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Efficiency of combining limestone, sawdust and microorganisms to treat Zinc and Manganese in AMD in Mao Khe, Quang Ninh

Hiệu quả của việc kết hợp đá vôi, mùn cưa và vi sinh vật cho việc xử lý kẽm và mangan trong nước thải axit mỏ Mạo Khê, Quảng Ninh

Research article

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This paper presents a novel technology combining limestone, sawdust and microorganisms to treat Zn and Mn in acid mine drainage (AMD) which brought a specially high efficiency. Hydraulic retention time is 1.1 day, aeration velocity is 0.6 L of air per 1 L of solution per min, cost only 0.2 USD/m^3. In the system, the process of adsorption, biological hydrolization of cellulose supply carbon source for dissimilatory sulfate reduction and the precipitation process of metals with sulfide. it was very convenient place. The concentration of heavy metals of AMD such as Mn, Zn... in the inflow are about 70 - 80 mg/L for Mn^{2+}; 40 - 48 mg/L for Zn^{2+}, outflow are only 0.4, 0.03 mg/L respectively. In conclusion, acid mine drainage wastewater treated by this technology can be reused for activities in the mines.

Bài báo này giới thiệu công nghệ mới kết hợp phương pháp vật lý, hóa học, sinh học cho việc xử lý Zn và Mn có trong nước thải axit mỏ đạt hiệu quả đặc biệt cao. Hệ thống được xử dụng trong nghiên cứu gồm đá vôi, mùn cưa, vi sinh vật và được kết nối với hệ thống lọc bằng, sỏi, cát vàng và than hoạt tính. Hệ thống được vận hành liên tục theo 3 giai đoạn khác nhau với thời gian lưu 1,5 ngày (giai đoạn A), 1,1 ngày, tốc độ sục khí 0,3 L không khí trong 1 phút trong 1 L. dung dịch (giai đoạn B) và 1,1 ngày, tốc độ sục khí 0,6 L không khí trong 1 phút trong 1 L. dung dịch (giai đoạn C). Trong hệ thống, nồng độ trung bình của Zn^{2+} ở đầu vào khoảng 40,81 đến 44,52 mg/L, ở đầu ra nồng độ trung bình chỉ còn lại 5,41; 1,10 và 0,03 mg/L tương ứng. Nồng độ đầu vào của ion Mn^{2+} khoảng 69,44; 75,84 và 76,48 mg/L tương ứng, tuy nhiên, ở đầu ra nồng độ của ion đạt 5,66 mg/L, 1,35 và 0,41 mg/L. Sử dụng công nghệ này thời gian lưu ngắn, chi phí khoảng 4000 VNĐ/m^3.

Keywords: treat Zn, Mn, limestone, sawdust and bacteria

1. Introduction

Zinc and manganese can be treated (neutralized) applying various physical, chemical and biological methods and various combinations (Brown et al., 2002; Merkel et al., 2005; Willscher, 2001). The choice of a specific method depends on a number of factors such as mass flows, pollutant loads, specific environmental laws, climatic conditions, local availability of limestone, infrastructure, financial and land use issues, subjective aspects, etc.

Using ionic exchange method to separate heavy metal ions from solution, simultaneously, an equivalent amount of other ions in solution. Ionic exchange method is used primarily in the treatment of hardness and salt removal in waste water and they can also be used for the removal and recovery of heavy metals in wastewater (Acheampong et al., 2010; Bahlo & Wach, 1992; Blume, 2001; Dietz et al., 2005). Although the use of ionexchange method is simple, but the material need to be frequently treated and recycled or storage of waste, so it can be an additional cost.

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Adsorption method is used widely to treat containing heavy metals in wastewater. It can be used to treat small concentrations of heavy metals and can be thoroughly treated with biological treatment wastewater or (with) chemical treatments (Meier et al., 2004; WRc/SevernTrent., 1996). When wastewater treated by adsorption method, first would be the removal of the neutral molecular substancesto ions then removal of disscociated subtances. Adsorption ability of compound in wastewater depends on temperature. In the low temperatures, the adsorption process occurs strong, but if too high temperature, it can occur the desoption process.

In treatment wastewater, the chemical methods such as neutralization and precipitation are offen used. Chemicals were used to neutralize and precipitate heavy metals mainly are NaOH, $Ca(OH)_2$ or Na_2CO_3 using these chemicals increase the cost and the soluble part of the amphoteric metals such as Zn, Al etc.

$$H^+ + OH^- \rightarrow H_2O$$
$$Me^{2+} + OH^- \rightarrow Me(OH)_2\downarrow$$
$$Me^{2+} + CO_3^{2-} \rightarrow MeCO_3\downarrow$$

Sulfur compounds are used such as Na_2S often precipitate the sulfur heavy metals very effectively, because the solubility of sulfur heavy metals are very low, but they are expensive and require special attention to the spread of H_2S into the atmosphere. In addition, the three valence metal ions could create hydroxide precipitate.

$$Me^{2+} + S^{2-} \rightarrow MeS\downarrow$$
$$Me^{3+} + S^{2-} + H_2O \rightarrow Me(OH)_3\downarrow + H_2S\uparrow$$

Treatment method for zinc and manganese in acid mine drainage in the laboratory by combining limestone, sawdust and bacteria.

Mechanism are taken in two stages:

➢ The first stage: The removal of heavy metals and neutralization in system.

Limestone mainly is mineral calcite (calcium carbonate $CaCO_3$). Calcite minerals have small solubility in water. Calcium carbonate is dissolved as the equation:

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \quad K_{sp} = 8{,}7\times10^{-9} \text{ ở } 25\ °C$$

Equivalent to:

$$2[CO_3^{2-}] + [H^+] + H_2O = 2[HCO_3^-] + 2[OH^-]$$

Most of heavy metals will precipitate as hydroxide and carbonate precipitation and separated from the solution.

For exemple: $Mn^{2+} + 2OH^- = Mn(OH)_{2\,(solid)}$

$$Mn^{2+} + 2OH^- + CO_3^{2-} = Mn_2(OH)_2CO_{3\,(solid)}$$
$$Mn^{2+} + CO_3 = MnCO_{3\,(solid)}$$
$$Zn^{2+} + 2OH^- = Zn(OH)_{2\,(solid)}$$
$$Zn^{2+} + 2OH^- + CO_3^{2-} = Zn(OH)_2CO_{3\,(solid)}$$
$$Zn^{2+} + CO_3^{2-} = ZnCO_{3\,(solid)}$$

In addition to the precipitation of heavy metal ions, limestone can neutralize acidity, which create a favorable environment for the microorganisms.

➢ The second stage: The removal of other anions and metal ions, which in the first stage processing unsatisfactory.

It plays roll as carbon source for microorganisms and simultaneously supplying for reducing process such as dissimilatory sulfate reduction:

$$(CH_2O)_n + SO_4^{2-} \rightarrow CO_2 + S^{2-} + OH^-$$

After the product of dissimilatory sulfate reduction, sulfide can generate alkaninity as well as precipitate heavy metal ions in the form of metal sulfide (reaction 2-6) (Bhagat et al., 2004; Kaksonen & Puhakka, 2007).

$$Me^{2+} + S^{2-} = MeS\downarrow$$

and the pH value is increased through the process:

$$S^{2-} + H^+ \rightarrow H_2S$$

Sawdust is an agricultural waste that contains mainly cellulose and it can be used as substrate for maintaining microbial activity in the system (Figure 1).

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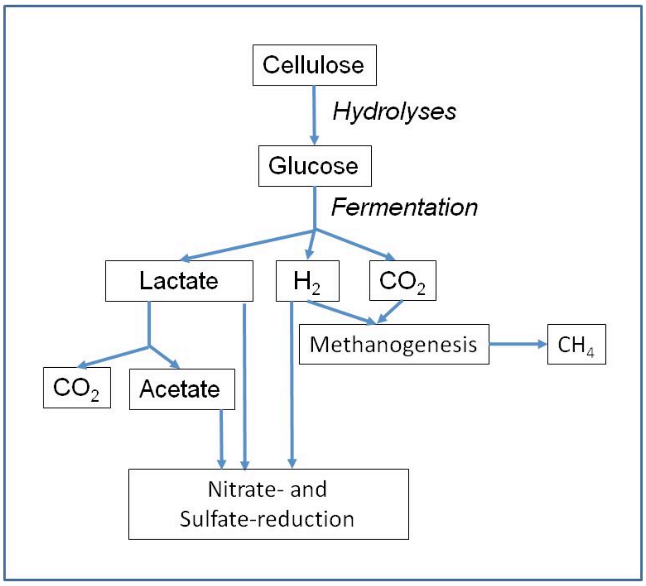

Figure 1. Organic substrate supply for the biological reduction of sulfate and nitrate in the treatment system

2. Material and methods

2.1. Experiment set up

The experiment system was presented in Figure 2. The tank made of polymer, the dimensions were 100 cm of length, 15 cm of width and 35 cm of height. The first 1/4 of the system is limestone and the second 3/4 is mixture of limestone, sawdust and enriched bacteria, which ratio is 10:1:0.1. A column consisting of sand and activated carbon was built and connected with the system. The system was operated continouostly in 3 phases A, B, C.

Phase A: Hydraulic retention time (HRT) is 1.5 day and the operation time is 2 months.

Phase B: Aeration machines are placed before and after the system. Also, after the aeration treatment in the end, the system is connected to a filtration column. HRT of the system is 1.1 day and aeration velocity is 0.3 L of air per 1 L of solution per min.

Phase C: Continue from phase B, HRT of the system is 1.1 day and aeration velocity is 0.6 L of air per 1 L of solution per min.

The culture of microbial limestone and sawdust was enriched in 1 month.

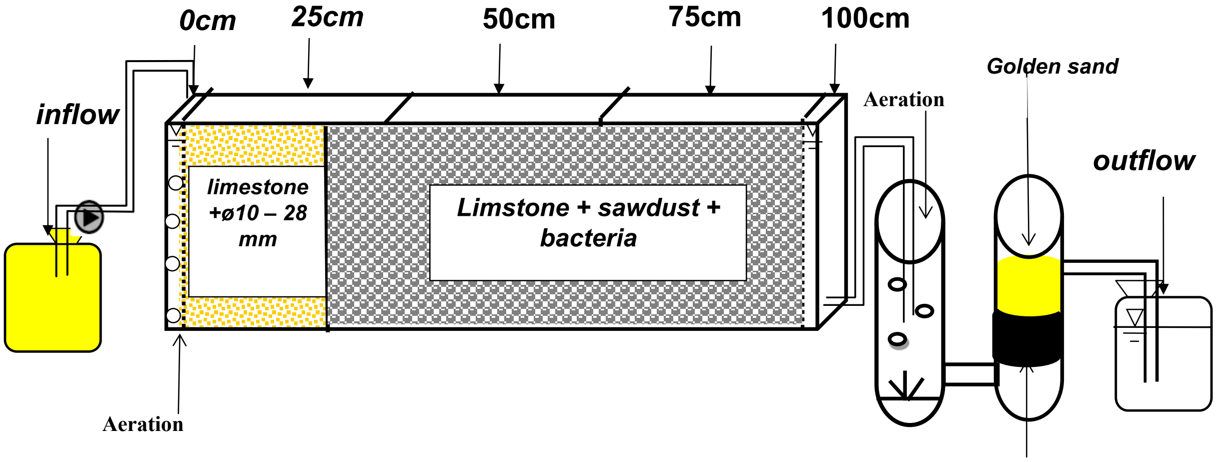

Figure 2: Scheme of the laboratory treatment system

2.2. Chacteristic inorganic wastewater

The used wastewater in this study was obtained from Mao Khe mine in Quang Ninh. The typical characteristics of the wastewater are listed below.

- Fe (total): 180 ÷ 320 (mg/L)
- Mn^{2+}: 2.4 ÷ 23.28 (mg/L)
- Zn^{2+}: 2.28 ÷ 42.12 (mg/l)
- SO_4^{2-}: 1600 ÷ 2770 (mg/L)
- pH: 1.26 ÷ 2.83

2.3. Sampling

Samples were taken twice a week from the inlet, middle (0 cm, 25 cm, 50 cm, 75 cm, 100 cm) and outlet of system unit with a syringe (60 ml).

2.4. Analytical methods

The samples were analyzed by following the standard methods.

The pH value was determined with pH meter 296 (WTW), acid and base capacity was determined with titration method. Sulfate, Sulfide, COD, was determined with Optizen 2120 UV/Shimadzu; heavy metals were determined with AAS Perkin Elmer and VA 757 Computrace, Metrohm.

3. Results and discussion

3.1. pH value

In all the three operation phases, pH value of the inflow wastewater was very low (about 1.7 - 2.1), however after the treatment, it increased up to neutral level. This could be explained that, the reaction of $CaCO_3$ with H^+ first occurred to form HCO_3^- or H_2CO_3. A part of $CaCO_3$ dissociated into CO_3^{2-}, then CO_3^{2-} and HCO_3^- could combine with H^+, the pH value increase. In system, the dissimilatory sulfate reduction formed S^{2-} which could react immediately with H^+ remaining in the wastewater to form H_2S. As a result, pH value was inreased continuously.

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$$
$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$
$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$
$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$
$$HCO_3^- + H^+ \rightarrow H_2CO_3$$
$$S^{2-} + H^+ \rightarrow H_2S$$
$$S^{2-} + H_2O \rightarrow HS^- + OH^-$$

Obviousely, the removal of H^+ in the combined biological and chemical methods was quite effective in increasing the pH value to neutral, which creates a suitable environment for microbial activity such as dissimilatory sulfate-reduction or hydrolyzation process.

3.2. Chemical Oxygen Demand

Chemical oxygen demand (COD) results shows that the concentration of organic compounds in the the inflow of the 3 phases is relatively low, the average value of COD is about 0.53 mg/L, in the tank COD changes according to the different stages.

In the phase A, HRT of 1.5 days, the COD value in the inflow was negligible in the tank (stage 50 cm), the average value of COD increased to 500 mg/L. Meanwhile in outflow the COD value decreased, which is of about 150 mg/L.

In the phases B and C, HRT of 1.1 days, the average value of COD in the tank (stage 50 cm) increased, but the addition of air into the system, COD decreased significantly. The decreased COD is proportional to the amount of air brought into the tank. The average value of COD was about of 190 mg/L for the phase B and only about of 160 for phase C. In the outflow the average COD value were of about 130 and 107 mg/L for phases B and C respectively.

In this system, organic carbon compounds come mainly from the sawdust in biological tank. Bacteria could hydrolyze cellulose sawdust into form short chain organic compounds such as glucose, which could be fermented to provide substrates for anaerobic dissimilatory reduction processes, for example organic acids, alcohols and hydrogen.

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow n\ C_6H_{12}O_6$$
$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$
$$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$$

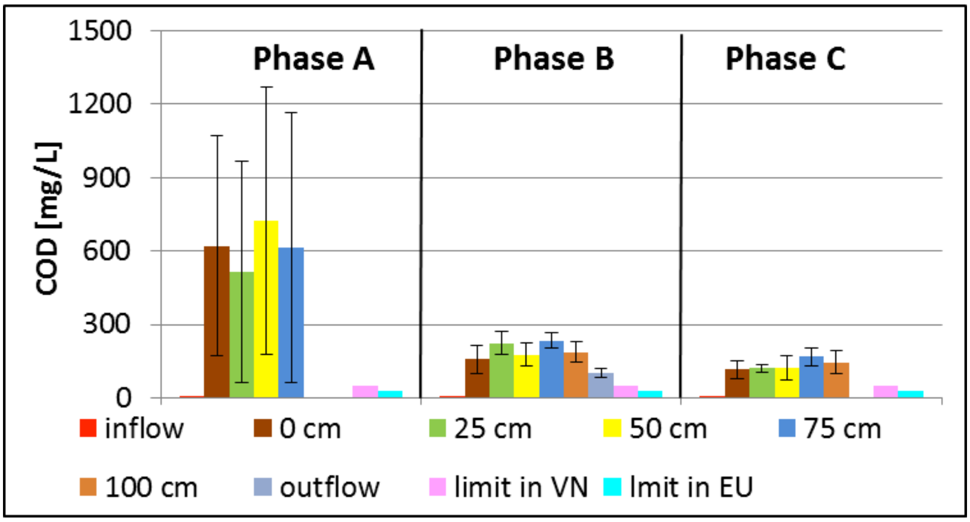

Figure 3. Chemical Oxygen Demand (COD) in the inflow and outflow in the stage (Phases A, B and C) n = 26-18-7 respectively

On the other hand, inorganic carbon in the form of CO_3^{2-}, HCO_3^-, with the presence of micro organisms, they can also change into a short circuit organic compounds such as acetate according to the following reaction equation:

$$CO_3^{2-} + H_2O \rightarrow CH_3COO^- + OH^-$$

These organic compounds play in very important roll for biological reduction process. On one hand, they could be as a electrodonors source for removing nitrate and sulfate, on the other hand, they plays in roll of carbon source for bacterial activities, in the treatment system.

The addition of air to the end of the system was removed a part of COD by oxidation process:

$$(CH_2O)_n + O_2 \rightarrow CO_2 + H_2O$$

3.3. Concentration of sulfide

The Figure 4 shows that the relatively high concentration of S^{2-} increases from stage 25 cm (about 75 mg/L) to stage 75cm (about 140 mg/L), This proves that S^{2-} was formed in the system very effective. The dissimilatory sulfatereduction in the system was very good (Battaglia-Brunet et al., 2000; Batty et al., 2008; Bhagat et al., 2004).

$$(CH_2O)_n + SO_4^{2-} \rightarrow CO_2 + S^{2-} + H_2O$$

With the presence of sulfide, the removal of heavy metals ion in AMD such as Zn^{2+} and Mn^{2+} were increased efficiency. The removal process is performed according to the following reaction:

$$Zn^{2+} + S^{2-} \rightarrow ZnS$$
$$Mn^{2+} + S^{2-} \rightarrow MnS$$

Forming sulfide through dissimilatory sulfatereduction create a suitable condition for zinc and manganese removal.

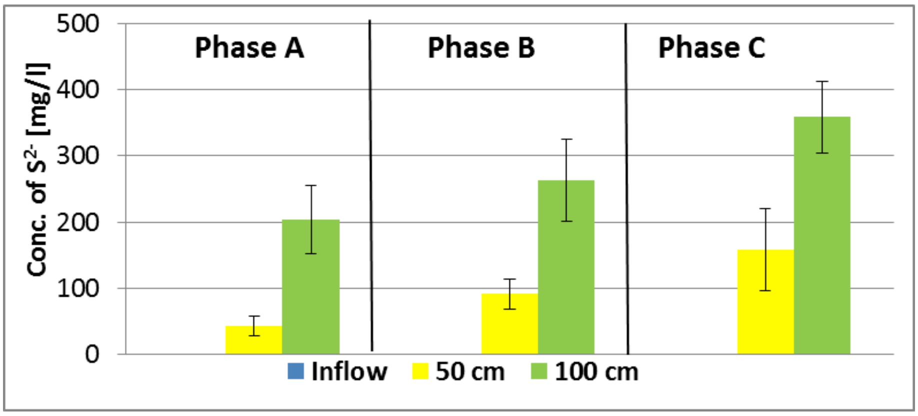

Figure 4. Average concentration of sulfide in the inflow and outflow in the stage (Phases A, B and C) n = 26-18-7 respectively

3.4. Concentration of Zn^{2+}

Zinc was removed effectively in all three phases (Figure 5). The results showes that, in 3 phases A, B and C, the removal efficiencies of Zn^{2+} are different. While the average concentration of Zn^{2+} in the inflow at about 40.81 to 44.52 mg/L, in the outflow average concentrations were only 5.41; 1.10 and 0.03 mg/L respectively.

In phase A, with the presence of NH_4^+, it prevents the elimination the Zn^{2+} through precipitation in the form of sulfide or carbonate precipitation. When aerate to system (Phase B and Phase C), in the presence of aerobic microorganisms, ammonia and nitrite will be converted into nitrates, making complicated amiacat into free zinc ions, which precipitate readily with ions CO_3^{2-} or S^{2-} according to the following reaction:

$$[Zn(NH_3)_4]^{2+} \leftrightarrow Zn^{2+} + 4\ NH_3$$
$$NH_3 + O_2 \rightarrow NO_2^- + H_2O$$
$$Zn^{2+} + CO_3^{2-} \rightarrow ZnCO_3\downarrow$$
$$Zn^{2+} + S^{2-} \rightarrow ZnS\downarrow$$

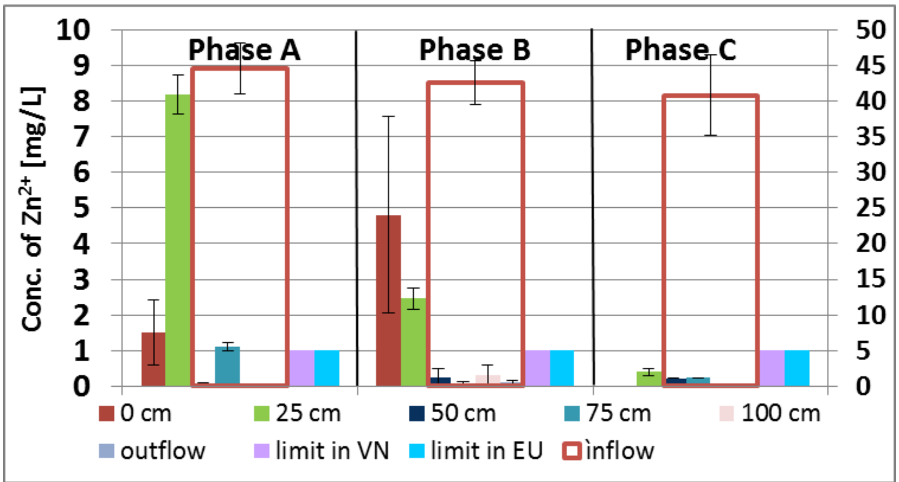

Figure 5. Concentration of Zn^{2+} in the inflow, stage of tank and outflow in the phases A, B and C. (n =26-18-7 respectively)

Thus, increasing aeration velocity in the system has increased the efficiency of the removal process Zn^{2+} ions out of the water and reached the standard of dometsic water.

3.5. Concentration of Mn^{2+}

The results showes that, in all 3 phases A, B and C, the concentration of Mn^{2+} ion in the inflow are relatively high, the average values are about 69.44; 75.84 and 76.48 mg/L respectively, however, in the outflow the concentration decreased significantly.

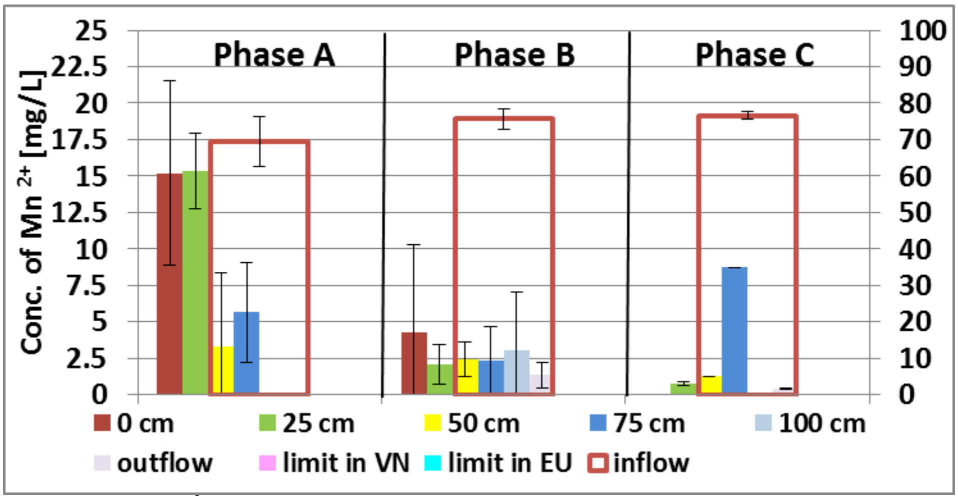

Figure 6. Concentration of Mn^{2+} in the inflow, stage of tank and outflow in the phases A, B and C. (n =26-18-7 respectively)

In the phase A non aeration, concentration reached 5.66 mg/L, while in phases B and C, they reached 1.35 and 0.41 mg/L respectively. This can be explained by aerating more into the system occure metabolic reactions:

$Mn^{2+} + O_2 \rightarrow MnO_2$

When the increased aeration (phase C), the removal of Mn is increased. Also, when in solution exist $CO_3^{2-}$and S^{2-}, $Mn^{2+}$is also removed through the precipitation of $MnCO_3$ và MnS form.

$$Mn^{2+} + CO_3^{2-} \rightarrow MnCO_3$$
$$Mn^{2+} + S^{2-} \rightarrow MnS$$

4. Conclusions

A lab-scale system using the combination of limestone, sawdust and bacteria was conducted to treat zinc and manganese in AMD effectively.. The treated waste water can directly into the environment.

Now, the system can treat AMD wastewater to reuse to bath or to provide for the production processes with the price of 0.2 USD/m^3. In the future, the system can be developed to have higher efficiency and can be applied to treat others kinds of wastewater, with an similar characteristic wastewater: such as industrial, electroplating, metallurgy waste water and an insignificants changes in price.

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