



## THE INFLUENCE OF SODIUM SILICATE ON REMOVAL OF HEAVY METALS BY IRON MINE TAILING

Le Sy Chinh<sup>1</sup>, Mai Trong Nhan<sup>2</sup>, Nguyen Xuan Hai<sup>2</sup>, Nguyen Thi Hai<sup>2</sup>, Dang Ngoc Thang<sup>2</sup>, Nguyen Tai Giang<sup>2</sup>, Doan Dinh Hung<sup>3</sup>, Nguyen Trung Minh<sup>3</sup>, Nguyen Manh Khai<sup>2</sup>, Tran Dang Quy<sup>2</sup> and Nguyen Thi Hoang Ha<sup>2</sup>

<sup>1</sup>Hong Duc University, Quang Trung, Thanh Hoa, Vietnam

<sup>2</sup>VNU University of Science, Vietnam National University, Hanoi, Nguyen Trai, Hanoi, Vietnam

<sup>3</sup>Vietnam National Museum of Nature, Vietnam Academy of Science and Technology, Hoang Quoc Viet, Hanoi, Vietnam

E-Mail: [nguyensexuanhai@hus.edu.vn](mailto:nguyensexuanhai@hus.edu.vn)

### ABSTRACT

Water pollution has been a major considering issue in recent years. Many technologies have been studied for the treatment of wastewater contaminated with heavy metals. The sorption of heavy metals has been emerged as a cost-effective and environment friendly technology. This study was conducted to assess the sorption capacity and removal efficiency of heavy metals at initial concentrations of 20 mg/l by iron mine tailing with different sodium silicate solution addition (0, 5, 10, and 15%). The results showed the proportionally increasing trend of sorption capacity and removal efficiency of Mn, Zn, Cd, and Pb to sodium silicate addition. Iron mine tailing without addition of sodium silicate demonstrated the highest removal efficiency of As. On the basis of modified material solubility,  $pH_{PZC}$ , sorption capacity, removal efficiency, and cost effectiveness, the results of this study indicate that iron mine tailing added with 10% sodium silicate and dried at 400°C was the most potential materials for removal of heavy metals from solutions.

**Keywords:** heavy metals, iron mine tailing, removal, sodium silicate, sorption.

### 1. INTRODUCTION

Heavy metals are elements with atomic weight in the range from 63.5 to 200.6 and density greater than 5.0 g/cm<sup>3</sup> [1,2]. Heavy metals are not biodegradable, they can be accumulated in living tissues via inhalation, ingestion or the skin [2,3]. A variety of treatment has been developed for the removal of these metals from water, including coagulation [4], adsorption [5, 6], ion exchange [7,8], and electrocoagulation [9], and biological processes [10]. Of which, the adsorption using natural materials has emerged as a cost-effective and efficiency alternative for the removal of heavy metals [11].

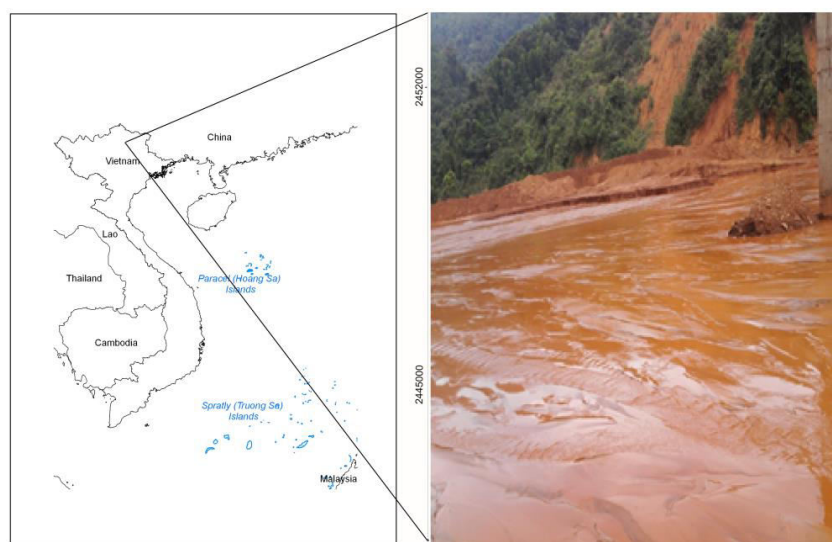
A wide range of adsorbents has been studied for heavy metal removal including laterite [12], zeolite [13], kaolinite [14], oxides and hydroxides of iron [6] ... High sorption capacity of red mud and coal mine tailing was reported [15-17]. However, few studies have investigated

the capacity of iron mine tailing to adsorb heavy metals. The broken incidence of the iron mine in Cho Don District, Bac Kan Province on July 20, 2015 highlights the need of using tailing materials for treatment purpose. A majority of clay and silt grain size of tailing adsorbents requires the addition of mixing materials. The objective of this research is to assess the influence of sodium silicate addition on sorption and removal of heavy metals.

### 2. MATERIALS AND METHODS

#### 2.1. Field survey and sampling

The survey was conducted in an iron mine in Cho Don District, Bac Kan Province, Northern Vietnam in October, 2015. Tailing materials in reservoir were collected for further laboratory study.



**Figure-1.** Iron mine tailing in Bac Kan Province.

## 2.2. Modification of iron mine tailing

The iron mine tailing samples were dried using the NIIVE OVER KD200 oven at 80 - 105°C until the

sample weight was constant. Samples were crushed into fine powder using the MRC laboratory Equipment Manufac Urer.

**Table-1.** Characteristics of modified iron mine tailing samples.

Modified samples	Characteristics
SBC2- 400	No sodium silicate solution, 400°C in 3 hours
SBC2-400-5S	5% sodium silicate solution, 400°C in 3 hours
SBC2-400-10S	10% sodium silicate solution, 400°C in 3 hours
SBC2-400-15S	15% sodium silicate solution, 400°C in 3 hours

Iron mine tailing was mixed with sodium silicate and deionized water to obtain the proportion of the silicate solution of 0, 5, 10, and 15%. The specific gravity, contents of Na<sub>2</sub>O and SiO<sub>2</sub> of sodium silicate solution is 1.46±0.01 g/ml, 11.5 ~ 12.2%, and 27.5 ~ 29.5%, respectively. The mixed samples were pressed using 2mm-diameter size machine and dried at 400°C in 3 hours (Table-1).

## 2.3. Heavy metal preparation

Five metals (Mn, Zn, Cd, Pb, and As) were added as standard solutions (Pb(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>HAsO<sub>4</sub>) provided by Merck corporation. The reagents were dissolved in Milli-Q water to obtain the desired contamination level (20mg/l). The resulting solutions were adjusted to pH 5.5 with NaOH 1M and HNO<sub>3</sub> 1M.

## 2.4. Experiment design

### Solubility of sorbents

Two grams of each modified iron mine tailing sample were placed in boxes containing 100 ml deionized water. This experiment was processed 3 months to examine solubility of modified samples. All of the laboratory experiments were repeated in triplicated.

### pH<sub>PZC</sub>

Two grams of each modified iron mine tailing sample were placed in boxes containing 100 ml deionized water and NaNO<sub>3</sub> 0.01M. pH<sub>i</sub> was adjusted by NaOH or HNO<sub>3</sub> at pH 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12. The samples were shaken for 24 hours (120 turns/min). All of the laboratory experiments were repeated in duplicated. The pH<sub>PZC</sub> values were determined by the equation (1):

$$\Delta\text{pH}_{\text{PZC}} = \text{pH}_i - \text{pH}_f \quad (1)$$

Where pH<sub>i</sub> and pH<sub>f</sub> are pH of solutions before and after 24 hour-shaking. The intersection of the trendline with the horizontal axis at the point ΔpH=0 determined pH<sub>PZC</sub>.

### Sorption of heavy metals

Two grams of each iron mine tailing sample were placed in 100 ml of water containing 20mg/l of each metal (Mn, Zn, Cd, Pb, and As). The samples were exposed to the solutions for 24 hours under shaking condition (120 turns/min). All of the laboratory experiments were repeated in duplicated.

The sorption capacity (*qe*) is calculated by the equation (2):

$$qe = \frac{(C_0 - C_e)V}{m} \quad (2)$$



Where  $q_e$ ,  $C_o$ ,  $C_e$ ,  $m$ , and  $V$  are sorption capacity (mg/kg), initial metal concentrations in water (mg/l), metal concentrations in water at equilibrium (mg/l), mass of material (g), and solution volume (ml), respectively.

The removal efficiency, which can be used to assess the potential of iron mine tailing for wastewater treatment, is calculated by the equation (3):

$$\text{Removal efficiency \%} = \frac{(C_o - C_e)100\%}{C_o} \quad (3)$$

Where  $C_o$  and  $C_e$  are initial metal concentrations in water (mg/l) and metal concentrations in water at equilibrium (mg/l), respectively.

## 2.5. Analytical methods

Mineral compositions of modified iron mine tailing samples were determined using the X-Ray Diffraction (XRD - Siemens D5000) at the Faculty of Physics, VNU University of Science. Particle Charge Detector (PCD - Mutek PCD-05) was performed for determination of surface charge density at the Faculty of Environmental Sciences, VNU University of Science. The surface area of iron mine tailing was determined using the Gemini VII 2390 Surface Area Analyzer (Micromeritics) at Hanoi University of Science and Technology. Elemental

analyses of water samples were performed by Atomic Adsorption Spectrometer AAS (280FS, VGA77, Agilent) at the Faculty of Geology, VNU University of Science.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Characteristics of modified Ban Cuon iron mine tailing

The results of mineral compositions (XRD) showed higher percentage of kaolinite, goethite, and hematite in SBC2-400 than that in Ban Cuon iron mine tailing added with sodium silicate (Table-2). The percentage of goethite in SBC2-400 sample was 6%, which was higher than that in SBC2-400-5S, SBC2-400-10S, SBC2-400-15S samples. The percentage of kaolinite in SBC2-400 and SBC2-400-15S samples were 11% and 10%, respectively, which were higher than that in SBC2-400-5S (7%), SBC2-400-10S samples (7%). The percentage of hematite in 4 samples varied within 7-8 % (Table 3). Iron mine tailing samples without addition of sodium silicate solution demonstrated the highest value of surface area (BET) (Table-3). The results of this study showed that surface charge density (PCD) was proportional to the percentage of sodium silicate addition (Table-3).

**Table-2.** Minerals composition of modified iron mine tailing.

Minerals	SBC2-400	SBC2-400-5S	SBC2-400-10S	SBC2-400-15S
Kaolinite	11%	7%	7%	10%
Goethite	6%	1%	1%	-
Hematite	8%	7%	7%	7%

**Table-3.** Surface area and surface charge density of modified iron mine tailing.

	SBC2 -400	SBC2 -400-5S	SBC2 -400-10S	SBC2 -400-15S
BET (m <sup>2</sup> /g)	47.8	29.5	39.4	26.1
PCD (mmol <sub>c(-)</sub> /kg)	69	87.7	91	116

### 3.2. Solubility of sorbents

The results of this study showed different solubility of modified sorbents after 3 months of incubation (Table-4). The modified iron mine tailing with 10% sodium silicate addition (SBC2-400-10S) demonstrated lowest solubility (<2%); by contrast, no addition of sodium silicate showed highest solubility (≈15%).

**Table-4.** Solubility of sorbents with different mixing sodium silicate ratios.

Sorbent materials	% solubility
SBC2-400	≈15
SBC2-400-5S	5-10
SBC2-400-10S	<2
SBC2-400-15S	≈10

### 3.3. Zero charge point (pHPZC) of sorbents

The zero charge points of SBC2-400, SBC2-400-5S, SBC2-400-10S, SBC2-400-15S were obtained at pH 5.6, 10.3, 10.5, and 9.7, respectively. An increase in pH values with the addition of sodium silicate was due to the hydrolysis process which was produced by reaction of weak acid and strong base (Na<sub>2</sub>SiO<sub>3</sub>). Low and positive charge sorbent surface indicate the preference of anion sorption (H<sub>2</sub>AsO<sub>4</sub><sup>+</sup>, HAsO<sub>4</sub><sup>2-</sup>). By contrast, negative charge tends to adsorb cation (e.g., Mn<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>) [17,18].

### 3.4. Influence of sodium silicate addition on removal of heavy metals from solutions

Of the four modified sorbents, SBC2-400 showed the highest sorption capacity and removal efficiency of As (555 mg/kg, 55.5%) and lowest values of Mn (288 mg/kg, 28.8%), Zn (332mg/kg, 33.2%), Cd (250mg/kg, 25.0%),



and Pb (708mg/kg, 70.8%) (Figure-3). This is in accordance with the finding of the effect of zero charge point on metal sorption [17,18]. SBC2-400-10S showed the highest sorption capacity and removal efficiency of Mn (656 mg/kg, 65.6%) and Pb (990 mg/kg, 99.0%) and lowest values of As (60 mg/kg, 6.0%). SBC2-400-15S demonstrated highest sorption capacity and removal efficiency of Zn (819 mg/kg, 81.9%) and Cd (610 mg/kg, 61.0%). In addition, no significant difference of Pb concentrations in the four modified sorbents (0, 5, 10, and 15% sodium silicate addition) was obtained (Figure-3).

The increasing trends of sorption capacity and removal efficiency of Mn, Zn, Cd, and Pb are proportional to the increasing addition of sodium silicate (Figure-3). The reverse result was obtained for As. These trends may result from the lower proportion of goethite (Table 2) and higher values of PCD (Table 3) in the samples added with sodium silicate (SBC2-400-5S, SBC2-400-10S, and SBC2-400-15S) than those in SBC2-400. The hydrolysis reaction in sodium silicate solution resulted in an increase of hydroxyl functional groups on the surface of modified

iron mine tailing. This process increased the sorption capacity and precipitation of heavy metal ions ( $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Pb^{2+}$ ) [17]. However, an increase of hydroxide also reduced positive charge functional groups on the surface and reduced the sorption capacity of As [17].

In the present study, the results of solubility,  $pH_{PZC}$ , sorption capacity, removal efficiency, and cost effectiveness indicate that the most feasible material for removal of heavy metals was SBC2-400-10S. However, considering the high pH values of modified samples (9.7 - 10.5), additional pretreatment of pH should be needed. In addition, most concentrations of metals in solutions after the experiment exceeded Vietnamese standard limits for industrial wastewater [19] (Table-5). This is due to high initial concentrations of metals (20 mg/l). Therefore, further studies on optimal conditions for metal removal, higher volume of mine tailing weight or additional technologies may be required for treatment of wastewater contaminated with heavy metals.

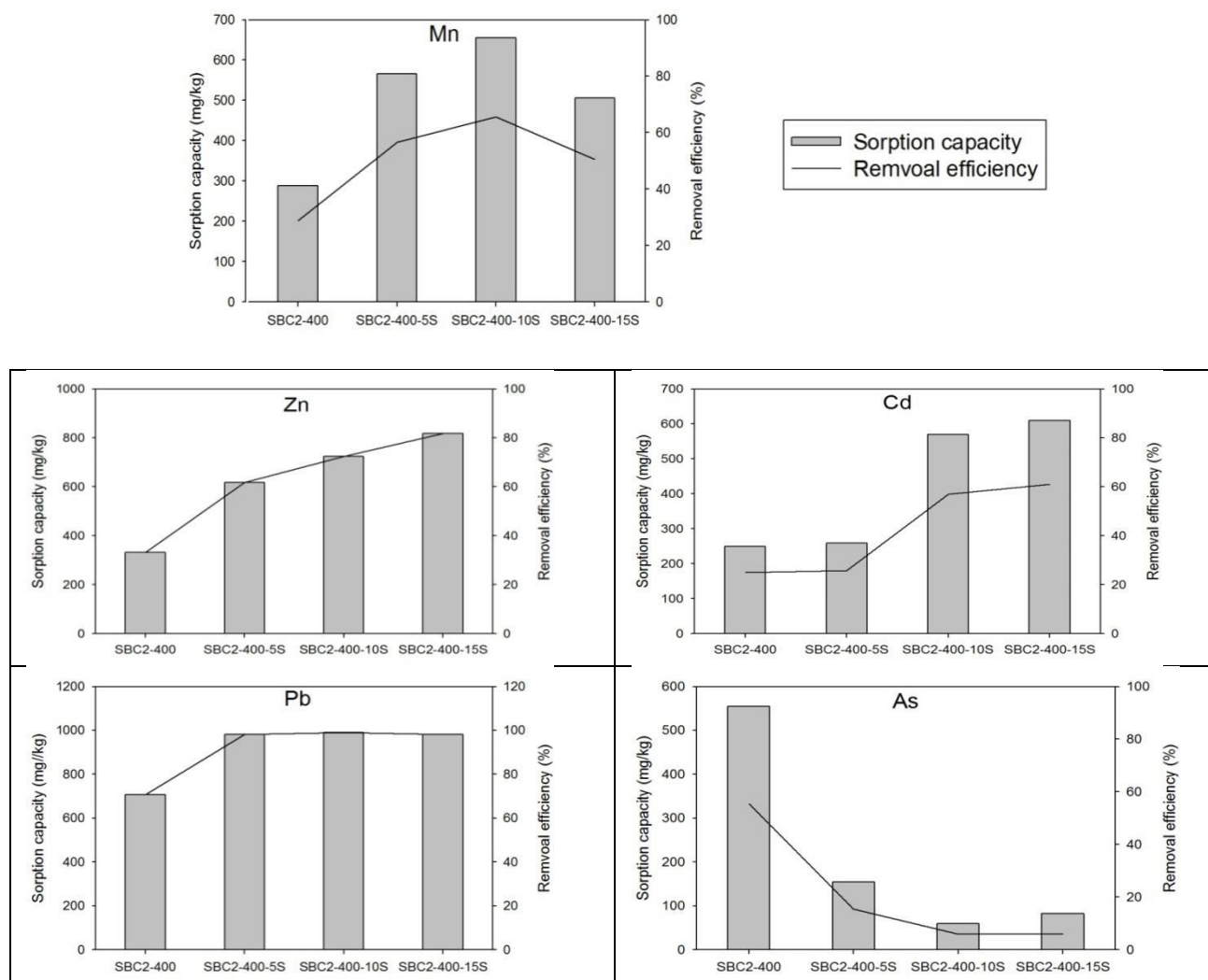


Figure-2. Sorption capacity and removal efficiency of iron mine tailing.

**Table-5.**Concentrations of metals in solutions after sorption experiments (mg/l).

Metals	SBC2-400	SBC2-400-5S	SBC2-400-10S	SB2-400-15S	QCVN40:2011/BTNMT	
					A	B
Mn	14.2	8.69	6.88	9.89	0.5	1
Zn	13.4	7.64	5.50	3.63	3	3
Cd	15.0	14.8	8.60	7.81	0.05	0.1
Pb	5.85	<b>0.37</b>	<b>0.21</b>	0.35	0.1	0.5
As	8.91	16.9	18.8	18.4	0.05	0.1

#### 4. CONCLUSIONS

The highest removal efficiency of Mn, Zn, Cd, Pb, and As was 65.6, 81.9, 61.0, 99.0, and 55.5%, respectively. Iron mine tailing without the addition of sodium silicate showed the highest removal efficiency of As. Highest removal efficiency of Mn and Pb was obtained in tailing added with 10% sodium silicate and that of Zn and Cd with 15% sodium silicate addition.

#### ACKNOWLEDGEMENTS

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