Sorption of heavy metals by laterite from Vinh Phuc and Hanoi, Vietnam

Nghiên cứu khả năng hấp phụ kim loại nặng của laterit đá argil concurrently with heavy metals from water, including precipitation (Gunatilake, 2015), ion exchange (Gaikwad et al., 2010), electrocoagulation (Turdean and Popescu, 2013), and biological processes (Dhokpande and Kaware, 2013). Of which, adsorption of heavy metals from solutions has emerged as a cost-effective and high removal efficiency technology. Several natural materials have been reported for treatment wastewater, including kaolinite (Adebowale et al., 2005), sludge (Gene et al., 2003; Doan and Nguyen, 2011), diatomite (Al-degs et al., 2001; Li et al., 2009), and laterite (Yu et al., 2008).

Laterite is the final product in the process of chemical weathering in the humid tropics with the accumulation of Fe and Al oxides and hydroxides. In Asia, the laterite is

1. Introduction

Water pollution by heavy metals has been a major considered issue in recent years. A variety of chemical - physical technologies have been applied to deal with the removal of these metals from water, including precipitation (Gunatilake, 2015), ion exchange (Gaikwad et al., 2010), electrocoagulation (Turdean and Popescu, 2013), and biological processes (Dhokpande and Kaware, 2013). Of which, adsorption of heavy metals from solutions has emerged as a

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**Keywords:** heavy metals, removal, laterite, solutions, sorption
very popular in China, India, Bangladesh, Vietnam, and Indonesia. In Vietnam, laterite is widely distributed in the north and central highlands. Laterite from Hanoi City was reported to have high sorption capacity of heavy metals such as Pb, As, Zn, Ni, Mn, Cu, Co, and Cd from solutions (Tran et al., 2004; Nguyen, 2010). However, no previous research has assessed the sorption of heavy metals by laterite from Vinh Phuc Province. The objective of this research is to assess the sorption capacity of laterite from Vinh Phuc Province in comparison with laterite from Hanoi City.

2. Materials and methods

2.1 Sampling

Laterite samples were collected at Thanh Van Commune, Tam Duong District, Vinh Phuc Province and Binh Yen Commune, Thach That District, Hanoi City. The laterite sample in Hanoi was taken at the same site as reported by Nguyen (2010) for comparison.

2.2 Heavy metals preparation

Five metals (Mn, Zn, Cd, Pb, and As) were added as standard solutions (Pb(NO₃)₂, Zn(NO₃)₂, Mn(NO₃)₂, Cd(NO₃)₂ and Na₃HAsO₄). The reagents were dissolved in Milli-Q water to obtain the desired contamination levels. Then the solutions were adjusted to pH 5.5 with NaOH and HNO₃.

2.3 Experiment design

2.3.1 pH_{PZC}

Two grams of each laterite sample were placed in boxes containing 100 ml deionized water and NaNO₃ 0.01M. pH was adjusted by NaOH or HNO₃ at pH 3, 4, 5, 6, 7 and 8. The samples were shaken for 24 hours (120 turns/min). All of laboratory experiments were repeated in duplicate. The pH_{PZC} values were determined by the equation 1.1:

\[ \Delta pH_{PZC} = pHi - pHf \]  

Where pHi and pHf are pH of solutions before and after 24 hour-shaking.

The intersection of the trendline with the horizontal axis at the point \( \Delta pH=0 \) determined pH_{PZC}.

2.3.2 Sorption of heavy metals

Two grams of laterite sample were placed in 100 ml of water containing 2.5, 5.0, 10, 20 and 50 mg/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 duplicate.

The sorption capacity (qe) is calculated by the following equation (1.2):

\[ qe = \frac{(Co - Ce)V}{m} \]  

Where qe, Co, Ce, 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 laterite for wastewater treatment, is calculated by the equation 1.3:

\[ \text{Removal efficiency} = \frac{(Co - Ce)100%}{Co} \]  

Where Co and Ce are initial metal concentrations in water (mg/l) and metal concentrations in water at equilibrium (mg/l), respectively.

2.4 Analytical methods

Samples were dried by NIIVE OVER KD200 temperature at 80-105°C and crushed by Equipment Manufacturer MRC at the Faculty of Geology, VNU University of Science, Vietnam National Univesity, Hanoi. Mineral compositions of the laterite samples were determined using the X-Ray Diffraction (XRD - Siemens D5005) at the Faculty of Physics, VNU University of Science. Particle Charge Detector (PCD - Mütek PCD-05) was performed for determination of surface charge density at the Faculty of Environmental Sciences, VNU University of Science. Elemental analyses of water samples were performed by Atomic Absorption Spectroscopy (AAS - 280FS, VGA77, Agilent) at the Key Laboratory of Geoenvironment & Climate change Response (GEO-CRE), Vietnam National University, Hanoi.

3. Results and discussion

3.1 Characteristics of laterite

The results of mineral compositions (XRD) showed high percentage of kaolinite and goethite in laterite (Table 1). The percentage of goethite and kaolinite in laterite from Vinh Phuc Province was 15% and 36%, respectively; that in laterite from Hanoi City was 42% and 40% (Table 1). The lower proportion of goethite and kaolinite in laterite from Vinh Phuc Province than that in Hanoi City may indicate the sorption capacity. The displacement of H⁺ ion from the edge site of kaolinite and the metals sorption are usually accompanied. The result of surface charge density (PCD) of laterite from Vinh Phuc Province demonstrated lower values than that from Hanoi City (Table 2).

The zero charge points of laterite from Hanoi and Vinh Phuc were obtained at pH 4.2 and 5.2, respectively. The results suggested that pH_{PZC} of laterite from two provinces was lower than pH value set in the present experiment (pH=5.5). Therefore, the two materials tended to adsorb cations such as Mn²⁺, Zn²⁺, Pb²⁺, and Cd²⁺ (Nguyen, 2010).
3.2 Sorption of heavy metals by laterite from Vinh Phuc Province

The sorption capacity of laterite from Vinh Phuc Province was proportional to initial concentrations of heavy metals in solutions. The highest sorption capacity of Pb, As, Cd, Zn, and Mn by laterite from Vinh Phuc was 1553, 756, 397, 281, 143 mg/kg, respectively (Figure 1) which was obtained at initial concentrations heavy metals of 50 mg/l. The highest removal efficiencies of Pb, As, Cd, Zn and Mn were 94, 76, 70, 56 and 37%, respectively (Figure 2). The sorption capacity of heavy metals by laterite was in the following order: Pb> As> Cd> Zn> Mn. This result is possibly due to the effect of cation radius in which larger radius indicates a smaller charge density and weakly hydrated cations. Cations with large charge density have strong resistance to the electrostatic force. Therefore, Mn is more difficult to be adsorbed than other metals. The radius of metal cations in descending order was Pb (1.2 Å) > Cd (0.97 Å) > Zn (0.74 Å) > Mn (0.67 Å). Arsenic can be adsorbed by the positive surface of the crystal structure of goethite. In addition, arsenic is also fixed in goethite according to following equation (Nguyen, 2014):

\[
\text{Fe-OH} + \text{AsO}_4^{2-} + \text{H} = \text{Fe-OAsO}_4^{2-} + \text{H}_2\text{O}
\]

Metal sorption capacity of laterite was tested to fit Langmuir and Freundlich models (Sparks, 2003) for further understanding of sorption mechanism. The results demonstrated that the sorption capacity of Pb, As, Cd, and Zn by laterite from Vinh Phuc Province was well fitted to the C linear type (Freundlich isotherm) (Sparks, 2003) with the correlation coefficient of 0.93, 0.89, 0.97, and 0.99, respectively. This result indicates that both adsorption and precipitation processes occurred simultaneously in the experimental solutions. In addition, experimental data of Mn on laterite from Vinh Phuc Province matched with L-type (Langmuir isotherm) (Sparks, 2003) with correlation coefficient of 0.99 which indicate that sorption capacity was inversely proportional to the initial concentrations of Mn in the experimental solutions. However, the increasing trend of sorption capacity with an increase in initial concentrations of heavy metals in solutions (Figure 1) indicates the need for further study on determination of sorption at equilibrium.

3.3 Comparison of sorption of heavy metals by laterite from Vinh Phuc and Hanoi provinces

The highest sorption capacity of Pb, As, Cd, Zn and Mn by laterite from Ha Noi Province was 1806, 1023, 503, 268, and 228 mg/kg, respectively (Figure 1). The highest removal efficiency of Pb, As, Cd, Zn and Mn by laterite from Ha Noi was 98, 96, 84, 61, and 53%, respectively (Figure 2). These results indicated that laterite from Vinh Phuc showed lower sorption capacity and removal efficiency than that from Hanoi (Figure 1, 2). The disparity adsorption capacity of Pb, As, Cd, Zn, and Mn between laterite from Hanoi and Vinh Phuc was 10.3–11.6, 11.9–17.9, 11.5–13.7, 9.5–17.6, and 11.1–14.3%, respectively. These results are possibly due to the higher percentage of goethite and kaolinite, higher values of surface charge density (PCD) of laterite from Hanoi than those from Vinh Phuc (Table 1, 2).

High sorption capacity and removal efficiency of heavy metals by laterite from Hanoi was in accordance with the results reported by Nguyen (2010). The difference in metal sorption by laterite from Thach That District, Hanoi City in this study than that in report of Nguyen (2010) may be due to the percentage of goethite (42%) and kaolinite (25%). In addition, the removal efficiency of heavy metals by laterite from Hanoi and Vinh Phuc was higher than that reported in bauxite, bentonite and zeolite (Naseem and Tahir, 2001; Le and Phan, 2008,Nibou et al., 2010; Nguyen, 2010).

4. Conclusions

Laterite from Tam Duong District, Vinh Phuc Province has a potential for sorption of heavy metals from solutions. The highest sorption capacity of Pb, As, Cd, Zn, and Mn by laterite from Tam Duong District was 1553, 756, 397, 281, and 143 mg/kg, respectively. The sorption capacity and removal efficiency of heavy metals by laterite from Tam Duong District were lower than those from Thach That District, Hanoi City, possibly due to differences in composition of goethite and kaolinite. The disparity sorption capacity of Pb, As, Cd, Zn, and Mn between laterite from Thach That and Tam Duong was 10.3–11.6, 11.9–17.9, 11.5–13.7, 9.5–17.6, and 11.1–14.3%, respectively.
Figure 1. Sorption capacity of Pb, As, Cd, Zn, and Mn by laterite from Vinh Phuc and Hanoi

Figure 2. Removal efficiency of Pb, As, Cd, Zn, and Mn by laterite from Vinh Phuc and Hanoi
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5. References

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