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Acid mine drainage treatment by integrated submerged membrane distillation –sorption system

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Abstract

Acid mine drainage (AMD), an acidic effluent characterized by high concentrations of sulfate and heavy metals, is an environmental and economic concern. The performance of an integrated submerged direct contact membrane distillation (DCMD) – zeolite sorption system for AMD treatment was evaluated. The results showed that modified (heat treated) zeolite achieved 26-30% higher removal of heavy metals compared to natural untreated zeolite. Heavy metal sorption by heat treated zeolite followed the order of Fe>Al>Zn>Cu>Ni and the data fitted well to Langmuir and pseudo second order kinetics model. Slight pH adjustment from 2 to 4 significantly increased Fe and Al removal rate (close to 100%) due to a combination of sorption and partial precipitation. An integrated system of submerged DCMD with zeolite for AMD treatment enabled to achieve 50% water recovery in 30 h. The integrated system provided a favourable condition for zeolite to be used in powder form with full contact time in a storing tank. Likewise, heavy metal removal from AMD by zeolite, specifically Fe and Al, mitigated membrane fouling on the surface of the hollow fiber

submerged membrane. The integrated system produced high quality fresh water while concentrating sulfuric acid and valuable heavy metals (Cu, Zn and Ni).

Keywords

Acid mine drainage, Heavy metal, Integrated process, Submerged membrane distillation, Sorption, Zeolite

1. Introduction

The formation of acid mine drainage (AMD) is a natural process attributed to the oxidation of sulfide minerals such as pyrites (Kalin et al., 2006; Mosley et al., 2018). Active and abandoned mines intensifies the formation of AMD due to open pits, mining waste rock, structures and tailings that are exposed to water, air and bacterial activity (Kalin et al., 2006; Mosley et al., 2018; Tolonen et al., 2014). AMD is characterized by low pH and high concentration of sulfate, as well as high concentrations of heavy metals activity (Kalin et al., 2006; Mosley et al., 2018; Tolonen et al., 2014). Nearby water streams are susceptible to AMD infiltration, resulting in discoloration of streams, decrease in pH and accumulation of heavy metals. In Australia, there are a significantly high amount of abandoned mines (more than 50,000 mines) compared to actively operating mines (around 380 mines) (Parbhakar-Fox et al., 2014; Unger et al., 2012). An estimated total land area of 215,000 km^2 around coastlines and inlands in Australia contain acid sulfate soils attributed to AMD (Fitzpatrick et al., 2009). The long-term impact of AMD contaminant on aquatic organisms, plant growth and human health is a significant concern, which necessitates AMD treatment (Mosley et al., 2018).

Conventionally, AMD is treated by using alkaline neutralizing chemicals such as caustic soda or limestone, to elevate the pH and precipitate metals (Tolonen et al., 2014). Although efficient, precipitation results in large volumes of sludge containing heavy metals that require safe disposal (Marcello et al., 2008). Various other active and passive remediation approaches such as bioremediation, wetlands, adsorption, phytoremediation are also used to treat AMD (Zhang, 2011; Vasquez et al., 2016; Crane and Sapsford, 2018). In this regard, the uptake of heavy metals by low-cost sorbents are especially promising as a cost effective treatment method for AMD.

In Australia, naturally occurring zeolites are available in large quantities at relatively low cost (Santiago et al., 2016). A significant advantage of zeolite is its tendency to adsorb cations. The ion exchange affinity of natural and synthetic zeolites for metal extraction from wastewater solution including acid mine drainage has been described by previous studies (Motsi et al., 2009; Rios et al., 2008; Wingenfelder et al., 2005). Castle Mountain, Australia produces a natural clinoptilolites (An et al., 2011). The uptake of heavy metals from AMD by Australian natural clinoptilolites may offer a low cost treatment option for AMD. In this regard, a number of approaches are used to enhance the sorption capacity of natural zeolite such as heat treatment, surface and chemical modification (Motsi et al., 2009; Taffarel and Rubio, 2010; Turner et al., 2000). Motsi et al. (2009) reported on the enhanced heavy metal removal of natural zeolite upon microwave and furnace heat treatment. Heat treatment for enhancing the performance of natural zeolite is especially attractive given that it requires no additional chemicals and complex processes.

Compared to the conventional approach of treat and discharge, more focus is now being placed on achieving water reuse for AMD treatment. Therefore, membrane technologies are

becoming favourable AMD treatment options. This is especially reflected by the increase in the implementation of membrane treatment processes such as reverse osmosis (RO) and nanofiltration (NF) at actual mining sites (Aguiar et al., 2016; Ambiado et al., 2017). Although NF and RO do meet good water reuse standards, membrane fouling and low recovery rate remain challenges. In view of this, recent studies are exploring the potential of alternative membrane processes such as electrodialysis, and forward osmosis for AMD treatment. For instance, Martí-Calatayud et al. (2014) reported on the promising capacity of electrodialysis for treating AMD but inorganic membrane precipitation by metals such as iron was a significant drawback. Similarly, Vital et al. (2018) explored the feasibility of using forward osmosis with NaCl as a draw solution for treating AMD. Although FO was able to achieve more than 98% rejection of ions, the phenomenon of reverse salt flux and dilution of draw solution were major limitations.

Alternatively, membrane distillation (MD), a thermal based membrane process, has shown promising potential for treating acid based wastewater from metal pickling industry (Tomaszewska et al., 2001), and concentrating various types of acid including sulfuric acid from AMD (Kesieme et al., 2012; Tomaszewska and Mientka, 2009). The suitability of MD for concentrating acid is attributed to its capacity to achieve high rejection of non-volatile compounds with up to 90% water recovery ratio, producing good quality fresh water by using vapor pressure difference as its driving force. Additionally, MD requires minimal electrical energy requirement compared to pressure operated systems such as RO and NF while the low thermal requirement (40 – 80 °C) can be met by alternative thermal sources such as solar or waste heat (Khayet, 2013). MD offers a promising potential for achieving near zero liquid discharge for small scale treatment such as AMD (Naidu et al., 2014; Naidu et al., 2017).

Direct contact MD (DCMD) is the most studied MD configuration due to its simplicity (Naidu et al., 2017). A number of operating approaches has been considered to improve the performance of DCMD. One such approach is using submerged DCMD, in which the membrane module is submerged directly into the feed solution tank (Choi et al., 2017). This configuration enables to achieve a compact system with reduced heat losses, attributed to the elimination of feed recirculation and reheating. Another promising aspect of submerged DCMD is its flexibility to be used as an integrated single system such as a submerged membrane–sorption system (Naidu et al., 2018). The application of submerged DCMD as an integrated single system for heavy metal removal while simultaneously producing fresh water and concentrating AMD has yet to be explored.

The focus of this study is to evaluate the performance of (i) Australia's natural and modified (heat treated) zeolite for heavy metal removal from AMD (ii) submerged DCMD for producing water for reuse from AMD and (iii) integrated submerged DCMD – sorption system for simultaneously removing heavy metals and producing water for reuse from AMD.

2. Material and methods

2.1 Acid mine drainage solution

A model acid mine drainage (AMD) solution was prepared based on AMD characteristics from actual mining sites reported by previous studies (Caraballo et al., 2009; Contreras et al., 2015) (**Table 1**). The model solution was prepared by dissolving analytical grade $CaSO_4$, $MgSO_4 \cdot (3H_2O)$, NaOH, FeO(OH), $Fe(SO_4) \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich and Thermo Fisher Scientific) in Milli-Q water. The solution pH was adjusted using 10 M of concentrated sulfuric acid (H_2SO_4) (10 M). The pH and total dissolved solids (TDS) contents of the AMD solution was detected by a portable multimeter (HQ40d, HACH, US). Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7900, US) was used to analyse the cation value in AMD. Sulfate concentration was measured by ion chromatography (IC, 790 Personal IC, Metrohm, Switzerland).

Table 1 Characteristics of synthetic AMD

Parameters	Values	Unit
pH	2.0 ± 0.2	-
TDS	6.35	g/L
Ca	170	mg/L
Mg	220	mg/L
Na	50	mg/L
Fe	340	mg/L
Zn	120	mg/L
Cu	90	mg/L
Al	150	mg/L

Ni	3.5	mg/L
SO_4	4.3	g/L

2.2 Zeolite

2.2.1 Natural zeolite

The performance of natural Australian zeolite sorbent in powder form (particle size < 75 µm) for heavy metal removal from AMD solution was evaluated. The mineral composition (as supplied by Castle Mountain, NSW, Australia) is listed in **Table 2**. This natural zeolite with a bulk density of is 2.7 g/cm^3 is mainly encompassed of clinoptilolite (~85 wt%) with minor percentages of quartz and mordenite (~15 wt%).

2.2.2 Heat treated zeolite

Heat treatment method was used to potentially enhance the performance of natural zeolite (Motsi et al., 2009; Turner et al., 2000). Heat treatment was chosen as it requires no additional chemicals and complex modification process. Heat treatment was carried out by placing an appropriate amount of powder form natural zeolite in a ceramic dish. The ceramic dish was then placed into preheated air atmosphere muffle furnace (Labec Laboratory Pty Ltd, NSW, Australia). Heat treatment was carried out at four different temperatures of 300, 400, 500 and 600 °C for 24 h. Upon heat treatment, the zeolite sorbents were stored in air tight containers in a desiccator.

Table 2 Natural zeolite chemical contents

Chemical content	wt.%
SiO_2	71.81
Al_2O_3	12.10

CaO	2.60
Na_2O	2.33
Fe_2O_3	1.14
K_2O	0.90
MgO	0.65
TiO_2	0.22
MnO	0.03
SrO	0.22
P_2O_5	<0.01

152

153 **2.3 Zeolite characteristics**

154 **2.3.1 Surface area and pore width distribution**

155 Nitrogen adsorption test was used to determine the Brunauer–Emmett–Teller (BET) specific
156 surface area and the Barrett–Joyner–Halenda (BJH) pore width distribution of the natural and
157 heat treated zeolite samples. Nitrogen adsorption test was measured with a Micrometrics
158 ASAP 2020 HD analyzer using low temperature, per the procedure of ISO 9277 and ISO
159 15901-2.

160

161 **2.3.2 Crystal structure**

162 X-ray diffraction (XRD) (Siemens D5000 diffractometer operating with Cu-Kα radiation
163 source) was used to detect the crystal structure of zeolite (natural and heat treated samples) in
164 powder form. A rotating sample stage was used to scan the samples at 2θ angular range of 10
165 to 80° in room temperature.

166

167 **2.3.3 Surface morphology and element contents**

A scanning electron microscopy (SEM) ((Zeiss Supra 55VP Field Emission) was used to analyse the zeolite surface characteristics (before and upon sorption). The SEM was integrated with energy dispersive X-ray spectroscopy (EDX) (15kV accelerating voltage) in order to analyse the element contents in zeolite.

2.3.4 Influence of pH and surface charge

The pH influence on heavy metal sorption by zeolite was determined by varying the pH of AMD solution from 2 to 5. The initial pH of the solution was adjusted using 10 M of H_2SO_4 and NaOH. Zeolite (10 g/L) was placed in beakers with 100ml AMD solution. The pH of the initial solutions were varied. The flasks were kept suspended for 12 h in a shaker (120 rpm) at ambient temperature (24 °C). The initial and final pH of the AMD solution in the beakers were recorded.

Zeolite surface charge was determined using zeta potential measurement. For this purpose, zeolite (1 g/L) placed in beakers with 100ml AMD solution. The pH of the initial solutions were varied from 1 – 9. The flasks were kept suspended for 12 h in a shaker (120 rpm) at room temperature (24 ± 1 °C). Zetasizer (nano instrument ZS Zen3600, UK) was used to analyse the zeolite surface charge.

2.4 Sorption study

2.4.1 Equilibrium

For equilibrium sorption in batch study, zeolite with varying doses ranging from 0.10 – 15 g/L was added to beakers containing 100 ml of AMD solutions. The beakers were kept suspended for 12 h in a shaker (120 rpm) at room temperature (24 ± 1 °C) to achieve equilibrium sorption. The solution pH was maintained at 2.0 ± 0.2 to evaluate the

performance of zeolite in actual acidic AMD condition and to ensure no precipitation of heavy metal occurred at increased pH. The concentration of heavy metals (Fe, Al, Zn, Cu and Ni) in AMD solution before and after sorption was analysed using ICP-MS. Q_e (mg/g), equilibrium sorption capacity, was represented by Eq. (1):

$$Q_e = \frac{V(C_i - C_e)}{M} \quad (1)$$

V (L)= solution volume and *M (g)* = sorbent mass. C_i and C_e are the concentrations of the heavy metals at initial and equilibrium, respectively.

Isotherm models (Langmuir and Freundlich) were used to analyse the equilibrium sorption data as below:

Langmuir isotherm: $Q_e = \frac{Q_m b C_e}{1 + b C_e}$ (2)

Freundlich isotherm: $Q_e = K C_e^{\,1/n}$ (3)

in which, Q_m (mg/g) is the sorption at maximum capacity and b (L/mg) is the Langmuir constant in relation to the affinity of site binding. K ($g^{1-n}\,L^n g^{-1}$) is Freundlich constant which relates to the affinity of the sorption and 1/n is a dimensionless parameter related to surface heterogeneity.

2.4.2 Kinetics

Sorption kinetics was conducted in beakers containing AMD solution (100 ml) and zeolite at a dose of 10 g/L. The solution pH was maintained at 2.0 ± 0.2. The beakers were kept suspended in a shaker (120 rpm) at room temperature (24 ± 1 °C). At varying time from 0.08 h up to 24 h, the solutions in the beaker was collected and the metal contents were measured. The kinetic sorption data were computed using kinetic models (pseudo-first and second order) as presented by Eq. (4) and (5):

$$\text{Pseudo first order: } \frac{dQ_t}{dt}_t = k_1(Q_e - Q_t) \quad (4)$$

$$\text{Pseudo second order: } \frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (5)$$

The parameters, k_1 and k_2, represent the adsorption rate (h^{-1}), Q_t and Q_e are the sorption capacity (mg/g) at time t and at equilibrium, respectively.

2.5 Submerged direct contact membrane distillation

A direct contact membrane distillation (DCMD) in submerged condition was used in this study to evaluate the potential of water reuse from AMD solution (**Fig. 1**). The set-up consists of a double wall feed tank containing AMD solution with a submerged hollow fiber membrane made of polyvinylidene fluoride (PVDF). The membrane was obtained from Econity, Republic of Korea) (Choi et al., 2017; Yao et al., 2018). The membrane pore size, inner and outer diameters, wall thickness, and contact angle are 0.1 μm, 0.7 mm and 1.2 mm, 250 μm and 106 ± 2° respectively. The membrane module was made of 18 fibers with 0.2 m length (active membrane area of 0.0136 m^2).

The outer wall of the double wall feed tank was circulated with heated water connected to a heating system, enabling to maintain a AMD feed solution temperature of 55.0 ± 0.5 °C. The permeate solution was maintained at 22 ± 0.5 °C using a cooling system. A gear pump was used to circulate the permeate solution at a flow rate of 0.8 L/min. The increase in permeate volume in the permeate tank was recorded over time using an electronic balance. This is used to compute the permeate flux over time. AMD solution was kept at constant volume of 0.9 L in the feed tank by replenishing fresh AMD feed solution (from a storage tank) at the same rate as the permeate production rate using a peristaltic pump.

This study evaluated the potential of combining submerged DCMD and zeolite into a single integrated process. For the integrated submerged DCMD–sorption process, AMD solution (pretreated with zeolite) was placed in the feed tank. Meanwhile in the storage tank, zeolite at a predetermined dose was kept suspended at a rate of 120 rpm (as per the batch sorption study) in 1.5 L of AMD solution. This enabled heavy metal removal by zeolite from AMD solution in the storage tank. A filter holder containing glass fiber membrane (Filtech, Australia) with a pore size of 1.1 μm was placed at the top of the holding tank to filter the used zeolite, ensuring only pretreated AMD solution enters the feed tank.

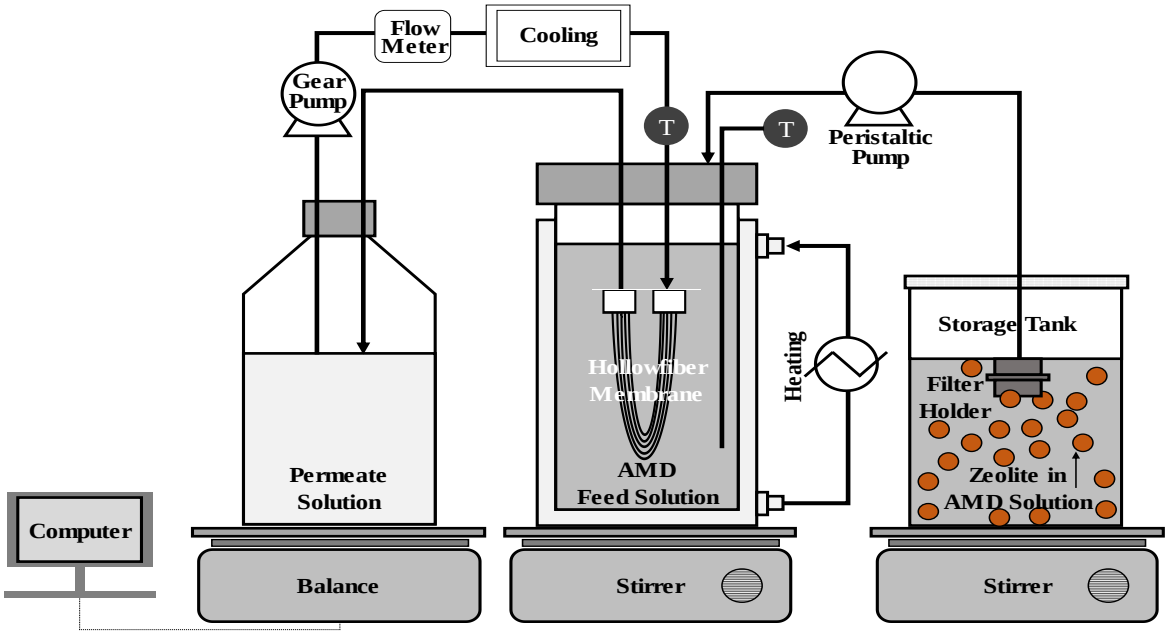


Fig. 1. Set-up of integrated submerged DCMD – sorption system

2.5.1 Membrane analysis

The morphology and element composition on the surface of the used and virgin membranes were analysed using SEM-EDX at a voltage of 15 kV as per the details mentioned in Section 2.3.3. The hydrophobicity of the virgin and used membranes were evaluated by measuring the water contact angle of the membrane using a goniometer (Theta Lite, Biolin Scientific, Sweden). Measurements were duplicated at different location of the membrane and the average value was used for this study.

3. Results and discussion

3.1 Performance of natural and modified (heat treated) zeolite

The sorption capacity of natural and modified (heat treated) zeolite was tested for heavy metal removal from AMD. Higher heavy metal removal was achieved with heat treated zeolite compared to natural untreated zeolite (**Table 3**). The removal of heavy metals increased from 1 – 12% with natural zeolite by up to 30 – 38% upon heating (500 °C).

Heating may have removed water on the surface as well as internal channels of the natural zeolite, resulting in vacant channels which enhances heavy metal sorption rate, as reported by previous studies (Ohgushi and Nagae, 2003; Turner et al., 2000). However, heavy metal removal by zeolite minimally improved beyond 500 °C of heating. This trend could be attributed to characteristics change of zeolite upon heat treatment.

Table 3 Performance of natural and heat treated zeolite with AMD solution (sorbent dose 5.0 ± 0.2 g/L, pH 2.0 ± 0.2).

Sorbent type	Heavy metal removal (%)				
	Fe	Al	Zn	Cu	Ni
Natural zeolite	12.8 ± 0.9	1.1 ± 0.2	9.4 ± 1.4	11.2 ± 0.7	10.8 ± 1.1
Heat treated zeolite					
300 °C	17.9 ± 1.6	15.7 ± 0.8	15.6 ± 2.4	17.1 ± 1.5	15.9 ± 2.0
400 °C	25.3 ± 2.2	26.1 ± 1.3	21.1 ± 2.0	22.8 ± 1.2	19.7 ± 1.9
500 °C	34.9 ± 2.7	36.3 ± 2.7	29.3 ± 2.3	31.3 ± 1.9	21.1 ± 1.3
600 °C	31.0 ± 2.5	30.8 ± 2.4	27.0 ± 2.3	29.1 ± 2.1	20.0 ± 2.9

3.1.1 Characteristics of zeolite

3.1.1.1 Surface area and pore width distribution

The surface area (BET) and pore width (BJH) of natural zeolite was 14.5 m^2/g and 147.59 Å. The surface area and pore width of zeolite showed an increasing trend with heat treatment up to 500 °C (**Table 4**). This implies that thermal heating contributed towards the activation of zeolite surface and possible removal of water (Akdeniz and Ülkü, 2007; Ohgushi and Nagae, 2005). In turn, metal removal increased (**Table 3**). On the other hand, the slightly lower surface area and pore width at 600 °C compared to 500 °C could explains the minimal changes in heavy metal removal above 500 °C (**Table 3**).

The results showed that heat treatment of zeolite at 500 °C was optimum to enhance its performance. Based on these results, 500 °C heat treated zeolite in powder form was used for all further experiments.

Table 4 Surface area and pore width of natural and heat treated zeolite.

Sorbent type	BET Surface area (m^2/g)	BJH Pore width (Å)
Natural zeolite	14.5	147.6
Heat treated zeolite		
300 °C	14.8	147.5
400 °C	15.0	148.2
500 °C	16.2	150.9
600 °C	14.9	147.9

3.1.1.2 Crystal structure

The XDR spectra (**Fig. 2**) showed similar diffraction pattern for natural and heat treated zeolite. This affirmed that heat treatment did not change the crystal structure. Further, the XRD spectra also established that the natural Australian zeolite used in this study corresponded to that of the structure of clinoptilolite, as reported by previous papers (Nguyen et al., 2015; Naidu et al., 2018).

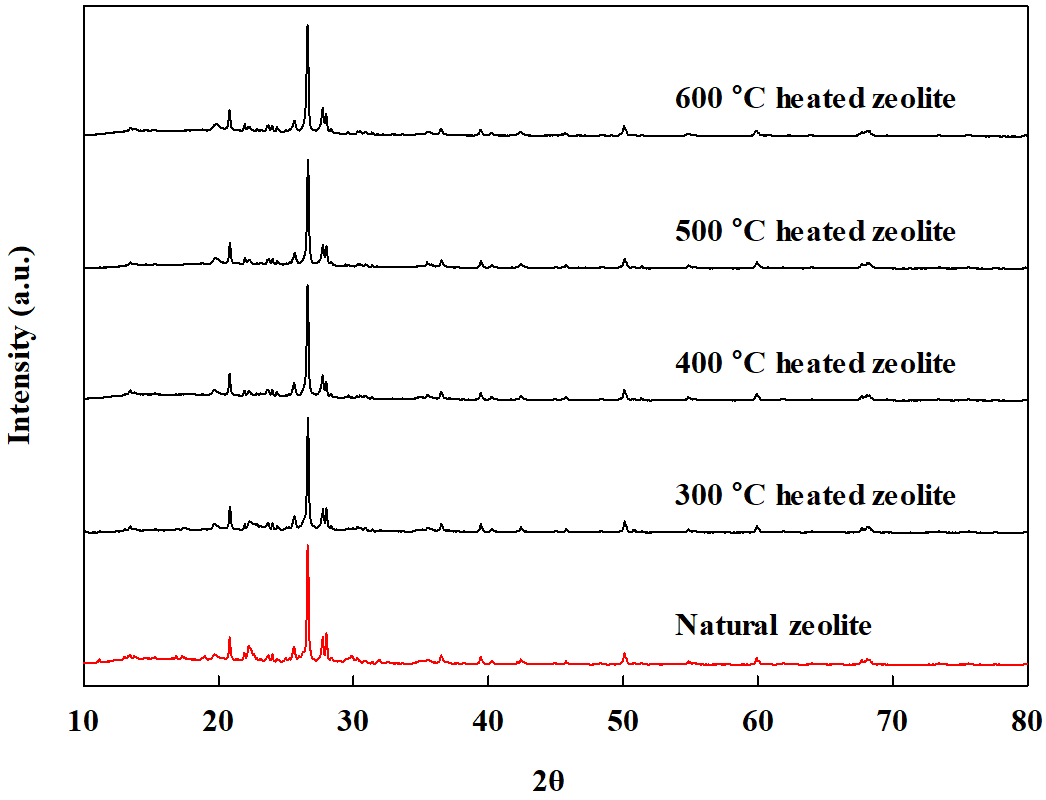


Fig. 2. XRD peaks of natural and heat treated zeolite

3.1.1.3 Surface morphology and element contents

The SEM images showed the heterogeneous condition of the zeolite (**Fig. 3**). No significant morphology changes were observed between the natural and heat treated zeolites.

The EDX established Si, O, K, Al, Mg, Na, Fe and Ca as the main element peaks in all zeolite structure (**Fig. 4**). The slight decrease of O atomic content from 67.52 in the natural zeolite to 66.61% upon heat treatment could be due to the removal of water in the internal channels (**Table 5**). The EDX analysis of heat treated zeolite (after sorption of heavy metals from AMD) showed reduction in Si, Na, Ca and K. Meanwhile the increase of Fe and Al as well as the presence of Cu, Zn and Ni establish the heavy metal sorption from AMD.

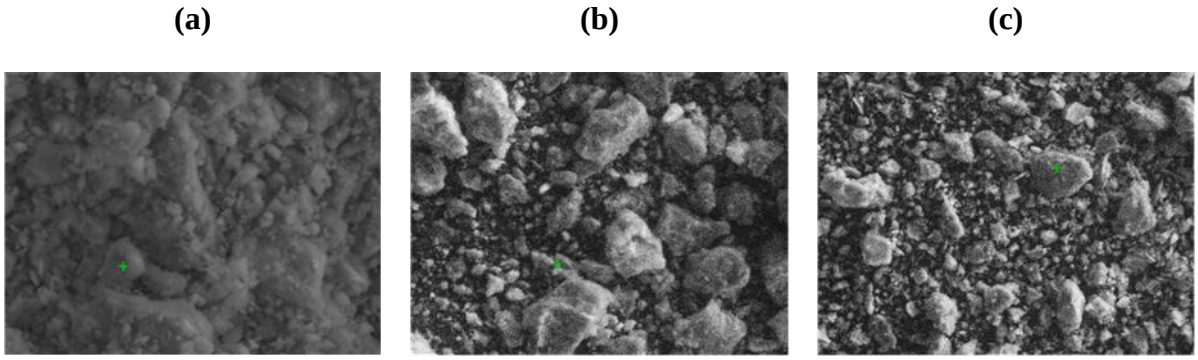


Fig. 3. SEM images of **(a)** natural untreated zeolite and 500 °C heat treated zeolite **(b)** unused/before sorption and **(c)** after heavy metal sorption

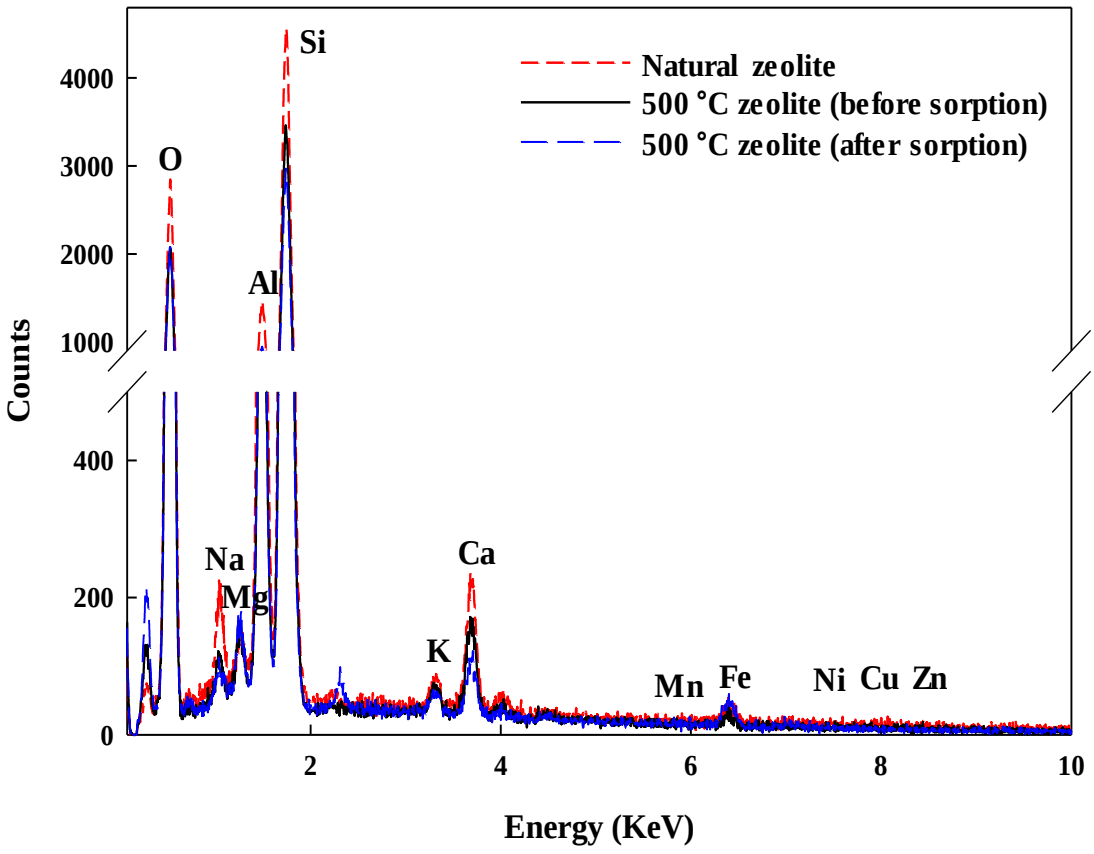


Fig. 4. EDX results of natural and 500 °C heat treated zeolite (before and after heavy metal sorption).

Table 5 EDX results of natural and 500 °C heat treated zeolite

Element	% atomic ratio		
	Natural zeolite	500 °C heat treated zeolite	
		Before sorption	After sorption
O	67.52	66.61	66.86
Si	20.95	24.68	22.56
Al	7.61	5.25	6.65
Fe	0.70	0.61	1.27
Ca	1.63	1.41	1.05
Mg	0.27	0.62	0.81
K	0.28	0.30	0.25
Na	1.06	0.54	0.39
Ni			0.10
Cu			0.04
Zn			0.02

3.1.2 Equilibrium sorption

3.1.2.1 Isotherm

Heavy metal sorption from AMD solution with 500 ºC heat treated zeolite was computed with Langmuir and Freundlich sorption isotherm (**Fig. S1** and **Table 6**).

The data satisfactorily fitted to Langmuir sorption isotherm (R^2 = 0.87 – 0.98) compared to the Freundlich sorption isotherm (R^2 = 0.79 – 0.89). Similarly, a number of studies on zeolite performance for heavy metal removal indicated the suitability of Langmuir isotherm (Motsi et al., 2009; Nguyen et al., 2015; Qiu and Zheng, 2009). Based on the sorption isotherm, heat treated zeolite capacity for heavy metal removal from AMD followed the order of

Fe>Al>Zn>Cu>Ni. Poor removal of Ni by a zeolite could be due to the high stability of its aqueous complex (Mondale et al., 1995).

The better Langmuir fitting indicated that the sorption sites were homogeneous with monolayer sorption coverage. However, not all the heavy metals achieved a fitting of R^2 above 0.95. This could be attributed to the mixed metals present at different concentrations in AMD (**Table 1**) resulting in competition of sorption. Nguyen et al (2015) compared the Langmuir fitting of heavy metal removal by zeolite and observed lower Langmuir capacity and fitting for each metal in a mixed metal solution compared to individual metal solution.

Table 6 Isotherm data (Langmuir and Freundlich) for heavy metal sorption from AMD solution at pH 2.0 ± 0.2 using 500 °C heat treated zeolite.

Heavy metal	Langmuir			Freundlich		
	Q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)(L/mg)$^{1/n}$	R^2
Fe	62.11	0.031	0.97	3.20	9.73	0.89
Al	44.64	0.072	0.90	1.40	1.34	0.83
Zn	39.06	0.114	0.98	3.65	10.38	0.85
Cu	36.10	0.075	0.95	2.67	6.11	0.81
Ni	1.09	1.326	0.91	1.96	0.62	0.90

3.1.2.2 Kinetics

Sorption of all heavy metals from AMD solution by 500 °C heat treated zeolite increased with time up to 12 hours and reached equilibrium at approximately 20 h. From the uptake curves in **Fig. S2**, it is evident that the rate of sorption was initially fast (within 4 h) and was gradually slow when approaching equilibrium. Kinetic experiment of heavy metal sorption was fitted to pseudo first and second order models (**Fig. S2** and **Table 7**). The experimental data was well matched to both pseudo first order (R^2 = 0.94 – 0.99) and pseudo second order (R^2=0.99). The calculated Q_e in both cases were almost similar to the experimental values of Q_e.

Table 7 Pseudo first and second order kinetic parameters for heavy metal sorption from AMD solution at pH 2.0 ± 0.2 using 500 °C heat treated zeolite (dose =10 ± 0.2 g/L)

Heavy metals	Q_e (exp) (mg/g)	Pseudo first order			Pseudo second order		
		Q_e (pre) (mg/g)	k_1 (hr^{-1})	R^2	Q_e (pre) (mg/g)	k_2 (g/mg/hr)	R^2
Fe	11.95	11.73	1.45	0.98	12.87	0.04	0.99
Al	6.07	6.11	2.06	0.99	6.27	0.20	0.99
Zn	3.89	3.65	1.48	0.94	4.20	0.11	0.99
Cu	3.15	2.98	1.57	0.95	3.36	0.16	0.99
Ni	0.11	0.10	1.55	0.95	0.11	5.17	0.99

3.1.3 Influence of sorbent dose and pH

Increased heavy metal removal was observed with higher zeolite dose **(Fig. 5a)**. The reducing trend of Al removal, especially above 10 g/L zeolite may be attributed to Al leaching out from the zeolite structure that contain around 12 wt% Al as Al_2O_3 (**Table 1**).

3.1.3.1 Ion exchange mechanism

Above zeolite dose of 10 g/L onwards, insignificant changes in heavy metal removal was observed. This is due to the decline in the remaining ion concentration in solution with increasing sorbent dose (Al-Haj and Ribhi, 1997). The uptake of heavy metal cations by zeolite has been well established as an exchange mechanism between the cations present in the solution and cations in the zeolite framework, mainly Na and Ca (Nguyen et al., 2015; Qiu and Zheng, 2009). The ion exchange mechanism suggest that zeolite may be more selective to monovalent cations. In this scenario, AMD solution (pH 2) contain high H ions and zeolite may preferentially adsorb monovalent H ions from the solution to divalent heavy metals (Sprynskyy et al., 2006). This could also explain the increase in the pH of AMD solution from 2.0 to 2.4 upon sorption. Thus, even as the dose of zeolite was increased, heavy metal removal rate remained low in the range of 35 to 40%.

3.1.3.2 Electrostatic sorption

Apart from the ion exchange mechanism, electrostatic sorption, which is the attraction of positively charged metal cations towards negatively charged zeolite surfaces, play an important role in influencing the uptake of heavy metals. Based on the zeta potential analysis, the zeolite surface charge showed a trend of increasing negativity from -11 mV to -30 mV as the pH of the solution was increased from 1 to 9 (**Fig. 5b**). Previous studies on natural zeolite characteristics reported similar observations of higher negative surface charge as the solution pH was increased (Englert and Rubio, 2005; Nguyen et al., 2015). Increased negative surface charge of zeolite enhances the sorption tendency onto cation metals through electrostatic sorption (outer sphere mechanism). The results of the zeta potential indicated the significant role of pH for improving metal removal from AMD.

3.1.3.3 Partial precipitation

In this study, a pH increase from 2 to 5, significantly increased the removal of Fe and Al by close to 100% (**Fig. 6**). Previous AMD studies have highlighted that, at higher pH, removal of Fe and Al is attributed to the combination of sorption and partial precipitation (Motsi et al., 2009; Wingenfelder et al., 2005). The high precipitation affinity of Fe and Al is due to the low solubility limit of both these metals at pH above 4.

Meanwhile, varying the pH from 2 to 5 only marginally improved the removal rate of Zn, Cu, and Ni. This result was contrary to a number of zeolite studies that reported on the increase in heavy metal removal rate at higher pH (Alvarez-Ayuso et al., 2003; Moreno et al., 2001; Motsi et al., 2009). Apart from heavy metals, the AMD solution used in this study contained Na and Ca that could have played a competitive role in minimizing the pH effect. Similarly, Wingenfelder et al (2005) reported on the poorer removal of heavy metals namely Cd and Zn in the presence of Ca.

Overall the results showed that modified (500 °C heat treated) zeolite in powder form enabled to remove heavy metals from AMD attributed to a combination of ion exchange, electrostatic sorption and partial precipitation. Nevertheless, it is a challenge to use the powdered form zeolite in ion exchange filter columns (Naidu et al., 2018). For this purpose, the potential of an integrated system, submerged DCMD with zeolite was evaluated in the subsequent section.

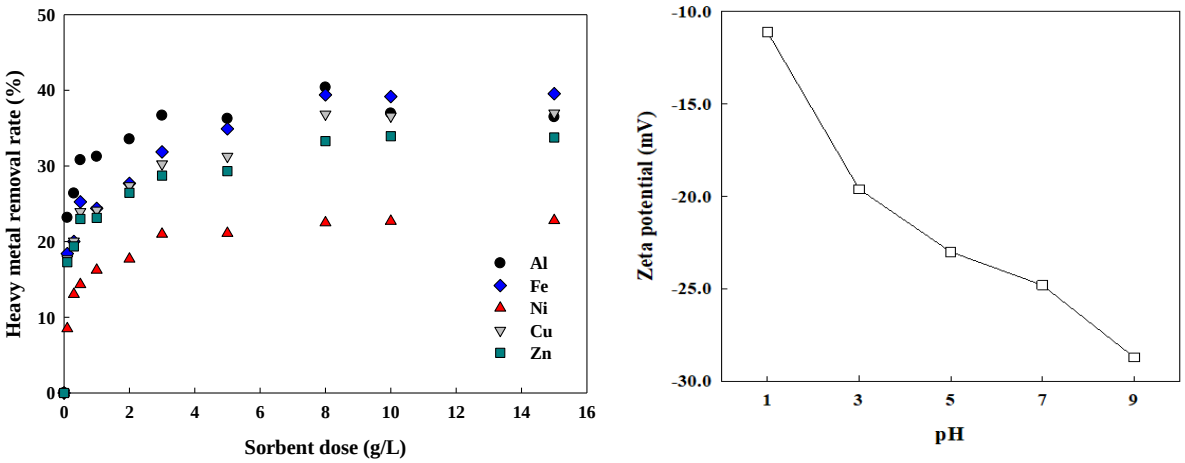
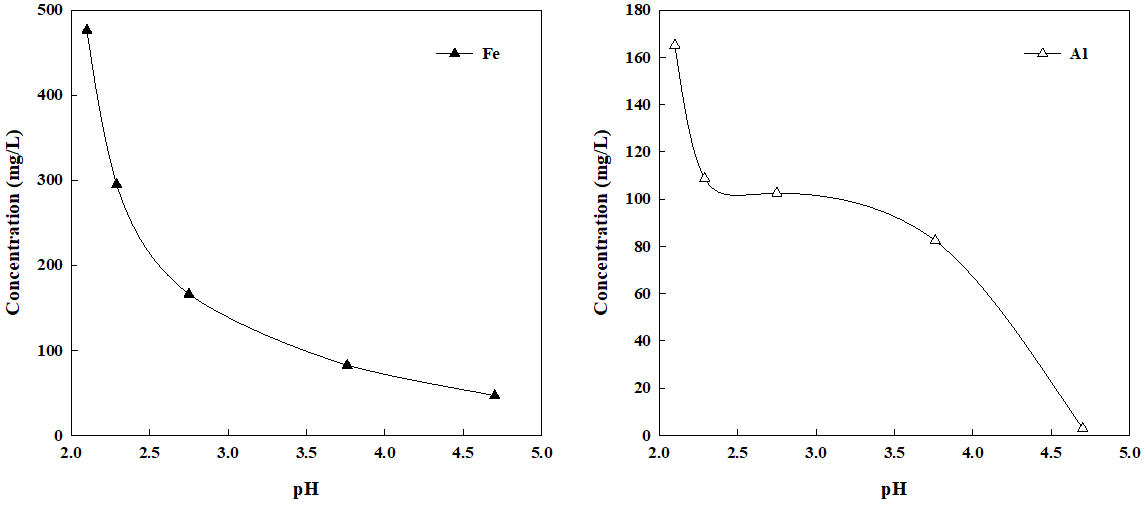


Fig. 5. 500 °C heat treated zeolite **(a)** heavy metal removal as a function of sorbent dose (pH 2.0 ± 0.2) **(b)** zeta potential as a function of pH (dose = 1.0 ± 0.2 g/L, 10^{-3} M KCl as electrolyte).



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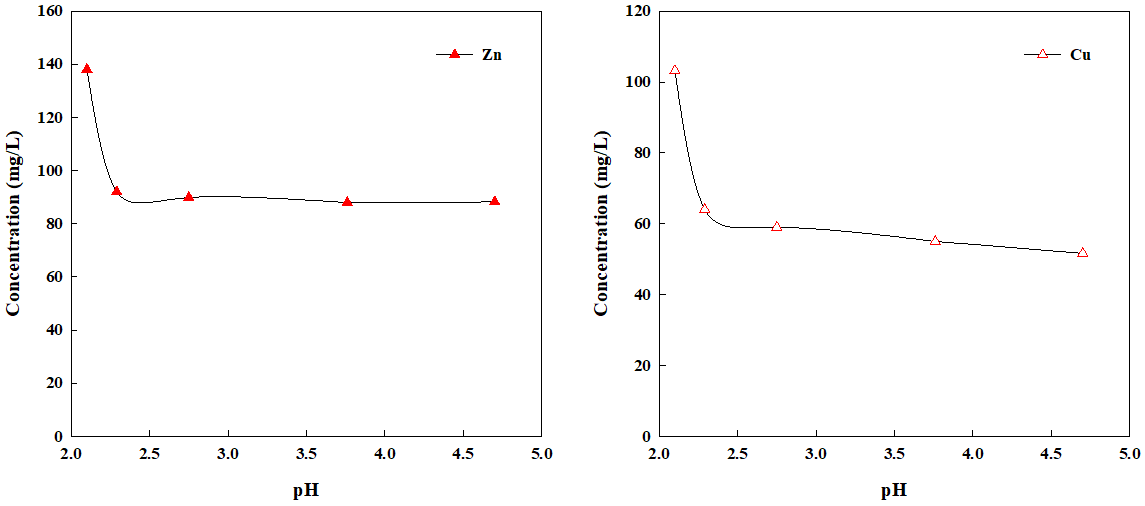

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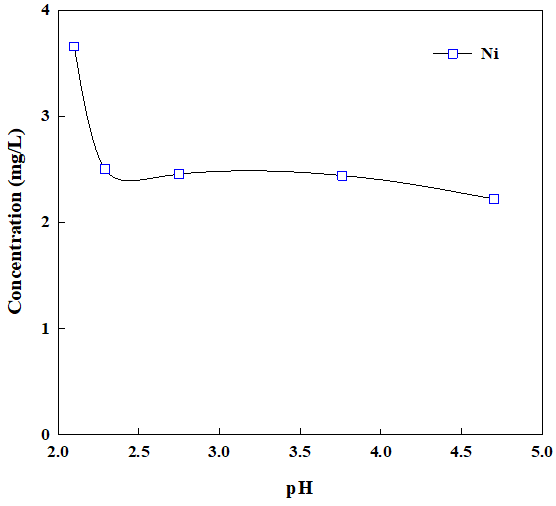


423
424

425 **Fig. 6.** Influence of pH on heavy metal removal from AMD solution with 500 °C heated

426 zeolite (dose = 10 ± 0.2 g/L)

3.2 Performance of submerged DCMD

The potential of achieving good quality water for reuse was evaluated using submerged DCMD.

3.2.1 Permeate flux and quality

An initial permeate flux of 2.5 ± 0.2 LMH was achieved (Choi et al., 2018) and the flux remained stable throughout the operation duration (30 h), enabling to achieve 50% water recovery (**Fig. 7**). The initial AMD solution (TDS of 6.4 g/L) was concentrated by 2 times (TDS of 12.9 g/L). Meanwhile, the concentration of permeate solution remained low (TDS less than 0.01 g/L). However, the sulfate concentration in the permeate solution increased significantly from 0.13 mg/L to 50 mg/L.

3.2.2. Membrane analysis

Visible brown deposition (resembling iron oxides) was observed on the used membrane (**Fig. 8b**) compared to the virgin membrane (**Fig. 8a**). SEM-EDX analysis revealed Fe, S and Al deposition on the membrane. The presence of Fe and Al on the membrane could be attributed to the high precipitation affinity of these metals at increased concentration under thermal condition (Gryta, 2007). The precipitated metals predominantly deposited on the membrane surface and was loosely attached to the surface. It is likely that the deposition only partially blocked the membrane pores, and therefore, a stable permeate flux was maintained throughout the operation duration. Nevertheless, the contact angle of the used membrane (68.6 ± 0.8°) reduced by 38 – 40% compared to the virgin membrane (109.5 ± 0.5°), suggesting that the Fe deposition resulted in the reduction of membrane hydrophobicity and partial wetting of sulfate ions.

3.3 Performance of integrated submerged DCMD-sorption

An integration of zeolite with submerged DCMD (**Fig. 1**) offers the potential for improving the performance of both processes in a single system. The integrated system enable zeolite to be used in fine powder form with long contact time (more than 24 h) when kept suspended in a storage tank. In return, the heavy metal removal by 500 °C heat treated zeolite (dose = 10.0 ± 0.2 g/L) at pH 4 will ensure minimal Fe and Al deposition onto the membrane during the submerged DCMD process.

3.3.1 Permeate flux and quality

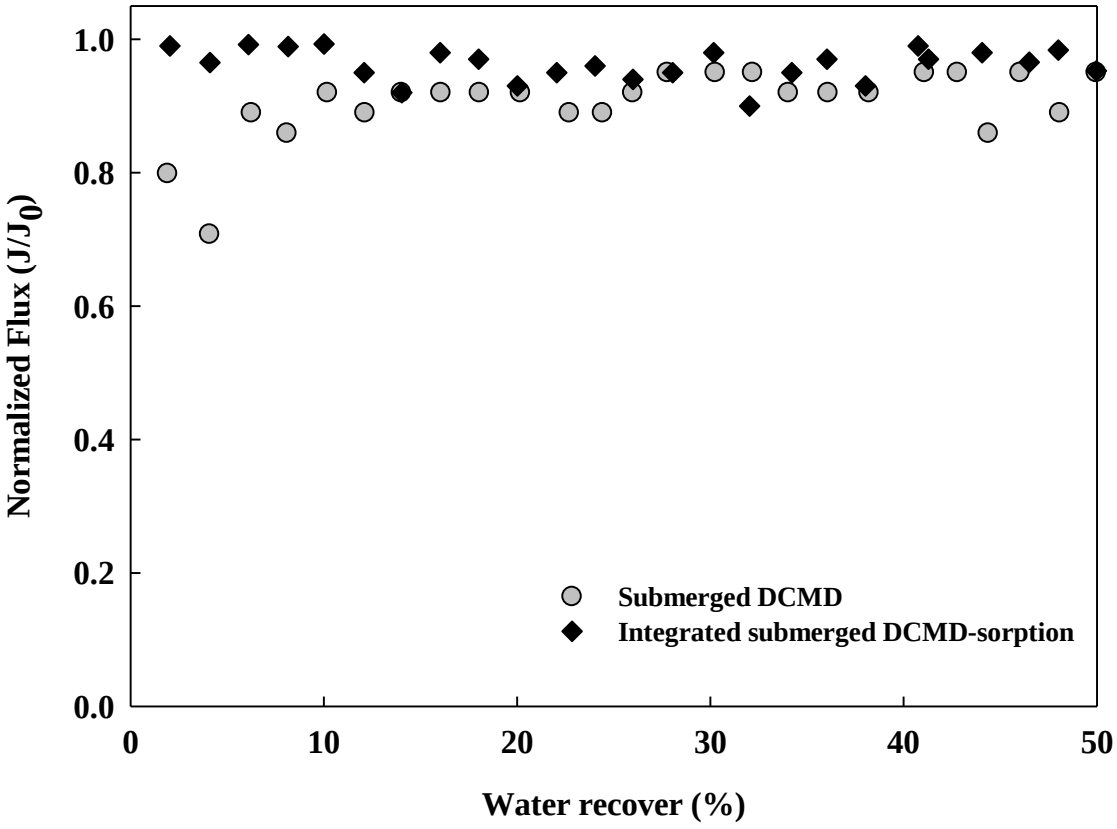
The integrated submerged DCMD-sorption system showed similar flux pattern as the submerged DCMD (**Fig. 7**), indicating that the DCMD performance was not affected by the presence of sorbent in the storage tank. The integrated system enabled to achieve high rejection of all ions, maintaining a permeate TDS of less than 0.01 g/L. The sulfate concentration in the feed solution was increased from 4.2 g/L to around 8.2 g/L, while the sulfate concentration in the permeate solution remained low (less than 0.13-0.15 mg/L).

3.3.2. Membrane analysis

The used membrane showed minimal Fe and Al depositions, according to the SEM-EDX analysis (**Fig. 8c**). The contact angle of the used membrane (99.7 ± 0.4°) only reduced slightly by 10% compared to the virgin membrane (109.5 ± 0.5°), suggesting that the membrane hydrophobicity was minimally affected. The membrane analysis established the stability of the membrane to be used to treat acidic AMD solution.

Overall, the results indicated the suitability of integrated submerged DCMD-sorption system for producing high quality water with simultaneous uptake of heavy metals by zeolite. The

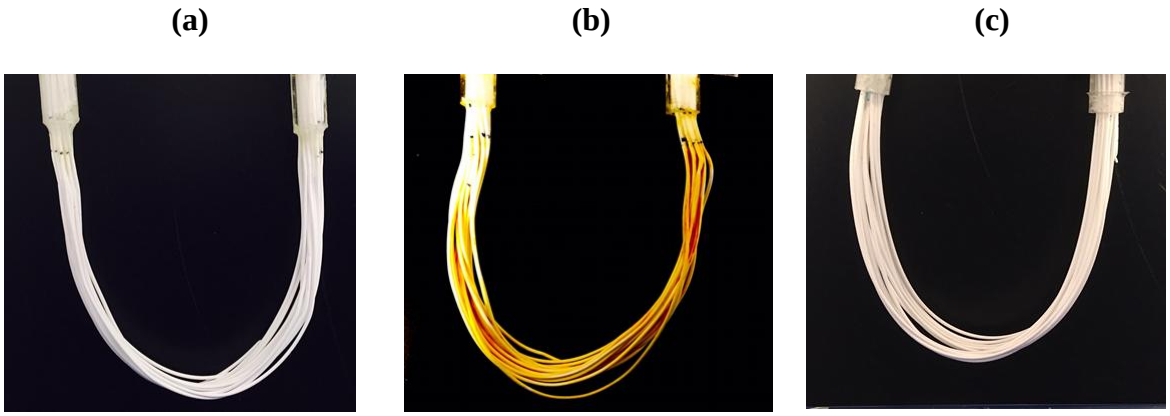
477 remaining AMD contained concentrated sulfuric acid as well as valuable metals of Cu, Ni
478 and Zn that can be selectively recovered.

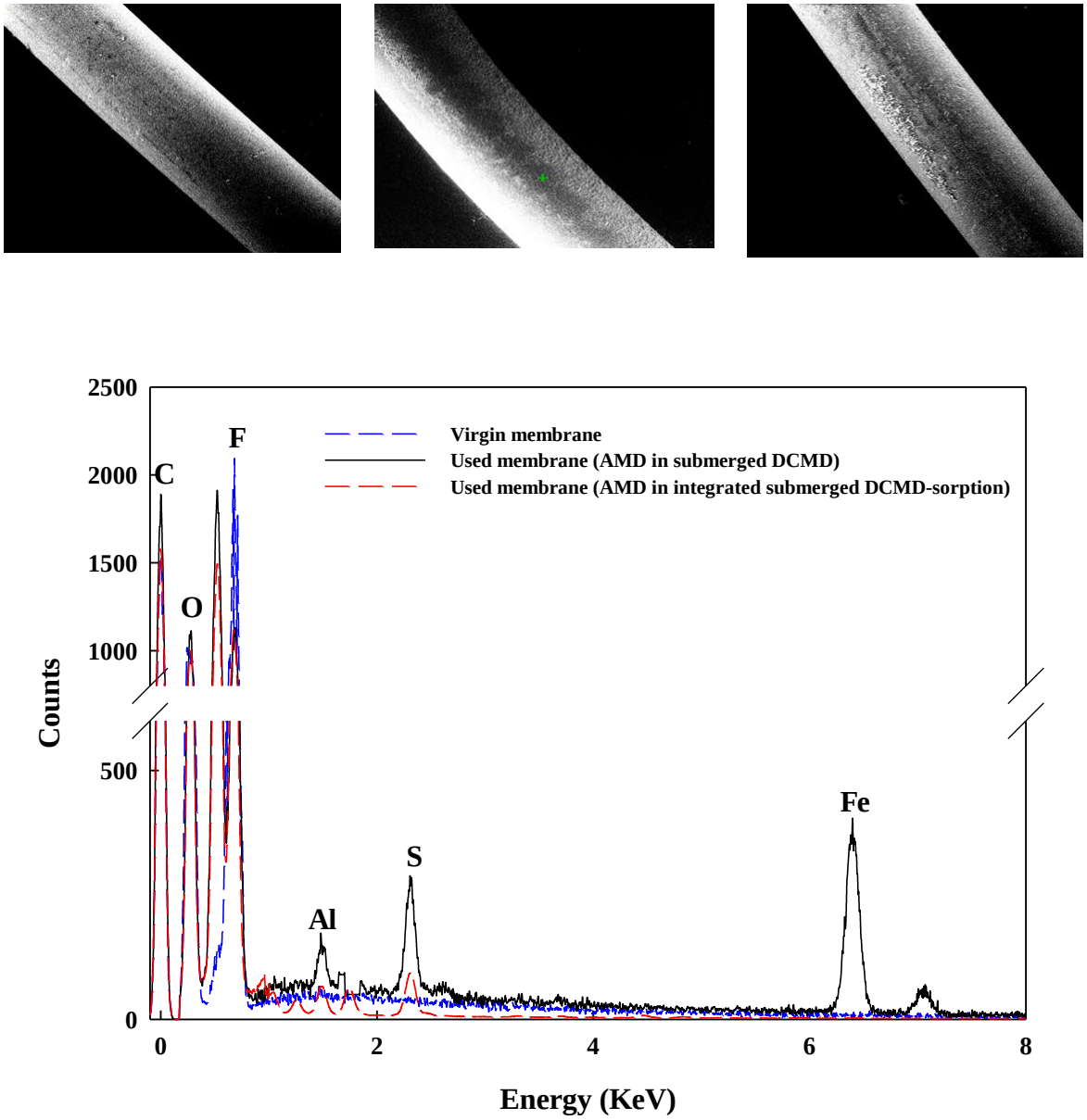


479

480 **Fig. 7.** Permeate flux for AMD treatment using submerged DCMD and integrated submerged
481 DCMD –sorption system

482





483 **Fig. 8.** SEM-EDX of hollowfiber membrane **(a)** virgin **(b)** used membrane with AMD in
484 submerged DCMD **(c)** used membrane with AMD in integrated DCMD-sorption.

485

4. Conclusion

An integrated submerged DCMD – zeolite sorption system for simultaneous removal of heavy metals and fresh water production from AMD was evaluated in this study. The results showed:

- A simple heat treatment was effective to increase the performance of natural zeolite for heavy metal removal from AMD solution. Heat treatment of natural zeolite at 500 °C enhanced heavy metal removal by 26-30%.
- The removal affinity for heavy metal was in the order of Fe>Al>Zn>Cu>Ni. The maximum sorption capacity (based on Langmuir Q_{max}) was 62.11, 44.64, 39.96, 36.10, 19.80 and 1.09 mg/g respectively.
- Fe and Al removal was close to 100% with 500 °C heat treated zeolite while 38-40% of Zn, Cu and Ni was achieved.
- Submerged DCMD enabled to treat AMD solution to achieve 50% water recovery while maintaining a stable flux. Nevertheless, Fe and Al precipitation from concentrated AMD deposited onto the hollow fibre membrane. This reduced the membrane hydrophobicity and caused partial wetting of sulfate ions.
- An integrated system of submerged DCMD with zeolite sorption provided a favourable condition to use 500 °C heat treated zeolite in powder form with a long contact time (30 h) in a submerged tank. In return, the simultaneous uptake of heavy metals by zeolite mitigated membrane fouling. At 50% water recovery, the integrated submerged DMCD – sorption system produced high quality fresh water for reuse while concentrating valuable Cu, Ni and Zn that can be recovered further.

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519 **References**

520 Aguiar, A.O., Andrade, L.H., Ricci, B.C., Pires, W.L., Miranda, G.A., Amaral, M.C.S., 2016.
521 Gold acid mine drainage treatment by membrane separation processes: An evaluation of the
522 main operational conditions. Sep. Purif. Technol. 170, 360-369.

523 Akdeniz, Y., Ülkü, S., 2007. Microwave effect on ion-exchange and structure of
524 clinoptilolite. J. Porous Mater. 14(1), 55-60.

525 Al-Haj, A.A., Ribhi, E.-B., 1997. Removal of Lead and Nickel Ions Using Zeolite Tuff. J.
526 Chem. Technol. Biot. 69(1), 27-34.

527 Alvarez-Ayuso, E., Garcia-Sanchez, A., Querol, X., 2003. Purification of metal electroplating
528 waste waters using zeolites. Water Res. 37(20), 4855-4862.

529 Ambiado, K., Bustos, C., Schwarz, A., Bórquez, R., 2017. Membrane technology applied to
530 acid mine drainage from copper mining. Water Sci. Technol. 75, 705-715.

531 An, W., Swenson, P., Wu, L., Waller, T., Ku, A., Kuznicki, S.M., 2011. Selective separation
532 of hydrogen from C_1/C_2 hydrocarbons and CO_2 through dense natural zeolite membranes. J.
533 Membr. Sci. 369(1-2), 414-419.

534 Caraballo, M.A., Rötting, T.S., Macías, F., Nieto, J.M., Ayora, C., 2009. Field multi-step
535 limestone and MgO passive system to treat acid mine drainage with high metal
536 concentrations. Appl. Geochem. 24(12), 2301-2311.

537 Choi, Y., Naidu, G., Jeong, S., Lee, S., Vigneswaran, S., 2018. Fractional-submerged
538 membrane distillation crystallizer (F-SMDC) for treatment of high salinity solution.
539 Desalination 440, 59-67.

540 Choi, Y., Naidu, G., Jeong, S., Vigneswaran, S., Lee, S., Wang, R., Fane, A.G., 2017.
541 Experimental comparison of submerged membrane distillation configurations for
542 concentrated brine treatment. Desalination 420, 54-62.

543 Contreras, J.O., Flores, D.P., Gutierrrez, P., Crooker, P.C., 2015. Acid Mine Drainage in
544 Chile: An Opportunity to Apply Bioremediation Technology. Hydrology Current Research
545 6(3), 1-8.
546 Englert, A.H., Rubio, J., 2005. Characterization and environmental application of a Chilean
547 natural zeolite. Int. J. Miner. Process. 75(1-2), 21-29.
548 Crane, R.A., Sapsford, D.J., 2018. Towards "Precision Mining" of wastewater: Selective
549 recovery of Cu from acid mine drainage onto diatomite supported nanoscale zerovalent iron
550 particles. Chemosphere 202, 339-348.
551 Fitzpatrick, R.W., Grealish, G., Shand, P., Simpson, S.L., Merry, R.H., Raven, M.D., 2009.
552 Acid sulfate soil assessment in Finniss River, Currency Creek, Black Swamp and Goolwa
553 Channel, South Australia. CSIRO land and water science report 26/09 CSIRO, Adelaide.
554 Gryta, M., 2007. Effect of iron oxides scaling on the MD process performance. Desalination
555 216(1-3), 88-102.
556 Kalin, M., Fyson, A., Wheeler, W.N., 2006. The chemistry of conventional and alternative
557 treatment systems for the neutralization of acid mine drainage. Sci. Total Environ. 366, 395–
558 408.
559 Kesieme, U.K., Milne, N., Aral, H., Cheng, C.Y., Duke, M., 2012. Novel application of
560 membrane distillation for acid and water recovery from mining waste waters. International
561 Mine Water Association Symposium 2012 Mine Water and the Environment, Curran
562 Associtates Inc., Bunbury, Australia.
563 Khayet, M., 2013. Solar desalination by membrane distillation: Dispersion in energy
564 consumption analysis and water production costs (a review). Desalination 308, 89-101.
565 Marcello, R.R., Galato, S., Peterson, M., Riella, H.G., Bernardin, A.M., 2008. Inorganic
566 pigments made from the recycling of coal mine drainage treatment sludge. J. Environ.
567 Manage. 88(4), 1280-1284.

568 Martí-Calatayud, M.C., Buzzi, D.C., García-Gabaldón, M., Ortega, E., Bernardes, A.M.,
569 Tenório, J.A.S., Pérez-Herranz, V., 2014. Sulfuric acid recovery from acid mine drainage by
570 means of electrodialysis. Desalination 343, 120-127.
571 Mondale, K.D., Carland, R.M., Aplan, F.F., 1995. The comparative ion exchange capacities
572 of natural sedimentary and synthetic zeolites. Miner. Eng. 8(4), 535-548.
573 Moreno, N., Querol, X., Ayora, C., Pereira, C.F., Janssen-Jurkovicová, M., 2001. Utilization
574 of Zeolites Synthesized from Coal Fly Ash for the Purification of Acid Mine Waters.
575 Environ. Sci. Technol. 35(17), 3526-3534.
576 Mosley, L.M., Biswas, T.K., Dang, T., Palmer, D., Cummings, C., Daly, R., Simpson, S.,
577 Kirby, J., 2018. Fate and dynamics of metal precipitates arising from acid drainage
578 discharges to a river system. Chemosphere 212, 811-820.
579 Motsi, T., Rowson, N.A., Simmons, M.J.H., 2009. Adsorption of heavy metals from acid
580 mine drainage by natural zeolite. Int. J. Miner. Process. 92(1-2), 42-48.
581 Naidu, G., Jeong, S., Choi, Y., Jang, E., Hwang, T.-M., Vigneswaran, S., 2014. Application
582 of vacuum membrane distillation for small scale drinking water production. Desalination 354,
583 53-61.
584 Naidu, G., Jeong, S., Choi, Y., Song, M.H., Oyunchuluun, U., Vigneswaran, S., 2018.
585 Valuable rubidium extraction from potassium reduced seawater brine. J. Clean. Prod. 174,
586 1079-1088.
587 Naidu, G., Jeong, S., Choi, Y., Vigneswaran, S., 2017. Membrane distillation for wastewater
588 reverse osmosis concentrate treatment with water reuse potential. J. Membr. Sci. 524, 565-
589 575.
590 Nguyen, T.C., Loganathan, P., Nguyen, T.V., Vigneswaran, S., Kandasamy, J., Naidu, R.,
591 2015. Simultaneous adsorption of Cd, Cr, Cu, Pb, and Zn by an iron-coated Australian zeolite
592 in batch and fixed-bed column studies. Chem. Eng. J. 270, 393-404.

593 Ohgushi, T., Nagae, M., 2003. Quick Activation of Optimized Zeolites with Microwave
594 Heating and Utilization of Zeolites for Reusable Desiccant. J. Porous Mater. 10(2), 139-143.
595 Ohgushi, T., Nagae, M., 2005. Durability of Zeolite Against Repeated Activation Treatments
596 with Microwave Heating. J. Porous Mater. 12(4), 265-271.
597 Parbhakar-Fox, A.K., Edraki, M., Hardie, K., Kadletz, O., Hall, T., 2014. Identification of
598 acid rock drainage sources through mesotextural classification at abandoned mines of
599 Croydon, Australia: Implications for the rehabilitation of waste rock repositories. J.
600 Geochem. Explor. 137, 11-28.
601 Qiu, W., Zheng, Y., 2009. Removal of lead, copper, nickel, cobalt, and zinc from water by a
602 cancrinite-type zeolite synthesized from fly ash. Chem. Eng. J. 145(3), 483-488.
603 Rios, C.A., Williams, C.D., Roberts, C.L., 2008. Removal of heavy metals from acid mine
604 drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites. J. Hazard. Mater.
605 156(1-3), 23-35.
606 Santiago, O., Walsh, K., Kele, B., Gardner, E., Chapman, J., 2016. Novel pre-treatment of
607 zeolite materials for the removal of sodium ions: potential materials for coal seam gas co-
608 produced wastewater. Springerplus 5, 571.
609 Sprynskyy, M., Buszewski, B., Terzyk, A.P., Namiesnik, J., 2006. Study of the selection
610 mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) adsorption on clinoptilolite. J. Colloid
611 Interface Sci. 304(1), 21-28.
612 Taffarel, S.R., Rubio, J., 2010. Adsorption of sodium dodecyl benzene sulfonate from
613 aqueous solution using a modified natural zeolite with CTAB. Miner. Eng. 23(10), 771-779.
614 Tolonen, E.-T., Sarpola, A., Hu, T., Rämö, J., Lassi, U., 2014. Acid mine drainage treatment
615 using by-products from quicklime manufacturing as neutralization chemicals. Chemosphere
616 117, 419-424.

617 Tomaszewska, M., Gryta, M., Morawski, A.W., 2001. Recovery of hydrochloric acid from
618 metal pickling solutions by membrane distillation. Sep. Purif. Technol. 22-23, 591-600.
619 Tomaszewska, M., Mientka, A., 2009. Separation of HCl from HCl–H_2SO_4 solutions by
620 membrane distillation. Desalination 240(1), 244-250.
621 Turner, M.D., Laurence, R.L., Conner, W.C., Yngvesson, K.S., 2000. Microwave radiation's
622 influence on sorption and competitive sorption in zeolites. AlChE J. 46(4), 758-768.
623 Unger, C., Lechner, A.M., Glenn, V., Edraki, M., Mulligan, D.R., 2012. Mapping and
624 Prioritising Rehabilitation of Abandoned Mines in Australia. Proceedings Life of mine
625 conference, Brisbane, QLD, 259-265.
626 Vasquez, Y., Escobar, M.C., Neculita, C.M., Arbeli, Z., Roldan, F., 2016. Biochemical
627 passive reactors for treatment of acid mine drainage: Effect of hydraulic retention time on
628 changes in efficiency, composition of reactive mixture, and microbial activity. Chemosphere
629 153, 244-253.
630 Vital, B., Bartacek, J., Ortega-Bravo, J.C., Jeison, D., 2018. Treatment of acid mine drainage
631 by forward osmosis: Heavy metal rejection and reverse flux of draw solution constituents.
632 Chem. Eng. J. 332, 85-91.
633 Wingenfelder, U., Hansen, C., Furrer, G., Schulin, R., 2005. Removal of Heavy Metals from
634 Mine Waters by Natural Zeolites. Environ. Sci. Technol. 39(12), 4606-4613.
635 Yao, M., Woo, Y.C., Tijing, L.D., Choi, J.-S., Shon, H.K., 2018. Effects of volatile organic
636 compounds on water recovery from produced water via vacuum membrane distillation.
637 Desalination 440, 146-155.
638 Zhang, M., 2011. Adsorption study of Pb(II), Cu(II) and Zn(II) from simulated acid mine
639 drainage using dairy manure compost. Chem. Eng. J. 172(1), 361-368.
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