



A continuous pilot-scale system using coal-mine drainage sludge to treat acid mine drainage contaminated with high concentrations of Pb, Zn, and other heavy metals

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ARTICLE INFO

Article history:

Received 8 August 2011

Received in revised form 15 February 2012

Accepted 17 February 2012

Available online 24 February 2012

Keywords:

Sludge

Acid mine drainage

Heavy metal

Stirring tank reactor

ABSTRACT

A series of pilot-scale tests were conducted with a continuous system composed of a stirring tank reactor, settling tank, and sand filter. In order to treat acidic drainage from a Pb–Zn mine containing high levels of heavy metals, the potential use of coal-mine drainage sludge (CMDS) was examined. The pilot-scale tests showed that CMDS could effectively neutralize the acidic drainage due to its high alkalinity production. A previous study revealed that calcite and goethite contained in CMDS contributed to dissolutive coprecipitation and complexation with heavy metals. The continuous system not only has high removal efficiencies (97.2–99.8%), but also large total rate constants (K_{total} , 0.21–10.18 h⁻¹) for all heavy metals. More specifically, the pilot system has a much higher Zn(II) loading rate (45.3 g m⁻³ day⁻¹) than other reference systems, such as aerobic wetland coupled with algal mats and anoxic limestone drains. The optimum conditions were found to be a CMDS loading of 280 g L⁻¹ and a flow rate of 8 L day⁻¹, and the necessary quantity of CMDS was 91.3 g L⁻¹ day⁻¹, as the replacement cycle of CMDS was determined to be 70 days.

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1. Introduction

Acid mine drainage (AMD), a highly acidic aqueous solution, is formed through the chemical reaction of surface and shallow subsurface water with rocks containing sulfur-bearing minerals to give sulfuric acid. Heavy metals can then be leached from rocks through contact with the acid. When AMD mixes with groundwater, surface water, and soils, it may have harmful effects on humans, animals, and plants. Specifically, in Pb–Zn mines, Zn(II) is released at high concentrations in AMD compared to other toxic heavy metals such as Fe(II), Fe(III), Al(III), Cu(II), Cd(II), and Pb(II). The oxidation of pyrite (FeS₂) and sphalerite (ZnS) in tailings of abandoned mines can occur spontaneously and may be catalyzed by iron oxidizing bacteria and Fe(III), resulting in the production of high acidity and Zn(II). Since high concentrations of Zn(II) are also observed in industrial wastewater discharged by metal processing, battery manufacturing, etc. [1], Zn(II) concentrations in surface, ground, and potable water are strictly regulated worldwide [2].

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amorphous micron- and submicron-sized iron oxide/hydroxide particles containing sulfate, and generally has a high surface area as well as numerous functional groups for removing dissolved trace metals through adsorption and co-precipitation [10–13]. To date, however, very little work has been reported on the removal mechanism of heavy metals.

Previously, the authors have aimed to elucidate the main mechanism of Zn(II) removal by CMDS produced from a full-scale electrolysis treatment plant by conducting a series of batch tests, such as isotherm, kinetic, and edge (pH effect) tests. In addition, spectroscopic analyses such as zeta potential, XRD, FT-IR, and SEM were conducted [9]. The results of the XRD analysis showed CMDS to have a heterogeneous composition with the main components being calcite (30%, w/w) and sulfate complexed iron (oxy)hydroxide (70%, w/w). The batch tests showed that the negatively charged groups coupled to the sulfate ions, FeOH-SO_4^{-2} , had an electrostatic attraction to Zn(II). However, the results of the FT-IR analysis showed that Zn(II) might be significantly precipitated as carbonate compounds, even though the Zn(II) removal by complexation with goethite could not be confirmed. Precipitation as carbonates may have occurred due to the solubility product (K_{SP} , $10^{-3.01}$) of ZnSO_4 being much higher than that of ZnCO_3 (K_{SP} , $10^{-10.8}$) or $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ (K_{SP} , $10^{-14.85}$) [14,15].

In this study, a treatment system consisting of a continuously stirred tank reactor, settling tank and sand filter was constructed and operated to determine the treatment efficiency for an acidic metallic mine drainage. For the tests, actual AMD from a Pb–Zn mine was applied to find the effect of the operating parameters, such as CMDS injection concentration and retention time. The ultimate objective is to optimize the main parameters needed for designing a full-scale treatment plant.

2. Material and methods

2.1. Analyses of CMDS

CMDS was prepared by drying sludge taken from a full-scale treatment facility, in which an electrolysis process had been adapted to treat acidic drainage coming from a coal-mine adit in South Korea. The CMDS was dried at 25 °C in open air for 5 days. The specific surface area of the CMDS was analyzed with a surface analyzer (ASAP 2010, Micromeritics Inc.). After shaking the CMDS in deionized water at a ratio of 1–5, the sludge pH was measured with a pH meter (Thermo Orion model 420A⁺). The concentrations of heavy metals in all samples were measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES, 5300DV, PerkinElmer).

2.2. System set-up and operation

Actual AMD was sampled onsite from the effluent of settling tanks for treating acidic drainage from a Pb–Zn mine in South Korea. Table 1 shows the chemical properties of the drainage used in this study. The wastewater was acidic (pH 2.65) and had a high acidity (288 mg L⁻¹). The concentrations of the cationic metal species Cu(II), Pb(II), Zn(II), and Fe(III) were 25.5, 0.091, 44, and 98 mg L⁻¹, respectively, while that of the sulfate ions was 2550 mg L⁻¹. After Fe(III), Zn(II) had the highest loading (44 times the regulatory limit) among the heavy metal species. Fig. 1 and Table 2 show a schematic and the properties of the treatment system, consisting of a stirring tank reactor [volume 2 L, diameter (*D*) 120 mm × height (*H*) 177 mm], a settling tank (volume 3.3 L, *D* 120 mm × *H* 292 mm) and a sand filter (volume 2.7 L, *D* 50 mm × *H* 1400 mm). In the sand filter, the grain size of the sand was in the range 0.25–0.5 mm. In the first test, the following operating conditions were setup for the

Table 1
Chemical property of target acid mine drainage (AMD) (unit: mg L⁻¹).

Item	Parameter	AMD	Limited
Anions	pH	2.65	5.5–8.5
	Alkalinity	0	NA
	Acidity	288	NA
	SO ₄ ²⁻	2550	250 (WHO)
	Cl ⁻	1.1	250
	PO ₄ ³⁻	0.04	NA
	Ca	125	NA
Trace metals	Fe	98	0.3
	Mg	1.35	NA
	Na	1.1	NA
	K	2.8	NA
	Al	0.082	0.2
	As	0.0009	0.05
Heavy metals	Cu	25.5	1
	Zn	44	1
	Ni	0.005	0.02
	Cd	0.196	0.01
	Pb	0.091	0.05

NA: not available.

pilot system: the influent flow of AMD was 8 L day⁻¹, and 560 g CMDS (dry wt. basis) was introduced into the stirring tank reactor (2 L, concentration 280 g L⁻¹). The retention times for the stirring tank reactor, settling tank, and sand filter were 0.25, 0.41, and 0.34 days, respectively. In this test, influent and effluent samplings in the settling tank and sand filter were conducted for 70 days. The flowrate of sludge return was set to be the same as that of the main system, in order to sustain a constant concentration of sludge in the stirring tank reactor. In the second tests, authors tried to find the optimum operational conditions for the continuous treatment system by testing different amounts (80–560 g L⁻¹ at stirring tank reactor) of CMDS and altering the flowrate (6–30 L day⁻¹).

2.3. Kinetics and treatment efficiency

Since the removal mechanisms of Zn(II) involve mainly the stirring tank reactor and the settling tank, in which most of the CMDS is retained, the value of the total rate constant (K_{total}) was obtained for the combined system of the stirring tank reactor and settling tank. The K_{total} value was also calculated using the equation below. If all parameters are assumed to be constant, except for the metal concentrations, this system follows a pseudo-first order reaction [16],

$$K_{\text{total}} = \frac{[C_{\text{influent}} - C_{\text{effluent}}]Q_{\text{total}}}{C_{\text{effluent}} \times V_{\text{reactor}}}$$

where V_{reactor} , Q_{total} , C_{influent} , and C_{effluent} are the reactor volume, flowrate, and metal concentration of influent, and metal concentration of effluent, respectively.

The treatment efficiency for the target metal species was obtained using the following equation:

$$\text{Treatment efficiency(\%)} = \frac{C_{\text{influent}} - C_{\text{effluent}}}{C_{\text{influent}}} \times 100\%$$

Table 2
Property of treatment system.

Composition	Volume (L)	Retention time (day) based on 8 L day ⁻¹ of flowrate	Dimension
Stirring tank reactor	2	0.25	<i>D</i> 120 mm × <i>H</i> 177 mm
Settling tank	3.3	0.41	<i>D</i> 120 mm × <i>H</i> 292 mm
Sand filter	2.7	0.34	<i>D</i> 50 mm × <i>H</i> 1400 mm

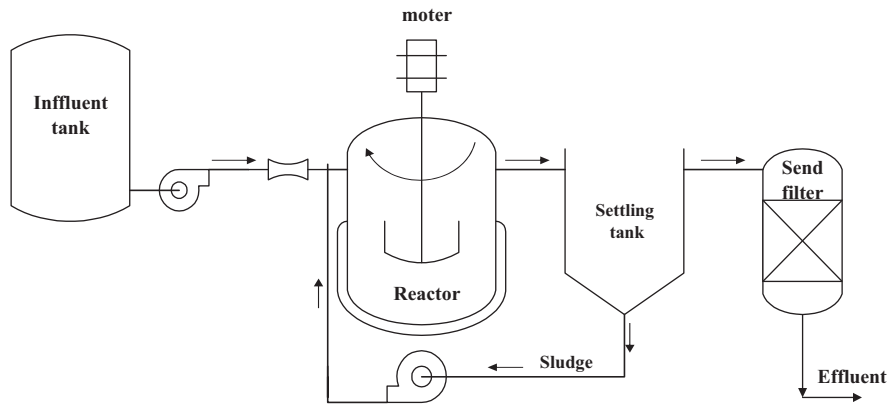


Fig. 1. Schematics of stirring tank reactor-settling tank-sand filter system.

where C_{influent} and C_{effluent} represent the average concentrations of the metal species in the influent and effluent from the sand filter. The Zn(II) loading rate was also calculated using the equation below [17].

$$\text{Zn(II) loading rate (g m}^{-3} \text{ day}^{-1}) = \frac{[C_{\text{influent}} - C_{\text{effluent}}](\text{g m}^{-3})Q(\text{m}^3 \text{ day}^{-1})}{V_{\text{total}}(\text{m}^3)} \times 100\%$$

3. Results and discussion

3.1. Characterization of the CMDS and AMD

Table 3 lists the physicochemical properties of CMDS, showing that it has a high pH (8.3) and alkalinity ($130 \text{ mg CaCO}_3 \text{ L}^{-1}$), and thus, it can be inferred that CMDS contains a high portion of alkaline materials, as was also shown in the previous XRD analysis [9]. Along with the mesopore structure (average pore size, 74.7 \AA), the CMDS had a comparably high Brunauer–Emmett–Teller (BET) surface area ($135.4 \text{ m}^2 \text{ g}^{-1}$). Interestingly, the CMDS showed a relatively low pH isoelectric point (pH_{IEP}) (4.5). This low pH_{IEP} might be due to the sulfate complexed surface [18]. Since CMDS is the sludge obtained from a full-scale electrolysis facility for treating drainage flowing from a mine site in which the bedrock consists of limestone, its main elements have been characterized as goethite and calcite. Previous results showed that sulfate ions participated in the structural networks (0.42 wt%) and were predominantly on the surface of the precipitated minerals (7.9 wt%) [9]. For comparison, in the case of schwertmannite, the sulfate usually participates in the mineral structure and on the surface at a ratio of 3:1 [19].

As the sulfate concentration is less than 3000 mg L^{-1} and the pH is acidic at 2.5–4.5 in the drainage, ferrous compounds are oxidized and precipitated as schwertmannite [$\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x \cdot n\text{H}_2\text{O}$ ($1 \leq x \leq 1.86$)], jarosite [$(\text{H,K,Na})\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2$], or goethite ($\alpha\text{-FeOOH}$). However, these precipitates are not stable and may be transformed to goethite over time [20–23]. The zeta potentials of the sulfate minerals, such as schwertmannite, jarosite, and goethite, are generally different from that of iron (oxy)hydroxide. For example, the pH_{IEP} of schwertmannite and jarosite ranges from 5.4 to 7.4 [4,18,24], while that of ferrihydrite is 7.1 [25]. However, as shown in Table 3, the pH_{IEP} (4.5) of CMDS was lower than those found in the previous studies.

3.2. Removal of Zn(II) by the pilot system

Tests using the pilot system were conducted to evaluate the potential capacity of CMDS for removing heavy metals from AMD.

For this system, 280 g L^{-1} of CMDS was put into the stirring tank reactor (2 L) and operated at 8 L day^{-1} (retention time for the whole pilot system was 1 day) for 70 days. Fig. 2 shows the pH change and Zn(II) content of the influent and effluent from the settling tank and sand filter, respectively. The filtration rate for the sand filter unit was 0.29 cm min^{-1} . The Zn(II) in the effluent from the settling tank and sand filter were relatively stable for 60 days. Based on the 60 days of operation, the average Zn(II) concentration in the influent was 45.4 mg L^{-1} , and in the effluent from settling tank and sand filter was 0.31 and 0.074 mg L^{-1} , respectively. After 60 days, however, Zn(II) in the effluents from the settling tank and sand filter steadily increased to about 1 and 0.8 mg L^{-1} , respectively. On the other hand, the influent pH varied between 2.0 and 3.2 for 18 days and then remained constant with an average pH of 2.6. The pH of the effluent from the sand filter was initially 6.3 and gradually increased to 8.0 over 16 days, and then maintained an

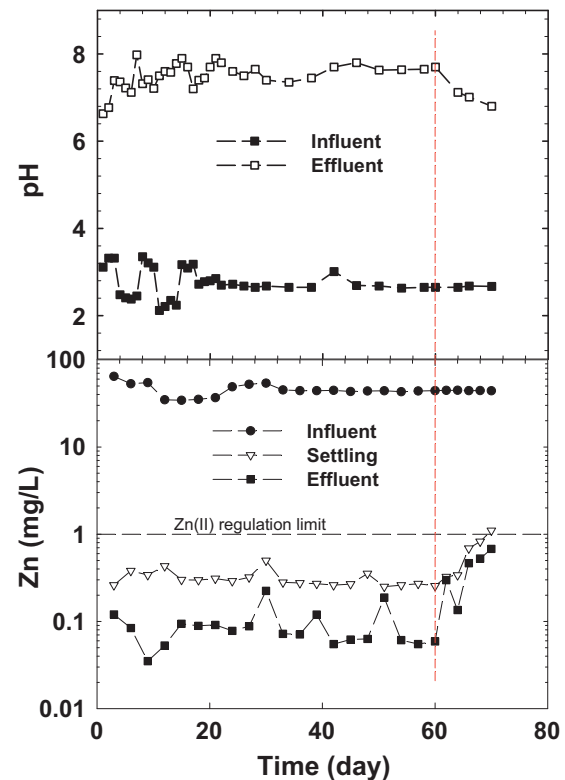


Fig. 2. Zn(II) and pH variation during stirring tank reactor-settling tank-sand filter operation for 70 days [HRT: 3 h; 280 g L^{-1} CMDS; temperature: 25°C AMD].

Table 3
Physico-chemical property of CMDS.

Item	pH	pH _{IEP}	Alkalinity (mg L ⁻¹)	Moisture content (wt.%)	BET (m ² g ⁻¹)	Pore size (Å)
CMDS	8.3	4.5	130	40.85	135.4	74.74

average of 7.5. This increase in pH was due to calcite dissolution from the CMDS. Importantly, Zn(II) was maintained at less than 0.1 mg L⁻¹ during the gradual increase of pH from the beginning, while Zn(II) linearly increased as the pH decreased between days 60 and 70. Judging from the relationship between pH and Zn(II) removal, it is suggested that Zn(II) is predominantly removed by complexation with goethite at the initial stage, and then it is controlled by co-precipitation followed by the dissolution of calcite in the CMDS, and finally Zn(II) increases because the CMDS is not able to generate more alkalinity. The previous study showed that the main mechanism of Zn(II) removal by CMDS was calcite dissolution followed by co-precipitation as smithsonite [Zn(II)CO₃] or hydrozincite [Zn(II)₅(CO₃)₂·(OH)₆], as well as the complexation of Zn(II) to goethite [9].

Using the equation given above, the treatment efficiency of Zn(II) was calculated to be 99.8%. For 60 days, the amount of Zn(II) removed by the CMDS was 38.8 mg Zn(II) per gram of CMDS. The K_{total} value for Zn(II) was calculated to be 9.15 h⁻¹ (Table 4). Mayes et al. [17] conducted experiments on Zn(II) removal using a hydrous ferric oxide (HFO) pellet system. The calculated K_{total} of their system was 0.84 h⁻¹, which was about 10 times lower than that of this pilot system.

For this pilot system (with a total volume of 8 L and a flow rate 8 L day⁻¹), the calculated Zn(II) loading rate was 45.3 g m⁻³ day⁻¹. Therefore, the efficiency of the pilot system in the Zn(II) loading rate was about 5.6 times that in the HFO pellet system (8.13 g m⁻³ day⁻¹) [26]. With respect to the removal efficiency, the system in this study had a much higher Zn(II) removal efficiency (99.8%) than the HFO pellet system (32%). In addition, although the scales were different, the pilot system had a much higher Zn(II) removal efficiency and loading rate than the other reference systems, such as aerobic wetland coupled with algal mats (31–91%, 0.55–0.8 g m⁻³ day⁻¹), and anoxic limestone drains (17%, 0.9 g m⁻³ day⁻¹), as shown in Table 5.

3.3. Removal of other heavy metals from the pilot treatment system

Fig. 3 shows the concentrations of other heavy metals with respect to time in the influent and effluents from the settling tank and sand filter. The average concentration of Cu(II) in the influent was 25.5 mg L⁻¹, while the effluents from the settling tank (0.14 mg L⁻¹) and sand filter (0.062 mg L⁻¹) contained much lower concentrations than the regulatory limit (1 mg L⁻¹). Although the inlet Fe(III) concentration was about 91 mg L⁻¹, the average concentrations of Fe(III) in the effluents from the settling tank and sand filter were 0.61 and 0.024 mg L⁻¹, respectively. Hence, the average concentration of Fe(III) in the effluent from the sand filter satisfied the regulatory limit of 0.3 mg L⁻¹. The influent contained on average 0.092 mg L⁻¹ Pb(II), which is higher than the regulatory limit (0.05 mg L⁻¹). However, the average concentration of Pb(II) in the effluents from the settling tank and sand filter decreased to 0.02 and 0.003 mg L⁻¹, respectively, which are much lower than the 0.05 mg L⁻¹ limit. The average inlet Cd(II) concentration (0.184 mg L⁻¹) also decreased to 0.042 and 0.004 mg L⁻¹ in the effluents from the settling tank and sand filter, respectively. It is important to note that other heavy metals did not have their breakthroughs under the same operating conditions, while Zn(II) had a

breakthrough at 70 days. The removal efficiencies of metal species were high, in the range 97.2–99.9%, and K_{total} of Zn(II), Cu(II) and Fe(III) were 9.15, 10.18, and 9.3 h⁻¹, respectively, while those of Cd(II) and Pb(II) were 0.21 and 0.23 h⁻¹, respectively. The lower K_{total} values might be due to their low concentrations. Accordingly, it was found that the pilot system using CMDS could remove all metal species simultaneously. Zn(II) was found to have the fastest breakthrough, in part due to its high loading. Thus, in the second phase of experiments using various CMDS flowrates and loading concentrations, the optimum operational conditions were found based on the removal efficiency of Zn(II).

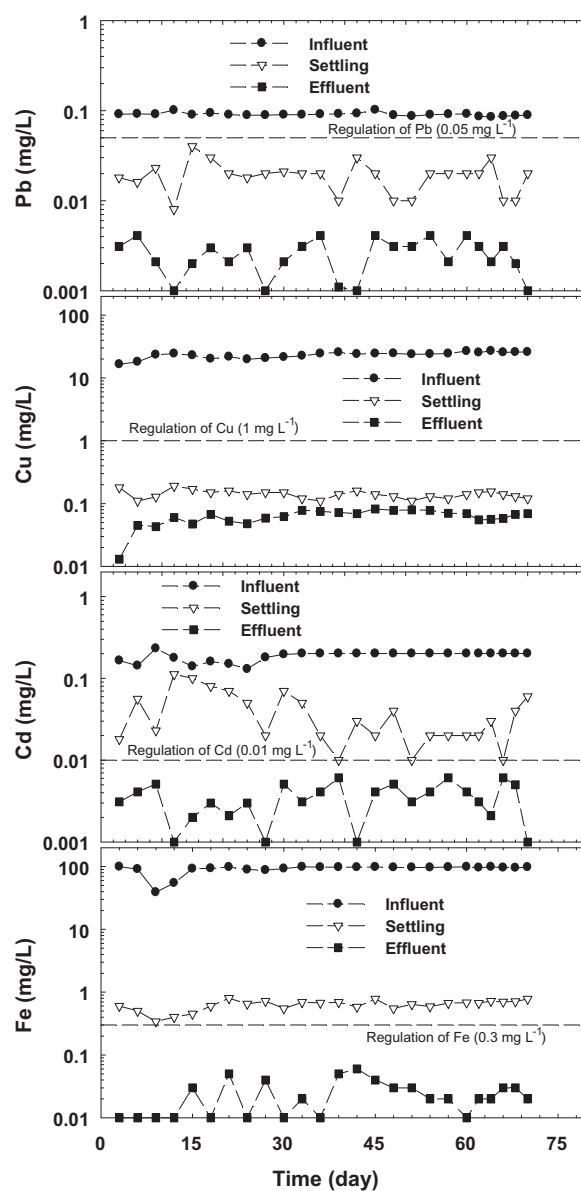


Fig. 3. Variation of lead, zinc, copper, cadmium and iron concentrations during stirring tank reactor-settling tank-sand filter operation for 70 days [HRT: 3 h; 280 g L⁻¹ CMDS; temperature: 25 °C].

Table 4
Average concentrations of heavy metal of influent and effluents from settling tank and sand filter for 60 days operation, calculated K_{total} , and removal efficiencies (stirring tank reactor 2 L, $Q=8 \text{ L day}^{-1}$).

Metal	$C_{influent} \text{ (mg L}^{-1}\text{)}$	$C_{effluent} \text{ from settling tank (mg L}^{-1}\text{)}$	$C_{effluent} \text{ 2008from sand filter (mg L}^{-1}\text{)}$	$K_{total} \text{ (h}^{-1}\text{)}$	Removal (%)
Zn	45.4	0.31	0.074	9.15	99.8
Cu	22.8	0.14	0.062	10.18	99.7
Cd	0.184	0.042	0.0035	0.21	98.1
Pb	0.092	0.0197	0.0026	0.23	97.2
Fe	90.85	0.61	0.024	9.3	99.97

Table 5
Treatment system performance of HFO and goethite/calcite compared to other passive treatment technologies, using various assessment metrics and mean values.

Wastewater type	System type	Flow (L min^{-1})	Volume (m^3)	Zn conc. of inlet/outlet (average for 60 days) (mg L^{-1})	Treatment efficiency (%)	Zn(II) loading rate ($\text{g m}^{-3} \text{ day}^{-1}$)	Reference
Mine water	Pilot scale HFO drain	1.8	0.16	1.7/1.2	32	8.13	[17]
Mine water	Pilot scale aerobic wetland/algal mat	2.4–10.2	240	16/1.2	91	0.8	[27]
Mine water	Full scale aerobic wetland/algal mat	510	6000	14.4/9.9	31	0.55	[27]
Mine water	Pilot scale anoxic limestone drain	1.2	2.25	6.91/5.74	17	0.9	[27]
Mine water	Stirring tank reactor (CMDS applied)-settling tank-sand filter	0.006	0.008	45.4/0.09	99.8	45.3	This study

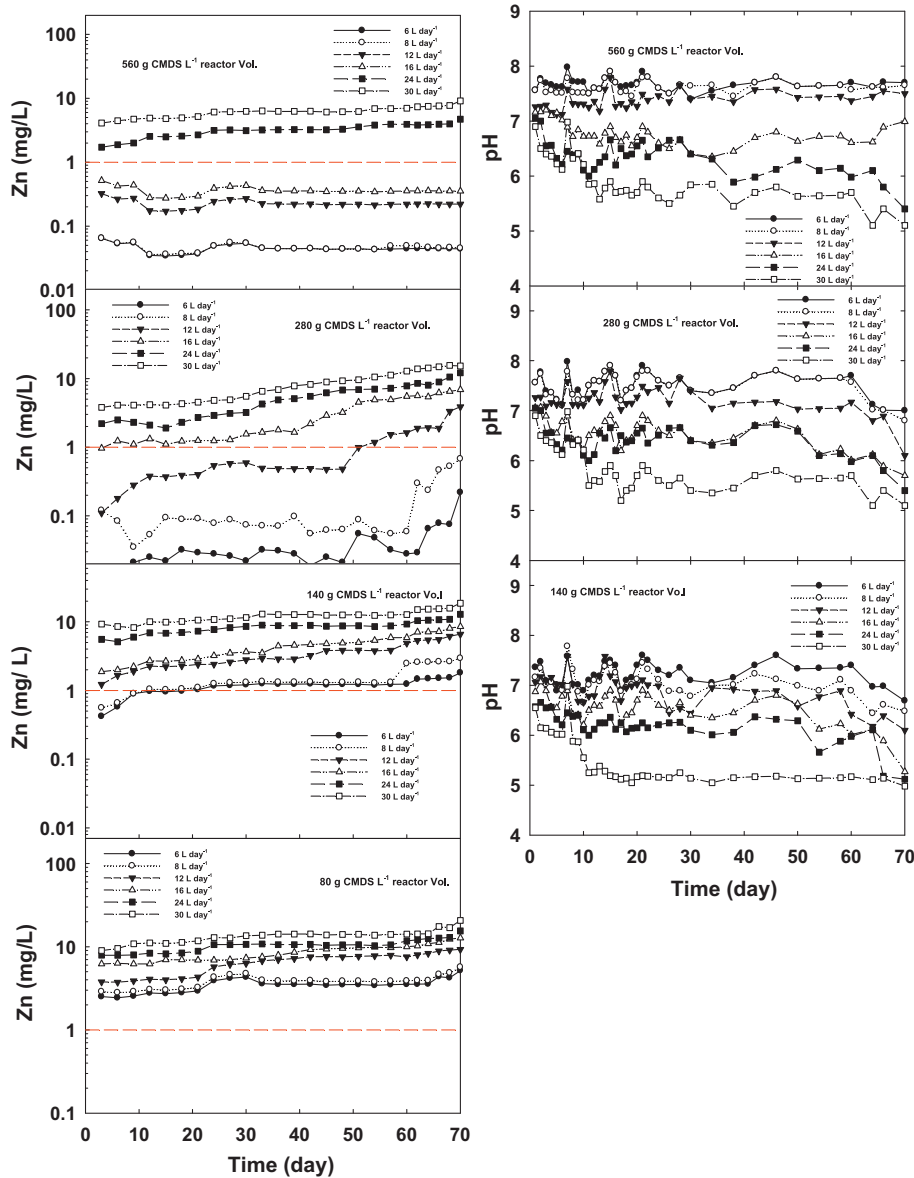


Fig. 4. Zn(II) and pH variations with different conditions of CMDS injected into stirring tank reactor and retention time.

3.4. Effect of CMDS loading and flowrate

Fig. 4 shows the experimental results [pH and Zn(II) of the influent and effluent from the sand filter] of the pilot system, for which different CMDS loadings (80–560 g L⁻¹ at stirring tank reactor) and flowrates (6–30 L day⁻¹) were used. By conducting these tests, the authors attempted to find the optimum operating conditions for treating the mine water. From the influent and effluents from the settling tank and sand filter, samples were obtained for 70 consecutive days to measure the pH and Zn(II). When operating with a CMDS loading of 80 g L⁻¹, the effluents in all cases did not meet the regulatory limit for Zn(II). With a loading of 140 g L⁻¹ and at two different flowrates (6 and 8 L day⁻¹), Zn(II) in the effluents was less than 1 mg L⁻¹ for only 10 days. With a flowrate greater than 8 L day⁻¹, Zn(II) was not removed to within the regulatory limit. While operating with a CMDS loading of 280 g L⁻¹, Zn(II) in the effluents were less than 1 mg L⁻¹ at flow rates of 6 and 8 L day⁻¹ for the whole operation period. However, the trend showed that Zn(II) increased steadily after 60 days, similarly as in the previous experiment, reflecting the reliability of the tested system. At 12 L day⁻¹, Zn(II) in the effluent gradually increased to exceed the regulatory limit at 50 days. However, the effluent met the regulatory limit for Zn(II) at the beginning with a higher flowrate (12 L day⁻¹). When the system was operated with a 560 g L⁻¹ CMDS loading, Zn(II) was effectively removed to levels much lower than 1 mg L⁻¹ for the entire operation period with a wide range of flowrates (6–16 L day⁻¹). Among various operational conditions, a CMDS loading of 560 g L⁻¹ resulted in the best removal efficiency of Zn(II). The poor removal performance with a higher flowrate might be due to the lower retention time of CMDS in the stirring tank reactor.

The graphs to the right in Fig. 4 also show the results of the pH of the effluent, except in the case of a CMDS loading of 80 g L⁻¹ in the stirring tank reactor. Overall, the removal efficiency of Zn(II) is highly correlated with pH. The pH of the effluent decreased as the flowrate increased. For a CMDS loading of 140 g L⁻¹ in the stirring tank reactor with a flowrate of 30 L day⁻¹, the initial pH (6.5) of the effluent abruptly decreased to 5 after 20 days, and then it remained constant. This decreasing trend of pH was also observed for a flowrate of 24 L day⁻¹. However, when operated more slowly, the pH stayed at 6. At the slowest flowrate, the pH varied in the range 6.5–7.5. The effluent pH remained greater than 7 with a CMDS loading of 280 g L⁻¹ and at a flowrate of 6–12 L day⁻¹, while the average pH was less than 6.5 at higher flowrates. With a CMDS loading of 280 g L⁻¹, the overall pH dropped after 60 days of operation, which was similar to previous results. When 560 g L⁻¹ CMDS was loaded into the stirring tank reactor, the pH was sustained in the range 7–8 with a flowrate of 6–12 L day⁻¹ for 70 days. However, the pH in the effluent decreased overall to values in the range 5–6.5 with flowrates of 24 or 30 L day⁻¹. Accordingly, as the loading of CMDS increased, the pH had less influence on reducing Zn(II) to below the regulatory limit.

4. Conclusions

By conducting continuous pilot tests for about 70 days using actual acid mine drainage obtained from a Pb–Zn mine, it was found that CMDS can effectively remove various heavy metals simultaneously. CMDS can also efficiently neutralize the acidic drainage due to its high alkalinity production by calcite dissolution, and the continuous pilot system using CMDS not only had high removal efficiencies for all heavy metals but also had high total rate constants for all heavy metals. Compared to other treatment systems, such as aerobic wetland coupled with algal mats and anoxic limestone drains, the pilot system in this study also had a much higher Zn(II) loading rate. As found in the pilot tests

conducted with different CMDS loadings and flowrates, Zn(II) was effectively removed to below 1 mg L⁻¹ over the entire operational period (70 days) at a CMDS loading of 560 g L⁻¹ and flowrate of 6–16 L day⁻¹. However, since mechanical damage of the mixing system and pooling problems could be a risk with high loadings of CMDS, the optimum operational conditions were considered to be a CMDS loading of 280 g L⁻¹ and a flow rate of 8 L day⁻¹. The replacement cycle for CMDS was determined to be 70 days, and the required amount of CMDS for the treatment flowrate was accordingly calculated to be 91.3 g L⁻¹ day⁻¹. The developed system using CMDS would be favorable in locations where only a small amount of space is available for a full-scale treatment plant to treat acidic mine water containing high levels of heavy metals.

Acknowledgment

This research is supported by the Korean Ministry of Environment as “The GAIA Project No: 173-091-003.”

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