >5 due to the two metals' low solubility limits. The finding is beneficial as Fe and Al were found to reduce selective adsorption capacities of both SBA15 and Cr-MIL-PMIDA (Lee et al., 2018; Ryu et al., 2019). Hence, pH 5.0 was determined as the best for valuable metal recovery and it coincides with optimum pH required for the adsorbents for maximum uptake.

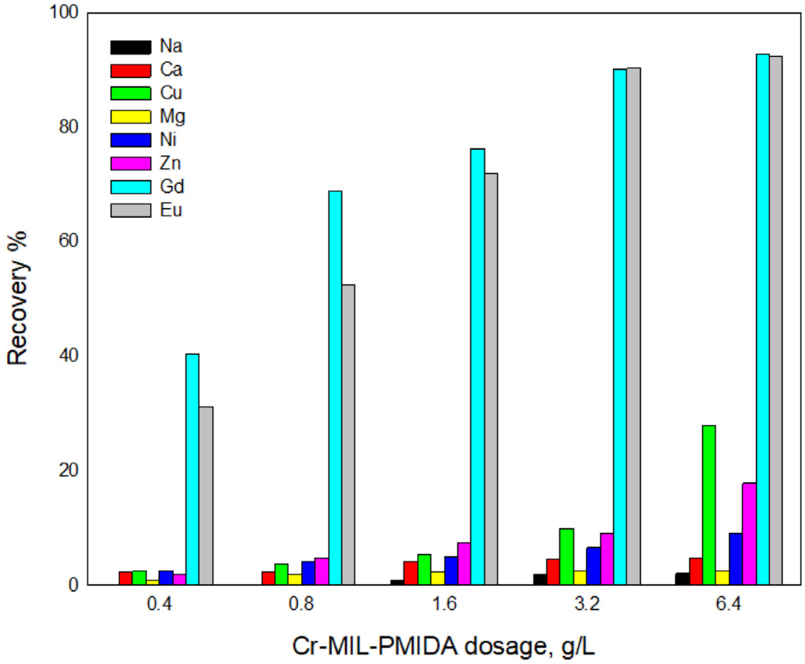

Fig. 4. Selective recovery of REE from pH adjusted concentrated NF feed (pH 5).

3.4. Selective adsorption studies

3.4.1. Selective adsorption of REE

The practical application of selectively recovering REE with Cr-MIL-PMIDA from pH adjusted concentrated feed was evaluated. 50 ml of pH adjusted solution was mixed with different Cr-MIL-PMIDA doses to identify the optimum adsorbent dose to selectively recover REE. Results from the experiment reveal that an adsorbent dosage of 3.2 g/L yields the best outcomes for selective recovery of REE (Fig. 4). At 6.4 g/L dosage the uptake of REE increased slightly, yet the uptake of Cu and Zn also increased more than 10%. This is attributed to the increased number of free sites present due to high adsorbent dosage. Also, Cr-MIL-PMIDA has residual or unreacted amine groups on its surface which is a beneficial functional group for Cu and Zn uptake (Ryu et al., 2019, 2021). Cr-MIL-PMIDA was also able to maintain significantly high REE uptake with very minimal Ca and Mg uptake, in spite of the high concentration of these elements over REE in the solution.

Similar high selectivity of REE over other transition metals were reported in recent research (Callura et al., 2018; Yang et al., 2020; Zhao et al., 2020). Most of these studies attributed selective recovery of REE to the functional group of the adsorbent, such as phosphonic, carboxyl and carbonyl groups. These functional groups are categorized into hard base groups and therefore, tend to exhibit high selectivity towards hard acidic groups such as REE over competing ions. Specifically, the synergistic effect created by the presence of different donor species in the same ligand, such as is the case with PMIDA, creates high selectivity towards REE in a multi-component solution (Reddy et al., 1999). It is also worth noting that a recent study conducted by Ryu et al. (2019) found that Cu demonstrates high chelating effect with amine groups on the adsorbent which results in high Cu adsorption. The low Cu uptake recorded in this experiment confirms the presence of a relatively low number of amine groups on the adsorbent, which can be attributed to successful reaction between the amine and PMIDA groups during the co-synthesis process. Furthermore, heavy trivalent REE such as Eu display a tendency for higher recovery due to favourable binding with active sites on the adsorbent surface compared to lower valent cations (Zhao et al., 2017). This may explain the reason for the significantly higher recovery of Gd and Eu as it favourably binds with active sites on the adsorbent surface compared to divalent cations with lower molecular weight such as Ca, Mg, Cu, Mn, and Zn.

Solvent extraction using organophosphorus acids is a widely used method to separate rare earth elements. A study conducted by Vera and Braga (2019) successfully used 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507) to separate Gd and Eu from chloride media. Another study by Li et al. (2018) found that combination of photochemical reduction and extraction chromatography can be successfully used to separate Gd and Eu with high purity.

3.4.2. Selective adsorption of Cu

The residual solution post-Cr-MIL-PMIDA adsorption was used in the experiment for Cu recovery. The experiment was conducted at pH 5.2 which was earlier identified as the optimum pH for selective Cu uptake. Varying dosages of

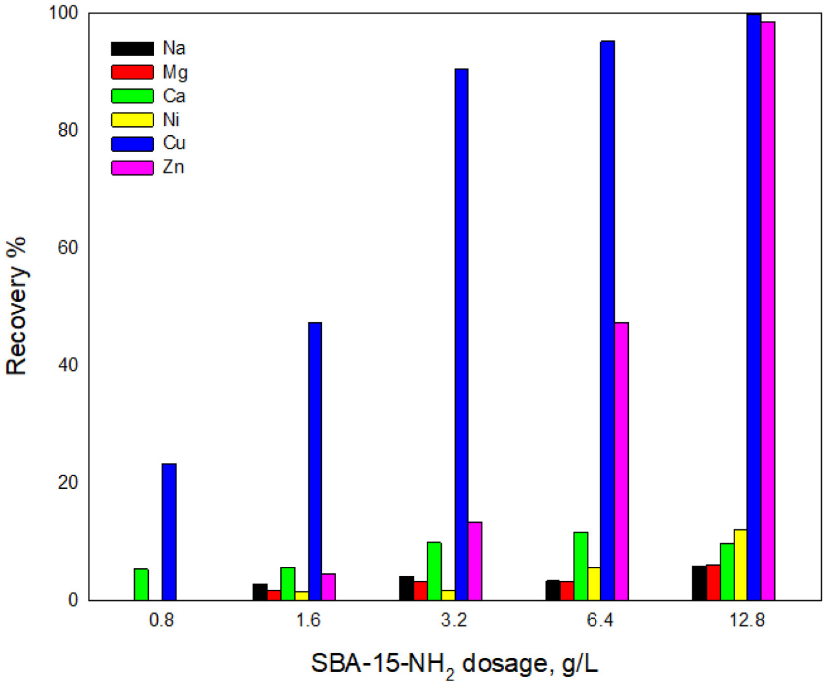

Fig. 5. Selective recovery of Cu from MOF-treated NF feed.

SBA15-NH$_2$ were mixed with 50 ml of the solution and the residual metal concentration was measured to determine the removal percentage. Fig. 5 shows Cu removal at more than 90% was recorded for adsorbent dosage above 3.2 g/L where the removal of other metals remained below 10%. At dosages of 6.4 g/L and beyond, Zn uptake on to SBA15 significantly increased. Hence SBA15-NH$_2$ dosage of 3.2 g/L was used. Previous studies show that Cu, Ni and Zn do not show any significant difference in chemical properties (Ryu et al., 2019). The ionic radius of all three metals was between 0.69 Å to 0.74 Å (Ryu et al., 2019).

Furthermore, all three metals have similar valency, and they appear next to each other in the periodic table. The absolute electro-negativity with amine groups for Cu and Zn was also found to be similar, i.e. 28.6 and 28.8, respectively (Liu et al., 2008). Ryu et al. (2019) go on to mention that theoretically Zn should have higher affinity towards ammine ligands because of its higher absolute hardness compared to Cu. Yet the high selectivity towards Cu in the presence of Zn in this experiment demonstrates that ion characteristics are not the dominant force in competitive adsorption.

High affinity of Cu towards ammine ligands can also be due to the formation of coordination complexes. Koong et al. (2013) mention that Cu forms strong chelating bonds with amine groups. Other studies also confirm that ammine ligands form strong coordination complexes that enable high selectivity (Aguado et al., 2009; Sierra and Pérez-Quintanilla, 2013). This further confirms that the formation of strong chelating bonds with amine ligands on SBA15 makes possible high selective recovery of Cu from competing metals.

3.5. Re-usability studies

The stability of Cr-MIL-PMIDA and SBA15-NH$_2$ was analysed over 5 adsorption/desorption cycles. Reusability of adsorbents is critical for practical application of this technology in industry. 0.1 M HCl solution served as the stripping agent for both adsorbents. Alkaline regeneration was used for SBA15-NH$_2$ to deprotonate ammine groups prior to subsequent application (Ryu et al., 2019). At pH below 3, protonation of ammine and phosphonic ligands occur which creates a repulsive force with positively charged REE and Cu ions (Ryu et al., 2019, 2021). This desorbs adsorbed metals onto the acidic solution. It has been reported that SBA15-NH$_2$ should be washed with NaOH to neutralize ammine charge (Ryu et al., 2019). Over 5 cycles, both Cr-MIL-PMIDA and SBA15-NH$_2$ retained over 95% of its initial adsorption capacity (Figure S5). This confirms the high structural stability of these adsorbents after repetitive use.

4. Conclusion

This experiment evaluated the efficiency of water recovery using low pressure NF from synthetic AMD and recovery of valuable metals from concentrated feed using novel adsorbents. The presence of organic pollutants decreased the flux of NF. Powdered eggshell was successfully employed as a low-cost adsorbent to remove OM prior to NF filtration resulting in a 52% flux increase (10.2 L/m^{2}h to 15.5 L/m^{2}h). 80% of water was recovered from synthetic AMD with over 95% solute rejection. Concentrated feed water was then used for selective recovery of valuable metals such as REE and Cu. Cr-MIL-PMIDA and amine-grafted SBA15 were successfully prepared in the lab and detailed characterization of the material was performed to determine their chemical and physical properties. The pH of concentrated feed was then adjusted to 5, where it was found that most of the Al and Fe precipitate while a majority of valuable metals remained dissolved.

Cr-MIL-PMIDA was found to recover over 90% of REE over highly concentrated competing ions present in pH adjusted solution. The optimum dosage was 3.2 g/L at which the uptake of competing ions remained below 10%. High selectivity towards Eu is attributed to affinity with carboxylate and phosphonic groups, coupled with electrostatic bonding with residual amine groups. Amine-grafted SBA15 was then used as an adsorbent to selectively recover Cu from residual solution. At 3.2 g/L dosage of SBA15-NH$_2$, over 90% of Cu was recovered while the uptake of other competing metals remained below 10%. Formation of coordination complexes between Cu and amine ligands was found to be the driving force behind the high selectivity.

Cyclic adsorption and desorption study showed that both Cr-MIL-PMIDA and SBA15-NH$_2$ retained over 95% of the initial adsorption capacity for recovering REE and Cu, respectively, even after 5 cycles. Discharge of untreated AMD has become a global environment concern. The sustainable approach to resolve this issue is through active industry participation. The study demonstrates that combining low pressure NF and adsorption for AMD treatment not only enables recovery of clean water for industrial operations, it also creates additional income through recycling of valuable metals which can offset treatment costs. Table S5 shows that 0.06 mg, 0.015 mg and 10.24 mg of Gd, Eu and Cu can be recovered, respectively, by processing 1L of AMD using this treatment process. This enables financially viable and sustainable treatment of AMD approaching zero liquid discharge.

CRediT authorship contribution statement

Charith Fonseka: Experiment execution and writing. **Seongchul Ryu:** Experiment modelling and review. **Gayathri Naidu:** Experiment review. **Jaya Kandasamy:** Supervision and review. **Saravanamuthu Vigneswaran:** Overall supervision, Experimental review, Writing and execution.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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