APPLICATION OF VOLCANIC ASH SOIL AND LATERITE TO WATER TREATMENT

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APPLICATION OF VOLCANIC ASH SOIL AND LATERITE TO WATER TREATMENT

By

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ABSTRACT

Volcanic ash soil and laterite are natural materials studied to use as treatment agents to remove contaminants from water. The present study aims to evaluate the applied ability of these materials to replace costly chemicals in water treatment. The flocculations of suspended clay particles and adsorption of phosphorous and heavy metals in contaminated water using volcanic ash soil and laterite materials were investigated.

In water treatment, water turbidity is a major factor increasing treatment costs. In order to eliminate water turbidity, suspended clay particles need to be removed. The removal efficiency is supposed to be strongly dependent on mineralogy of self-clay particles as well as treatment agents. This study examined the effects of clay mineralogy and interfacial chemistry of clay suspensions on the performance of a flocculant prepared from weathered volcanic ash rich in allophane and imogolite. Upon addition of the flocculant into the clay suspension and stirring, fluffy flocs formed and settled after a standing time. The absorbance of the supernatant gradually decreased to near zero at an optimum addition and then increased again when more flocculant was added. The optimum flocculant addition differed significantly among the clay suspensions. Inspection of the results of the flocculation tests and characterization of the sample clays, particularly stepwise multiple regression analyses, suggested that the major factors affecting the performance were the effective cation exchange capacity (ECEC), content of micaceous minerals and average particle size. This was interpreted as indicating the importance of the amount of negative charge on the external surfaces of particles in the clay suspensions.

Volcanic ash soil has high potentials in wastewater treatment due to consist of iron and aluminum oxides. To evaluate the relative flocculating power of allophane and imogolite, we conducted a series of flocculation experiment using allophane and imogolite sols and their mixtures. Imogolite was more effective than allophane for all five clay suspensions used. Therefore, weathered volcanic ash containing more imogolite is suitable for manufacturing flocculating agent. The residual turbidities of montmorillonite suspensions after treatment with mixed allophane and imogolite sols were nearly equal to those calculated under the assumption that the contribution of allophane and imogolite was additive. But the experimental turbidity was much higher than the calculated result for a soil clay suspension.

In the similar way, the study examined the removal capacity of suspended clay particles by the laterite samples distributed in Viet Nam. Mineralogy of the laterite and their use as flocculating agents for suspended clay particle removal were investigated. The laterite sample collected in Thach That region (1-TT) performed the best flocculation efficiency followed by the laterite sample collected in

Hoa Lac region (2-HL). The sample collected in Quynh Tam commune (3-QT) worked less efficiently than other two samples. Goethite, gibbisite and hematite are considered to be the main components that are responsible for flocculation action.

Adsorption of phosphate in artificial model solutions onto laterite was studied by batch experiments. Equilibrium isotherms and other adsorption experiments showed that phosphate adsorption was slightly pH dependent whereas the materials containing ferric and aluminum compounds are proven to be strongly pH dependent. Adsorption capacities of 1.1-1.6 mg P g^{-1}at pH 3 and 1.0-1.4 mg P g^{-1}at pH 9 and an equilibrium concentration of less 2 mg P L^{-1} can be reached. The presence of other anions, e.g., sulfates and carbonate was shown to decrease adsorption of phosphate. In competitive adsorption in the mixed solutions of phosphate, sulfate and carbonate, laterite samples preferred phosphate to sulfate and carbonate. The order of adsorption selectivity was phosphate > sulfate > carbonate. From the technological viewpoint, natural laterite is low cost material sources to remove phosphorous in contaminated water. However, laterite rich in quart mineral is not recommended to remove phosphorous at alkaline pH range.

The batch experiments of adsorption of Cu^{2+}, Pb^{2+}and Cd^{2+}were carried out at laboratory scale with artificial model solutions. Adsorption capacity was determined based on Langmuir models. The results showed that both volcanic ash soil and laterite displayed high adsorption capacity for lead (up to 1.0-1.2 mg Pb g^{-1}is recorded at pH 5). Adsorption capacity for copper, though not as high as that of lead, is acceptable if used in water treatment (about 0.5-0.8 mg Cu g^{-1} at pH 5). Cadmium seemed to have been hardly removed by laterite and volcanic ash soil. The calculated adsorption capacities were 0.4 mg Cd g^{-1}for laterite and less than 0.1mg Cd g^{-1} for volcanic ash soil at an initial concentration of 25 mg L^{-1}. The adsorption of heavy metals by laterite and volcanic ash was strongly pH dependent. At pHs lower than 4, these materials were not effective for metal removal. From a viewpoint of implementation, the laterite should be used after pH adjustment to over 4 for Pb, Cu, Cd removal from wastewater. Similar way in use of volcanic ash soil is recommend for Pb and Cu, but volcanic ash soil is not recommended for Cd removal from wastewater.

Volcanic ash soil and laterite are environmental friendly and effective materials in water treatments. The laterite is an abundantly available resource in tropical and sub-tropical areas whereas volcanic ash soil is widely distributed in volcanic zones. Their ability in contaminant adsorption was described by the present study. Therefore, these materials are recommended to use as bed medium which may replace sand and gravel materials in water filtering process.

LIST OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1. GENERAL INTRODUCTION

1.1. BACKGROUND

Water is essential for human and development on earth, but water is a finite and vulnerable resource which has quantitative limitations and qualitative vulnerability. Water covers more than 70% of the earth's surface, but water shortage is becoming a global problem due to increasing population, economic growth and climate change. As be reported by UNDP (2006), from the early years of the 21st century, around 1.2 billion people, or almost one-fifth of the world's population, live in areas of water shortage, and 500 million people are approaching this situation. Another 1.6 billion people (one quarter of the world's population) are facing economic water shortage where countries lack the necessary infrastructure to take water from rivers and aquifers. It is not surprising that most of people experiencing these challenges are in developing countries. Water shortage is becoming the greatest threat to food security, human health and health of natural ecosystems. An attention of professionals and policy makers involved in water supply should be put in urgently, particularly in the arid and semi-arid regions of the world like Asia and the Middle East (Seckler, 1999).

The statement of water shortage in the world is believed to be more serious in current decade due to effects of climate change. The large rivers such as Yellow River in China, Colorado River in North America are drying up and becoming bare. In the Mediterranean regions including the parts of southern Europe, North Africa, Middle East, North East and South India, Northern China and Sub-Sahara Africa, people will face severe problems of water shortage in the coming years. Many European regions are also facing the same problem, because half of its lakes have already atrophied (Cosgrove, 2000). Ground water has contributed 10% water demand in agricultural production in the world, but water table fall up to several meters per year will put heavy stress to countries basing on ground water irrigation such as Mexico, Yemen and India (Serageldin, 2000). Drinking water supply in some big cities (Beijing, Mexico, Bangkok, etc.) is facing many challenges because of aquifer dependence and saltwater intrusion (UNEP, 2000; Cosgrove, 2000).

Water shortage is a natural, and at the same time, human-made phenomenon, water quantity has been a concerned issue since history began, but water quality degradation becomes a new problem reaching crisis level in many parts of the world. A number of approximately 50% of the world's population or more than 3 billion people was recorded in 2000 to lack access to sanitation (Cosgrove, 2000). A little improvement in the statistics was made after a decade. According to analyses from UNEP and UNESCO, about 80% of all illnesses and more than one third of all deaths in developing countries are related to water. It is estimated that worldwide, around 7 million die yearly from diseases linked to water. Every eight seconds a child dies from a water-related illness. Water pollution has risen problems of both human health and ecosystem in recent years in many countries. Japan, a

developed country in the world, has been well known by their industry development and economic growth. Though Japan is ranked in the top country group with safe environment at present, they have experienced a terrible unforgettable past that engraved in their mind with diseases brought about by cadmium and mercury pollution of water which are called "*Minamata and itai-itai* diseases". Alzheimer's disease caused by aluminum accumulation in human brain is not strange for people. Alzheimer's disease has no survivors. It destroys brain cells and causes memory changes, erratic behaviors and loss of body functions. Alzheimer's disease affects at least 4 million people in the United States and probably over 11 million more world-wide, chiefly in the developed countries.

Arsenic contamination in groundwater is a major problem threatening to environment, ecosystem and human health. Historical arsenic contamination exists in Cornwall in UK, and an example of a recent arsenic pollution is that of Ron Phibun town in southern Thailand, Guizhou Province of China where arsenic-related human health effects have been reported. Bangladesh, a developing country in Asia, now is facing the serious problem of arsenic contamination. Arsenic is detected to be present in large quantities in the shallow tube-well water of many districts in rural and small urban areas of Bangladesh. Within two decades, especially the northern areas, many people have been found to be affected by arsenic toxicity because of drinking tube-well waters were contaminated with arsenic. Some new publications summarized that more than 90 % of the shallow tube-wells have been found to contaminate arsenic at concentrations exceeding 0.05 mg L^{-1} and more than 7000 arsenicosls patients have been identified in arsenic affected areas in Bangladesh. The arsenic disease is very dangerous. According to a study in 1999 by the National Academy of Sciences, arsenic in drinking water causes bladder, lung and skin cancer, and may cause kidney and liver cancer. The study also found that arsenic harms the central and peripheral nervous systems, as well as heart and blood vessels, and causes serious skin problems. It also may cause birth defects and reproductive problems.

A large load of contaminants from effluent of industry, drained water of agriculture and municipal sources discharging directly into the water bodies is a major reason of water pollution worldwide. Nitrogen and phosphorous contamination in surface water causes eutrophication in the lakes, rivers and aquaculture ponds which damages aquatic ecosystem and biodiversity. In addition to biological problems, eutrophication also poses effects on peoples' health and livelihoods. Excess nutrients can directly and indirectly lead to a decline in drinking water quality. Besides that, treatment cost of water contaminated nutrient elements is also raised to high level because the costs of advanced equipments are needed. Unfortunately, nutrient water contamination exists as a big problem in almost of countries and puts a high pressure on control and mitigation methods. We should look at the case of Gulf of Mexico as a specific example of economical losses and environmental impacts due to eutrophication. The Gulf of Mexico is a zone with area varies between 6,000 and 7,000 square miles is used to store drained water for all the major rivers and tributaries in the Midwestern United States

of which have run way through farm lands. Now, it becomes a "dead zone" because the bloom of algae exhausted dissolved oxygen in water and aquatic organism cannot exist due to lack of oxygen.

Development of new treatment technology and conservation solution of water resource has been an important task for every country, particularly, in the context of global climate change and increasing pollution. The use of conventional chemicals such as poly aluminum chloride and poly acrylamide is effective in reducing turbidity of water, but it has several environmental consequences (Nakanishi and Wada, 2007) (i) an increase in metal concentration in water; (ii) production of large volumes of (toxic) sludge; (iii) dispersion of acrylamide oligomers which may also be a health hazard. The more advanced agents that are environment-friendly and highly efficient (charcoal, granule active carbon-GAC, biopolymers, etc,.), are known. However, the cost for treatment is high and not suitable for the people getting low income. The local materials such as chitosan, rice husk, straw, moringa seed are low cost adsorbents and work well in removal of contaminants, but the use at high dose may increase biological oxygen demand in water (Tripathy and De Ranjan, 2006, Gupta *et al.*, 2011). The clay minerals and lime stones could not get expected treatment efficiency, but they bring safe for environment and save treatment cost (Babel and Kurniawan, 2002, Gupta *et al.*, 2011). In search for materials that may exhibit higher treatment efficiency, I noticed some volcanic ash soils and laterite fulfill most of the requirement if they are slightly modified. Volcanic ash soils and laterites are natural materials which are available in Japan and Viet Nam. In order to investigate their possibility in contaminated water treatment, the present study was carried out.

1.2 MOTIVATION

The suspended particles causing turbidity in water can be removed by using flocculants while the removal of heavy metals needs adsorbents. Volcanic ash soils and laterites consist of aluminum and iron bearing minerals which function as both flocculant and adsorbent to remove suspended clay particles, anions and cations from water. Therefore, these materials are used for primary tests at laboratory scale aiming to investigate their ability of water purification. The results from the present study will contribute to develop new trend in water treatment technology and to find new materials that may be applicable to water filtration process in Viet Nam where sand and gravel are conventionally used.

1.3. OBJECTIVES

The present study aims to:

i) To give the answer why a flocculant made from volcanic ash soil exhibit different efficiency in the removal of turbidity for waters from different construction sites in Japan, the study focuses on the effects of mineralogy of suspended particles that cause turbidity.

ii) To investigate flocculation behavior of allophane and imogolite in the removal of suspended particles, the study compares allophane and imogolite sols as flocculating agents for suspended clay particles.

iii) To find the ability of laterite from Viet Nam in removal of suspended particles from water, flocculation experiments at laboratory scale are conducted with clay suspensions and some laterite samples.

iv) To investigate anion adsorption capacity and kinetics of volcanic ash soil and laterite, phosphorous adsorption experiments are conducted on these materials

v) To characterize heavy metals adsorption capacity and kinetics of volcanic ash soil and laterite, adsorption experiments of copper, lead and cadmium absorption onto these materials are conducted.

1.4. THESIS OUTLINE

A general introduction on the research is presented in chapter 1. The literature review is presented in chapter 2. This chapter lists conventional water treatment methods with description about mechanism, their advantages and disadvantages. The natural materials applied for water treatment is also presented in this chapter. Chapter 3 presents mineralogy effects of suspended particles on flocculation performance of volcanic ash soil flocculant. The content of the chapter 3 was published in the journal of Clay Science volume 16, number 1 on June, 2012. Chapter 4 shows the power of allophane and imogolite sols in flocculation clay suspensions. This chapter was also published in the journal of Clay Science volume 16, number 3 on September, 2012. Chapter 5 presents mineralogy of laterite from Viet Nam and their performance as flocculating agents to remove suspended clay particles from water. This content was published in the Journal of Faculty of Agriculture, Kyushu University, volume 58, number 1 on February, 2013. Chapter 6 describes the removal of phosphorous in water using laterite from Viet Nam. And the removal of heavy metals by volcanic ash and laterite is presented in the chapter 7. The last chapter is devoted to general discussion on the ability of volcanic ash and laterite in water treatment.

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CHAPTER 2. LITERATURE REVIEW

2.1 CONVENTIONAL WATER TREATMENT METHODS

Until now, conventional technologies including key steps of coagulation, flocculation, sedimentation, and rapid gravity sand filtration have greatly contributed to water quality improvement. These are well-proven technologies for the removal of suspended solid matter, bacteria, and other microorganisms. Iron, manganese, tastes and odors may also be removed from the water by these processes.

2.1.1 Coagulation and flocculation process

The particles existing in water would settle down on their own if enough time is given.-But settling may take time of days or months due to small particle size and to electrostatic repulsion between the particles as well as to Brownian motion. Most particles existing in water have negative charges, so they tend to repel each other. In order to remove suspended particles from water effectively, coagulation/flocculation process is recommended to apply.

Coagulation is a treatment process that includes chemical addition, rapid mixing, and flocculation. Coagulation is often the first unit operation in water treatment and it is very crucial for the removal of suspended particles. Coagulation and flocculation processes are intended to form particles large enough to be separated and removed by subsequent sedimentation or neutralization the charges on the colloidal particles in the raw water. Destabilizing stable colloidal particles in the suspension is essential. In most cases, coagulation is optimized for the removal of inorganic colloidal particles. It is also used for the removal of natural organic matter by the process of enhanced coagulation (Gregor *et al*., 1997). In natural waters, colloids are predominantly negatively charged and they are stable by virtue of the hydration and electric charges on their surfaces. Coagulation can remove colloidal particles and natural organic matter in water by three mechanisms:

i) Colloidal destabilization, accomplishment by electrical double layer compression, charge neutralization, enmeshment, or bridging;

ii) Precipitation;

iii) Co-precipitation (sweep flocculation), primarily by occlusion or surface adsorption but conceivably by no isomorphic inclusion. Rapid, high energy mixing (for example mechanical mixers, inline blenders, jet spurge mixing) is necessary to ensure that the coagulant is fully mixed into the process flow to maximize its effectiveness. The coagulation process occurs very quickly, probably in a second or minute. Poor mixing can result in poorly developed flocs.

Flocculation is a process following coagulation, allows smaller particles formed during the rapid coagulation stage to agglomerate into larger particles that are settleable and/or filterable floc particles. After coagulant addition, a process of slow mixing of 10-30 minutes is conducted. The

optimum flocculation time will vary depending on the raw water quality and downstream clarification process. Gentle mixing conducted in this stage makes small particles contact together to form larger flocs. Effectiveness of flocculation depends on the delay (or contact) time and mixing clarification processes. Coagulation process is summarized in Fig 2.1.
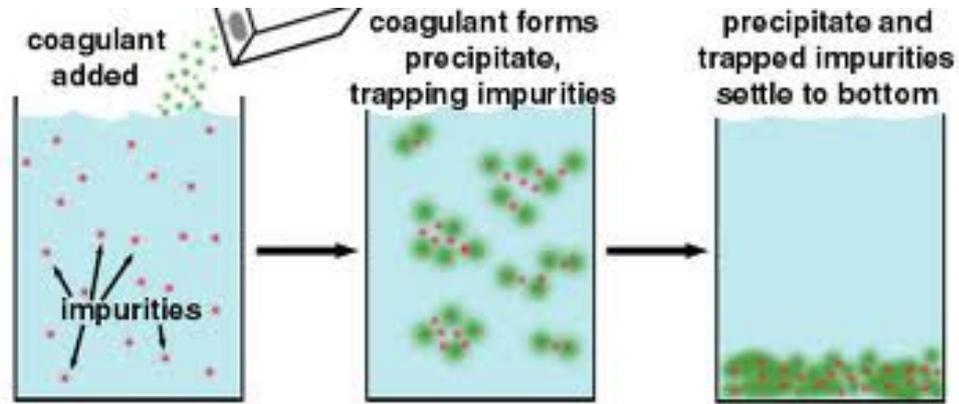
Fig.2.1. Coagulation process as be theoretically described

(*Source: http://water.me.vccs.edu/courses/env110/lesson4.htm*)

2.1.1.1 The chemistry of coagulation and flocculation

The coagulation and flocculation is primarily to electrostatic interactions, i. e., the attraction and repulsion among negatively or positively charged particles. Like charges (two negatively charged particles or two positively charged particles) repel each other while opposite charges (a positively charged particle and a negatively charged particle) attract each other.

Most particles suspended in natural waters have negative charges, so they tend to repel each other. As a result, they stay dispersed to form stable colloidal aqueous suspensions.
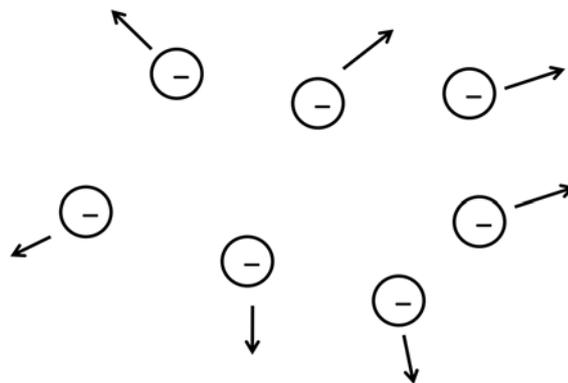
Fig. 2.2. Negatively charged particles repel each other due to electrostatic repulsion.

The purpose of addition of coagulant chemicals is to neutralize the negative charges on the particles to reduce electric repulsion. The amount of coagulant which should be added to the water depends on the zeta potential, a measure of the electrical potential at a shear plane around charged particles. If the zeta potential is large, more coagulant is needed. Coagulants having positive charge isadded it is attracted to the negative charges on the particles as shown below.
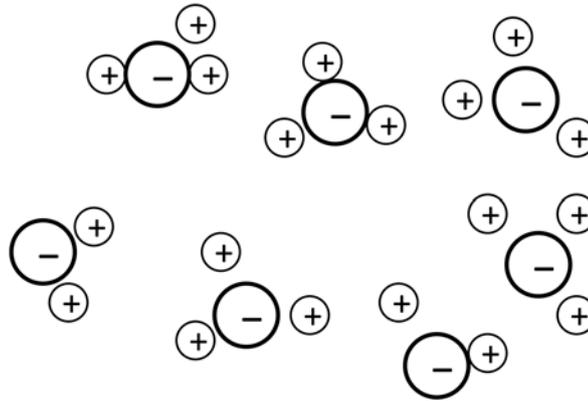
Fig. 2.3. Positively charged coagulants attract to negatively charged particles due to electricity.

The associationof positive and negative charges results in charge neutralization, and the particles no longer repel each other. The next force which will affect the particles is known as van der Waal forces. This is the molecular force that occur when moleculeshavingno charge come to close contact.
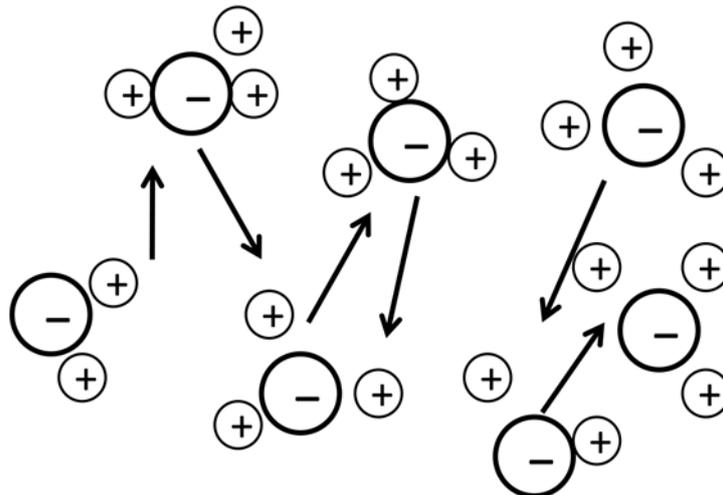
Fig. 2.4. Neutral particles attract due to van der Waal forces.

Van der Waal forces make the particles adhered each other to form agglomerates. When enough particles have attachedtogether, they become flocs and will settle down. The removal of particulate contaminants from water will be achievedby filtration. The following picture schematically illustrates thestructure of a floc made in flocculation process (Fig. 2.1)

8
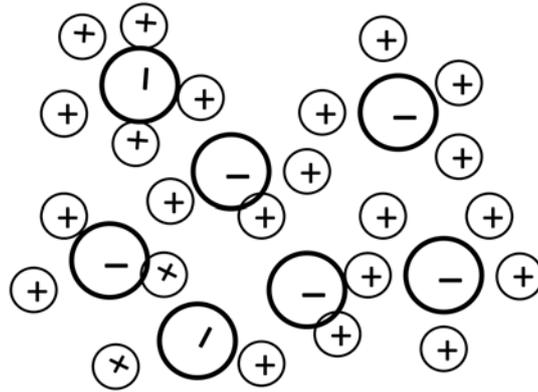
Fig. 2.5. Particles and coagulants associate together to form flocs.
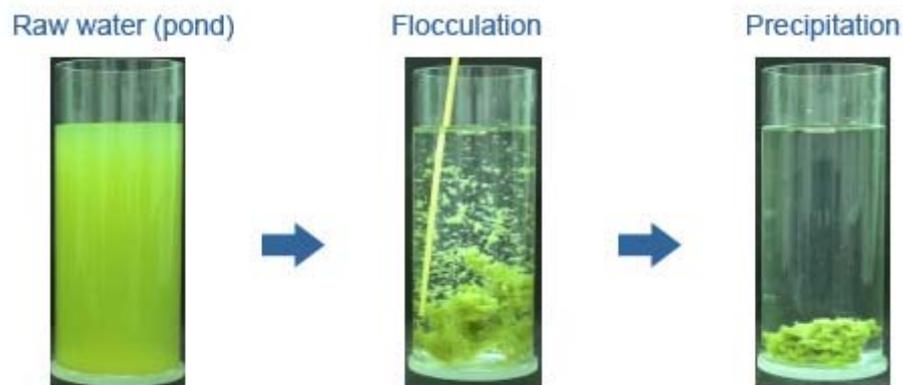
Fig.2.6. An Example of water sample treated by flocculation/coagulation process.

(*Source: http://www.et.byu.edu/~wanderto/homealgaeproject/Harvesting%20Algae.html*)

2.1.1.2 Coagulants and flocculants

Coagulants are chemicals that destabilize suspended particles (particularly colloidal sized particles). Hydrolyzing metal ions, e. g., aluminum or iron, are widely used as coagulants in water treatment. The high cationic charge makes them effective for destabilizing colloids. When coagulants are added into water, destabilization of colloids occurs due to adsorption, charge neutralization or particle entrapment (Duan and Gregory, 2003).

Flocculants (also known as flocculant aids or coagulant aids) assist the agglomerating and enmeshing particles together. When flocculants are added, particles increase in the size, strength and settling ability. Flocculants may be cationic, anionic, or non-ionic. They are produced from materials having varying degrees of ionizing tendency and a wide range of molecular weight.

Although flocculants and coagulants are effectively and widely used in water treatment, their drawbacks are big problems for applications. Using flocculant aids may change pH of the water, increase soluble residues, volume and metal content of the sludge. Besides aluminum- and iron-based

coagulants, organic chemicals known as poly electrolytes may also be used as coagulant or flocculant aids to reduce turbidity of water. Pre-hydrolysed forms of metals such as polyaluminum chloride and poly iron sulfate are good examples. In some cases, organic chemicals are more effective, produce strong flocs and result in less sludge volume (Duan and Gregory, 2003) compared with aluminum and iron salts.

2.1.1.3 Factors affecting coagulation and flocculation process

The coagulation/flocculation process is affected by pH, salts, alkalinity, turbidity, temperature, mixing, and coagulant chemicals.

The effectiveness of a coagulant is generally **pH** dependent. Colored waters are better treated at low pH (4.4-6) with aluminum.

Alkalinity is needed to form in soluble compounds to precipitate them out. It could be naturally present in the water or needed to be added as hydroxides, carbonates, or bicarbonates.

The higher **temperature**, the faster reaction, and the coagulation are more effective.

Time is an important factor as well. Proper mixing and detention times are very important for coagulation.

The higher **velocity** causes the shearing or breaking of floc particles and lower velocity will let them settle in the flocculation basins. Velocity around 1 ft/sec in the flocculation basins should be maintained.

Zeta potential is the charge at the boundary of the colloidal turbidity particle and the surrounding water. The higher **zeta potential** creates higher repulsion between particles; as a result, higher zeta potential requires the higher coagulant dose. An effective coagulation may obtain at zeta potential reduced nearly zero.

2.1.2 Gravity filtration

Rapid gravity filtration follows processes of coagulation, flocculation and sedimentation. Solid particles are separated from liquid solution by mixing with bed materials. Sand is common traditional material to keep suspended particles. As water passes through a bed filter media, matter (including micro-organisms) is trapped within the media by a two-step process in which particles are moved to the surfaces of media grains or captured flocs, and then become attached (adsorbed) to these surfaces. Mechanical straining and adsorption are factors of successful filtration through media. By mechanical straining, granular filters can remove particles that are much smaller than the dimensions of the interstices between their grains. A granular filter is able to capture very fine particles, even in the absence of particles with large size to bridge the interstices. Adsorption is a process in which the efficiency depends on the surface properties of both adsorbents and small particles. Small particles in close proximity to a solid surface are subjected to either electrical attraction or repulsion and also subjected to the hydraulic forces resulting from the movement of water.

2.2 REMEDIATION TECHNOLOGY FOR HEAVY METALS CONTAMINATEDWATER

In order to reduce water pollution and remedy heavy metals polluted water, great efforts for technological and technical development of treatment have been made during the past decades.

2.2.1 Chemical precipitation

The process involves the transformation of dissolved contaminants into insoluble solids, and then contaminants are subsequently removed from liquid phase by physical methods, such as clarification and filtration (NEESA, 1993; Nomanbhay and Palanisamy, 2005). In a precipitation process, chemical precipitants (also known as coagulants and flocculants) are used to increase particle size through aggregation. Treatment efficiency depends on pH and alkalinity of the water. As conventional treatment methods, heavy metals in water are precipitated by adding sodium hydroxide or lime during neutralization. However, complete hydroxide precipitation does not take place especially in the presence of complexing agents (NEESA, 1993; EPA, 2000; Xu and Xu, 2008).

Chemical treatment of contaminated groundwater to remove heavy metals has been performed in column and pilot scale experiments. Granulated lime and calcium carbonate were used as coagulants (Lee *et al*., 2007). Furthermore, some investigators have developed and selectively used 1,3-benzenedaimidoethathiol to irreversibly bind soft heavy metals in aqueous solution. In the study of Matlock *et al*. (2002), the chemical compound named Metx was found to remove over 90% of several toxic heavy metals from acid mine drainage samples. In South Africa, acid mine water from gold mine has been treated by the precipitation of heavy metals with lime and sulfides, followed by ion exchange. The oxidation and precipitation of heavy metals with lime and subsequent sulfide-carrier magnetite was observed to be particularly suitable for the removal of heavy metal ions from the effluent of gold mine (Feng *et al*., 2000). Despite their simplicity, they are not recommended for use since they release toxic hydrogen sulfide when pH is acidic, hence causing great hazards in case of accidental release or over-dosages. The best suggested alternative to the traditional sulfide treatment is the dithiocarbonate precipitation (METALSORB, 2004).

Chemical precipitation of metals has advantages: convenience, self-operation, and low maintenance cost. However, the following disadvantages are still observed in practicing this technique:

- The precipitates are in the form of light tiny flocs requiring an extra coagulation/flocculation.

- Large volumes of sludge are generated, inducing additional waste-disposal costs. The addition of treatment chemicals may increase the waste sludge up to 50% (EPA, 2000).

- Regulation requirements are not always met using hydroxide and carbonate precipitation alone. Each dissolved metal has its own distinct pH level for maximum hydroxide precipitation.

- Corrosive chemicals are used during process; thereby increase safety concerns (EPA, 2000; METALSORB, 2004).

2.2.2 Ion exchange

Ion exchange is a reversible chemical reaction where metal ions from aqueous solution are attached to charged particles. Normally, hydrocarbon derived from polymer resins is used as agents (Vaca *et al.*, 2001; Volesky *et al.*, 2003). The authors reported that it successfully removed lead, cadmium and chromium by ion exchange operation with clinoptilolite. Their study revealed effective removal of dissolved lead and cadmium removed within 18 h in batch reactors, with higher removal efficiencies that was greater than 95% in the acidic pH range.

2.2.3 Reverse osmosis

Reverse osmosis is membrane treatment process that use membrane as a molecular filter to remove almost all of solutes. In this process, water molecular is passed through membrane while ionic contaminants are inhibited to pass through. In comparison with conventional methods, this method displays more significant advantages in removal of ionic and dissolved organic molecular contaminants (Volesky *et al.*, 2003; Pawlak *et al.*, 2005). The reserve osmosis has been applied to treat heavy metals in both small and large scale installations. However, high cost and complexity of operation are disadvantages in using this technology.

2.2.4 Phytoremediation

Phytoremediation, is called *green remediation* in other word, is a remediation process that use plants to remedy surface waters, waste waters, ground waters, soils and sediments that are contaminated by some types of substances. The functions of plants (e.g. adsorption at root zone, accumulation by shoot and up take by left) are involved in removal of contaminants. This method is known to be cost effective and have fewer negative effects than physical and chemical approaches; therefore, it has gained increasing popularity in both academic and practical sites. Studies have demonstrated that plants such as *Brassica juncea*, *Salsola kali*, and *Prosopis* species cultivated in hydroponics and agar are able to uptake significant amounts of heavy metals, suggesting possible utilization in phytoremediation processes.

Researchers have also realized that phytoextraction can be used for the recovery of precious metals such as gold, silver, platinum, and palladium (Gardea *et al.*, 2005). In addition, phytoremediation of heavy metals contaminated waters by using aquatic macro phytes have been investigated in recent years (Kumar, 2008). Their study used roots, stems and leaves of seven representative species of native aquatic plants (biomonitors): *Ipomoea aquatica*, *Eichhorniacrassipes*, *Typhaangustata*, *Echinochloacolonum*, *Hydrillaverticillata*, *Nelumbonucifera* and *VallisneriaspiralisL* to uptake heavy metals. The results showed that cadmium and lead fall within

normal range while that of cobalt and nickel were within the critical range. However, zinc and copper showed the highest accumulation at alarming toxicity levels (Kumar *et al*, 2008).

Phytoremediation has advantages such as economical cost, ability to remedy more than one contaminant in one site, but its disadvantages are dependence on region climatic condition that affects growth and tolerance of plants as well as requirement for long time to purify the contaminants.

2.2.5 Microbial remediation

Microbial bioremediation is defined as the process by which microorganisms are stimulated to rapidly degrade hazardous organic contaminants. Microbes decompose poisonous chemicals by using enzymes to convert one chemical into another form and taking energy or utilizable matter from this process. The chemical transformations generally involve breaking of large molecules into several small molecules in simpler forms. Studies on the interactions of microorganisms with heavy metals are gaining increasing interest in recent years. Some of these studies have indicated different metal resistance mechanisms, interactions and processes of bacteria, protozoa and fungi. The bio-sorbents was reported to be quite effective for the removal of metal ions from contaminated solution in low cost and environmental friendly manner (Rani *et al*., 2009). Metals were removed by biosorption onto microbial biofilm and recovered from biofilm so that the biofilm may be reused in multiple cycles (Hutchins *et al*., 1986; Costley and Wallis, 2001). The study carried out by Sharma *et al*. (2000) revealed that *Klebsiella pneumoniae* had potential ability to bioaccumulate heavy metals at high concentrations (15 mM), showing the potential of this bacterium for remediation of heavy metals contaminated environment. Also, the survival of *Euplotesmutabilis* (a ciliate protozoa) in industrial wastewater containing high concentrations of heavy metals (cadmium, lead copper and chromium) was shown by Rehman *et al*. (2008).

Similarly, the remediation of aqueous lead and cadmium ions by the fungus *Fusariumoxysporum* was investigated by Sanyal *et al*. (2005). The use of immobilized non-living algae biomass (bioresins) for the stripping of metals from solution was also studied (Brown, 1996). In the result, bioresins derived from one biomass type were found to be highly effective in binding copper, nickel and lead ions in water.

Although the advantages of microbial remediation including low-cost, required moderate capital investment, environmental safety due to natural process have been investigated, the application of this technology is limited to biodegradable compounds. Not all compounds are susceptible to rapid and complete degradation. There are some concerns that the products of biodegradation may be more persistent or toxic than the primary compound. The success is dependent on the presence of metabolically capable microbial populations, suitable environmental growth conditions, and appropriate levels of nutrients and contaminants.

2.3 ADSORPTION THEORY AND ENVIRONMENTAL APPLICATIONS

When adsorbate contacts with adsorbent, adsorption takes place. Adsorption is a process that occur when a gas or liquid solute accumulates on the surface of a solid or a liquid adsorbent to form a molecular or atomic film (the adsorbate). A reverse process of adsorption is desorption which is defined as substances diffuse into solution.

2.3.1 Mechanism of Adsorption

Adsorption arises due to the fact that the surface atoms of the adsorbent are not in the same environment as the atoms inside the bulk. Inside the adsorbent all the forces acting between the atoms are balanced but on the surface the atoms are not surrounded by atoms or molecules on all sides, and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface. The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words, ΔH (enthalpy change) of adsorption is always negative. When a gaseous atom or molecule is adsorbed, its freedom movement becomes restricted. This amount to decrease in the entropy change of the gas after adsorption, i.e., ΔS is negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG (decrease in Gibbs free energy) must be negative, i.e., there is a decrease in Gibbs free energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $-T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds ΔH becomes less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state, equilibrium is attained.

There are mainly two types of adsorption of gases on solids. If accumulation of gas on the surface of a solid occurs on account of weak van der Waals forces, the adsorption is termed as physical adsorption or physisorption. When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed chemical adsorption or chemisorption. The chemical bonds may be covalent or ionic in nature. Chemisorption involves a high energy of activation and is, therefore, often referred to as activated adsorption. Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, dehydrogenate is first adsorbed on nickel by vander Waals forces. Molecules of hydrogen then dissociate to form

hydrogen atoms which are held on the surface by chemisorption. Some of the important characteristics of both types of adsorption are described below:

(i) Lack of specificity: A given surface of an adsorbent does not show any preference for a particular gas as the van der Waals forces are universal.

(ii) Nature of adsorbate: The amount of gas adsorbed by a solid depends on the nature of gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed as van der Waals forces are stronger near the critical temperatures. Thus, 1 g of activated charcoal adsorbs more sulfur dioxide (critical temperature 630K), than methane (critical temperature 190K) which is still more than 4.5 mL of dihydrogen (critical temperature 33K).

(iii) Reversible nature: Physical adsorption of a gas by a solid is generally reversible. Thus, Solid + Gas/ Gas/Solid + Heat

More gas is adsorbed when pressure is increased and the volume of the gas decreases (the Le–Chateliers's principle) and the gas can be removed by decreasing pressure. Since the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increasing temperature (the Le-Chatelier's principle).

(iv) Surface area of adsorbent: The extent of adsorption increases with the increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.

(v) Enthalpy of adsorption: No doubt, physical adsorption is an exothermic process but its enthalpy of adsorption is quite low (20 - 40 kJ mol^{-1}). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals forces.

2.3.2 Characteristics of chemisorption

(i) High specificity: Chemisorption is highly specific and it will only occur if there is some possibility of chemical bonding between adsorbent and adsorbate. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is absorbed by transition metals due to hydride formation.

(ii) Irreversibility: As chemisorption involves compound formation, it is usually irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, adsorption often increases with rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually high pressure is also favorable for chemisorption.

(iii) Surface area: Like physical adsorption, chemisorption also increases with increase of surface area of the adsorbent.

(iv) Enthalpy of adsorption: Enthalpy of chemisorption is high (80-240 kJ mol^{-1}) as it involves chemical bond formation.

Adsorption is usually described through isotherms that determine the amount of adsorbate on the adsorbent. From literature, several models describing process of adsorption, namely Freundlich isotherm, Langmuir isotherm, BET isotherm, etc. are reported.

The **Langmuir adsorption model** is the most common model used to quantify the amount of adsorbate adsorbed on an adsorbent as a function of partial pressure or concentration at a given temperature.

The Langmuir isotherm is given below:

$$\frac{Y}{M} = \frac{abC}{1 + aC}$$

Where:

Y = concentration of pollutant adsorbed, mg/L

M = PAC concentration, mg/L

C = equilibrium concentration of pollutant, mg/L

a = constant (determined graphically)

b = constant (determined graphically)

Alternatively, the equation can be manipulated to linear form, as be shown below

$$\frac{1}{YM} = \frac{1}{ab}x\frac{1}{C} + \frac{1}{b}$$

To calculate "b" for the Langmuir isotherm:

$$b = \frac{1}{\text{y\,\,intercept}}$$

To calculate "a" for the Langmuir isotherm:

$$\text{Slope} = \frac{1}{ab}$$

The **Freundlich equation** is an adsorption isotherm, which is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. There are basically two well established types of adsorption isotherm: the Freundlich adsorption equation is modified from the Langmuir equation.

The Freundlich Adsorption Isotherm is mathematically expressed as

$$\frac{x}{m} = Kp^{1/n}$$

Or

$$\frac{x}{m} = Kc^{1/n}$$

where

x = mass of adsorbate

m = mass of adsorbent

p = Equilibriumpressure of adsorbate

C = Equilibrium concentration of adsorbate in solution.

K and $1/n$ are constants for a given adsorbate and adsorbent at a particular temperature.

Stephen Brunauer, Paul Emmet and Edward Teller published this theory in 1938. It is a theory for multi-layerphysisorption and is of profound significance in the development of this field.

The Brunauer-Emmett-Teller (BET) equation is:

$$q = \frac{qm\ kb\ C}{[Cs-C]\{1+[Kb-1][C/Cs]\}}$$

where C_s = concentration at which all layers are filled and K_b = a coefficient

Its assumptions are:

- Adsorbed molecules stay put
- Enthalpy of adsorption is the same for any layer
- Energy of adsorption is the same for layers other than the first
- A new layer can start before another is finished.

2.4. NATURAL MATERIALS AND THEIR APPLICATIONS IN WATER TREATMENT

Contaminated water has ringed warning alarms for of environment degradation in the world during the past decades. Water quality improvement plays an essential role in human life. Water technology with treatment materials has been continuously studied and innovated and widely applied for environment. Materials including traditional and advanced ones have obtained the increasing interests of t scientists.

2.4.1 Plant origin coagulants

A number of effective coagulants have been proven from plant origin. Some of the common coagulants include nirmali (Tripathi *et al.*,1976), *M. oleifera* (Olsen, 1987; Jahn, 1988), okra (Al-Samawi and Shokrala, 1996), *Cactus latifaira* and *Prosopis juliflora* (Diaz *et al.*, 1999), tannin from valonia (Özacar and Sengil, 2000), apricot, peach kernel and beans (Jahn, 2001), and maize (Raghuwanshi *et al.*, 2002). Bhole (1995) compared 10 natural coagulants from plant seeds. The study indicated that those from maize and rice had good coagulation efficiency when they were used as primary coagulants or coagulant aid.

The seeds from *M. oleifera* have been shown to be one of the most effective as a primary coagulant for water treatment. *M. oleifera* is a small plant, fast growing, drought resistant. Since the early 1970's a number of studies have been carried out to determine the effectiveness of its seeds for the treatment of surface water (Olsen, 1987; Ghebremichael, 2004) using different extraction methods for the active coagulant from *M. oleifera.* Utilizing artificially prepared turbid water and naturally

turbid raw waters, laboratory investigations have confirmed the seeds to be highly effective in the removal of suspended solids from waters containing medium to high initial turbidities (Sutherland *et al.*, 1994). Pilot and full-scale plant trials carried out in Malawi water treatment works demonstrated that the water treated by *oleifera* seeds may be similar in quality to that treated by aluminum sulfate (Ghebremichael, 2004).

Chitosan, a natural coagulant from animal origin is also an effective coagulant (Pan *et al.*, 1999; Guibal *et al.*, 2006). It has unique properties among biopolymers due to the presence of primary amino groups and has characteristics of both coagulants and flocculants such as high cationic charge density, long polymer chains, bridging of aggregates, and precipitation (in neutral or alkaline pH conditions). It has also been used for the chelating of metal ions in near-neutral solution and the complexation of anions in acidic solution (cationic properties due to amine protonation). Its coagulation and flocculation properties can be used to treat particulate suspensions (organic or inorganic) and also to treat dissolved organic materials. It has also been reported that chitosan possesses antimicrobial properties (Chung *et al.*, 2003).

By using natural coagulants, considerable savings in chemicals and sludge handling cost may be achieved. Al-Samawi and Shokrala (1996) reported that 50 - 90% of alum requirement could be saved when okra was used as a primary coagulant or coagulant aid. Apart from being less expensive, natural coagulants produce readily biodegradable and less voluminous sludge. For example, sludge produced from *M. oleifera* coagulated turbid water is only 20 - 30% of that of alum treated water (Narasiah *et al.*, 2002). The coagulation process in water treatment is complimented by filtration. The successfulness of coagulation in most cases determines the performance of the filtration system, which may be of a mono medium or dual media type.

2.4.2 Filtration media

Some of the locally available filter media that have been used in single or multimedia filtration include crushed coconut shells, burned rice husk (Frankel, 1974),crushed apricot shell (Aksogan *et al.*, 2003), pumice (Ghebremichael, 2004) and palm leaves and shrimp shells (Aly *et al.*, 2005). Paramasivan *et al.* (1973) reported that high-grade bituminous coal, used in dual media filtration, could be a good substitute for anthracite coal. In his study, Ghebremichael (2004) showed that pumice obtained from Eritrea could be used as a dual filter media to give longer filter runs than a single medium (sand) filter. In addition to these materials, another material that has not received much attention and could be used for water treatment is volcanic ash.

Carboxyl methyl cellulose (CMC) (Petrov and Nenov, 2004; Barakat, 2008b), diethylaminoethyl cellulose (Trivunac and Stevanovic, 2006), and polyethyleneimine (PEI) (Aroua *et al.*, 2007) were used as efficient water-soluble metal-binding polymers in combination with ultrafiltration (UF) for selective removal of heavy metals from water. Barakat (2008b) investigated

the removal of Cu (II), Ni (II), and Cr (III) ions from synthetic wastewater solutions by using CMC and polyethersulfon ultrafiltration membrane.

Ferella *et al.* (2007) examined the performance of surfactants enhanced ultrafiltration process for removal of lead and arsenic by using cationic (dodecylamine) and anionic (dodecylbenzenesulfonic acid) surfactants. The removal of lead ions was over 99%, while that for arsenate ions was 19%, in both systems. Modified UF blend membranes based on cellulose acetate (CA) with polyether ketone (Arthanareeswaran *et al.*, 2007), sulfonatedpolyetherimide (SPEI) (Nagendran *et al.*,2008) and polycarbonate (Vijayalakshmi *et al.*, 2008) were recently tested for heavy metals removal from water. It was found that CA/blend membranes displayed higher permeate flux and lower rejection compared to pure CA membranes.

2.4.3 New adsorbents

Various low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently developed and applied to the removal of heavy metals from metal-contaminated wastewater. In general, three main steps are involved in pollutant sorption onto solid sorbent: (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle. Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent.

Natural zeolites gained a significant interest, mainly due to their ion exchange capability. Among the most frequently studied natural zeolites, clinoptilolite were shown to have high selectivity for certain heavy metal ions such as Pb (II), Cd (II), Zn (II), and Cu (II). It was demonstrated that the cation-exchange capability of clinoptilolite depends on the pre-treatment method and its ion exchange ability (Babel and Kurniawan, 2003; Bose *et al.*, 2002). The role of pH is very important for the selective adsorption of different heavy metal ions onto zeolite (Basaldella *et al.*, 2007; R´ıos *et al.*, 2008; Barakat, 2008a). Barakat reported that Cu (II) and Zn (II) were adsorbed at neutral and alkaline pH. Cr (VI) was adsorbed at acidic pH while the adsorption of Mn (IV) was achieved at high alkaline pH values. Nah *et al.* (2006) prepared synthetic zeolite magnetically modified with iron oxide (MMZ). MMZ was showed high adsorption capacities for the Pb (II) ion and a good chemical resistance in a wide pH range 5 - 11. The natural clay minerals can be modified with a polymeric material in a manner that this significantly improves their capability to remove heavy metals from aqueous solutions (Vengris *et al.*, 2001; So¨lenera *et al.*, 2008; Abu-Eishah, 2008). Phosphate was calcined at 900°C, nitric acidficated phosphate and zirconium phosphate have been employed as new adsorbents for removal of heavy metals from aqueous solution (Aklil *et al.*, 2004; Moufliha *et al.*, 2005; Pan *et al.,* 2007).

Industrial by-products such as fly ash, waste iron, iron slags, hydrous titanium oxide, can be chemically modified to enhance their removal performance for metal removal from wastewater. Lee *et al.* (2004) studied green sands, another by-product from the iron foundry industry to remove Zn (II). Feng *et al.* (2004) investigated Cu (II) and Pb (II) removal using iron slag Fly ashes were also investigated as adsorbents for removal of toxic metals. Gupta *et al.* (2003) explored bagasse fly ash, a solid waste from sugar industry, for Cd (II) and Ni (II) removal from synthetic solution at pH ranging from 6.0 to 6.5. Alinnor (2007) used fly ash from coal-burning for removal of Cu (II) and Pb (II) ions. Sawdust treated with 1,5-disodium hydrogen phosphate was used for adsorption of Cr (VI) at pH 2 (Uysaland Ar, 2007). Iron based sorbents such as ferrosorp plus (Fuhrman *et al.*, 2008) and synthetic nanocrystalline akaganeite (Deliyanni *et al.*, 2007) were recently used for simultaneous removal of heavy metals. Ghosh *et al.* (2003) and Barakat (2005) studied hydrous titanium oxide for adsorption of Cr (VI) and Cu (II), respectively. Barakat reported that, the adsorbed Cu (II) aqueous species can undergo surface hydrolysis reaction as pH rises. This yields a series of surface Cu (II) complexes such as $TiO–CuOH^+$, $TiO–Cu(OH)_2$, and $TiO–Cu(OH)_3$ species.

2.4.4 Modified agriculture and biological wastes (bio-sorption)

Recently, a great deal of interest in the research for the removal of heavy metals from industrial effluent has been focused on the use of agricultural by-products as adsorbents. The use of agricultural by-products in bioremediation of heavy metal ions is known as bio-sorption. This utilizes inactive (non-living) microbial biomass to bind and concentrate heavy metals from waste streams by purely physico-chemical pathways (mainly chelation and adsorption) of uptake (Igwe *et al.*, 2005). New resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk can be used as an adsorbent for heavy metal after chemical modification or conversion by heating into activated carbon. Ajmal *et al.* (2000) employed orange peel for Ni (II) removal from simulated wastewater. They found that the maximum metal removal occurred at pH 6.0. The applicability of coconut shell charcoal (CSC) modified with oxidizing agents and/or chitosan for Cr (VI) removal was investigated by Babel and Kurniawan (2004). Cu (II) and Zn (II) removal from real wastewater were studied using pecan shells-activated carbon (Bansode *et al.*, 2003) and potato peels charcoal (Amana *et al.*, 2008). Bishnoi *et al.* (2003) conducted a study on Cr (VI) removal by rice husk-activated carbon from an aqueous solution. They found that the maximum metal removal by rice husk took place at pH 2.0. Rice hull, containing cellulose, lignin, carbohydrate and silica, was investigated for Cr (VI) removal from simulated solution (Tang *et al.*, 2003). To enhance its metal removal, the adsorbent was modified with ethylene diamine. The maximum Cr (VI) adsorption of 23.4 mg g^{-1} was reported to take place at pH 2. Other type of biosorbents, such as the biomass of marine dried green algae (biological materials) (Gupta *et al.*, 2006), were investigated for uptaking of some heavy metals from aqueous solution. Some of the used algae wastes were *Spirogyra* species (Gupta *et al.*, 2006), *Ecklonia maxima* (Fenga and Aldrich, 2004), *Ulvalactuca* (El-Sikaily *et al.*, 2007), *Oedogoniumsp* and *Nostoc*

sp. (Gupta and Rastogi, 2008), and brown alga *Fucusserratus* (Ahmady-Asbchin *et al*., 2008). On the whole, an acidic pH ranging 2-6 is effective for metal removal by adsorbents from biological wastes.

The mechanism of up-taking heavy metal ions can take place by metabolism-independent metal-binding to the cell walls and external surfaces (Deliyanni *et al*., 2007). This involves adsorption processes such as ionic, chemical and physical adsorption. A variety of ligands located on the fungal walls are known to be involved in metal chelation. These include carboxyl, amine, hydroxyl, phosphate and sulfhydryl groups. Metal ions could be absorbed by complexion with negatively charged reaction sites on the cell surface.

2.4.5 Volcanic ash soil and its environmental applications

Volcanic ash is formed during explosive volcanic eruptions. It consists of very fine rock and mineral particles less than 2 mm in diameter, and is rich in volcanic glass. The volcanic glass alters in the soil formation process via incongruent dissolution to form non crystalline and poorly crystalline aluminum silicate minerals: typically allophane and imogolite. Volcanic ash soils have been employed for environment, water treatment and industry areas. The study of Fujita *et al*, 2003 indicated volcanic ash soils adsorbed some pesticides. Allophane and imogolite bear positive charges that might attract anions at the low pH. Phosphate anions are absorbed by allophone and imogolite at edge sites, consequently, the phosphate was removed by using these minerals (Clark and Mcbride, 1984). Some organic compounds, particularly organic acids, are adsorbed onto allophane surfaces via ligand exchange (Parfitt *et al.* 1977) and up to 25% C is associated with allophanic soil clay fractions in some volcanic ash soils (Parfitt and Henmi, 1982; Churchman and Tate, 1986). In contrast, positively charged organic ions are adsorbed mainly by physical adsorption and occupy a part of the pore space (Theng, 1972).

Natural and synthetic allophanes (Parfitt and Henmi, 1980; Clark and McBride, 1984) strongly adsorbed phosphate in fairly large amounts ranging between 50 and 200 mmol g^{-1}, equivalent to 2-8 phosphate ions per allophane spherule. Sulfate adsorption is strongly dependent on pH, the adsorbed amount increased as the pH decreased from 7 to 4 (Bohn *et al.,* 1986). Sulfate was absorbed by displacing the H_2O and OH groups at defect sites; the positive charge reduced and negative charge increased (Rajan, 1979). The amount of sulfate adsorbed can be up to 9 times greater than the positive charge measured by chloride adsorption at pH 5. Adsorption capacity of allophanic soils was indicated to be100mmol S g^{-1}inthe areas with high rainfall. Sulfate is probably added to the soil as salts in rain water. In comparison with soils containing mainly vermiculite and micas, much less sulfate was leached from allophanic soils (Bolan *et al.,* 1988). Yujiarai *et al*. (2005) investigated arsenate As (V) reactivity and surface speciation on amorphous aluminosilicate mineral (synthetic allophane) by batch adsorption experiments. The adsorption isotherm indicated that As (V) uptake increased with increasing As (V) concentration from 50 to 1000 µM .Suspended allophone-like

nanoparticles could contribute to the rapid transport processes (e.g., surface runoff and preferential flow) of phosphate and As (V) in subsurface environments.

The ability of Andisols to adsorb heavy metals was demonstrated by Forbes (1976) and Abd-Elfattah and Wada (1981). Cu and Co was specifically adsorbed on both allophane and imogolite adsorption increased with increasing alumina content. The ESR spectra suggested that monomeric Cu^{2+} adsorbed on an alumina-like surface sites where surface bonding occurred at a second site. Distribution of Cu between these two surface sites is dependent on the SiO_2/Al_2O_3 ratio, pH, and adsorbate concentration. The second site was probably a SiOH or AlOH group that bonded Cu (II) with less energy by displacement of a single proton from the surface (Clark and Mc Bride, 1984).

2.4.6 Laterite and environmental applications

Laterites are highly weathered and altered residual soils formed by the in-situ weathering and decomposition of rocks under tropical condition (Blight, 1997). Laterites are rich in sesquioxides (Fe_2O_3 or Al_2O_3) and low in bases and primary silicates but may contain appreciable amounts of quartz and kaolinite. Due to the presence of iron oxides lateritic soils are red in color ranging from light through bright to brown shades. Laterite has been well known in Asian countries as a building material for more than 1000 years. Besides, the material also has various applications in environment remediation that has been reported in previous studies.

Udoeyo (2010) carried out batch experiments and investigated the possibility of lateric soil for using as an adsorbent for heavy metals (Pd, Cu and As) in water. Laterite was a potential alternative for removal of arsenic in groundwater (Maiji *et al*., 2006; Rahman, *et al*., 2008). His study estimated the life-time of laterite as a column packing-adsorber. It worked for 70 days to achieve WHO safe limitation (0.01 mg L^{-1}) for water having initial arsenic concentration from 0 to 30 mg L^{-1}. Avinash *et al*, 2009 studied treatment of municipal wastewater in Mumbai, India using laterite-based constructed soil filter. The results indicated increase of dissolved oxygen levels and reduction of chemical oxygen demand (COD) from 135.4±79.4 to 28.8±19.5 mg L^{-1}. The biological oxygen demand (BOD) reduced from 92 to less than 10 mg L^{-1}. Suspended solids reduced by 12–18 mg L^{-1} when initial value was 180 mg L^{-1}. Turbidity reduced from mean 140 to 5.0±3.4 NTU. The total coliform, fecal coliform were 3.2±0.9, 2.8±0.4, respectively.

In addition, laterite adsorbed phosphorus in natural lakes and landfills (Zhang, *et al*, 2011). Wood and Atamney, (1996) examined the use of laterite in the bed medium to remove phosphorus and heavy metals from waste water in Northern Ireland where phosphorus enrichment of lakes due to agriculture problem and heavy metal emission from landfill sites. This study, using both laboratory tests and pilot-scale constructed wetlands, reported the effectiveness of granular laterite in removing phosphorus and heavy metals from landfill leachate. The laboratory studies showed that laterite was capable of removing 99% of phosphorus from solution. A pilot-scale experiment containing laterite

achieved 96% removal of phosphorus. Initial removals of aluminium and iron by pilot-scale CWs were up to 85% and 98% respectively. Percolating columns of laterite reduced Cd, Cr and Pb to undetectable concentrations. Mitali *et al.* (2006) investigated kinetics and mechanism of fluoride removal using laterite from Bankura in West Bengal. The laterite was found to be efficient for removal of fluoride from aqueous sample, (83.3-74.4% in the temperature range 293-313 K for initial concentration of 10 mg L^{-1}. The removal of other anions such as Cl^-, SO_4^{2-}, and NO^{3-} by laterite was also reported to be satisfactory.

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CHAPTER 3. EFFECTS OF MINERALOGY OF SUSPENDED MATERIALS ON PERFORMANCE OF WEATHERED VOLCANIC ASH-BASED FLOCCULANT

ABSTRACT

We examined the effect of clay mineralogy and interfacial chemistry of clay suspensions on the performance of a flocculant prepared from weathered volcanic ash rich in allophane and imogolite. Upon addition of the flocculant into the clay suspension and stirring, fluffy flocs formed and settled after a standing time. The absorbance of the supernatant gradually decreased to near zero at an optimum addition and then increased again when more flocculant was added. The optimum flocculant addition differed significantly among the clay suspensions. Inspection of the results of the flocculation tests and characterization of the sample clays, particularly stepwise multiple regression analyses, suggested that the major factors affecting the performance were the effective cation exchange capacity (ECEC), content of micaceous minerals and average particle size, of which the contribution of the former two factors seemed weightier. This was interpreted as indicating the importance of the amount of negative charge on the external surfaces of particles in the clay suspensions.
Key words: Water treatment, flocculation, volcanic ash, allophane, imogolite

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3.1 INTRODUCTION

Removal of suspended materials is an essential operation in drinking water supply and waste water treatment. In water treatment, flocculation process is commonly used to eliminate suspended materials. Typical suspended materials in natural waters including silicate minerals, humic substances and algae carry mostly negative surface charges and they are compensated by diffuse cation swarm around the particles (Hunter and Liss, 1979). This arrangement of surface charge and counter cations are termed diffuse double layer (DDL). Since the cations in DDL are not in close contact with particle surfaces, electrostatic repulsive force operates between suspended particles to prevent their agglomeration. A common way to remove suspension materials is to add flocculating agents to overcome electrostatic repulsion and promote coalescence of the suspended particles to form large flocs that settle down rapidly (Tripathy and De Ranjan, 2006). Salts of multivalent cations, e.g., Al^{3+} and cationic hydroxide clusters of aluminum are commonly used as flocculants. The latter is available on the market under the trade name of PAC and being used worldwide. Multivalent cations tend to be adsorbed onto the counter particle surface and the development of DDL is suppressed. Consequently, the electrostatic repulsion is overcome by London-van der Waals attraction making particles come near and coalesce to form large flocs. Long chain synthetic polymers are also popular

flocculating agents applied to remove suspended materials under bridging and electrostatic patch mechanism (Tripathy and De Ranjan, 2006).

There are little performance and safety problems in using these conventional flocculants in closed environments like in water purification plants. However, in water processing in the open environment, the use of the aluminum salts and synthetic polymers is often avoided in consideration of possible physiological effects on organisms (Nakanishi and Wada, 2007). In removal of prolonged turbidity in reservoir and lakes by flocculation-sedimentation, safer flocculants are required because the flocs are not recovered but they are left on the lake floor for long time. Some natural substances are gaining increasing interests as the flocculant that may have less environmental impacts in water treatment in lakes, reservoirs and construction sites. The use of starch, guar gum, derivatives of chitin, chitosan and carboxymethyl cellulose was reviewed by Tripathy and De Rajan (2006). Zhang *et al.* (2010) reported that a microbial polymer was effective for flocculating synthetic kaolinite suspensions. Kashiwai and Yuki (2006) tested natural allophane separated from weathered pumice and found that it was effective for flocculating suspended clays in natural waters. Kuchibune *et al*. (2006) used slurry of weathered allophanic volcanic ash to remove suspended clay particles from reservoir water.

Generally, the natural organic polymer flocculants are nontoxic to organisms and available from renewable resources, but they have relatively low flocculation efficiency (Tripathy and De Rajan, 2006) and are not stable against microbial attack during storage. Although they are nontoxic, the high dosage may increase the biological oxygen demand of processed water. The flocculants prepared from allophonic weathered volcanic ash, on the other hand, were found to be as effective as PAC for flocculating suspended clay particles in some natural reservoirs (Kuchibune *et al*., 2006). One of the authors (Ienaga) has applied flocculants manufactured from weathered volcanic ash for the removal of suspended clay particles from reservoir waters and muddy waste waters from construction sites and found that the flocculant basically worked well, but the performance differed greatly among the waters even when the concentrations of suspended materials were similar.

A possible flocculation mechanism is hetero-coagulation of negatively charged layer silicate minerals and positively charged allophane, suggesting that the flocculation efficiency depends on charge characteristics of clay particles in water environment. The present study aims to elucidate effects of clay mineralogy and surface charge characteristics of suspended particles on the flocculation efficiency of flocculant prepared from weathered volcanic ash.

3.2 MATERIALS AND METHODS

3.2.1 Flocculant

A commercial flocculant supplied from Astec.Co. under a trade name of TRP-Ai was used throughout the present study. This product is made from subsurface layer of weathered volcanic ash soil rich in allophane and imogolite by mechanical dispersion treatment followed by pH adjustment

with HCl. The product was thick slurry with a solid content of 132 g L^{-1}. It was diluted three times with distilled water just before use in the flocculation experiments.

3.2.2. Clay suspensions

Five gram portion of a soil or clay sample (Table 3.1) was mixed with 1 L of deionized water and sonicated at 250 W for 15 min after pH adjustment to about 8 with 0.1 mol L^{-1} NaOH. The dispersed suspension was put into sedimentation cylinder and the fraction having equivalent spherical diameter of <2 μm was separated once by siphoning. This procedure was repeated for several times to obtain sufficient amount of clay suspension for flocculation tests. The separated stock clay suspensions were mixed and kept in a polypropylene bottle with fitted stopper and diluted with deionized water just before use.

Table 3.1. Source of soil and clay samples

Sample name	pH	Organic carbon/g kg^{-1}	Source
K1	4.7	7.1	B horizon of Dystrochrept in Gyeonggi-Do, Korea
K4	5.1	3.4	IIB23 horizon of Hapludult in Gyeongsangnam-Do, Korea
K7	5.1	1.9	B22 horizon of Hapludalf in Jeollanam-Do, Korea
T5	5.3	4.3	B22 horizon of Haplustox in NakhonRatchasima, Thailand
O1	4.6	3.7	B21 horizon of Hapludultin Okinawa, Japan
F	5.7	18	Ap horizon of Fluvaquents in Fukuoka, Japan
Kaolinite		tr.	Iriki mine, Kagoshima, Japan
Montmorillonite		tr.	Kunipia-F supplied byKunimine Co., Tokyo, Japan

3.2.3. Characterization of clay suspensions and flocculant

Exchangeable cation composition was determined by 1 mol L^{-1}NH$_4$OAc extraction. A clay suspension containing 200 mg of clay was placed on a 0.1 μm membrane filter and washed with 50 mL of the NH$_4$OAc solution under suction. The filtrate was analyzed for Ca^{2+}, Mg^{2+}, Na$^+$ and K$^+$ by atomic absorption spectroscopy (Z2300, Hitachi, Japan).

Particle size distribution of the suspended clay minerals was determined by photon correlation spectroscopy (ELSZ, Photal Co, Japan). The spectrometer was calibrated with spherical colloidal latex having a diameter of 100 nm. Zeta (ζ) potential of the suspended clay particles was determined by a ζ potential analyzer (Zetasizer 2000, Malvern Instruments, UK). The average ζ potential was calculated with the preinstalled software from the electrophoretic mobility measured by laser-Doppler velocimetry. The apparatus was calibrated with a standard latex suspension supplied by the manufacturer.

Mineralogical analysis of the clay suspensions by X-ray diffraction (XRD) was carried out following the procedure described by Wada and Umegaki (2001) with a Cu K$_\alpha$ radiation at 40 kV and

20 mA. The approximate contents of layer silicate clay minerals, gibbsite, quartz and feldspars were estimated from the XRD peak intensities following the procedure described by Moslehuddin (1998). Free iron oxide and hydroxide content was determined by the selective dissolution (Wada and Greenland, 1970) using sodium dithionite, sodium citrate and sodium hydrogen carbonate. The dissolved iron was determined by atomic absorption spectroscopy (Z2300, Hitachi, Japan). The approximate weight of oxide and hydroxide of iron was calculated by multiplying the amount of the extracted iron by a factor of 1.5.

3.2.4. Characterization of flocculant

The allophane plus imogolite content of the flocculant used was determined by the selective dissolution method (Blakemore *et al*, 1981; ParfittandWilson,1985) with a modification by Schuppli *et al*. (1983). The Si, Al and Fe concentrations in the extract were determined by atomic absorption spectroscopy (Z2300, Hitachi, Japan). The particle size distribution was determined by repeated sedimentation and sieving following procedure of Nguyen and Egashira (2005). This is because the photon correlation spectrometer did not accept particles larger than several μm and the software for calculating the particle size distribution was not suitable for fibrous imogolite. The clay fraction separated in the particle size analysis was subjected to X-ray diffraction in the same manner for clay suspensions. The clay fraction of the flocculant was also examined in an electron microscope (JEM 100CX, JEOL Co., Japan)

3.2.5 Flocculation experiments

The flocculation experiments were performed by the Jar-test device (MJS-3H, Miyamoto Co., Japan) in a room at 20-24 °C. A 400 mL portion of a 500 mg L^{-1} clay suspension was placed in a 500 ml tall beaker in the jar tester and the impeller rod was put in the suspension. Immediately after the addition of 0 to 40 mL of diluted flocculant, the suspension was stirred at a speed of 300 rpm for 3 min and at 50 rpm for 5 min. The flocs were allowed to settle for 30 min. A 10 mL portion of the supernatant then was collected from 2cm below the water surface and absorbance was measured at a wave length of 660 nm by a spectrophotometer (U1900, Hitachi, Japan). All of tests were carried out in triplicate.

3.3 RESULTS AND DISCUSSION

3.3.1 Mineralogy of flocculant and soil clay samples

X-ray diffraction patterns of the Mg-saturated and glycerol-solvated clay samples and flocculant are shown in Fig. 3.1. The flocculant gave faint diffraction peaks only at about 1.4, 0.7 and 0.334 nm after Mg-saturation and glycerol-solvation but the former two peaks disappeared after heating at 550 °C (not shown). This suggests that these peaks arose mostly from imogolite but not from layer silicate minerals. The 0.334 nm peak persisted after heating, indicating that the flocculant contained small

amount of quartz. The particle size distribution showed that the flocculant comprised of 28% of coarse sand (200-2000 μm), 12% of fine sand (20-200 μm), 13% of silt (2-20 μm) and 47% of clay (< 2 μm) by weight. The allophane plus imogolite content determined by the selective dissolution using ammonium oxalate-oxalic acid (Blakemore, 1981; Parfitt and Wilson, 1985) was 19% on the oven-dry basis. This value combined with the solid content of the flocculant (132 g L^{-1}) gives the allophane plus imogolite concentration in the flocculant to be 25 g L^{-1}. The average Si/Al molar ratio of the allophane and imogolite in the flocculant calculated from the selective dissolution data was 0.82. The oxalate-oxalic acid soluble iron mineral content was 20 g kg^{-1} as Fe_2O_3. This is equivalent to the concentration of 2.6 g L^{-1} in the flocculant.
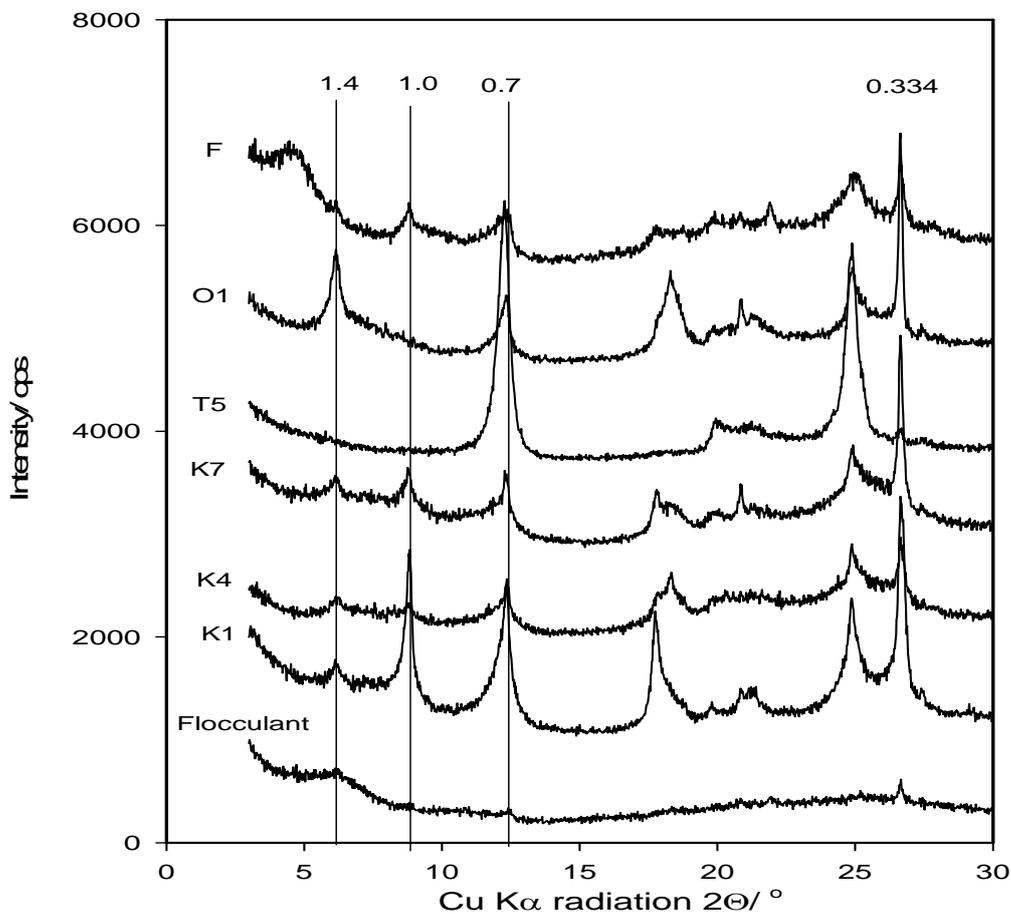
Fig. 3.1. X-ray diffraction patterns of the clays in suspensions used for flocculation experiments. Patterns for Mg-saturated and glycerol solvated specimens are shown.

Fig. 3.2 shows an electron micrograph of the < 2 μm fraction of the flocculant. The aggregates of very fine granules and threads indicate the dominance of allophane and imogolite. Although thread like imogolite is conspicuous in this micrograph, faint peaks in the X-ray diffractogram (Fig 3.1) and

the fact that pure imogolite shows fairly strong diffraction peak at around 1.2-2.0 nm (Wada, 1989) suggest that the relative abundance of imogolite is low.
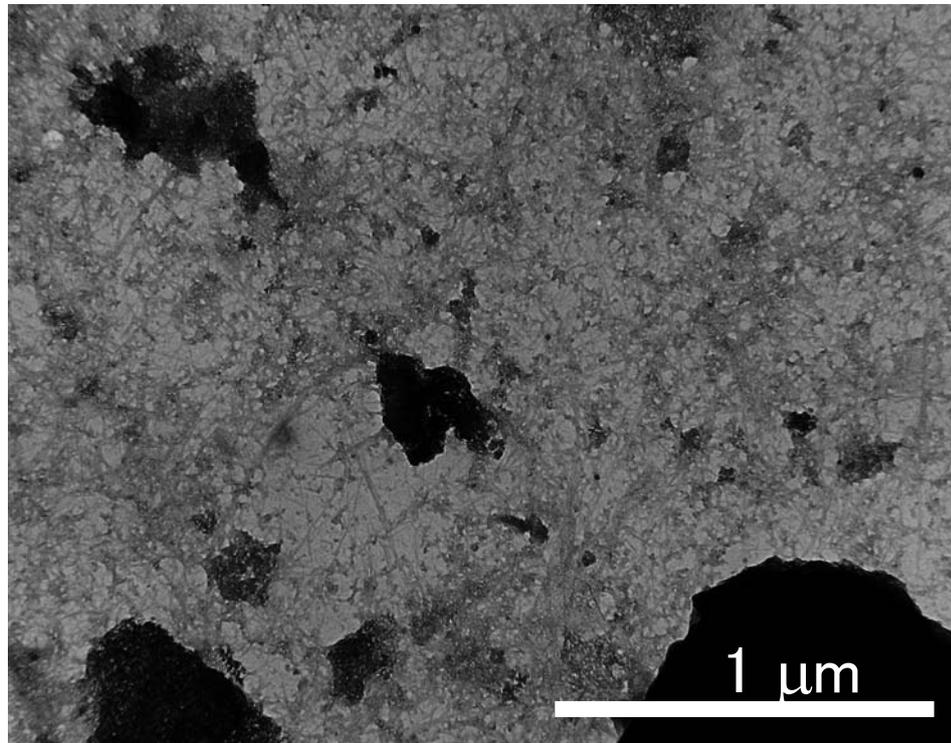
Fig. 3.2. Electron micrograph of < 2 μm fraction of flocculant.

Table 3.2. Approximate mineral contents of clay samples

Sample	Approximate clay mineral percentage										
	Mc	Ch	Vt	VtCh	Sm	Kt	Other LS	Gb	Qz	Fd	Fe
K1	36	0	5	5	0	20	2	5	19	5	3
K4	20	0	10	20	0	20	5	0	14	9	2
K7	21	0	14	8	0	15	0	4	29	6	3
T5	0	0	0	0	0	96	0	0	0	0	4
O1	2	0	1	34	0	20	0	17	21	4	1
F	18	1	17	3	11	18	0	4	14	11	3
Montmori-llonite	0	0	0	0	100	0	0	0	0	0	0
Kaolinite	0	0	0	0	0	100	0	0	0	0	0

(Mc= Mica, ChVt = Vermiculite-Chloriteintergade, Sm= Smectite, Kt= Kaolinite, Qz=Quartz, Fd = Feldspar, Gb = Gibbsite, Other LS = Mixed layer minerals including kaolinite-smectite and mica-vermiculaite, Fe = Oxides and hydroxides of iron)

The soil clay samples used for the flocculation test had mixed clay mineralogy except for the T5 sample that contained only kaolinite. The major clay minerals in the K1, K4 and K7 samples were

micaceous minerals, vermiculite-chlorite intergrade, kaolinite and quartz. The O1 sample also contained vermiculite-chlorite intergrade, kaolinite and quartz but it lacked in micaceous minerals (Fig. 3.1). The F sample contained significant amount of smectite as indicated by the broad diffraction peak at 1.7-1.9 nm (Fig. 3.1). The approximate relative contents of layer silicate minerals, quartz, feldspars and gibbsite were estimated following the procedure described by Mosslehuddin (1998) and Nguyen (2008) and combined with the free iron oxide content determined by selective dissolution (Wada and Greenland, 1970) to calculate the approximate mineralogical composition of the clay samples used. Thus estimated mineralogical composition of the clay samples are listed in Table 3.2.

3.3.2 Colloidal properties of clay suspensions

The pH and electric conductivity of the suspension, exchangeable cation composition, average particle size and the average ζ-potential of the suspended particles are tabulated in Table 3.3. The histograms showing the particle size distribution are shown in Fig.3. The suspension pH was in a narrow range from 6.79 to 6.86. The electric conductivity was also not much different among samples. The major exchangeable cation was Na^+ followed by Ca^{2+} and Mg^{2+} and K^+ content was low. The prevalence of Na^+ is due to the use of NaOH in the clay dispersion and separation process. Some soils used for clay preparation were acidic (Table 3.1) and contained a significant amount of exchangeable aluminum (data not shown). The neutral pH values of the clay suspensions indicate that the adsorbed aluminum was replaced by Na^+ and precipitated as hydroxides. The neutral pH value for the montmorillonite suspension is due to the low clay/water ratio. The effective cation exchange capacity (ECEC), i.e., the sum of the exchangeable cations, was 12.3, 13.5, 16.6, 6.14, 10.5, 29.8, 99.0 and 3.67 cmol$_c$ kg^{-1} for the K1, K4, K7, T5, O1, F, montmorillonite and kaolinite samples, respectively.

Table 3.3. Colloidal properties of clay samples

Samples	pH	EC/ dS m^{-1}	Exchangeable cations/cmol$_c$kg^{-1}				Average particle size/ nm	Average ζ potential/ mV
			Na$^+$	K$^+$	Ca^{+2}	Mg^{2+}		
K1	6.83	0.03	6.61	0.78	3.18	1.72	161	-59.7
K4	6.80	0.02	8.34	0.40	2.66	2.05	183	-82.7
K7	6.86	0.03	5.03	0.42	4.69	6.51	285	-12.6
T5	6.82	0.02	3.35	0.40	1.68	0.72	86	-45.1
O1	6.79	0.02	8.98	0.32	0.26	0.97	128	1.1
F	6.81	0.03	4.95	2.11	17.22	5.53	187	-36.6
Montmorillonite	6.86	0.04	77.41	1.96	14.83	4.82	224	-55.7
Kaolinite	6.86	0.04	2.75	0.21	0.40	0.31	384	16.7

Fig. 3.3. Size distribution of suspended particles in clay suspensions used for flocculation experiment.

Table 3.3 and Fig. 3.3 show that the size of the suspended clay particles is far less than 1 μm. Since the clay particles are basically platy in shape, the size information from the photon correlation spectroscopy is not straightforward. The size distribution shown in Fig. 3.3 and the calculated average particle diameter should be taken as a matter of relativity. The T5 sample had the smallest average particle diameter of 86 nm, while the kaolinite sample had the largest average diameter of 384 nm.

The measured ζ-potential of the clay particles of the clay suspensions distributed mostly over -40 to -50 mV ranges. Table 3.3 lists only the averaged values. The average ζ-potential was negative except for the O1 and kaolinite samples. The ζ-potential of the kaolinite sample ranged from about -50 mV to 100 mV with a peak at around -15 mV but the averaged value was positive.

3.3.3 Flocculation experiments

Upon addition of the diluted flocculant and vigorous stirring at a speed of 300 rpm, fluffy flocs formed. During the continued stirring at 50 rpm, the flocs grew in size and they loosely deposited on the bottom of the beaker after 30 min of the standing time. Only a small number of flocs holding air bubbles still floated in the suspension. Since the supernatant of the suspension after the settling time was almost homogeneous, i.e., there was no visible turbidity gradient, a 10 mL portion of the supernatant was sampled from a depth of 2 cm from the surface and its absorbance at 660 nm was measured. The results of the flocculation experiments were graphically summarized in Fig. 3.4, where the averaged absorbance and standard deviation of the three replications were plotted against the flocculant dose. The error bar fell within the circle, indicating that the flocculation test was excellently reproducible. As the flocculant dose increased, the absorbance decreased to near zero and increased again. The increase in absorbance past the optimum dose is probably due to the presence of the excess flocculent and/or re-dispersed clay particles. The near zero absorbance at the optimum dose indicates that all the suspended clay particles interacted with the added flocculant, i.e., allophane and imogolite, to have formed large flocs. The minimum amount of the flocculant to be added to decrease the absorbance below 0.005 was defined as the optimum dose in the present study.

The measured optimum dose was 26, 8, 4, 6, 8, 18, 14 and 0.8 mL for the K1, K4, K7, T5, O1, F, montmorillonite and kaolinite samples, respectively. The K1 and F samples required the larger amount of the flocculant before all the suspended particles were flocculated followed by the K4 and O1 samples. Of the two standard clay samples the kaolinite sample required much less dose than the montmorillonite sample did, i.e., 0.8 mL vs.14 mL. Horikawa *et al*. (1976) studied the flocculation in binary imogolite-layer silicate mixed suspensions and reported that montmorillonite almost completely flocculated at an imogolite to montmorillonite ratio of 0.25 by weight. The observed optimum dose for the montmorillonite sample corresponds to an allophane plus imogolite to montmorillonite ratio of 0.23. According to Horikawa (1976), the imogolite to kaolinite ratio at complete flocculation was about 0.01 and the kaolinite started to re-disperse at the higher ratios and

showed positive electrophoretic mobility. The trend in absorbance for kaolinite shown in Fig. 3.4 is good agreement with his observation. Horikawa (1976) interpreted the difference between montmorillonite and kaolinite in terms of the amount of surface negative charge of these minerals.

The amount of the surface negative charge would be surely one of the most important factor that affect the flocculant requirement but the results obtained in the present study suggest that it is not necessarily the dominant factor. For example, the K1 and K7 samples have comparable ECEC but the optimum dose for the K1 sample was much higher than that for the K7 sample. Similarly, the optimum dose for the K1 and F samples were larger than that for montmorillonite in spite of their lower ECEC. It is interesting to note that the K1 and F samples having relatively high micaceous mineral contents required larger amounts of the flocculant. To explore the factors affecting the flocculant requirement, stepwise multiple linear regression analysis was carried out using Mathematica 8.0. The selected variables giving the highest r^2 adjusted for the degree of freedom were the ECEC, micaceous mineral content and average particle size. The best regression equation was:

$$9.1295 + 0.1203\ x_1 + 0.4289x_2 - 0.03263x_3\ \ (r^2\ \text{adjusted} = 0.517) \qquad (3.1)$$

Where x_1, x_2 and x_3 represent ECEC in $cmol_c$ kg^{-1}, micaceous mineral percentage and average particle size in nm, respectively. Fig. 5 shows the relationship between the measured optimum dose and that predicted with the regression equation. The regression equation significantly overestimated the optimum dose for the K4 and K7 samples and underestimated that for the kaolinite sample. For the rest of the samples, the predicted optimum doses were fairly close to the measured ones. The analysis of variance on the fitted model showed that the most highly contributed variable is the micaceous mineral percentage followed by the ECEC and average particle size.

Since the leading mechanism of flocculation is the neutralization of the surface negative charge on the suspended layer silicate mineral particles, it is reasonable to have positive coefficient for the ECEC. The larger the ECEC, more flocculant is needed to neutralize the surface charge in general. The negative coefficient for the average particle size is also acceptable because the larger the particle size the smaller the number of the particles in suspensions having the same particle concentration by weight per unit volume. However, the inclusion of the micaceous mineral percentage in the regression equation is not straight forward. One possible interpretation is that the ECEC alone cannot account for the amount of the surface negative charge that contributes to interparticle interaction.

The charges that are responsible for the interparticle interaction would be those on the exterior planar surfaces of clay crystals or packets as well as those on the edge surfaces. The charges on the interior surfaces of clay particles made up of several stacked unit silicate layers would not contribute to the interparticle interaction. If these assumptions are correct, the ECEC is not a good measure of the amount of the surface charges that are responsible for electrostatic interparticle interaction particularly for clay minerals having exchangeable interlayer cations, since the ECEC represents all the surface charges to which ammonium ions are accessible. On the other hand, it is a good estimate of exterior surface charge for non expandable micaceous minerals. Thus, the ECEC cannot be used as

a single measure of the exterior surface charge of suspended particles for clays having mixed mineralogy. The linear regression analysis using the sum of the smectite and vermiculite percentages gave the following equation:

$$10.2899 + 0.1170x_1 + 0.4236x_2 - 0.03425x_3 \quad \text{(adjusted } r^2 = 0.496) \qquad (3.2)$$

Where x_1, x_2 and x_3 represent the sum of vermiculite and smectite percentages, micaceous mineral percentage and average particle size in nm, respectively. The similar goodness of fit of these models suggests that the amount of the exterior surface charge is the dominant factor affecting the flocculant requirement. The smaller coefficient for smectite plus vermiculite percentage may indicate that smaller fraction of the surface charge on these minerals contribute to interparticle interaction.

Fig. 3.4 shows that the excessive addition of the flocculant resulted in the increased absorbance. This may be due either to the remnants of the flocculant or to the re-dispersed clay particles that were stabilized by the excessive amounts of allophane and imogolite. Horikawa (1976) reported that the addition of allophane and/or imogolite to the suspensions of layer silicate minerals caused initial flocculation and re-dispersion upon excessive addition. The electrophoretic mobility of the re-dispersed clay particle resembled that of allophane and imogolite (Horikawa, 1976). The range of the flocculant dose in which the absorbance was kept below 0.005 was 26 to 30 mL, 8 to 10 mL, 4 to 10 mL, 6 to 12 mL, 8 to 13 mL, 17 to 23 mL and 0.8 to 5 mL for the K1, K4, K7, T5, O1, F and kaolinite samples, respectively. There were no clear relationships between these ranges and the properties of the suspended materials.

The flocculant used in the present study was prepared from the weathered volcanic ash containing both allophane and imogolite. It is interesting to discuss the relative contribution of allophane and imogolite to the removal of suspended layer silicate particles via flocculation by charge neutralization. Both allophane and imogolite exhibit positive and negative surface charges depending on the suspension pH (Clark and McBride, 1984) but their charge characteristics are different in terms of the location of charge. Allophane develops both positive and negative charges on its external surface as evidenced by its negative and positive electrophoretic mobility (Horikawa, 1976). Imogolite develops positive charges on its external surface but the negative charges are confined to internal surface of its tubular structural unit. Since the negative charges on the internal surface of the tube are balanced by cations retained in the tube, imogolite does not show positive electrophoretic mobility even when it bears net negative charge (Horikawa, 1976). Recent electronic structure calculations on imogolite showed that the external surface of imogolite is always positively charged (Guimaraes *et al.*, 2007). All these suggest that imogolite would be more effective for charge neutralization. In addition, the fibrous morphology of imogolite would favorable for bridging layer silicate particles to form larger flocs. Using freeze-etching technique, Horikawa *et al.* (1976) observed numerous layer silicate particles connected by imogolite fibers. On the other hand, imogolite is much less abundant than allophane in weathered volcanic ash and overall contribution to the flocculation may be smaller.

It is difficult to collect allophane and imogolite separately from a weathered volcanic ash but it is possible to prepare nearly pure imogolite and allophane specimens from gel-like films and weathered pumice grains (Wada and Wada, 1977). It would be not only scientifically interesting but also practically important to evaluate relative efficiency in flocculating dispersed layer silicate particles using sols of pure allophane and imogolite.
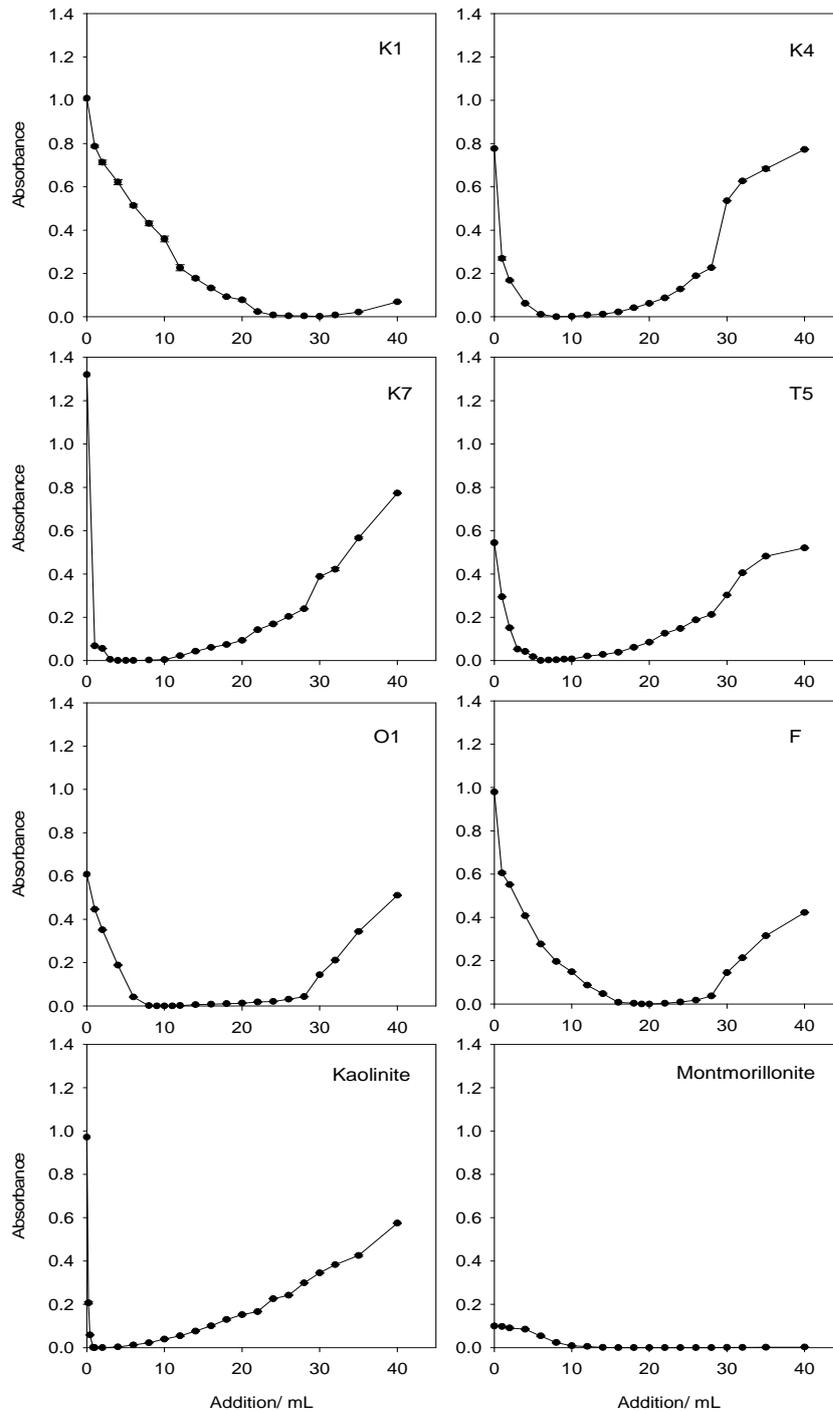
Fig. 3.4. Results of the flocculation experiments.
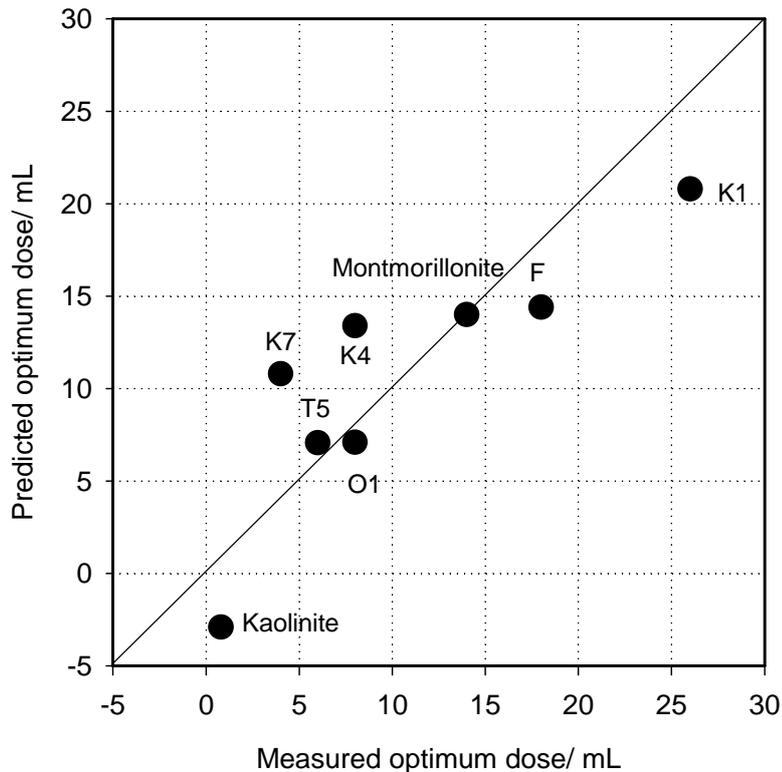
Fig. 3.5. The relationship between the measured optimum dose and predicted dose.

3.4 CONCLUSIONS

The flocculant made from volcanic ash soil rich in allophane and imogolite can effectively remove suspended clay particles at an optimum addition of the flocculant. The optimum dose depends on the mineralogy of the suspended particles. The major factors affecting the optimum dose are the ECEC, micaceous mineral content and average particle size. The ECEC and micaceous mineral content positively correlate, on the other hand, the average particle size negatively correlates with the optimum dose. This trend indicates that the amount of the negative charge on the external surfaces of the suspended clay particles is the dominant factor that determines the flocculant requirement.

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CHAPTER 4. COMPARISON OF ALLOPHANE AND IMOGOLITE SOLS AS A FLOCCULATING AGENT FOR SUSPENDED CLAY PARTICLES IN WATER

ABSTRACT

To evaluate the relative flocculating power of allophane and imogolite, we conducted a series of flocculation experiment using allophane and imogolite sols and their mixtures. Imogolite was more effective than allophane for all five clay suspensions used. The residual turbidities of test montmorillonite suspensions after treatment with mixed allophane and imogolite sols were nearly equal to those calculated under the assumption that the contribution of allophane and imogolite was additive. But the experimental turbidity was much higher than the calculated one for a soil clay suspension.

Key word: allophane, imogolite, flocculation, water treatment

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4.1 INTRODUCTION

Flocculation-sedimentation is the most commonly used techniques for removal of suspended materials in drinking water purification and waste water treatment. Popular flocculant used in these fields are inorganic salts of multivalent cations and synthetic soluble polymers. Although aluminum ions are highly phyto-toxic (Nakanishi and Wada, 2007) and some synthetic organic polymers are mutagenic (Mallevialle *et al.*, 1984), there is little toxicity concern in water treatment plants because the dose is optimized so as to minimize the residual concentration in the processed waters and the sediments are recovered and disposed properly. However, in water processing in the open environment, the use of the aluminum salts and synthetic polymers is often unwelcome in view of possible adverse effects on organisms. In removal of prolonged turbidity in reservoir and lakes by flocculation-sedimentation, safer flocculants are required because the flocks are not recovered but they are left on the lake floor for long time. To meet these requirements, the uses of natural biopolymers and inorganic materials have been tested as reviewed by Tripathy and De Rajan (2006). The starch, guar gum, derivatives of chitin, chitosan and carboxymethyl cellulose are the examples for the biopolymers (Tripathy and De Rajan, 2006; Zhang *et al.*, 2010) and allophanic soils (Kashiwai and Yuki, 2006; Kuchibune *et al.*, 2006) are the examples for inorganic substances. Generally, the natural organic polymer flocculants are nontoxic to organisms and available from renewable resources, but they have relatively low flocculation efficiency (Tripathy and De Rajan, 2006) and are not stable against microbial attack during storage. Although they are nontoxic, the high dosage may increase the biological oxygen demand of processed water and sediment. The flocculants prepared from allophanic

weathered volcanic ash, on the other hand, are biologically inert and were found to be as effective as PAC for flocculating suspended clay particles in some natural reservoirs (Kuchibune *et al.*, 2006).

According to the pioneering basic research works by Horikawa (1976) and Horikawa *et al.* (1976), the dominating mechanism of the flocculation of suspended clay particles by imogolite is the surface charge neutralization as evidenced by the drastic reduction in the electrophoretic mobility. Nga *et al.* (2012) examined the effect of mineralogy of suspended materials on the performance of a commercial flocculant made from weathered volcanic ash rich in allophane and imogolite and reached a similar conclusion. However the flocculation mechanism of allophane and imogolite may not be the same. Single thread of imogolite can bridge many layer silicate particles as seen from the electron micrographs of freeze-etched binary suspensions of kaolinite-imogolite and montmorillonite-imogolite (Horikawa *et al.*, 1976), while such bridging is not expected for allophane. If imogolite is more effective for flocculating layer silicate particles, the imogolite content can be used as a criterion in searching for weathered volcanic ash resources suitable for producing flocculants.

In the present study, relative flocculation efficiency of allophane and imogolite were compared. The imogolite sample was prepared from gel-like films filling weathered pumice grains and allophane sample was extracted from interior of the pumice grains. Flocculation experiments were conducted on suspensions of three soil clays, kaolinite and montmorillonite.

4.2 MATERIALS AND METHODS

4.2.1 Allophane and imogolite sols

Both allophane and imogolite were separated from weathered pumice collected from the Murasakino pumice bed in Kitakami, Iwate prefecture, Japan. For preparation of imogolite suspension, gelatinous films filling the interstices of pumice grains were collected by hand picking using tweezers. The collected films were suspended in deionized water and sonicated for 1 min at 24 kHz and 110 W (W-113 MkII, Honda Electronics Co., Japan) to remove fine pumice granules occluded in the films. The purified imogolite films free from pumice granules were gently ground, re-suspended in fresh deionized water, and the pH of the suspension was adjusted to 4.5 with HCl. 0.1 mol L^{-1}. Imogolite was dispersed by sonication for 30 min at 19.5 kHz and 200 W (Type 4280, Kaijo Co., Japan). The resulted uniform imogolite sol was stored in a polypropylene bottle.

The sol of allophane was prepared following the method described by Wada (2001). The weathered pumice grains after removing imogolite films were gently crushed in a mortar and < 0.2 nm fraction was collected. Allophane was dispersed by pH adjustment to 4.5 with 0.1 mol L^{-1} HCl followed by sonication for 15 min at 19.5 kHz and 200 W (Type 4280, Kaijo Co., Japan). The fraction having an equivalent spherical diameter of less 0.2 μm was repeatedly collected by centrifugation and stored in a polypropylene bottle.

The purity of the separated allophane and imogolite was checked by electron microscopy. The Na$^+$ and Cl$^-$ retentions by the allophane and imogolite from 0.1 mol L^{-1} NaCl solution were measured as a function of solution pH basically following the method described by Wada and Okamura (1980). For imogolite, the purified gelatinous film was used instead of dispersed imogolite sol for convenience of solid-liquid separation by centrifugation.

4.2.2 Clay suspensions

Clay suspensions used for flocculation tests were prepared from three soil samples and two specimen clays (Table 4.1) following the procedure described by Nga *et al*. (2012).

Table 4.1. Source of soil and clay samples

Sample name	Source
K4	IIB23 horizon ofHapludult in Gyeongsangnam-Do, Korea
T5	B22 horizon of Haplustox in NakhonRatchasima, Thailand
F	Ap horizon of Fluvaquents in Fukuoka, Japan
Kaolinite	Iriki mine, Kagoshima, Japan
Montmorillonite	Kunipia-F supplied by Kunimine Co., Tokyo, Japan

Five gram portion of a soil or clay sample (Table 4.1) was mixed with 1 L of deionized water and sonicated for 15 min after pH adjustment to about 8 with 0.1 mol L^{-1} NaOH. The dispersed suspension was put into sedimentation cylinder and the fraction having equivalent spherical diameter of <2 µm was separated once by siphoning. This procedure was repeated using several portions of the sample to obtain sufficient amount of clay suspension for flocculation tests. The separated stock clay suspensionswere kept in a polypropylene bottle with fitted stopper and diluted with deionized water just before use.

The clays in the prepared suspensions were characterized for exchangeable cation composition, particle size distribution, and clay mineralogy. The detailed procedures for the characterization were described by Nga *et al*. (2012).

4.2.3 Flocculation experiments

The concentration of the purified imogolite and allophane suspensions were adjusted to 4800 mg L^{-1} by diluting with deionized water. The flocculation experiments were performed by a jar tester (MJS-3H, Miyamoto Co., Japan) in a room at 20-24 °C following Nga *et al*. (2012). A four hundred mL portion of a 500 mg L^{-1}clay suspension was placed in a 500 ml tall beaker and the impeller rod was put in the suspension. Immediately after the addition ofthe allophane or imogolite sol, the suspension was stirred at a speed of 300 rpm for 3 min and at 50 rpm for 5 min. The flocs were allowed to settle for 30 min. A 10 mL portion of the supernatant was collected from 2cm below the

water surface and absorbance was measured at a wave length of 660 nm by a spectrophotometer (U1900, Hitachi, Japan). All of the tests were carried out in triplicate.

To evaluate the allophane to imogolite ratio in the flocculant, a series of mixed sols whose allophane to imogolite ratios were 4:0, 3:1, 2:2, 1:3 and 0:4 were prepared by mixing stock allophane and imogolite suspensions. The flocculation test was carried out in a similar way described above at a predetermined dose. Approximately 10 mL of the sediment was pipetted and spread in a petri dish, and the morphology of the flocs was recorded by photographing.

4.3 RESULTS AND DISCUSSION

4.3.1 Properties of clay suspensions

Properties of the clay suspension used for the flocculation test were summarized in Table 2. The K4 and F sample had mixed clay mineralogy but the T5 sample contained almost only kaolinite. The pH of the suspension was in a range from 6.80 to 6.86. The effective cation exchange capacity of the suspended clays, i. e., the sum of exchangeable cations was in a fairly large range from 3.7 to 99 $cmol_c$ kg^{-1}. The exchangeable cation compositions (Ca, Mg, K and Na) are not shown in the table but the fraction of Na was the largest because NaOH was added for pH adjustment (Nga *et al*., 2012).

Table 4.2. Colloidal properties of clay samples

Samples	pH	EC/ dS m^{-1}	Average particle size/ nm	ECEC/ $cmol_c$ kg^{-1}	Clay mineral composition (Approximate %)
K4	6.80	0.02	183	13.5	Kaolinite(27), Vermiculite-chlorite(22), intergrade(22), Mica(19), Vermiculite(10)
T5	6.82	0.02	86	6.2	Kaolinite(96), Iron oxide(4)
F	6.81	0.03	187	29.8	Kaolinite(19), Vermiculite(19), Mica (17), Smectite(10), Quartz (13)
Montmorillonite	6.86	0.04	224	99.0	Montmorillonite(100)
Kaolinite	6.86	0.04	384	3.7	Kaolinite(100)

(ECEC; Effective Cation Exchange Capacity)

4.3.2 Surface charge characteristics of allophane and imogolite

Fig. 4.1 shows the surface charge characteristics of allophane and imogolite used in the present experiments, where the chloride adsorption was plotted as the amount of positive charge and sodium adsorption was plotted as negative charge. The crosses in the figure indicate the net surface charge, i. e., chloride adsorption minus sodium adsorption. The allophane exhibited both positive and negative charges over the entire pH range examined and the positive charge increased as pH decreased while the negative charge showed the opposite trend. The charge characteristic of the imogolite was essentially similar to that of allophane but the magnitude of the charges is fairly large and less pH dependent. The point of zero net charge (PZNC; Sposito, 1981) was 6.04 for allophane and 6.63 for imogolite.
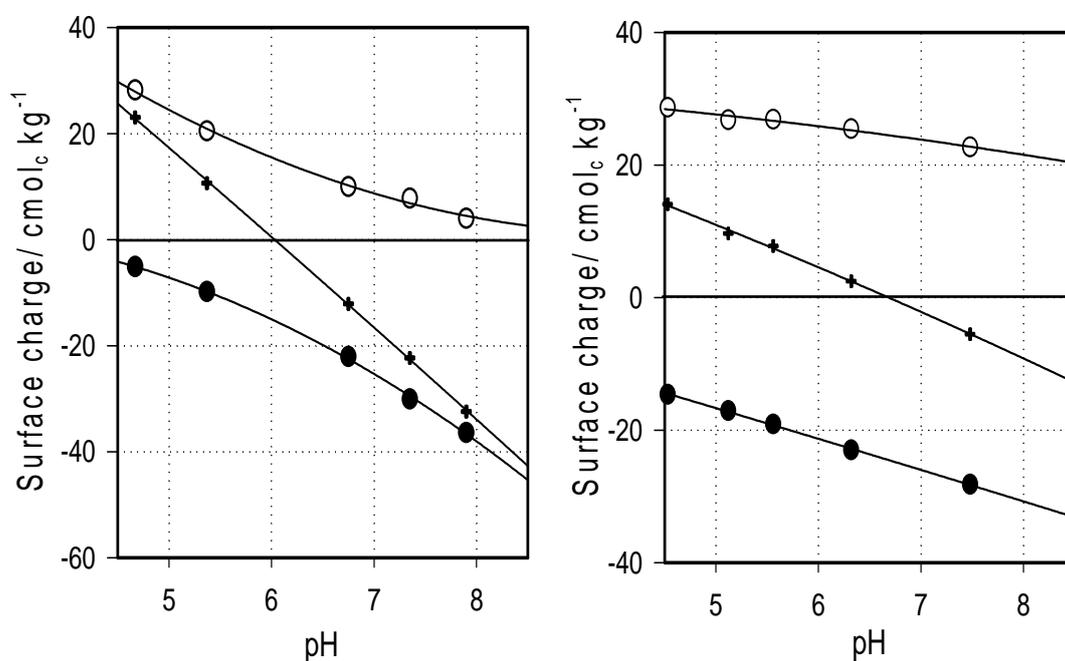
Fig. 4.1. Surface charge characteristics of allophane (left) and imogolite (right). Open and closed circles indicate Cl- adsorption (positive surface charge) and Na+ adsorption (negative charge), respectively. The cross indicates the net surface charge.

4.3.3 Relative flocculating power of allophane and imogolite

The results of the flocculation tests for montmorillonite, kaolinite and the F soil clay are graphically presented in Fig. 4.2, where the relative absorbance of the suspension after standing time was plotted against flocculant dose. The relative absorbance is defined as the ratio of the absorbance after flocculation test to that of the original clay suspension. For all of the suspensions, the absorbance of the suspension was exactly proportional to the clay concentration in a range from 0 to 500 mg L^{-1} and it is basically possible to calculate the concentration of clay after flocculation and sedimentation.

However, the relative absorbance but not the calculated clay concentration was plotted in this figure because a part of the added allophane or imogolite may have remained in the supernatant after flocculation test and contributed to the absorbance. The pHs of the suspension after flocculation test did not differ significantly from the original ones.
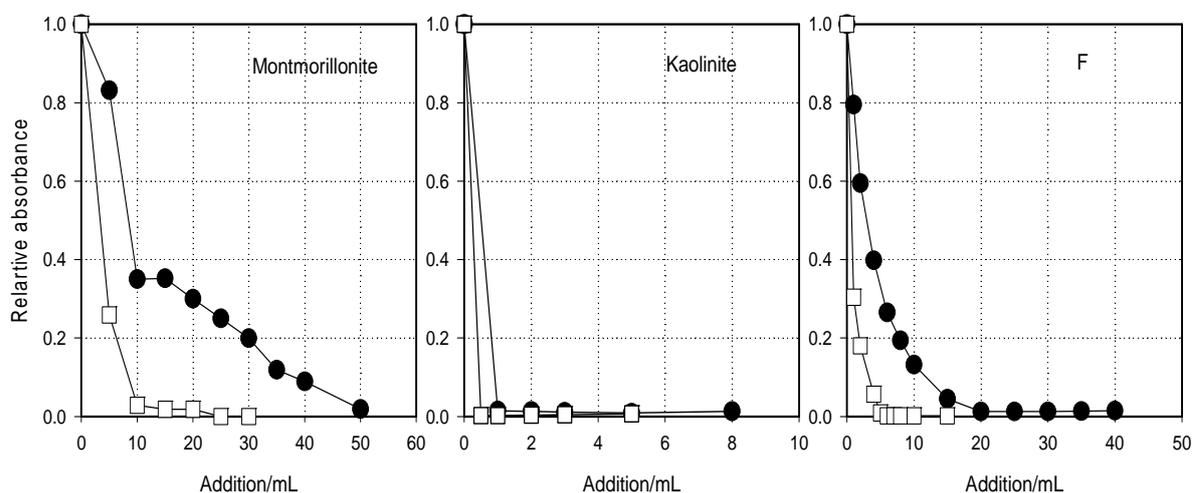
Fig. 4.2 Relative turbidity of montmorillonite (left) and F soil clay (right) suspentions after addition of allophane sol (closed circle) or imogolite sol (open square).

For montmorillonite, the absorbance sharply dropped after 10 mL addition of the imogolite suspension. The addition of allophane was also effective but 50 mL was required to reduce the relative absorbance below 0.01. If the remnant allophane and imogolite is negligible, the montmorillonite concentration after an addition of 10 mL of allophane and imogolite sol is calculated to be 172 and 10 mg L^{-1}, respectively, indicating that imogolite sol is much more effective for removing suspended montmorillonite particles than allophane sol. Imogolite sol was also more effective than allophane sol for flocculating the F soil clay. At an addition of 5 mL of allophane and imogolite sol, the clay concentration is estimated to have dropped to 165 and 3.6 mg L^{-1}, respectively. These values indicate that the allophane and imogolite sols are approximately twice as much effective for the F soil clay than for montmorillonite. Kaolinite was much more sensitive than montmorillonite and the F soil clay and it flocculated almost completely with an addition of < 1 mL of allophane or imogolite sol. The lowest absorbance was achieved at 5 m L- and 1 mL-addition for allophane and imogolite, respectively. The slight increase in the absorbance at larger than optimum additions is probably due to the remnant of excessive allophane or imogolite.

The flocculation of suspended layer silicate clays by allophane and imogolite is a typical hetero-flocculation. Unlike homo-flocculation, colloidal particles of different kind coalesce even when their surfaces carry electric charge of the same sign if the difference in the surface potential is large enough (Kitahara and Furusawa, 1990). Even so, the experimental results of Nga *et al*. (2012) that the

optimum dose of an allophanic flocculant depended on the amount of negative charge on the suspended clay particles rather than on their ζ-potential indicated that the charge neutralization is an important factor. Since imogolite exhibits more positive charge as well as net positive charge at around pH 6.8 (Fig. 4.1), the higher performance of imogolite is considered to be at least partly due to the larger extent of charge neutralization.
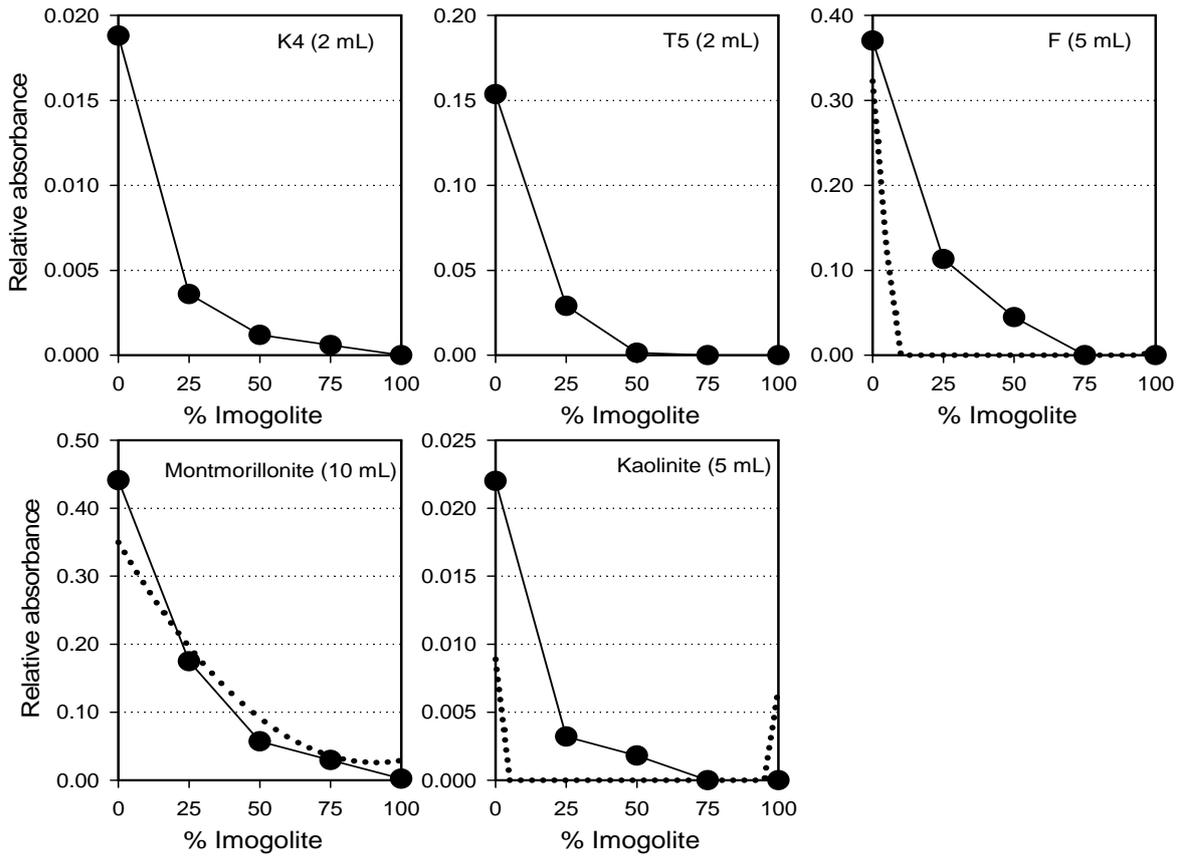
Fig. 4.3. Relationship between relative absorbance of clay suspension after the addition of a fixed volume of mixed sols and its imogolite content. The sample name and the added volume are indicated in each graph. The dotted lines in graphs for the F soil clay and montmorillonite are calculated lines assuming allophane and imogolite contributed independently.

Each graph in Fig. 4.3 shows the relationship between relative absorbance of a clay suspension after addition of a predetermined volume of the mixed allophane-imogolite sol and the percentage of imogolite in the mixed sol. The volume of the sol added was 2 mL for the K4 and T5 soil clays, 5 mL for the F soil clay and kaolinite and 10 mL for the montmorillonite. These volumes correspond to the minimum dose of the imogolite sol required to reduce the relative absorbance to below 0.01 which were determined by a series of preliminary experiments. The graphs in Fig. 4.3 clearly show that the

imogolite sol was more effective for flocculating all five clay suspensions. Particularly for the T5, F soil clays and montmorillonite, the relative absorbance after addition of the allophane sol was as high as 0.15, 0.37 and 0.44 as compared to that of < 0.01 after addition of imogolite sol.
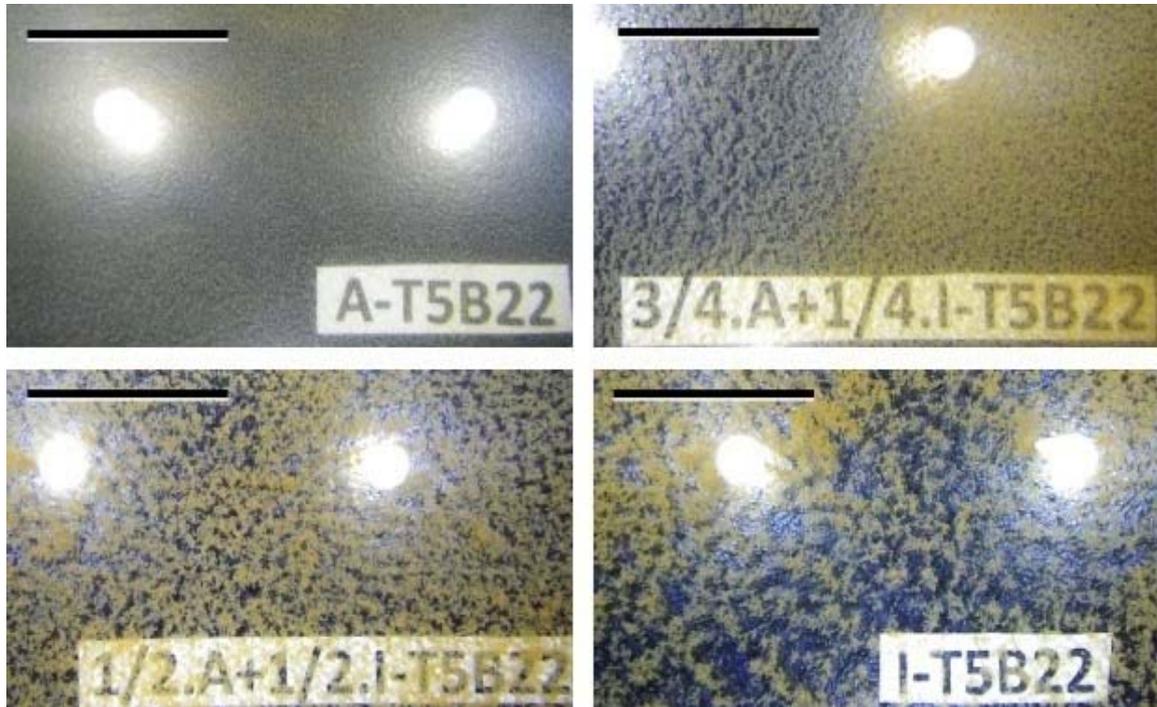
Fig. 4.4. Photographs of flocs formed after flocculation experiments on the T5 soil clay suspension. Top left: imogolite sol, top right: mixed sol containing 25% imogolite, bottom left: mixed sol containing 50% imogolite, and bottom right: imogolite sol. White spots appears on the photographs are reflections of illuminating LED lights.

Fig. 4.4 shows the photographs of the flocs formed and settled when the T5 soil clay was treated with the sols containing 0, 25, 50 and 100% of imogolite. The morphologies of the flocs formed by mixed sols containing 75% (not shown) and 100% imogolite were similar. The size of the flocs was so small to resolve by naked eyes when allophane sol was applied. As the percentage of imogolite in the mixed sol increased the size of the formed flocs distinctly increased. The treatment with the imogolite sol yielded fairly large flocs having a span of a few mm, although it was difficult to define the exact size and shape. These trends were common to all of the clay suspensions. The photographs show that the flocs formed are fluffy and porous particularly when the imogolite content of the sol was >50%. This is probably they were made up of imogolite thread bridging layer silicate clay particles. The electron microscopic examination of a freeze-etched suspension of mixed montmorillonite and imogolite (Horikawa *et al*., 1976) showed such assemblages.

All the experimental plots in Fig. 4.3 are concave. This is a natural result since the imogolite sol is more effective than allophane sol for flocculating suspended clay particles. But it is difficult to

judge from these plots whether the flocculating action of allophane and imogolite was additive, synergic or negatively synergic. If the action of allophane and imogolite is additive, the relative absorbance of a clay suspension treated with a mixed sol can be calculated from the results of a series of flocculation experiments with pure allophane and imogolite. The relative absorbance of a clay suspension after an addition of 10 mL of mixed allophane-imogolite sol containing 20% imogolite, for example, is given by the following equation;

$$R_{mix20,10} = 1 - \{(1 - R_{I,2}) + (1 - R_{A,8})\}$$

Where $R_{mix,20,10}$ is the expected relative absorbance after addition of 10 mL of the mixed sol containing 20% of imogolite, $R_{I,2}$ is the relative absorbance after addition of 2 mL of the imogolite sol, and R_{A8} is the relative absorbance after addition of 8 mL of the allophane sol. The latter two quantities were read from the regression curves for the plots shown in Fig. 4.2. The R_{mix} value was set to 0 when the calculated value was < 0. The dotted lines in Fig. 4.3 are the calculated curves for montmorillonite, kaolinite and the F soil clay. The comparison of the experimental and calculated curves formontmorillonite indicates that the flocculation action of allophane and imogolite was additive. On the other hand, the calculated curves lies far below the experimental curves for kaolinite and the F soil clay, indicating that the flocculation action of allophane and imogolite was negatively synergic.

The negative synergy observed for the F soil clay and kaolinite can be explained by the association of allophane and imogolite in mixed suspensions. Horikawa *et al*. (1976) examined freeze-etched suspensions of mixed allophane and imogolite and found that aggregates of allophane attached on the threads of imogolite. Horikawa (1976) measured the electrophoretic mobility of particles in mixed allophane and imogolite suspensions and reported that the particles in the mixed suspensions behaved like pure imogolite. These results suggest that allophane and imogolite in mixed suspensions do not behave independently and at least a part of allophane attaches on imogolite fibers, resulting in less frequent collision of allophane and suspended clay particles. If all of the allophane associates with imogolite and it no longer functions in flocculation, the relative absorbance of the F soil clay after treatment of 5 mL of mixed sol containing 25 and 50% imogolite may approximate to the relative absorbance after addition of 1.25 and 2.5 mL of the pure imogolite sol, respectively. The values read from the experimental curve for imogolite in Fig. 4.2 (right) are 0.30 after 1.25 mL addition and 0.092 after 2.5 mL addition, which are significantly higher than the experimental values after mixed sol addition. This indicates that allophane also contributed to the flocculation to a certain extent.

It is difficult to draw a general conclusion from this study because the number of experimental data was limited due to the limited availability of the pure imogolite sol. A possible tentative conclusion about the mode of interaction of allophane-imogolite mixture and layer silicate clay minerals is that the flocculation action of allophane and imogolite is basically negatively synergic due

to their close association in the mixture but the extent of negativity differs depending on the properties of layer silicate minerals. The observation of the flocs formed in ternary allophane-imogolite-layer silicate suspensions by cryo-transmission electron microscopy will be useful in elucidating the flocculation mechanism.

The experimental results from this study and considerations indicate that imogolite is much more effective as a flocculating agent for layer silicate suspensions. Weathered volcanic ash containing more imogolite is suitable for a material for manufacturing flocculating agent for processing soil clay suspensions. The graphs for the K4 and T5 clays and kaolinite, the relative absorbance steeply decreased as the imogolite content increased from 0 to 25%. This implies that the imogolite to allophane ratio of 1:3 is a criterion in screening weathered volcanic ash to prepare a high performance flocculating agent. Unfortunately, however, there is no reliable and convenient method for quantifying allophane and imogolite. Developing such method will be important in utilization of weathered volcanic ash resources.

4.4 CONCLUSIONS

Imogolite is much more effective as a flocculating agent for layer silicate suspensions than allophane. Weathered volcanic ash containing more imogolite is suitable for a material for manufacturing flocculating agent.

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CHAPTER 5. MINERALOGY OF LATERITE SAMPLES FROM VIET NAM AND THEIR USE AS FLOCCULATING AGENTS FOR REMOVAL OF SUSPENDED CLAY PARTICLES FROM WATER

ABSTRACT

The existence of suspended clay particles is one of main factors for high turbidity in water. Flocculation is a common technique used to eliminate suspended materials from water. Currently, a variety of flocculating agents have been found as commercial products and applied to purify water. Most of agents works well and bring positive effects on environment. However, the use of some agents has shown problems relating to economic benefits and environment. The treatment cost and environmental safety evoke the increasing interests in not only developing countries but also in developed countries. To solve these problems, many researchers have been carrying out researches to improve materials for treatment. The present study aims at understanding mineralogy of the laterite samples distributed in Viet Nam and at evaluating their use ability as flocculating agent for suspended clay particle removal. Three laterite samples were used for experiments in this study. The laterite sample collected in Thach That region (1-TT) performed the best flocculation efficiency followed by the laterite sample collected in Hoa Lac region (2-HL). The sample collected in Quynh Tam commune (3-QT) worked less efficiently than other two samples. Goethite, gibbisite and hematite are considered to be the main components that are responsible for flocculation action.

Key words: Clay particle, flocculation, geothite, hematite, laterite, water processing
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5.1 INTRODUCTION

The suspended clay particles in water are main pollutants that cause turbidity in water environment. Removal of suspended particles is an essential operation in water treatment. Flocculation technique is a common way that is used to remove suspended materials from natural waters. In flocculation process, flocculating agents are added to overcome electrostatic repulsion and promote coalescence of the suspended particles to form large flocs that settle down rapidly (Tripathy and De Ranjan, 2006).

The synthetic agents, such as poly-diallyl dimethyl ammonium chloride (PDADMAC or Cat-Floc), used either alone or in combination with alum, have been reported to be effective in flocculation of negatively charged suspended particles in water (O'Melia, 1972; Faust and Aly, 1983). Long chain synthetic polymers are also popular flocculating agents to remove suspended materials via

bridging and electrostatic patch mechanism (Tripathy and De Ranjan, 2006). Zhang *et al.* (2010) reported that a microbial polymer was effective for flocculating synthetic kaolinite suspensions. Chitosan, a product made from crab shell, is very effective to remove suspended organic materials (Tripathy and De Ranjan, 2006) with less negative effects on the environment.

The flocculating agents have brought undoubted benefits in water treatment. However, negative effects on the environment have been found by the use of some agents. Aluminum salts and synthetic polymers cause possible physiological effects on organisms (Nakanishi and Wada, 2007) as well as aluminum accumulation in the environment and its connection with Alzheimer disease (Stauber *et al*, 1999). Some natural substances such as chitosan and carboxymethyl cellulose are nontoxic to environment, available from renewable resources and very effective for pollutant removal (Divakaran and Pillai, 2001) but they are not stable against microbial attack during storage (Tripathy and De Rajan, 2006; Zhang *et al.,* 2010) and may increase the biological oxygen demand of processed water if high dose is used. Therefore, flocculating agents with high treatment efficiency and less negative effects on the environment is needed for advanced water treatment in aquatic systems.

Flocculants made from natural volcanic ash soil were reported by Nga *et al*. (2012b), which were effective in removing pollutants from water at a low treatment cost. The flocculant made from volcanic soil was found to be as effective as PAC for flocculating suspended clay particles in some natural reservoirs but their flocculation efficiency largely depended on clay mineralogy (Kuchibune *et al*., 2006; Nga *et al.,* 2012a). Laterite, the *in-situ* weathering and decomposition products of rocks, is abundant in the tropical and sub-tropical regions and rich in sesquioxides (Fe_2O_3 or Al_2O_3). Thus they are possibly applied for water treatment (Blight, 1997; Nga *et al*., 2012b). The study of Udoeyo *et al.* (2010) indicated high absorption capacity for heavy metals of laterite materials. Lateritic soils have been used as effective sorbents for arsenic in groundwater (Maji*et al*., 2006; Rahman *et al.*, 2008; Maiti *et al.*, 2010). In addition, laterite adsorbs phosphorous in natural lakes and landfills (Zhang *et al.*, 2011).

The laterite is abundantly distributed in many regions in Viet Nam due to strong laterization. The characteristics of laterite would be different depending on regional climate and geology. The laterite materials are of high potential use in environmental treatments, but the laterite materials in Viet Nam have not been received due attention. Mineralogy of materials has been considered as an important factor affecting the removal of suspended particles (Nga *et al*., 2012a). Therefore, in the present study, mineralogy of laterite samples from Viet Nam and their ability as a flocculating agent to remove suspended clay particles were investigated.

5.2 MATERIALS AND MOTHODS

5.2.1 Laterite samples

Three laterite samples, 1-TT, 2-HL and 3-QT, were collected from lateric soil zones in Viet Nam indicated in Fig 5.1. The 1-TT sample was collected from a layer at a depth of 1.5m in Thach That town where completely weathered laterite is distributed. The original sample is a hard block with dark yellow color. The 2-HL sample was found in excavated soil at a construction site. It is a hard block containing red solid gravels. The 3-QT sample was taken from a laterite profile at a depth of 0.5 m from the surface. The raw sample was a hard block with black grey color.

The original samples were washed with tap water and air-dried at a room temperature. They were gently crushed to pass through a 2-mm screen. Aliquot of the treated samples was mixed well with distilled water, and adjusted to pH 5-6 with0.1 mol L^{-1} HCl and sonicated. The prepared three flocculant samples had dry matter content of 131 gL^{-1}, 127$gL^{-1}$and 91gL^{-1}for1-TT, 2-HL and 3-QT, respectively.

Fig. 5.1. Sampling locations and imagines of raw laterite samples.

5.2.2 Clay suspensions

Clay suspensions used for flocculation tests were prepared from two soil samples and two specimen clays (Table 5.1) following the procedure described by Nga *et al*. (2012a). A five-gram portion of the soil or clay sample was mixed with 1 L of deionized water and sonicated for 15 min

after pH adjustment to about 8 with 0.1 mol L^{-1}NaOH. The dispersed suspension was put into sedimentation cylinder and the fraction having equivalent spherical diameter of <2 μm was separated by siphoning. This step was repeated using several portions of the samples to obtain sufficient amount of clay suspension for flocculation tests. The separated stock clay suspensions were kept in a polypropylene bottle with fitted stopper and diluted with deionizer water just before use.

Table 5.1. Source of soil and clay samples

Sample name	Source
T5	B22 horizon of Haplustox in NakhonRatchasima, Thailand
F	Ap horizon of Fluvaquents in Fukuoka, Japan
Kaolinite	Iriki mine, Kagoshima, Japan
Montmorillonite	Kunipia-F supplied by Kunimine Co., Tokyo, Japan

5.2.3 Mineralogy and surface characteristic analysis of clay suspensions and laterite samples

Mineralogy of the laterite samples were analyzed for four components (clay, silt, fine sand and coarse sand) by X-ray diffraction (RINT-2000V, Rigaku) following the procedure of Nga *et al.* (2012a).

Mineralogical analysis of the clay suspensions by X-ray diffraction was carried out following the procedure described by Wada and Umegaki (2001) with a Cu Kα radiation at 40 kV and 20 mA.

Exchangeable cation composition was determined by 1 mol L^{-1}NH$_4$OAc extraction. For clay suspensions, the principle of Nga *et. al.* (2012) was applied. A clay suspension containing 200 mg of clay was placed on a 0.1μm membrane filter and washed with 50 mL of the NH$_4$OAc solution under suction. For laterite samples, the method of Muramoto *et al.* (1992) was applied. Two gram portion of a laterite sample was extracted three times with 30 mL the NH$_4$OAc solution. The extract was analyzed for Ca^{2+}, Mg^{2+}, Na$^+$ and K$^+$ by atomic absorption spectroscopy (Z2300, Hitachi, Japan).

Particle size distribution of the laterite samples was determined by siphoning method. The air-dried samples after organic matter digestion were separated by sonication for 15 minutes. Clay, silt and sand fractions were collected after respective settling time by siphoning.

Surface charge of laterite samples was determined by serial potentiometric titration method. Five gram portion of the sample was equilibrated with NaCl solutions having different pHs for 4 hours keeping ionic strength at 0.005 mol L^{-1}, 0.02 mol L^{-1}or 0.1 mol L^{-1}. The point of zero salt effect (PZSE), which is the pH value where net proton surface charge density is unaffected by changes in ionic strength, was determined as the crossover pH value of potentiometric acid-base titration analysis performed at different ionic strengths. Effects of PZSE on the vanishing of surface charge component is indirect. Therefore, PZNC (the point of zero net charge) is interpreted instead of PZSE in this study.

5.2.4 Thermal analyses

Differential thermal and gravimetric analysis (DTA-TG) was carried out simultaneously using the system of Rigaku Thermo plus EVO. The samples were heated from 20 to1000ºC for at a heating rate of 10 ºC min^{-1}. The amount of sample used in each test was 10mg.

5.2.5 Flocculation experiments

The flocculation experiments were performed witha jar tester (MJS-3H, Miyamoto Co., Japan) in a room at 20-24 ºC following the procedure of Nga *et al.* (2012a). A four hundred mL portion of a 500 mg L^{-1}clay suspension was placed in a 500 mL tall beaker and the impeller rod was put in the suspension. Immediately after the addition of predetermined dose of laterite flocculants, the suspension was stirred at a speed of 300 rpm for 3 min and at 50 rpm for 5 min. The flocs were allowed to settle for 30 min. A 10 ml portion of the supernatant was collected from 2cm below the water surface and absorbance was measured at a wave length of 660 nm by a spectrophotometer (U1900, Hitachi, Japan). All of the tests were carried out in triplicate.

5.3 RESULTS AND DISCUSSION

5.3.1 Mineralogy and surface charge characteristics of laterite samples

X-ray diffraction patterns of the Mg-saturated and glycerol-solvated clay fractions and fine sand fractions of three laterite samples are shown in Fig. 5.2. The clay fractions of the 1-TT and 2-HL samples showed fairly strong peaks at 0.7, 0.418, 0.35 and 0.269 nm, indicating that these samples contain kaolinite and goethite and hematite. In addition, the 1-TT sample showed weak peak at 1.4 nm, indicating that it contain small amount of non-expandable 2:1 layer silicates. The weak peak at 0.487 nm indicates that all the samples contain gibbsite. The 3-QT sample showed a significantly different mineralogy in that it is dominated by quartz and contained much less amount of kaolinite but it contained goethite and hematite. The dominance of 0.425 and 0.334 nm peaks in the X-ray diffraction patters for fine sand samples indicate that the major mineral in the fine sand fraction is quartz. The small but distinct peak at 0.418 and 2.69 nm shows that the fine sand fractions also contain goethite and hematite. The silt and coarse sand fractions exhibited similar X-ray patterns.
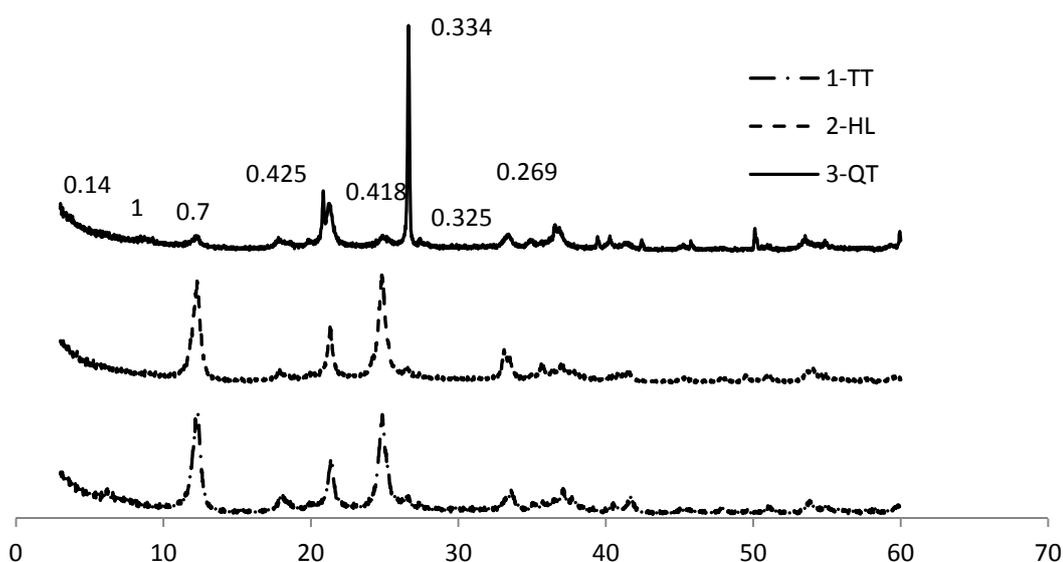
Fig. 5.2. X-ray diffraction diagram of 1-TT, 2-HL and 3-QT.

The results of thermal analyses are shown in Fig. 5.3. All the samples showed clear endothermic peaks centered at around 50, 320°C and corresponding weight losses. The 1-TT and 2-HL samples exhibited an additional large endothermic peak at 480°C but the 3-QT sample showed only a faint peak at that temperature. The endothermic peak at 50°C obviously came from desorption of adsorbed water. And the peaks at 320 and 480°C are assigned to dehydration reaction of hydroxide minerals and kaolinite, respectively. Although goethite dehydrates at lower temperature than gibbsite, the endothermic peak centered at around 320°C contains contribution of both gibbsite and goethite. These results harmonize with X-ray diffraction patterns shown in Fig. 5.2, particularly in that the 3-QT sample showed very weak diffraction peak at 0.7 nm. The 2-HL and 3-QT samples showed large endothermic peaks at around 840°C but they did not accompany weight loss. The origin of these endothermic peaks was not identified.

The dehydration reaction of gibbsite and kaolinite are expressed as

$$2Al(OH)_3 = Al_2O_3 + 3H_2O \qquad (5.1)$$

and

$$Si_4Al_4O_{10}(OH)_8 = SiO_2.Al_2O_3 + 4H_2O \qquad (5.2)$$

The weight loss from 200 to 400°C was about 0.5 mg for all three samples. If this came from the dehydration of gibbsite, the stoichiometry in the reaction (5.1) gives the gibbsite weight of 1.4 mg in 10 mg sample. Similarly, the weight of kaolinite in is estimated to be 1.4 mg for the 1-TT and 2-HL samples and 0.71 mg for the 3-QT sample.
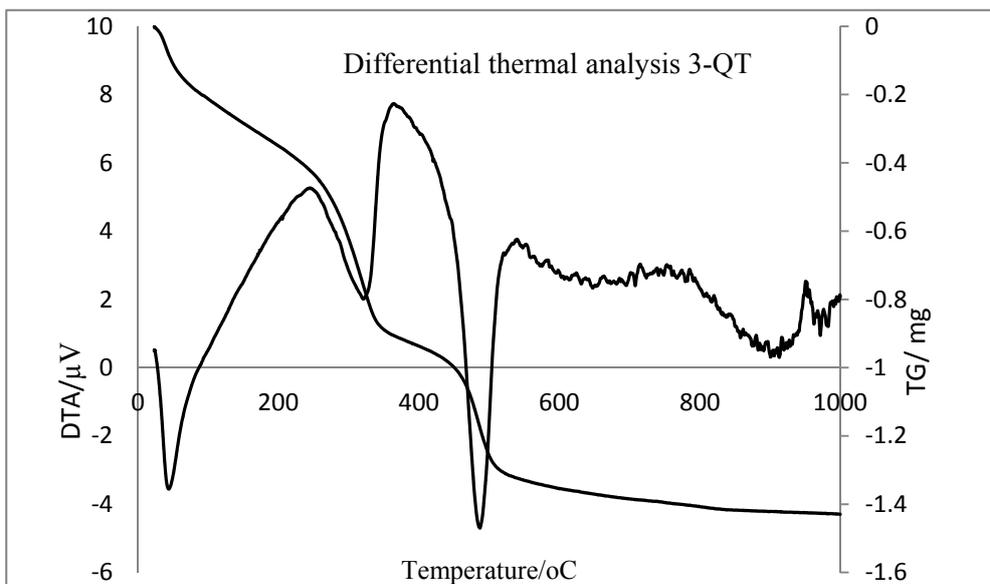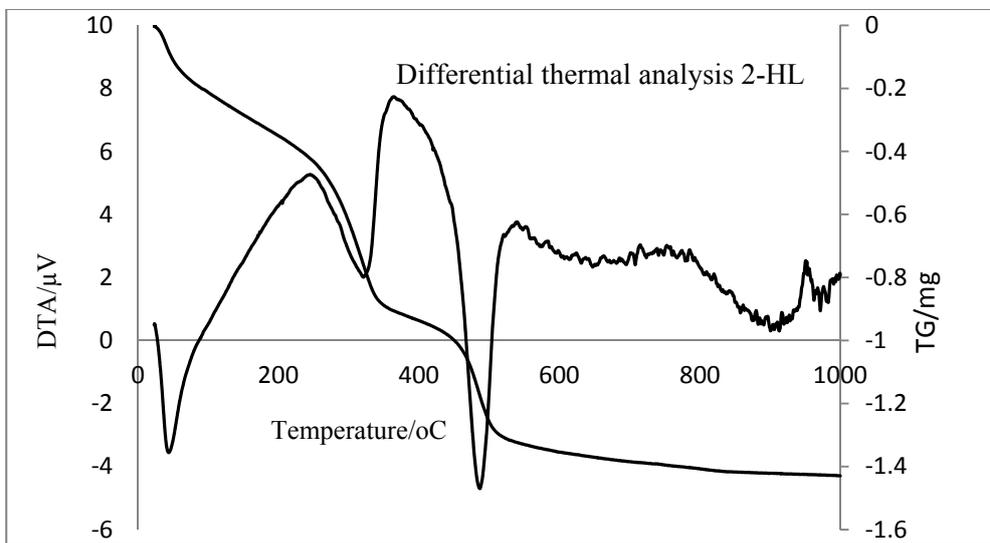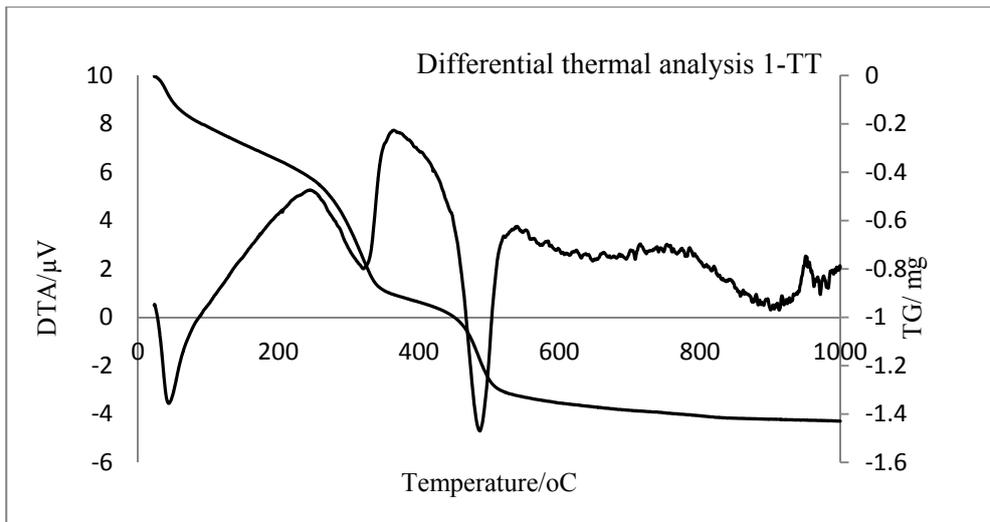
Fig.5.3. Results of differential thermal analysis and thermogravimetric analysis

Basic chemical properties are summarized in Table 5.2. The pH (H₂O) was in a range from 5.3 to 5.6 and the pH (KCl) was similar, indicating that the samples contained little exchangeable Al. The 1-TT sample showed the highest clay content of 67% followed by the 2-HL and 3-QT samples. The clay content of the 3-QT sample was only 30% and it had fairly high sand content. Although the clay content was high, the effective cation exchange capacity, i. e. the sum of exchangeable cations, was very low. This is a reflection of the virtual lack in 2:1 type layer silicate minerals as indicated by X-ray diffraction (Fig. 5.2).

Table 5.2. Some physic-chemical characteristics of laterite samples

No	pH_{H2O}	pH_{kcl}	TOC (%)	Clay (%)	Silt (%)	Fine sand (%)	Coarse sand (%)	ECEC (cmolc/kg)
1-TT	5.30	5.03	0.18	67.42	6.29	7.71	18.58	1.359
2-HL	5.56	4.95	0.13	57.03	6.24	9.89	26.83	1.001
3-QT	5.35	5.18	0.13	30.93	8.04	24.65	36.38	0.773

Fig. 5.4 shows the surface charge characteristics of laterite samples used in the present study, where the net surface charge was plotted against solution pH. The net charge decreased as pH increased and the sign of the net charge reversed at pHs 5.1, 5.0 and 5.4 for the 1-TT, 2-HL and 3-QT samples, respectively. These pH values, i. e. the point of zero net charge (PZNC) were not much different from pH values measured in water (Table 5.2). Since PZNC for goethite and gibbsite lie around pH 8, the observed lower PZNC values may be due to the presence of kaolinite and quartz.

Based on the mineralogical and chemical data, the approximate mineralogical composition of the laterite samples is summarized in Table 5.3.
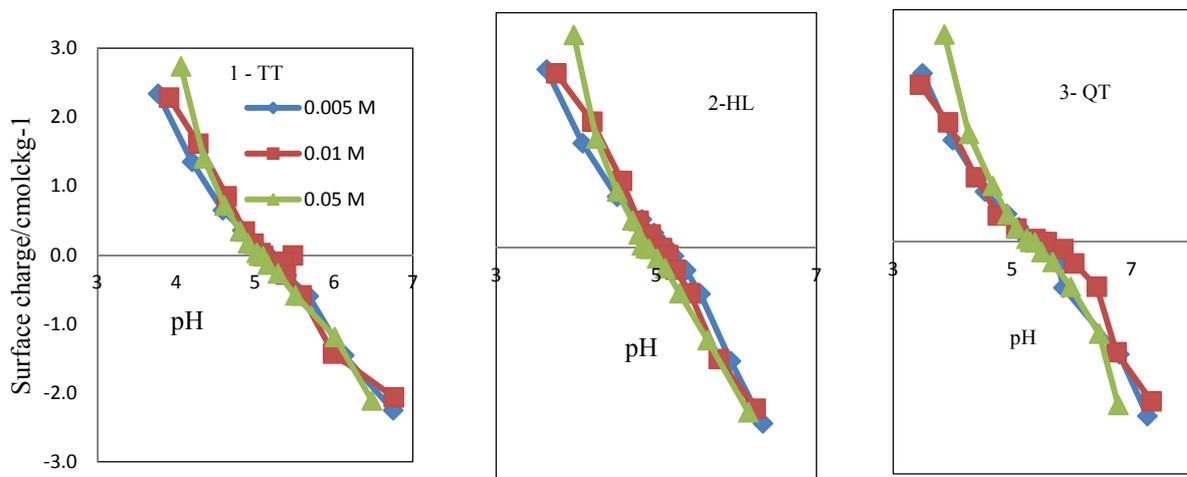
Fig.5.4. Surface charge diagrams of laterite samples:1-TT; 2-HL and 3-QT.

Table.5.3. Mineralogy identification of laterite samples

Sample	Fraction	Identification
1-TT	Clay	Mica; kaolinite; Geothite; feldspars
	Silt	Kaolinite; Geothite; Quazt; Feldspars
	Fine sand	Quazt; Geothite
	Coarse sand	Kaolinite; Geothite; Quazt
2-HL	Clay	Kaolinite; Geothite; Feldspars
	Silt	Kaolinite; Geothite; Quazt; feldspars
	Fine sand	Geothite; Quazt
	Coarse sand	Kaolinite; Geothite; Quazt; hematite, Feldspars
3-QT	Clay	Kaolinite; hematite; Quazt; Feldspars
	Silt	Quazt
	Fine sand	Quazt
	Coarse sand	Geothite; Quazt

5.3.2 Mineralogy and colloidal properties of clay suspensions

The X-ray diffraction patterns of the soil clay samples used for the flocculation tests are shown in Fig. 5.5. The strong peak at 0.7 and 0.35 nm in the T5 sample indicate that kaolinite predominates. The broad at 1.7-1.9 nm and 1.0 nm in the F sample show that it contains smectite and micaseous minerals. The approximate contents of layer silicate minerals and quartz that were estimated by the procedure described by Mosslehuddin (1998), Nguyen (2008) and Wada and Greenland (1970) were already reported by Nga *et al*. (2012a).
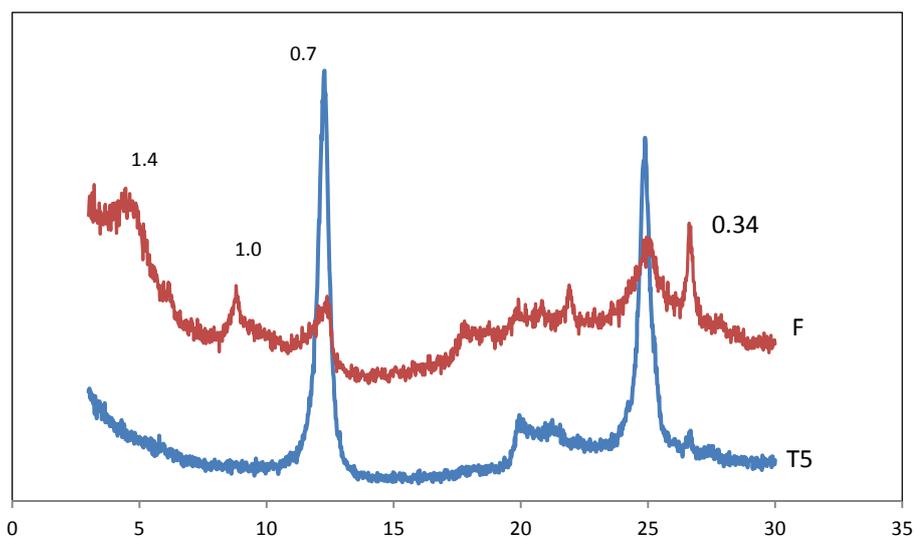
Fig.5.5.Mineralogy of soil clay suspensions (T5 and F samples).

Properties of the clay suspensions used for the flocculation tests were summarized in Table 4. The suspension pH ranged from 6.81 to 6.86. The electric conductivity was low and not much different among samples. The T5 sample had the smallest average particle diameter of 86 nm, while the kaolinite sample had the largest average diameter of 384 nm. The ECEC of the suspended clays was in a large range from 3.7 to 99 cmol$_c$ kg^{-1}. The fraction of Na was the largest among the exchangeable cations because NaOH was added for pH adjustment (Nga *et al*., 2012a).

Table 5.4. Colloidal properties of clay samples

Samples	pH	EC/ dS m^{-1}	Exchangeable cations/cmol$_c$kg^{-1}				Average particle size/ nm	Average zeta potential/ mV
			Na$^+$	K$^+$	Ca^{+2}	Mg^{2+}		
T5	6.82	0.02	3.35	0.40	1.68	0.72	86	-45.1
F	6.81	0.03	4.95	2.11	17.22	5.53	187	-36.6
Montmorillonite	6.86	0.04	77.41	1.96	14.83	4.82	224	-55.7
Kaolinite	6.86	0.04	2.75	0.21	0.40	0.31	384	16.7

5.3.3 Flocculation tests

The fluffy flocks formed when the flocculants were added and clay suspensions were vigorously stirred at a speed of 300 rpm. During the continued stirring at 50 rpm, the flocs grew in size and they loosely deposited on the bottom of the beaker after 30 min of the standing time. A 10 mL portion of the supernatant was sampled from a depth of 2 cm from the surface and its absorbance at 660 nm was measured. The results of the flocculation experiments are graphically presented in Fig 6, where the averaged relative absorbance at three replications was plotted against the flocculant dose. In general, the absorbance decreased as the flocculant dose increased and then increased again past optimum dose. The re-increase in absorbance is probably due to the presence of the excess flocculent and/or re-dispersed clay particles (Nga *et al*., 2012a).This observation was also in good agreement with the results by Nga *et al.* (2012b) on the kaolinite removal from water by volcanic and laterite materials. The montmorillonite suspension showed different response when the 3-QT slurry was added in that the absorbance exceeded that of the original montmorillonite suspension by about 20% (Fig. 5.6).

The lowest relative absorbance of about 0.01 indicates that 99% of the suspended clay particles were removed from the suspension. Considering the pHs of the clay suspensions and the PZNC the mutual flocculation of the added laterite and clay particles were due to the charge neutralization. The suspension pHs during flocculation experiment were close to those of the original clay suspensions, i. e., around 6.8, because the volume of the added flocculants remained mostly < 10% of the volume of the clay suspension. Since the PZNCs are around 5, the net surface charge is negative at round pH 6.8.

This is seemingly contradictory to the charge neutralization. But it is not unreasonable to expect the mechanism because gibbsite and goethite would have had positive surface charge even at pH7. Follett (1965) proved that electrostatic attraction force was dominated in retention of amorphous and colloidal ferric hydroxides by kaolinite. He also concluded that no bonding rearrangement occurred upon sorption of ferric colloids onto kaolinite. Weiss and Russow (1963) also indicated a similar association behavior of positively charged AgI particles by clay particles.
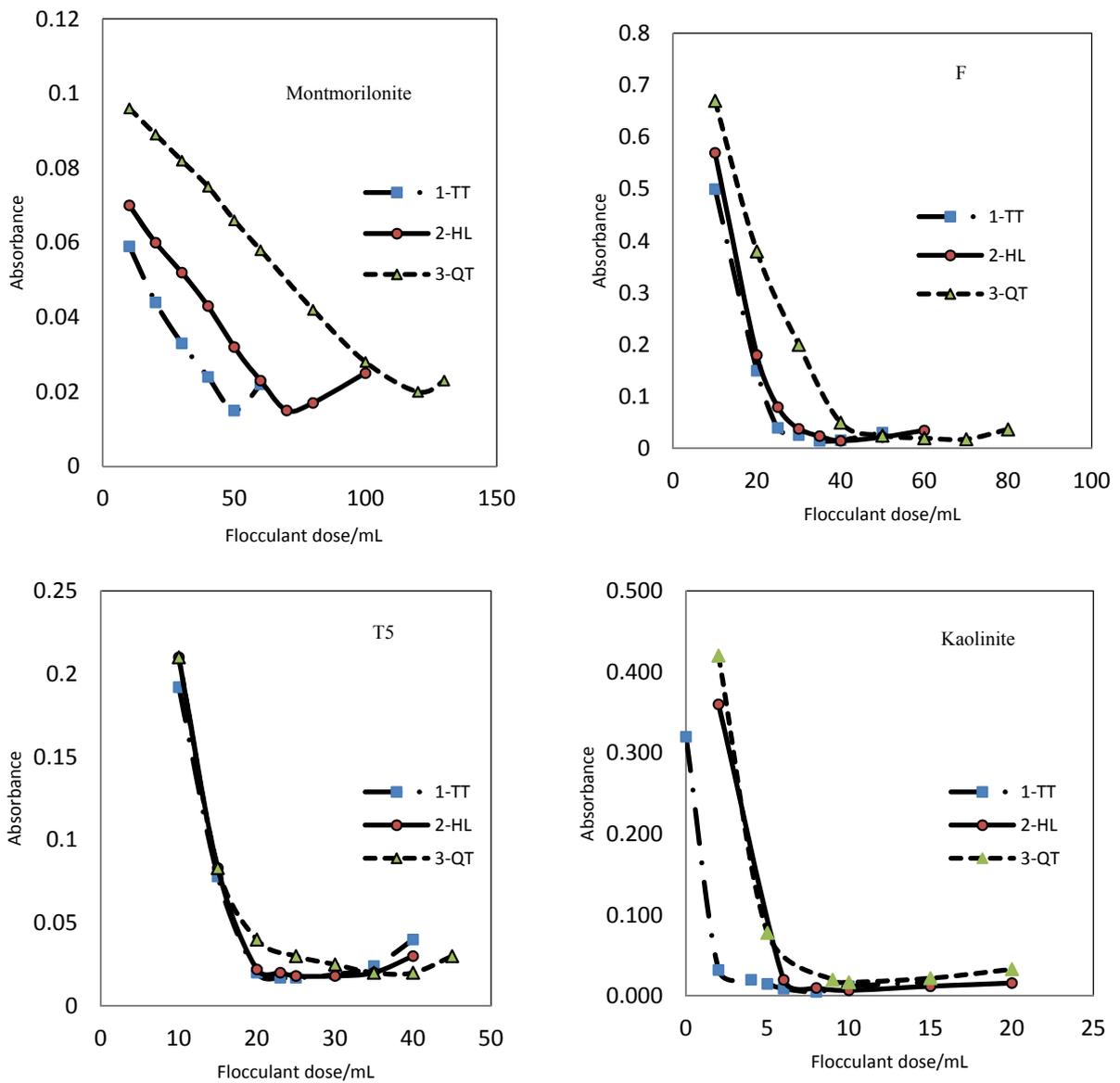
Fig. 5.6. Flocculation experiments of clay suspensions by laterite flocculants.

The results of the flocculation tests indicated that the amount of flocculant required to achieve the lowest absorbance was different for clay suspensions. The respective optimum dose of the flocculant made from 1-TT, 2-HL and 3-QT were 50, 70 and 120 mL for montmorillonite, 35, 40 and 60 mL for the F sample, 20, 25 and 35mL for T5 sample and 5, 6, and 9 mL for kaolinite. Nga *et al*. (2012a) reported that the mineralogical characteristics of clay suspensions affected the flocculation

efficiency. According their experimental results, suspensions containing smectite required larger flocculant dose (Nga *et al.,* 2012a). The present results are in accordance with that, the T5 sample a kaolinite having low ECEC needed small amount of flocculants whereas montmorillonite and the F clay sample needed much more flocculant dose. Another factor for the very high flocculation efficiency for kaolinitic suspensions is that kaolinite has PZNC of about 3.0 as interpreted by Nga *et al.* (2012b) and Horikawa (1976).

The flocculation performance of the three laterite flocculants was obviously different. The 1-TT sample gave the highest flocculation efficiency followed by the 2-HL sample, and 3-QT and this trend was common to the results from all four clay suspensions. The trend was marked for montomorillonite (Fig. 5.6). The gibbsite and goethite content of the 3-QT laterite seems comparable with those of other laterite samples (Fig. 5.2 and 5.3). The surface charge characteristics for the three laterite samples were also similar (Fig. 5.4). One possible reason for the observed lower flocculation efficiency is the lower goethite content as indicated by the X-ray diffraction pattern in Fig. 5.2. In addition fine quartz particles may have remained in the suspension. This may explain the relative absorbance over 1 observed for montmorillonite (Fig. 5.6).

5.4 CONCLUSIONS

The flocculants made from laterites in Viet Namare able to remove suspended clay particles via charge neutralization mechanism. The flocculation efficiency significantly depends on mineralogy and surface charge characteristics of both clay suspensions and laterite flocculants. Iron oxide minerals, e. g, geothite and hematite in the laterite are considered to be the factors contributing to flocculation.

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CHAPTER 6. REMOVAL OF PHOSPHATE FROM WATER BY LATERITE FROM VIET NAM

ABSTRACT

Adsorption of phosphate in artificial model solutions onto laterite was studied by batch experiments. Equilibrium isotherms and other adsorption experiments showed that phosphate adsorption was slightly pH dependent whereas the materials containing ferric and aluminum compounds are proven to be strongly pH dependent. Adsorption capacities of 1.1-1.6 mg P g^{-1}at pH 3 and 1.0-1.4 mg P g^{-1}at pH9 and an equilibrium concentration of less 2 mg P L^{-1} can be reached. The presence of other anions, e.g., sulfates and carbonate was shown to decrease adsorption of phosphate. In competitive adsorption in the mixed solutions of phosphate, sulfate and carbonate, laterite preferred phosphate over sulfate and carbonate. The order of adsorption selectivity was phosphate>sulfate>carbonate.

Key words: Adsorption, phosphorous, laterite, iron oxide mineral

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6.1 INTRODUCTION

6.1.1 Back ground

Phosphorus (P) is an essential nutrient for the growth of organisms, but excessive amount of phosphorus in water bodies can also cause eutrophication resulting in the bloom of aquatic plants, growth of algae and depletion of dissolved oxygen in water and hence deteriorate water quality. Phosphorus is released into aquatic environments in many ways including industrial, agricultural, mining activities and mineralization of natural forest coverage. Although phosphorus contamination in aqueous environment has attracted increasing interests recently because of damages to ecosystem, loads of phosphorus discharged into environment has been increasing. Therefore, phosphorous removal from water is an urgent demand for water quality improvement and environmental protection.

In recent years, several techniques for phosphorus removal from wastewater have been developed and attracted much attention. The methods including adsorption, physical settling and filtration process, chemical precipitation with aluminum and iron compounds, and biological processes that rely on biomass growth of bacteria, algae, plants or intracellular bacterial polyphosphates accumulation are mentioned in a review by Bashana and Basan (2004). Finding advanced adsorbents to bring about high efficiency for treatment process is gaining increasing interest of scientists. Several low-cost and natural materials such as clays, waste materials and by-products such as montmorilonite, kaolinite, illite (Edzwald *et al*., 1976), palygorskite (Ye *et al*., 2005; Cheng

and Sheng, 2006), La(III)-chelex resin (Wu *et al*., 2007), dry iron oxide tailings (Zeng, 2009) fly ash (Cheng *et al*., 2007), blast furnace slag (Oguz, 2004), hydroxides sludge (Golder *et al*., 2006), activated aluminum oxide and ferric hydroxide (Genz *et al*., 2004), have all been investigated as effective adsorbents to remove phosphorous in water. Despite the abundance of literature on phosphate adsorption capacity of clay minerals and natural materials, only few studies are available for the ability of laterite.

Laterite is formed by deep weathering in tropical and subtropical environments. The heavy rainfall in these regions leaches out all soluble weathering products in such soils, leaving behind clay minerals, rutile, and hydrated Al and Fe oxides which have been known for their strong interaction with arsenate and phosphate ions in solution (Cornell and Schwertmann, 2003).So far various studies have focused on applications of laterite for water treatment. Frederick (2008) investigated removal of arsenic from drinking water sources of laterite thanks to metal oxy-hydroxides of aluminum and iron in composition. Udoeyo *et al*. (2010) indicated high absorption capacity of laterite for aqueous heavy metals. Lateritic soils have been used as effective sorbents for arsenic removal from groundwater (Majiet *et al*., 2006; Rahman *et al.*, 2008; Maiti*et al*., 2010). Nga *et al*. (2013) indicated good performance of laterite materials collected from Viet Nam in removal of suspended clay particles from water.

Instead of using synthetic compounds of high cost and toxicity to environment to remove pollutants from water, development of natural adsorbents of low cost should be paid attention. Laterite might be an alternative material which is effective, inexpensive and environmentally friendly. In Viet Nam, laterite is abundant and distributed in many regions due to strong lateritirization, but their applications to water treatment have been very few. The objective of this study is to demonstrate that laterites from Viet Nam are effective as adsorbents in removing phosphorous from aqueous solution. The present study focuses on evaluating the effects of pH on phosphate sorption, determining phosphate adsorption capacity and selectivity for phosphate through a series of batch experiments using simple and multicomponent solutions.

6.1.2Chemistry, occurrence and environmental relevance of phosphorus

6.1.2.1 Chemistry and natural occurrence

Phosphorus (P), having the atomic number 15 and an atomic weight of 30.97376is the eleventh most abundant element in the earth's crust and widely present in rocks, soils, waters and in living organisms. Phosphorus compounds play a crucial role in life processes, forming the backbone of the DNA and being involved in metabolic energy transfer as ATP and related compounds. Phosphorous is released to environment and also among the most toxic substances known, used as chemical warfare agents and as pesticides. There are more than 100,000 known phosphorus compounds of which the majority contains linkages to oxygen, carbon, nitrogen and metals. Under most conditions, naturally

occurring phosphorus is exclusively combined with four oxygen atoms, forming the phosphate oxyanion (Bryant, 2004).

Phosphorus in natural and waste waters is distributed between various physical compartments, including a dissolved fraction comprising both inorganic and organic P species, a colloidal fraction associated with both inorganic colloids such as clays and organic macromolecules including humic and fulvic acids, particulate component including P species adsorbed to particle surfaces or retained in the particle matrix and also a biological constituent associated with aquatic organisms such as algae or bacteria (Dennison,1998).

In nature, phosphorus passes through several interconnected cycles. The geological cycle of phosphorus includes erosion, transport to the oceans, sedimentation, tectonic uplift and alteration of phosphate-containing rocks into plant-available phosphate in soils. The cycle time is several million years (Jones,2004). Besides the geological cycle, phosphorus is cycled as part of the food chain on land and in aquatic systems, with cycle times ranging between a few weeks and up to one year (Jones, 2004). The global P cycle has been modified extensively by modern human (agricultural, urban and industrial) practices. As a result, fluxes of P have doubled during the past several centuries due to a high rate of extraction of P from mineral deposits followed by widespread use in fertilizers and detergents. Figure 6.1 illustrates the geological and biological phosphorus cycles including anthropogenic influences.
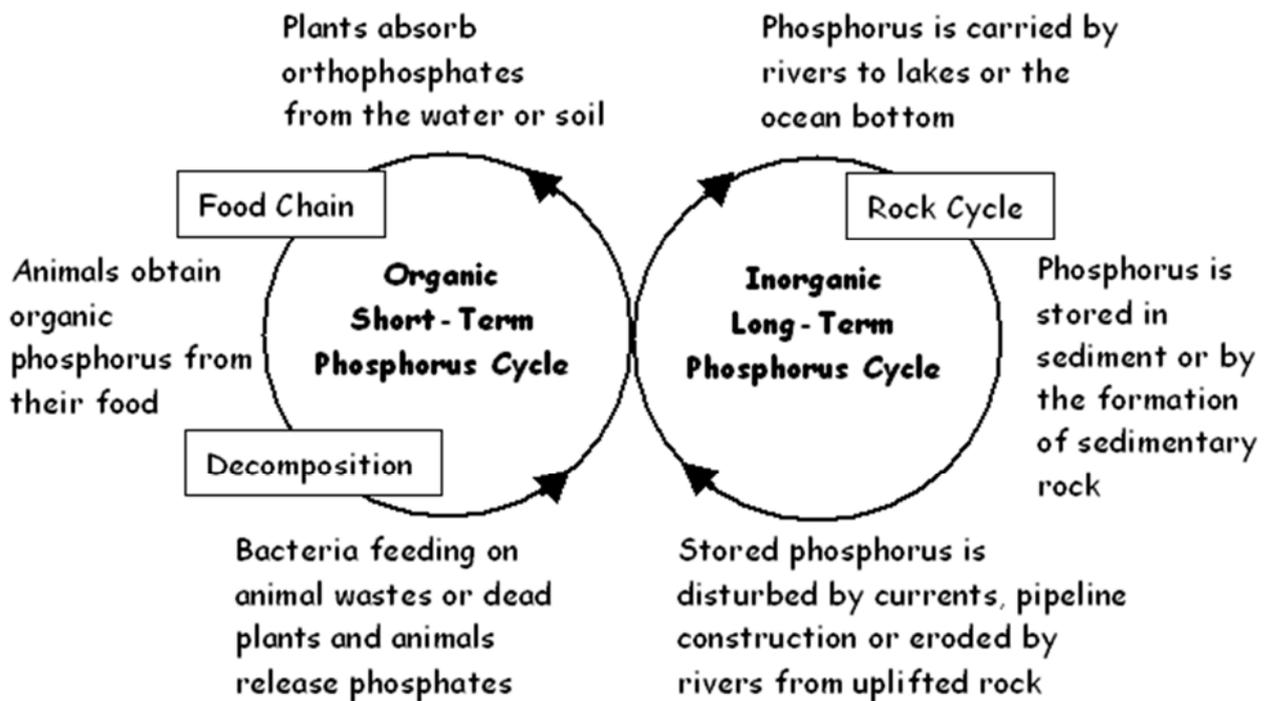
Fig. 6.1. Geological and biological phosphorus cycle in nature.

In aqueous environment, phosphorous exists under different behavior depending pH values of solutions. Figure 6.2 shows the aqueous speciation of phosphoric acid (orthophosphate). In the pH range of most natural waters and wastewaters (pH 6-9.5), the monovalent ($H_2PO_4^-$) and the divalent (HPO_4^{2-}) anions are the dominating species. For the dissociation of phosphoric acid, the equilibrium constants are $pK_a1 = 2.12$; $pK_a2 = 7.21$, and $pK_a3 = 12.67$ (ionic strength of zero, $T=25°C$). Speciation and charge of the phosphate influence the adsorption onto metal oxide surfaces, in turn, phosphate removal is pH dependent.
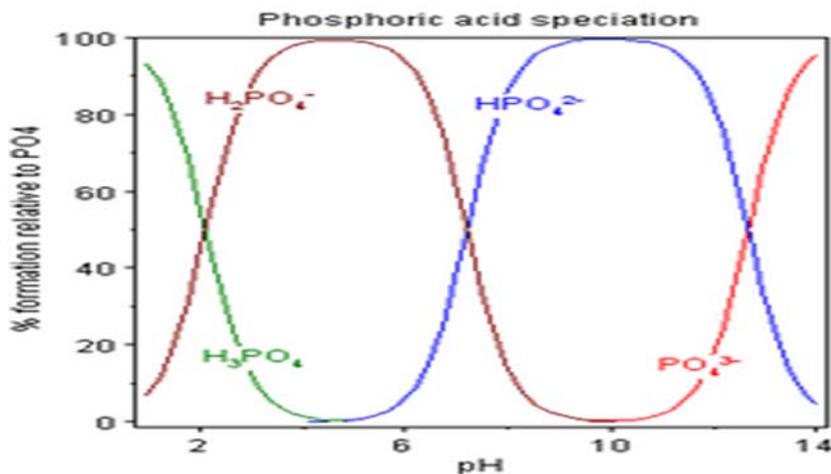
Fig. 6.2. Aqueous speciation of phosphorus as function of pH.

6.1.2.2 Eutrophication

The pollution of surface waters by phosphates is the main cause for eutrophication and was recognized as a problem in the middle of the twentieth century. Phosphorus is an essential nutrient for plants and excess quantities results in extensive growth of phytoplankton, macroalgae, and higher plants. In some cases, this includes harmful algal blooms and depletion of dissolved oxygen that subsequently results in the decline of aquatic life (Chorus, 1999; Farmer, 2004). The research of a survey on the extent of the problem on a global level has found that 53% of lakes and reservoirs in Europe are eutrophic. The proportions for Africa, South East Asia, North and South America are 28%, 54%, 48%, and 41%, respectively (EU council, 1993). Point sources (e.g., from municipal wastewater treatment plants, industrial and some agricultural) account for more than half of the phosphorus discharged in Europe. The principal sources of phosphorus in wastewater originate from human excreta and, in some countries, from the use of detergents. Phosphorus release to surface waters has led to legislations, such as the European Union Urban Wastewater Directive designed to remove phosphorus from domestic and industrial wastewater. Consequently, phosphorus removal has become more widely employed in wastewater treatment and emissions of phosphorus from sewage into surface waters, across Europe, have typically fallen by 30-60% since the mid-1980's, with

considerable variations across the continent. Similar control measures have been implemented in the U.S.A. and Japan. The U.S. EPA has established a maximum contaminant level for phosphorus to be <20 mgL^{-1} in rivers and streams and in lakes and reservoirs during summer growing season (Report of United State Environment Protection Agency, 2000). While sewage discharges are gradually tackled, the relative importance of diffuse phosphorus sources, such as agriculture and soil erosion will increase. Despite improvements in discharge and surface water quality in recent years, phosphorus pollution remains a significant issue in developed countries. Developing countries have also severe eutrophication problems driven by increasing fertilizer use, as well as very poor treatment of urban wastewater from increasing populations (Farmer, 2004).

6.1.2.3 Phosphorus removal technologies

Today, the most widely applied phosphorus removal processes are chemical and biological phosphorus removal. The principle of chemical P removal from wastewater is to transfer dissolved phosphates into particulate form by producing chemical precipitates of low solubility by addition of di- and tri-valent metal ions or lime. The formed precipitates and particulate phosphates are usually removed by solid separation processes such as sedimentation, flotation or filtration (Cooper, 1994; Tchobanoglous, 2003). Polyphosphates and organic phosphorus may take part in adsorption reactions, but only to a limited extent and thus represent the partly removable phosphorus fraction. The proportions of easily vs. partly removable phosphorus fractions influences process performance and achievable levels of residual phosphorus in the effluent, which are also governed by the raw water quality, type and dose of precipitant, location of dose application, chemical speciation, mixing conditions, process configuration, and the target water quality. The process is robust and flexible and phosphorus removal of more than 90% is achievable under optimized conditions.

The phenomenon of biological phosphate removal was first recognized by Greenberg *et al.* (1995) who proposed that under certain conditions, activated sludge had the ability to accumulate phosphate in excess of that required for balanced microbial growth. In later years, this was frequently referred to as 'luxury' phosphate uptake and its exploitation appeared to provide the basis of a biological alternative to chemical precipitation for phosphate removal from wastewater. Ultimately, this led to the development of the enhanced biological phosphate removal (EBPR) process. EBPR can be achieved through the activated sludge process by recirculating sludge through anaerobic and aerobic conditions. This is achieved by configuring the treatment system such that an anaerobic zone is added upstream of the traditional aerobic phase. A specialized group of microorganisms known as polyphosphate accumulating organisms is able to gain a selective advantage by taking up carbon sources such as volatile fatty acids under anaerobic conditions and storing them intracellularly as carbon polymers (Tchobanoglous, 2003). When operated successfully, the EBPR process is a relatively inexpensive and environmentally sustainable option for phosphate removal.

Although less frequently used in large-scale phosphorus removal from wastewater, a great number of adsorbents have been studied and used in a variety of phosphorus removal applications as diverse as wastewater treatment, maintenance of potable water supplies and constructed wetlands (Douglas *et al*., 2004). Adsorbents enriched with Ca, Fe and/or Al performed well in phosphate uptake capacity (Driro *et al*., 1999; Johansson, 1999). Table 6.4 shows a summary of phosphorus adsorbents which have been tested in laboratory. Laterite is available adsorbent and approved for drinking water application. Consequently, this work focuses on the potential application of laterite in phosphorous removal.

6.2 MATERIALS AND METHODS

6.2.1. Materials

The present study used three laterite samples (1-TT, 2-HL and 3-QT) collected from lateric soil zones in Viet Nam as adsorbents. The 1-TT sample was collected from a layer at a depth of 1.5 m in Thach That town where completely weathered laterite distributes. The original sample is a hard block with dark yellow color. The 2-HL sample was found in excavated soil at a construction site. It is a hard block containing red solid gravels. The 3-QT sample was taken from a laterite profile at a depth of 0.5 m from the surface.

The initial raw samples were washed with tap water and air-dried at a room temperature. The fraction that passed through a 2-mm screen after gentle crushing was used as adsorbents. Their physical and chemical properties are shown in Table 6.1.

Table 6.1. Some physic-chemical characteristics of laterite samples

No	pH_{H2O}	pH_{kcl}	TOC (%)	Clay (%)	Silt (%)	Fine sand (%)	Coarse sand (%)	ECEC ($cmol_c/kg$)
1-TT	5.30	5.03	0.18	67.42	6.29	7.71	18.58	1.36
2-HL	5.56	4.95	0.13	57.03	6.24	9.89	26.83	1.00
3-QT	5.35	5.18	0.13	30.93	8.04	24.65	36.38	0.77

The phosphate stock solution containing 10 mmol L^{-1} was prepared by dissolving pure chemical of sodium dihydrogen orthophosphate (NaH_2PO_4) in distilled water. Phosphate working solutions of different concentrations were prepared by diluting the phosphate stock solution in 0.005M $MgCl_2$ solution for adjusting ionic strength. The pH value of the phosphate working solution was measured before and after adsorption experiments.

6.2.2. Mineralogy and surface charge analysis of laterite

Mineralogy of the laterite samples were analyzed for four particle size fractions (clay, silt, fine sand and coarse sand) by X-ray diffraction (RINT-2000V, Rigaku) with a Cu K$_\alpha$ radiation at 40 kV and 20 mA following the procedure of Nga *et al*. (2013).

Surface charge of laterite samples was determined by serial potentiometric titration method. Five gram portion of the sample was equilibrated with NaCl solutions having different pHs for 4 h ationic strengths of 0.005 mol L^{-1}, 0.05 mol L^{-1} or 0.01 mol L^{-1}. Proton and hydroxide ion adsorption by laterite was calculated from pHs before and after equilibration and plotted against pH. The pHpzse were determined from the intersection point of the curves for different ionic strengths. The net surface charge was set to zero at pHpzse.

6.2.3. Thermal analysis

Differential thermal and gravimetric analysis (DTA-TG) was carried out simultaneously using Rigaku thermo plus EVO. The samples were heated from room temperature to 1000°C at a heating rate of 10 ^{o}C min^{-1}. The amount of sample used in each test was 10mg.

6.2.4. Phosphorous adsorption experiments

To construct adsorption isotherm, 0.3 g of laterite and 50 mL of phosphate working solution at concentrations of 0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.8; 1.0 mmol L^{-1}were mixed in centrifuge tubes. The tubes were capped and placed on a shaker at 170 rpm for 24 h at room temperature to ensure equilibrium. The suspension was separated by centrifugation (2500 rpm, 15 min) and the supernatant was filtered through a 0.45μm membrane filter. The residual concentration of phosphate was determined by the molybdate blue spectrophotometric method. Each experiment was duplicated.

A similar procedure was adopted in the experiment on the effect of pH on phosphate adsorption. The fixed initial phosphate concentration of 0.5 mmol L^{-1} was employed and the pH was adjusted by 0.1M HCl and 0.1M NaOH to cover a range from 4 to 9. The pH measurement was implemented before shaking and after equilibration.

Phosphate adsorption kinetics was examined at 25°C and phosphate working solution at concentration of 0.5mmol L^{-1}. A 3 g portion of a laterite sample was added to 500 mL phosphate solution in a 1-L bottle and shaken at 170 rpm without pH adjustment. Several mL of equilibrium solution was sampled intervals between 0 and 24 h, immediately filtered through a 0.45 μm membrane filter and then analyzed for P concentration.

The competitive adsorption experiments of phosphate was conducted with solutions containing 0.5 mmol L^{-1} sulfate, 0.5 mmol L^{-1}carbonate and 0.5 mmol L^{-1}phosphate, which were prepared from

sodium sulfate, sodium carbonate and sodium dihydrogenate orthophosphate (NaH_2PO_4), respectively. Centrifuge tubes are used to contain 0.3 g of laterite and 50 mL of solution and then shaken for 24 h at room temperature. The solutions examined include single phosphate, complex of sulfate and phosphate and complex of phosphate, sulfate and carbonate.

The P concentration was measured after filtering through 0.045μm. The analysis of phosphate was done by spectrophotometer using method described in standard methods of Kuo (1996). The experiments were done in triplicate and the results were averaged.

6.3 RESULTS AND DISCUSSION

6.3.1. Mineralogy and surface charge characteristics of laterite samples

X-ray diffraction patterns of the Mg-saturated and glycerol-solvated clay fractions and fine sand fractions of three laterite samples are shown in Fig.6.3.
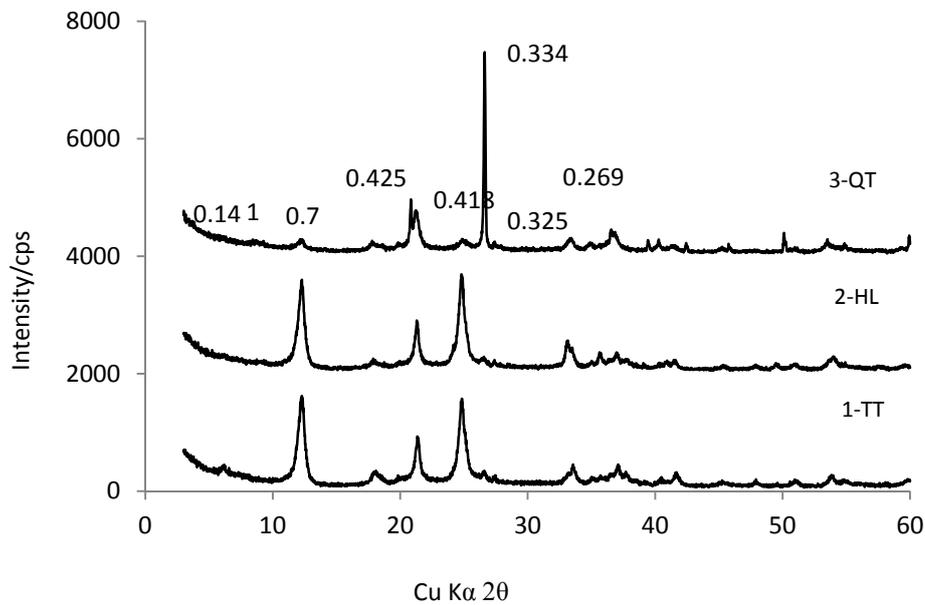
Fig.6.3. X-ray diffraction pattern of laterite samples/ Clay fraction. The figures indicate d-spacings in nm.

The clay fractions of the 1-TT and 2-HL samples showed fairly strong peaks at 0.7, 0.418, 0.35 and 0.269 nm, indicating that these samples contain kaolinite and goethite and hematite. In addition, the 1-TT sample showed weak peak at 1.4 nm, indicating that it contain small amount of non-expandable 2:1 layer silicates. The weak peak at 0.487 nm indicates that all the samples contain gibbsite. The 3-QT sample showed a significantly different mineralogy in that it is dominated by quartz and contained much less amount of kaolinite and goethite. The dominance of 0.425 and 0.334 nm peaks in the X-ray diffraction patters for fine sand samples indicate that the major mineral in the

fine sand fraction is quartz. The small but distinct peak at 0.418 and 2.69 nm shows that the fine sand fractions also contain goethite and hematite. The silt and coarse sand fractions exhibited similar X-ray patterns.

Basic chemical properties are summarized in Table 6.1. The pH (H_2O) was in a range from 5.3 to 5.6 and the pH (KCl) was similar, indicating that the samples contained little exchangeable Al. The 1-TT sample showed the highest clay content of 67% followed by the 2-HL and 3-QT samples. The clay content of the 3-QT sample was only 30% and it had fairly high sand content. Although the clay content was high, the effective cation exchange capacity, i. e. the sum of exchangeable cations, was very low. This is a reflection of the virtual lack in 2:1 type layer silicate minerals as indicated by X-ray diffraction (Fig. 6.3).

The results of thermal analyses are shown in Fig. 6.4. All the samples showed clear endothermic peaks centered at around 50, 320°C and corresponding weight losses. The 1-TT and 2-HL samples exhibited an additional large endothermic peak at 480°C but the 3-QT sample showed only a faint peak at that temperature. The endothermic peak at 50°C obviously came from desorption of adsorbed water. And the peaks at 320 and 480°C are assigned to dehydration reaction of hydroxide minerals and kaolinite, respectively. Since goethite dehydrates at lower temperature than gibbsite, the endothermic peak centered at around 320°C suggests that the contribution of gibbsite was larger. These results harmonize with X-ray diffraction patterns shown in Fig. 6.3, particularly in that the 3-QT sample showed very weak diffraction peak at 0.7 nm. The 2-HL and 3-QT samples showed large endothermic peaks at around 840°C but they did not accompany weight loss. The origin of these endothermic peaks was not identified.

The dehydration reaction of gibbsite and kaolinite are expressed as

$$2Al(OH)_3 = Al_2O_3 + 3H_2O \qquad (6.1)$$

And

$$Si_4Al_4O_{10}(OH)_8 = SiO_2.Al_2O_3 + 4H_2O \qquad (6.2)$$

The weight loss from 200 to 400°C was about 0.5 mg for all three samples. If this came from the dehydration of gibbsite, the stoichiometry in the reaction (6.1) gives the gibbsite weight of 1.4 mg in 10 mg sample. Similarly, the weight of kaolinite is estimated to be 1.4 mg for the 1-TT and 2-HL samples and 0.71 mg for the 3-QT sample. But actually the dehydration of both gibbsite and goethite occurs at around 300°C and it is difficult to quantify these two minerals separately.
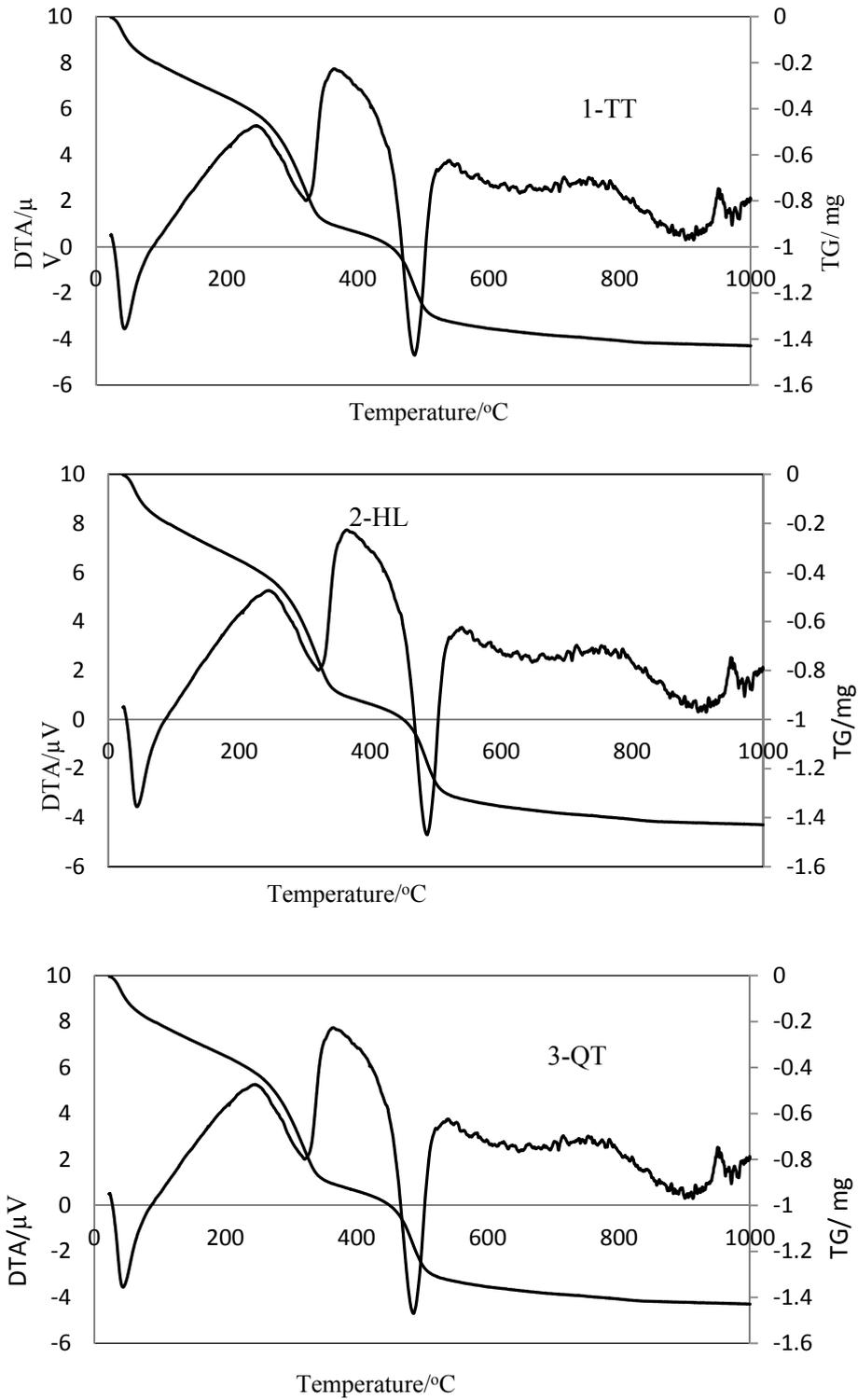
Fig. 6.4. Results of differential thermal analysis and thermo gravimetric analysis.

Fig. 6.5 shows the surface charge characteristics of laterite samples used in the present study, where the net surface charge was plotted against solution pH. The net charge decreased as pH

increased and the sign of the net charge reversed at pHs 5.1, 5.0 and 5.4 for the 1-TT, 2-HL and 3-QT samples, respectively. These pH values, i. e. the point of zero net charge (PZNC) were not much different from pH values measured in water (Table 6.1). Since PZNC for goethite and gibbsite lie around pH 8, the observed lower PZNC values may be due to the presence of kaolinite and quartz.
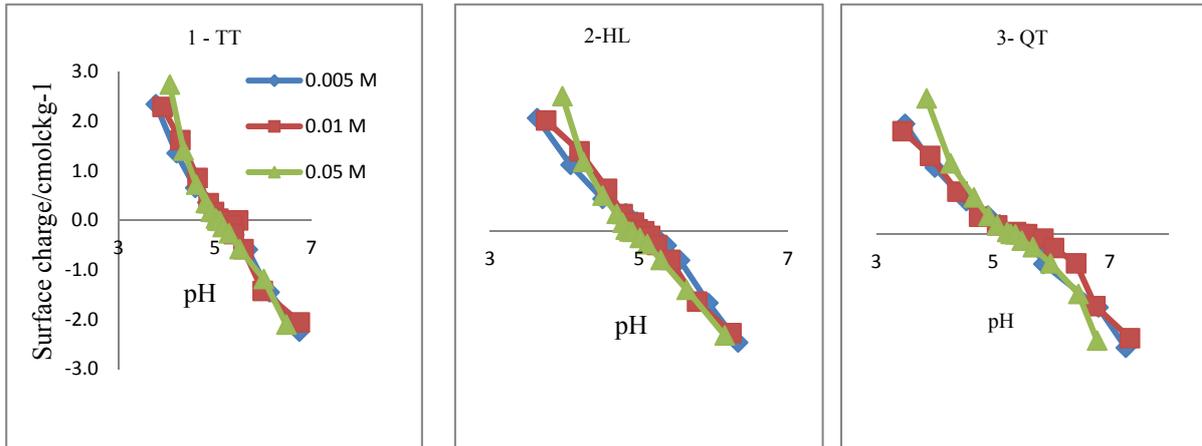
Fig.6.5. Surface charge diagrams of laterite samples.

Based on the mineralogical and chemical data, the approximate mineralogical composition of the laterite samples is summarized in Table 6.2.

Table6.2. Mineralogy identification of laterite samples

Sample	Fraction	Identification
1-TT	Clay	Mica; kaolinite; Geothite; feldspars
	Silt	Kaolinite; Geothite; Quazt; Feldspars
	Fine sand	Quazt; Geothite
	Coarse sand	Kaolinite; Geothite; Quazt
2-HL	Clay	Kaolinite; Geothite; Feldspars
	Silt	Kaolinite; Geothite; Quazt; feldspars
	Fine sand	Geothite; Quazt
	Coarse sand	Kaolinite; Geothite; Quazt; hematite, Feldspars
3-QT	Clay	Kaolinite; hematite; Quazt; Feldspars
	Silt	Quazt
	Fine sand	Quazt
	Coarse sand	Geothite; Quazt

6.3.2 Phosphate adsorption isotherm

The phosphate adsorption isotherms of the laterite samples are shown in Fig.6.6. The phosphate adsorption capacity increased with increasing equilibrium phosphate concentration from 0 to 1mmol L^{-1}. The adsorption capacity is determined at equilibrium phosphate concentration of 0.5 mmol L^{-1} and at pH 5-6 which corresponding to approximately 0.048 mmol g^{-1}, 0.045 mmol g^{-1} and 0.032 P mmol g^{-1} for 1-TT, 2-HL and 3-QT, respectively. The adsorption of phosphate onto laterite samples is believed to be complexation between surface hydroxyl groups of goethite, hematite and the phosphate ions (Seiki, *et al.*, 2003) as expressed, for example, by equation (6.3). With further increase of the phosphate concentration, the phosphate adsorption plateaued. As indicated by values of q_m (Table 6.3), the 1-TT sample gave the highest adsorption efficiency followed by the 2-HL sample, and 3-QTsample. The gibbsite and goethite content of the 3-QT laterite seems comparable with those of other laterite samples (Figs. 6.3 and 6.4). The surface charge characteristics for the three laterite samples were also similar (Fig. 6.5). One possible reason for the observed lower phosphate adsorption is the low gibbsite content of the 3-QT sample. The Langmuir and Freundlich equations expressed in Eqs. (6.4) and (6.5) were used for evaluating the experimental data

$$Fe\text{-}OH + HPO_4^{2-} + H = Fe\text{-}OPO_3^{2-} + H_2O \tag{6.3}$$
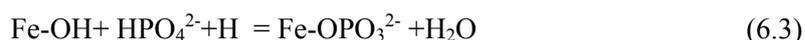
$$q_e = q_m bc_e/(1 + bc_e) \tag{6.4}$$

$$q_e = K_f c_e^{1/n} \tag{6.5}$$

where c_e (mg L^{-1}) and q_e (mg g^{-1}) are the equilibrium phosphorus concentrations in the aqueous and solid phases. Here, q_m (mg g^{-1}) is the maximum adsorption capacity and b is the affinity parameter. K_f and $1/n$ are the Freundlich adsorption constant and n is interpreted as a measure of adsorption intensity. The constants determined by least squares method are summarized in Table 6.3. The regression coefficients (R^2) are also shown in Table 6.3. The R^2 values obtained for the Freundlich and Langmuir isotherms were both above 0.976, indicating that both models can be used to describe the adsorption of phosphate onto laterite. The Langmuir isotherm appears to be slightly better suited to describe the equilibrium data.

Table 6.3. Estimated isotherm parameters for phosphate adsorption

Sample	Langmuir Equation			Freundlich Equation		
	q_m (mg g^{-1})	b	R^2	K	$1/n$	R^2
1-TT	1.01	20.2	0.991	0.055	0.233	0.993
2-HL	0.84	17.16	0.991	0.05	0.246	0.994
3-QT	0.46	13.04	0.992	0.037	0.266	0.976
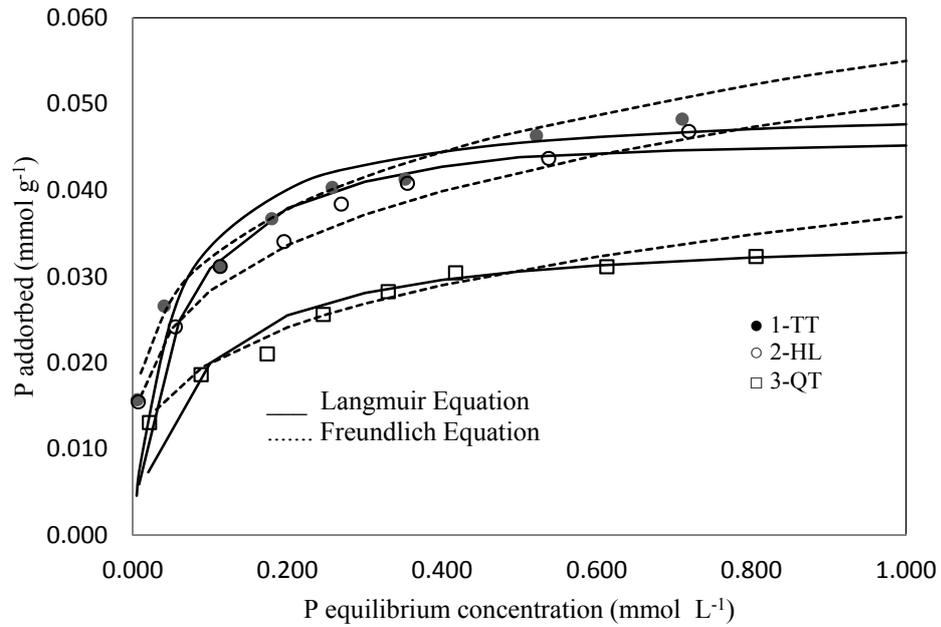
Fig.6.6. Phosphorous adsorption isotherm at 25°C and pH 5-6.

Table 6.4. Phosphorous adsorption capacities of different materials

Adsorbent	pH	Initial Phosphate concentration (mg P L^{-1})	Phosphate adsorption capacity (mg P g^{-1})	Data source
Fly ash	6-7	30	6.6	Cheng *et al*. (2007)
Blast furnace slag	5.5	40	10.5	Johansson and Gustafsson (1999)
Natural palygorskite	7.1	50	4	Ye *et al*. (2006)
Montmorillonite	7.6	3.5-20	0.746	Edzwald (1976)
Kaolinite	7-8.3	4-40	0.091	Edzwald (1976)
Illite	7.5	10-30	2.51	Edzwald (1976)
La(III)-chelex resin	5.5	15.5	3.038	Wu (2007)
Dry iron oxide tailings	3.5	10	8	Zeng (2004)
Laterite 1-TT	5.3	0-31	1.5	This study
Laterite 2-HL	5.2	0-31	1.4	This study
Laterite 3-QT	5.4	0-31	1.0	This study

The phosphate adsorption capacities of laterite determined in the present study is compared with those of common adsorbents in Table 6.4. Because the experimental conditions including initial phosphate concentrations and pH were not exactly the same, the adsorption capacities of various adsorbents are not strictly comparable. It is found that the adsorption capacities of laterite (1-1.5 mg P g^{-1}) are lower than of palygorskite, illite and blast furnace slag but higher than those of common clays (montmorillonite, kaolinite). Therefore, laterite may be potentially attractive adsorbents for the removal of phosphate from aqueous solutions.

6.3.3 Effect of initial pH on phosphate adsorption

Fig. 6.7 shows the dependence of phosphate adsorption on solution pH
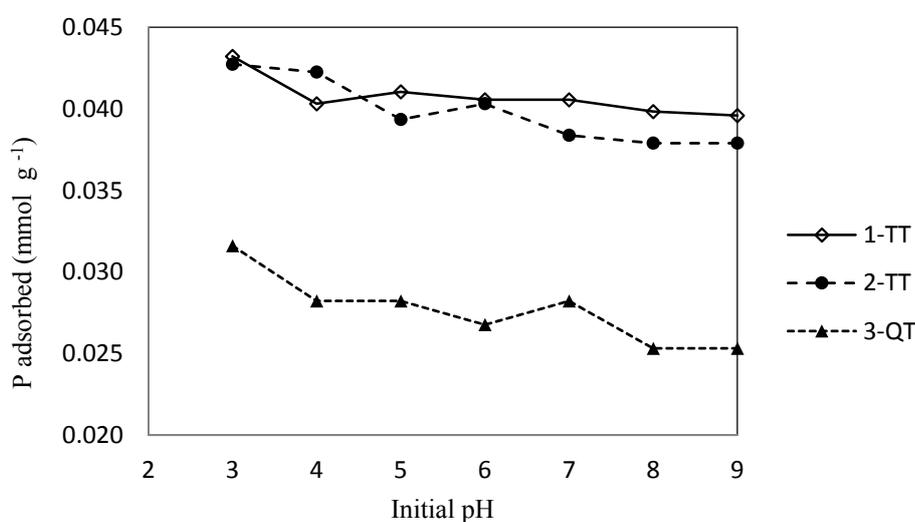
Fig.6.7. Effect of initial pH on phosphate adsorption by laterite. (P concentration 0.5mmolL^{-1}, contact time 24 h, adsorbent dose 6 g L^{-1})

At pH 3, phosphate adsorption was highest: approximately 0.034-0.045 mmol g^{-1} at an equilibrium concentration of 0.5 mmol L^{-1}. The higher pH values lead to slight reduction in phosphate adsorption. Fig. 6.7 shows that phosphate adsorption by laterite is only slightly pH-dependent. Compared to the maximum amount of adsorbed phosphate at pH 3, less than 10% decrease was observed at pH 9. The adsorption is possibly hindered at high pHs, because both surface of laterite and phosphate carries more negative charges at higher pHs, which induces more intensive repulsion between the negatively charged surface and phosphate.

6.3.4 Adsorption kinetics

The phosphate adsorption kinetic was examined under conditions of room temperature 25°C, equilibrium concentration of 0.5 mmol L^{-1} and pHs 5-6. The adsorption kinetic of phosphate on the three adsorbents performed a similar trend. Phosphate adsorbed onto laterite increased with time, significant increase was in first 8 h and reached equilibrium at about 24 h (Fig. 6.8).

Experimental data was evaluated by kinetic adsorption equations, Power function equation (6.6) and Elovich equation (6.7)

$$\text{Power function equation: } q = at^{b} \tag{6.6}$$

$$\text{Simple Elovich equation: } q = a + b \ln t \tag{6.7}$$

Where q is the amount adsorbed (mg g^{-1}) and t is the adsorption time. The other parameters are kinetic constants, which can be determined by regression of the experimental data. Since the power function gave low correlation coefficients (R^2) for the present experimental data (0.7) and this model was ruled out. On the other hand, the simple Elovich equation gave acceptable correlation coefficients (R^2) of 0.84, 0.82 and 0.7, for 1-TT, 2-HL and 3-QT, respectively. Therefore, the fitted curves by Elovich equation are overlain in Fig 6.8. The suitability of the simple Elovich equation was also reported by Ye *et al*. (2006) and Chen and Seng (2006).
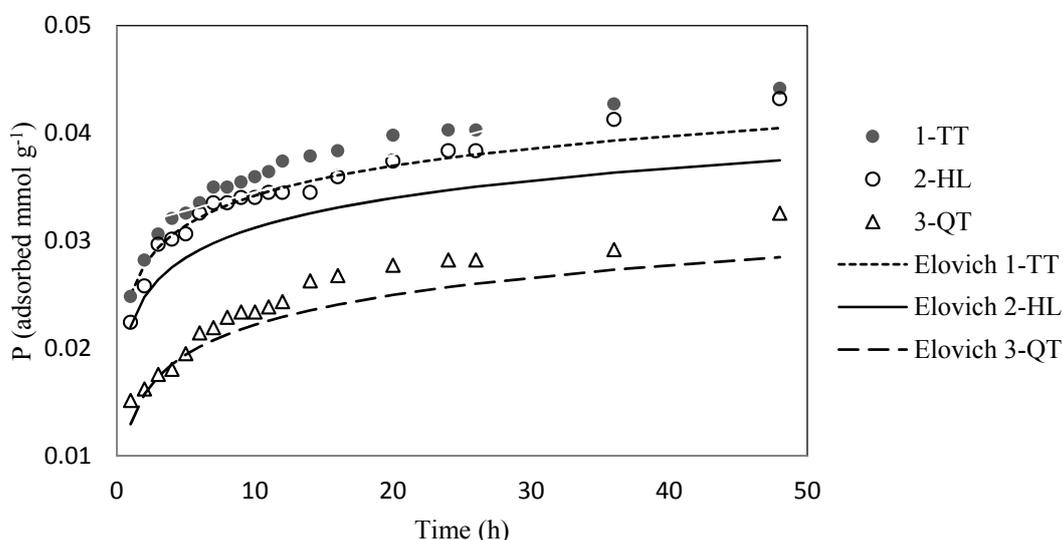
Fig.6.8. Phosphorous adsorption kinetic data at 25°C and pH 5-6.

6.3.5 Competitive adsorption of phosphate

Table 6.5. Amount of Phosphorus adsorbed (mmol kg^{-1}) in mixed solution of ions

	Samples			Comparison (%)		
Solution	1-TT	2-HL	3-QT	1-TT	2-HL	3-QT
Single solution of phosphate	40.32	38.38	28.23	100.00	100.00	100.00
Complex solution of phosphate and sulfate	36.50	34.87	26.12	90.53	90.85	92.53
Complex solution of phosphate, carbonate and sulfate	35.33	34.02	25.22	87.62	88.64	89.34
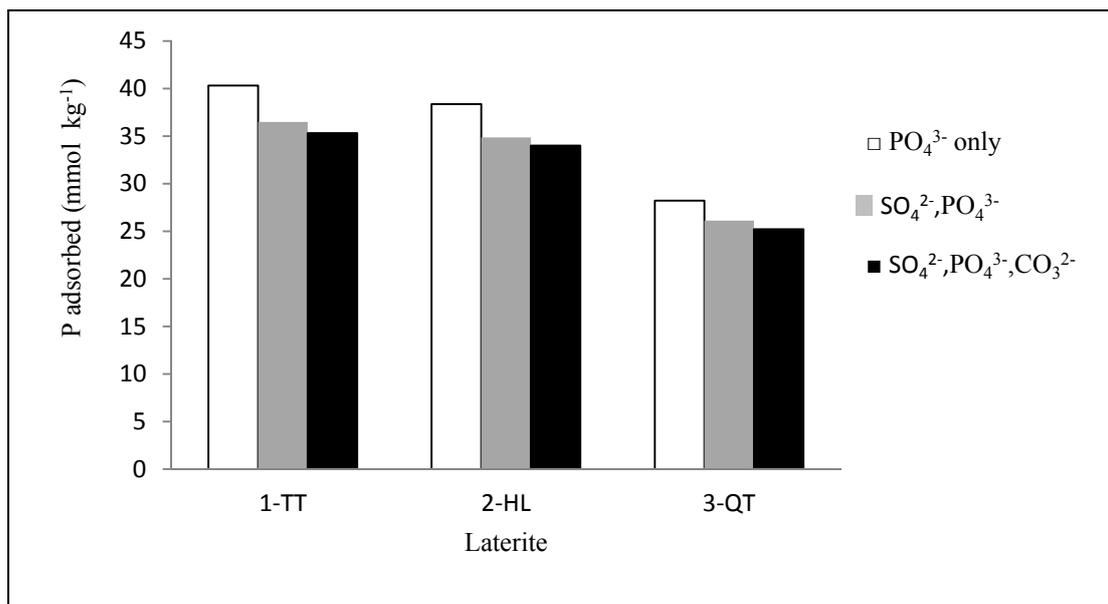
Fig. 6.9. Phosphorous adsorbed on laterite from single and complex solution. Single solution: NaH_2PO_4 (0.5 mmol). Complex solution: $NaHCO_3$ (0.5 mmol), Na_2SO_4 (0.5 mmol), NaH_2PO_4 (0.5 mmol).

Adsorption experiments were carried out separately with simple phosphate solutions, binary solutions of phosphate and sulfate, ternary solutions of phosphate, sulfate and carbonate. A fixed concentration of 0.5 mmol L^{-1} phosphate is mixed with the same concentration of sulfate and carbonate anions. Amount of phosphate anion adsorbed onto laterite in the presence of sulfate and carbonate anions is presented in Table 6.5 and plotted in Fig. 6.9. The adsorbed phosphate decreases when sulfate and carbonate anions presented in the solutions. The amount of phosphate adsorbed on laterite in mixed solutions was less than that in simple solutions (Table 6.5). However, the rate of phosphate adsorbed is still higher than the rate of sulfate and carbonate adsorptions onto laterite. Thus, the results of competitive adsorption experiments indicate that laterite could selectively adsorb phosphate ion and is suitable for the removal of phosphate from aqueous solution. In addition, experimental data shown in Table 6.5 also indicate the order of selectivity of adsorption of anions is phosphate > sulfat e >carbonate.

6.4 CONCLUSIONS

In this study, three laterite samples distributed in different regions in Viet Nam were examined for the removal of phosphate ions from aqueous solutions. The adsorption isotherms, kinetics, pH effect, competitive adsorption and equilibrium time of phosphate onto laterite were investigated. The combined effects of surface group of goethite and zero point charge determined the adsorption capacity for phosphate. 1-TT performed the highest adsorption capacity (0.045 mmol g^{-1}), followed by 2-HL (0.04 mmol g^{-1}) and 3-QT (0.035 mmol g^{-1}).The adsorption was rapid in first 8 h and slowly reached adsorption equilibrium in 24 h. The results of equilibrium adsorption data fitted to both the

Freundlich and Langmuir models. The simple Elovich equation fairly accurately described the phosphate adsorption kinetics onto laterite. Phosphate adsorption of laterite was less pH-dependent and laterite could selectively adsorb phosphate ion in mixed solutions containing sulfate and carbonate. The natural laterite is a low cost adsorbent to remove phosphorous in water. However, laterites containing smaller amount of goethite, e.g., 3-QT sample, is not recommended for water treatment at high pHs.

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CHAPTER 7. REMOVAL OF HEAVY METALS FROM WATER BY VOLCANIC ASH SOIL AND LATERITE

ABSTRACT

The batch experiments of adsorption of Cu^{2+}, Pb^{2+} and Cd^{2+} were carried out at laboratory scale with artificial model solutions. Adsorption capacity was determined based on Langmuir models. The results showed that both volcanic ash soil and laterite displayed high adsorption capacity for lead (up to 1.0-1.2mg Pb g^{-1} is recorded at pH5). Adsorption capacity for copper, though not as high as that of lead, is acceptable if used in water treatment (about 0.5-0.8 mg Cu g^{-1} at pH5). Cadmium seemed to have been hardly removed by laterite and volcanic ash soil. The calculated adsorption capacities were 0.4mg Cd g^{-1} for laterite and less than 0.1mg Cd g^{-1} for volcanic ash soil at an initial concentration of 25 mg L^{-1}. The adsorption of heavy metals examined by laterite and volcanic ash was strongly pH dependent. At pHs lower than 4, these materials were not effective for metals removal. From a viewpoint of implementation, the laterite should be used after pH adjustment to over 4 for Pb, Cu, Cd removal from wastewater. Similar way in use of volcanic ash soil is recommend for Pb and Cu, but volcanic ash soil is not recommended for Cd removal from wastewater.

Key words: Adsorption, water treatment, heavy metals, lateirte, allophane, imogolite.

7.1 INTRODUCTION

7.1.1 Background

The removal of heavy-metals from wastewater discharged to effluent is one of the most important environmental issues in the world. Pollution by heavy metals is of great concern due to the potentially hazardous effects on the environment (Huang *et al*., 2008). Heavy metal pollution of water bodies has been caused by wastes from many sources such as metal plating, mining, tanneries, painting, car radiator manufacturing, as well as agricultural chemicals like fertilizers and fungicides (Aman *et al*., 2008; Jiang *et al*., 2008). The industrial activities have significantly contributed to heavy metal pollution in various ecosystems. Because of their high solubility in water, heavy metals can be absorbed by living organisms. Once they enter the food chain, high concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they may cause serious health disorders (Babel and Kurniawan, 2004). Hence, immobilization or removal of toxic metals from water is a long-term research goal aiming at protecting human health and environment from pollution risks.

Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent and adsorption is one of the alternative treatment methods. The conventional methods to remove heavy metals from contaminated waters are chemical precipitation, filtration, ion exchange, evaporation, reverse osmosis, solvent extraction, and electrochemical treatment. However, these methods are either inefficient or expensive when heavy metal exists in lower concentrations consequently it is important to find new methods for removing heavy metals from natural and wastewaters. Comparing with conventional methods, adsorption method is quite popular due to its simplicity and high efficiency, as well as due to the availability of a wide range of adsorbents (Babel and Kurniawan, 2002). As reviewed by Babel and Kurniawan (2002), many materials such as waste of olive oil factory (WPOOF), tea factory waste, barely straw untreated, *Partheniumhysterophorus L.* activated carbon, cone biomass of *T. orientalis*, dye loaded sawdust, dye groundnut shell, fly ash, peat moss, coir pith, modified coir pith, black carrot residues, deactivated protonated yeast have been tested for nickel (II) removal from water and wastewater systems by many scientists and engineers.

There are several reviews on water treatment through sorption. Use of chitin and chitosan to remove metal ions from wastewater was reviewed with particular emphasis on sorption capacities and kinetics (Gupta *et al*., 2011). Clay is one of the potential adsorbent as well. Similar to zeolites, clay minerals are also important inorganic components in soil. Their sorption capabilities come from their high surface area and exchange capacities. The negative charge on the structure of clay minerals gives clay the capability to attract metal ions (Babel and Kurniawan, 2002). The feasibility of using kaolinite and montmorillonite clay minerals as adsorbents for removal of toxic heavy metals was reviewed by Gupta *et al*. (2011).

Industrial waste is also one of the potentially low-cost adsorbent for heavy metal removal. It requires little processing to increase its sportive capacity. Generally, industrial wastes are generated as by-products. Since these materials are locally available in large quantities, they are inexpensive. In India, various types of industrial wastes such as waste slurry, lignin, iron(III) hydroxide, and red mud, have been explored for their technical feasibility to remove heavy metals from contaminated waters (Babel and Kurniawan, 2002).

Although these adsorbents can be employed for heavy metal removal from waste water, finding new adsorbents with low cost, availability in local conditions is still essential for water treatment. Laterite is the weathered product under tropical and sub-tropical condition. These products are rich in iron and aluminum oxides which have been known with high adsorption capacity for anions and cations in water. Laterite can remove arsenic from drinking water sources (Frederick, 2008), besides that, they were also applied to adsorb heavy metals in industrial waste water (Udoeyo *et al*., 2010). Lateritic soils have been used as effective sorbents for arsenic removal in groundwater (Maji *et al*.,

2006; Rahman *et al*., 2008; Maiti *et al*., 2010). Nga *et al*. (2013) investigated good performance of laterite materials collected from Viet Nam in removal of suspended clay particles and phosphorous from water (Chapter 6).

In the current research, we continue to characterize the metal adsorption of laterites and volcanic ash soil samples that may be applied as adsorbents to remove heavy metals from contaminated waters. This study will focus on experiments of adsorption isotherm and the influence of pH on metal adsorption by laterite and volcanic ash materials.

7.1.2 Chemistry, and environmental relevance of copper, lead and cadmium

7.1.2.1 Copper

Heavy metals (elements with an atomic density greater than 6 g/cm^3) are one of the most persistent pollutants in water. Unlike other pollutants, they are difficult to degrade, but can accumulate throughout the food chain, producing potential human health risks and ecological disturbances. Their presence in water is due to discharges from residential dwellings, groundwater infiltration and industrial discharges. The occurrence and accumulation of heavy metals in the environment is a result of direct or indirect human activities, such as rapid industrialization, urbanization and anthropogenic sources (Gardea-Torresdey *et al*., 2005; Martin-Gonzalez *et al*., 2006). The common heavy metals that have been indentified to pollute water include arsenic, copper, cadmium, lead, chromium, nickel, mercury and zinc.

Copper may occur as the metal and in oxidation states as copper (I) and copper (II). An unstable copper (III) is also known. In aqueous solution, copper is present mainly as the copper (II) ion, depending on pH, temperature, the presence of bicarbonate and sulfide, and the potential to form ligands with organic species, such as humic, fulvic, and amino acids, certain polypeptides, and detergents (Stiff, 1971). The free copper (I) ion can exist in aqueous solution only in exceedingly low concentrations, and the only copper (I) compounds that are stable in water are the highly insoluble ones, such as chloride or cyanide (Cotton and Wilkinson, 1972). Some copper (II) salts, including chloride, nitrate, and sulfate, are soluble at low pH under oxidizing conditions. The carbonate, hydroxide, oxide, and sulfide are less soluble, particularly at pH 7 or higher. In alkaline waters with high carbon dioxide content, copper may precipitate as copper carbonate.

Copper and its compounds are widely distributed in nature, and copper is found frequently in surface water and in some groundwater. Distributed water contains considerably more copper than the original water supply because of the dissolution of copper from copper piping. Soft waters with low pH, low alkalinity, and low conductivity are often more corrosive than hard waters, but these factors alone cannot be used to predict the degree of metal mobilization. Eleven water chemistry variables potassium, sodium, calcium, magnesium, manganese, chloride, nitrate, hydrogen, sulfate, dissolved

oxygen, and conductivity, all related to the degree of elevation of copper in the water (Maesen *et a*l., 1985).

It is most likely that much of the copper reported in surface waters comes from contamination with industrial metallurgic waste. Besides, it may occur in areas contaminated by mining or smelting activity. Welding operations, due to types of electrodes, welding on brass material, welding on material painted with copper-containing paints, etc, are also major emission sources. Factors affecting the balance between copper and the parent rock and the derivative soil include the degree of weathering, the nature and intensity of the soil formation, drainage, pH, oxidation-reduction potential and the amount of organic matter in the soil (Baker, 1956). Alkaline conditions in the soil and the surface water favor precipitation of copper. This may cause deficiencies in plants and minimize the effectiveness of copper-containing molluskicides. Acid conditions promote solubility of copper, increase the concentration of ionic copper and thereby change the microorganism and other aquatic animal populations, depending on tolerance for various levels of copper in solution (Broadbent and Nakashima, 1971).

Copper is an important element for body metabolism, enzymatic reactions and iron utilization. Copper deficiency (less than 2 mg day^{-1}) is accompanied by anemia because of the inability of body to synthesize ferric micronutrient from iron (III) at normal rate. Copper deficiency has caused anemia, neutropenia, and disturbances of bone formation in children. Although copper is essential element for body, it is observed to bring reverse effects in which the high level is used. Ingestion of more than 15 mg of copper has been reported to be toxic to humans. Ingestion of gram quantities of copper sulfate resulted in death by suicide. Exceed copper consumed is accumulated in kidney, lung, liver, brain, etc., causing serious cancer diseases. Copper in dust, fumes or sprays cause congestion of the nasal membrane. Various damages to lung tissue have been reported in cases of severe intoxication after exposure to copper sulfate sprays. Exposure to copper dust causes discoloration of the skin.

Environmental and aquatic organism problems have been found from copper accumulation. The binding of excess copper to specific sites in protein, however, can disrupt several metabolic processes of all living organisms (Viarengo *et al*., 1981). Sublethal toxicity has been shown to induce changes in many aspects of animal behavior, could mediate ecological death by disrupting the normal function and life history of the exposed organism (Rand, 1985). When copper ends up in soil it strongly attaches to organic matter and minerals. In surface water copper can travel great distances, either suspended on sludge particles or as free ions.

Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils, a few of plants can be survival. That is why there is not much plant diversity near copper-disposing factories. Due to the effects upon plants copper is a serious threat to the productions of farmlands. Copper can seriously influence the proceedings of certain farmlands, depending upon the acidity of the soil and the presence of organic

matter. Despite of this, copper-containing manures are still applied. Copper can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The decomposition of organic matter may seriously slow down because of this. When the soils of farmland are polluted with copper, animals will absorb concentrations that are damaging to their health. Mainly sheep suffer a great deal from copper poisoning, because the effects of copper are manifesting at fairly low concentrations.

7.1.2.2 Lead

Lead is a widespread element on the earth crust. Ionic lead, Pb (II), lead oxides and hydroxides, and lead metal oxy anion complexes are the general forms of Pb that are released into the soil, groundwater, and surface waters. The most stable forms of lead are Pb (II) and lead-hydroxy complexes. Lead (II) is the most common and reactive form of Pb, forming mononuclear and polynuclear oxides and hydroxides. The predominant insoluble Pb compounds are lead phosphates, lead carbonates (form when the pH is above 6), and lead hydroxides (Raskin and Ensley, 2000). Lead sulfide (PbS) is the most stable solid form within the soil matrix and forms under reducing conditions, when increased concentrations of sulfide are present. Under anaerobic conditions a volatile organo lead (tetramethyl lead) can be formed due to microbial alkylation.

The main sources of lead entering an ecosystem are atmospheric lead (primarily from automobile emissions), paint chips, used ammunition, fertilizers and pesticides and lead-acid batteries or other industrial products. The transport and distribution of lead from major emission sources, both fixed and mobile, are mainly through air (UNEP, 1991). Lead is present in tap water as a result of its dissolution from natural sources, but primarily from household plumbing systems in which the pipes, solder, fittings or service connections to homes contain lead. Polyvinyl chloride (PVC) pipes also contain lead compounds that can be leached from them and result in high lead concentrations in drinking-water. The other major sources of lead emission are from waste plumbing system or iron sedimentation from pipe system. The most serious source of exposure to soil lead is through direct ingestion (eating) of contaminated soil or dust.

Lead has not been considered to be an essential element but its necessity is still a controversial matter. It is well known to be toxic in slight excess and its effects have been more extensively reviewed than the effects of other trace metals. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys (Baldwin and Marshall, 1999). Lead performs no known essential function in the human body, it can merely do harm after uptake from food, air, or water. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains. Lead accumulates in the soil, particularly soil with a high organic content (US EPA, 1986). Lead deposited on the ground is transferred to the upper layers of the soil surface, where it may be retained for many years (up to 2000 years). In undisturbed ecosystems, organic matter in the upper layer of soil surface retains atmospheric lead. In cultivated soils, this lead is mixed with soil to a

depth of 25cm (i.e., within the root zone). Atmospheric lead in the soil will continue to move into the micro-organism and grazing food chains, until equilibrium is reached. Distribution of lead in ecosystems can displace other metals from the binding sites on the organic matter. It may hinder the chemical breakdown of inorganic soil fragments and lead in the soil may become more soluble, thus being more readily available to be taken up by plants. Plants on land tend to absorb lead from the soil and retain most of this in their roots. Although lead does not readily accumulate in the fruiting parts of vegetable and seed products (e.g., corn, beans, squash, tomatoes, strawberries, and apples), the risks of lead poisoning may be caused by uptake of lead from soil by leaf or dust deposits on leaf surface of plants (Josen, 2002).

7.1.2.3 Cadmium

In the earth's crust, cadmium appears mainly in association with ores containing zinc, lead, and copper (in the form of complex oxides, sulfides, and carbonates). Elemental cadmium is a soft, silver-white metal, which is recovered as a by-product of zinc mining and refining. Cadmium enters the aquatic environment from numerous diffuse (e.g, agricultural and urban run-off, atmospheric fall-out) and point sources, both natural and anthropogenic. Weathering and erosion of cadmium-containing rocks result in the release of cadmium not only to the atmosphere, but also to the soil and the aquatic system. Natural and anthropogenic sources (e.g., mine/smelter wastes, commercial fertilizers derived from phosphate ores or sewage sludge, municipal waste landfills) contribute to the levels of cadmium found in soil and sediments. Reported sediment concentrations of cadmium range from 0.03–1 mg kg^{-1} in marine sediments to as high as 5 mg kg^{-1} in river and lake sediments. Relatively high concentrations of cadmium (>1 mg kg^{-1}) have been measured in the soil near smelters and other industrialized areas (WHO, 2000).

The solubility of cadmium in water is influenced by the acidity of the medium. Acid rain and the resulting acidification of soils and surface waters have increased the geochemical mobility of Cd, and as a result its surface water concentrations tend to increase as water pH decreases (Campbell, 2006). Dissolution of suspended or sediment-bound cadmium may increase in acidity (Fleischer *et al*., 1974). The concentration of cadmium in unpolluted fresh waters is generally less than 0.001 mgL^{-1}, the concentration of cadmium in seawater averages about 0.00015 mg L^{-1} (Fleischer *et al*., 1974, Kirpichtchikova *et al*., 2006; McLaughlin, 2000). Surface waters containing in excess of a few micrograms of cadmium per liter have probably been contaminated by industrial wastes from metallurgical plants, plating works, plants, manufacturing cadmium pigments, textile operations, cadmium-stabilized plastics, or nickel–cadmium batteries, or by effluents from sewage treatment plants (Fleischer, 1974).

Although cadmium is very biopersistent but it has few toxicological properties. Once it is absorbed by anorganism, remains resident for many years. Cadmium in the body is known to affect several enzymes. It is believed that the renal damage that results in proteinuria is the result of Cd

adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules. Cadmium also reduces the activity of delta-aminolevulinic acid synthetase, arylsulfatase, alcohol dehydrogenase, and lipoamide dehydrogenase, whereas it enhances the activity of deltaaminolevulinic acid dehydratase, pyruvate dehydrogenase, and pyruvate decarboxylase (Manahan, 2003). The most spectacular and publicized occurrence of cadmium poisoning resulted from dietary intake of cadmium by people in the Jintsu River Valley, near Fuchu, Japan. The victims were afflicted by *itai-itai* disease, which means *ouch, ouch* in Japanese. The symptoms are the result of painful osteomalacia (bone disease) combined with kidney malfunction. Cadmium poisoning in the Jintsu River Valley was attributed to irrigated rice contaminated from an upstream mine producing Pb, Zn, and Cd. The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction. Food intake and tobacco smoking are the main routes by which Cd enters the body (Manahan, 2003).

7.2 MATERIALS AND METHODS

7.2.1 Materials

The present study used natural materials including lateite and volcanic ash samples as adsorbents. Three laterite samples (1-TT, 2-HL and 3-QT) collected from lateric soil zones in Viet Nam. The 1-TT sample was collected from a layer at a depth of 1.5m in Thach That town where completely weathered laterite is distributed. The original sample is a hard block with dark yellow color. The 2-HL sample was found in excavated soil at the construction site. It is a hard block containing red solid gravels. The 3-QT sample was taken from the laterite profile at a depth of 0.5 m from the surface.

The initial raw samples were washed with tap water and air-dried at a room temperature. The particle fraction were gently crushed and passed through a 2-mm screen. The particle fraction less than 2mm was used as adsorbents. Their physical and chemical properties are indicated in the Table 7.1.

Table 7.1. Some physic-chemical characteristics of laterite samples

No	pH_{H2O}	pH_{Kcl}	TOC (%)	Clay (%)	Silt (%)	Fine sand (%)	Coarse sand (%)	ECEC ($cmol_c kg^{-1}$)
1-TT	5.30	5.03	0.18	67.42	6.29	7.71	18.58	1.359
2-HL	5.56	4.95	0.13	57.03	6.24	9.89	26.83	1.001
3-QT	5.35	5.18	0.13	30.93	8.04	24.65	36.38	0.773

Laterite soil sample collected from Hawaii Island was also used for adsorption experiments. Soil sample was air-dried at room temperature and ground in mortars. A particle fraction less than 2mm was used as adsorbent in the present study.

A volcanic ash sample was supplied from Astec.Co. under a trade name of TRP-Ai, which was used in flocculation experiments of suspended clay particles presented in Chapter 4. This product is made from subsurface layer of weathered volcanic ash soil rich in allophane and imogolite by mechanical dispersion treatment followed by pH adjustment with HCl. The product is thick slurry with a solid content of 132 g L^{-1}. The liquid sample was dried at 105°C for overnight, and then softly ground by mortars to collect small particles. The particle fraction less than 2mm was used as adsorbent in this study.

Hawaii soil collected from a soil profile in Hilo, Hawaii was formed in volcanic ash under perhumid climate. Its mineralogy and physic-chemical characteristics are presented in the Table 7.2. Hematite, goethite, silicate minerals are dominant in mineral composition of Hawaii soil (Wada, K and Wada, S-I, 1976). The absence of allophane and imogolite minerals in the Hawaii soil may be ascribed to a fairly dry climate where soil was formed. The predominance of noncrystalline hydrous alumina and iron oxides in soil reflects the strong effects of desilication in weathering of volcanic ash (Wada, K and Wada, S-I, 1976).

Table 7.2. Mineralogy and characteristics of Hawaii soil

Mineral component	Hematite, goethite (H>G), kaolinte, illite, gibbsite, quazt
Particle size distribution	
2000-200μm	15.0 %
200-20μm	18.8 %
20-2μm	12.6 %
<2μm	53.7 %
Composition	
SiO2	2.8 %
Al2O3	17.4 %
Fe2O3	37.1 %
SiO2/Al2O3 molar ratio	57.3
Total C	2.6 %
Al	3.74 %
Fe	14.6 %
pHkcl	5.3

Simulated solutions of Cu (II), Pb (II) and Cd (II) were made from commercial reagent of analytical grade. The stock solutions containing 1000mg/L were prepared by dissolving 3.775 g of copper (II) nitrate trihydrate $Cu(NO_3)_2.3H_2O$; 1.598 g of lead (II) nitrate $Pb(NO_3)_2$ and 2.744 g of cadmium nitrate tetra hydrate $Cd(NO_3)_2.4H_2O$ in one liter of deionizer water. The working solutions were diluted from the stock solutions at appropriate concentration. Solution of $Ca(NO_3)_2$ 0.01M was used to control ionic strength, solutions of HNO_3 0.1M and NaOH 0.1M were used to adjust pH.

7.2.2 Analysis of mineralogy and surface charge of laterite and volcanic ash samples.

Mineralogy of particle size fractions (clay, silt, fine sand and coarse sand) of the samples were analyzed by X-ray diffraction (RINT-2000V, Rigaku) with a Cu K_α radiation at 40 kV and 20 mA following the procedure of Nga *et al*. (2013).

Surface charge of the samples was determined by serial potentiometric titration method. Five gram portion of the sample was equilibrated with NaCl solutions having different pHs for 4 h to keep ionic strength at 0.005mol L^{-1}, 0.05 mol L^{-1}or 0.01 mol L^{-1}. Proton or hydroxide ion adsorption was calculated from pH difference between before and after reaction, then pHpzse were determined from the intersection point of the curves where proton and hydroxide adsorptions were plotted against pH at different ionic strengths. The surface charge was set to zero at pHpzse and for other pH charges were determined by shifting the proton and hydroxide adsorption isotherms. The detail procedure is described by Lucian and Liming (1996) as below:

Place fixed amount of samples (5 g for laterite samples and 3 g for TRP-Ai) in each of capped centrifuge plastic tube (39 tubes in total and arranged in three rows of 13 for one sample). The middle tube in a row will be zero-addition of acid or base. Each tube in a row will contain a NaCl solution of the same ionic strength i.e., 0.005, 0.01 and 0.005M, respectively) (Table 7.2).

To establish a pH range (i.e., 3-11) increasing amounts of 0.005M HCl or 0.005M NaOH (standardized) was added to the tubes (0.5 mL-25 mL) as presented in Table.7.3. For the 0.005M ionic strength row, 0.005M NaCl was added to bring the total volume in each tube to 50 mL. The remaining ionic strength solutions (i.e., 0.05 and 0.01 M) have 1 similar sequential addition of acid and base with further additions of ionic strength salt (0.02 and 0.1M) and distilled water to provide a 50 mL solution aliquot at a fixed ionic strength (Table 7.3).

Samples were shaken for 4 h to get equilibrium at room temperature and a speed of 170 rpm. Centrifuge and determine the pH of supernatant. Conductivity measurement of supernatant was performed to determine the precise final ionic strength of equilibrium solution.

Blank sample (without soil added) was carried out in the same manner with laterite and volcanic ash soil samples. Similarly to the procedure of the soil suspension titration, known amounts of electrolyte, standardized acid or base and deionizer water were mixed to produce a solution of desired pH and ionic strength. The blank sample has the same total volume as used in the soil titrations. Equilibrium and pH measurements were all performed similar to those described above. Calculate a ΔH-ΔOH (cmolckg^{-1}) for each sample at each ionic strength examined and plot vs. equilibrium pH.

$$\Delta H\text{-}\Delta OH = \frac{[10^{-pHB} - 10^{-pHS}] - [10^{-(14-pHB)} - 10^{-(14-pHS)}]}{\gamma} \times \frac{0.1}{w}$$

where

$\Delta H\text{-}\Delta OH$ = apparent proton surface charge density calculated by titration at given ionic strength and pH in $cmol_c kg^{-1}$

ΔH= The different between the final H^+ concentration of suspension solution and that of the blank

ΔOH = The different between the final OH^- concentration of suspension solution and that of the blank

pHB = pH of the blank solution

pHS = pH of the solution equilibrated with the sample

14= conditional dissociation product of water

γ = Single ion activity coefficient calculated with the Davies equation (0.71)

w= oven-dried soil sample weight (g)

Table 7.3. Amount (mL) of acid, base, ionic strength salt and distilled water necessary to establish a 50 mL aliquot consisting of a sequential pH change while maintaining an ionic strength of 0.005, 0.01 and 0.05M.

Tube No	0.005M HCl	0.005M NaOH	0.005M 0.005M NaCl	0.01M 0.02M NaCl	Distilled water	0.05M 0.1M NaCl	Distilled water
1	25	0	25	18.8	6.2	23.2	1.8
2	15	0	35	21.2	13.8	24.2	10.8
3	8	0	42	23	19	24.6	17.4
4	4	0	46	24	22	24.8	21.2
5	2	0	48	24.5	23.5	24.9	23.1
6	0.5	0	49.5	24.2	25.3	25	24.5
7	0	0	50	25	25	25	25
8	0	0.5	49.5	24.2	25.3	25	24.5
9	0	2	48	24.5	23.5	24.9	23.1
10	0	4	46	24	22	24.8	21.2
11	0	8	42	23	19	24.6	17.4
12	0	15	35	21.2	13.8	24.2	10.8
13	0	25	25	18.8	6.2	23.2	1.8

7. 2.3. Thermal analysis

Differential thermal and gravimetric analysis (DTA-TG) was carried out simultaneously using the system of Rigaku Thermo plus EVO. The samples were heated from 20 to1000°C at a heating rate of 10 $^{\circ}$C/min. The amount of sample used in each test was 10mg.

7.2.4 Adsorption experiments

7.2.4.1 Determine dosage of adsorbents

For Copper adsorption

The adsorption of Cu^{2+}from solutions of 5 mg L^{-1}, 10 mg L^{-1}and 20 mg L^{-1}were examined with increasing amount of adsorbents added. Amount of 0.3 g; 0.5g; 1 g; 1.5 g and 2 g of samples were placed in centrifuge tubes and then a 50 mL volume of Cu^{2+} solutions were added. The samples were shaken at a speed of 170 rpm at room temperature for equilibration (i.e., 4 h for HW sample and 24 h for TRP-Ai and laterite samples). The supernatants were collected after centrifugation at 2500 rpm for 15 min. Copper concentration in the collected supernatants was measured by atomic absorption spectroscopy (Hitachi, Z2300).

For Lead adsorption

The adsorbents used for this experiment are TRP-Ai, HW and three laterite samples. The different amount of sorbents (i.e., 0.1g; 0.2g; 0.5g; 1g; 1.5 g; 2 g and 3 g) were placed in the centrifuge tubes. A volume of 50 ml of solution of 10 mg L^{-1}lead then was added in. The samples were shaken for 24 h at 170 rpm at room temperature for equilibration. The supernatants were collected by centrifugation at 2500rpm for 15 min. Copper concentration was measured by atomic absorption spectroscopy (Hitachi, Z2300).

For cadmium adsorption

Different amount of adsorbents (i.e., 0.5g; 1g; 1.5g; 2g; 2.5g; 3g; 4g for laterite samples and HW and 0.5g; 1g; 2g; 3g; 4g; 6g for TRP-Ai) was placed in centrifuge tubes. The volume of 50 mL of solution Cd^{2+} was added and then shaken for 24 h for equilibration. Supernatant was collected by centrifugation at 2500rpm for 15 min. The Cd^{2+} concentration in supernatant was measured by atomic absorption spectroscopy (Hitachi, Z2300).

7.2.5 Adsorption isotherm experiment

For the copper adsorption isotherm experiment, an appropriate amounts of adsorbents (1 g for HW, TRP-Ai) and (2 g for laterite samples) were placed in the centrifuge tubes. Then a volume of 50mL of Cu^{2+}solutions with concentration range from 0-30mgL^{-1}were added. For equilibration, the suspensions were shaken for 24 h at 170 rpm at room temperature. Centrifugation at 2500 rpm was conducted for 15 min after equilibration and the supernatants were collected by centrifugation.

Copper concentration was measured by atomic absorption spectroscopy (Hitachi, Z2300). Each experiment was duplicated.

For the lead adsorption isotherm experiment, 1 g portions of the adsorbents were placed in the centrifuge tubes. Then a volume of 50 mL of Pb^{2+} solution with concentration range from 0-20 mg L^{-1} were added. The equilibration and Pb determination in the equilibrium solutions were done in the same way to that for Cu.

For the Cadmium adsorption isotherm experiment, 3 g portions of adsorbents were placed in the centrifuge tubes. Then a volume of 50 mL of Cd^{2+} solution with various concentrations from 0-20 mg L^{-1} was added. The equilibration and Pb determination in the equilibrium solutions were done in the same way to that for Cu.

7.2.6 pH effects on heavy metal adsorption

For copper adsorption, an appropriate amount of samples (1 g of HW, TRP-Ai and 2 g of laterite samples) were placed in centrifuge tubes. 25 mL of 0.01 M $Ca(NO_3)_2$ solution was added to maintain ionic strength at 0.005M. In order to adjust pH to desired values, predetermined volumes (Table 7.4) of 0.1 M HNO_3 or NaOH solution was added. Distilled water was used to fill up to 40 mL (Table 7.4). Finally, 10 ml portions of 50 mg L^{-1} Cu^{2+} solution were added. Then, samples were shaken for 24 h at 170 rpm to equilibrate. Supernatant was separated after centrifugation at 3000 rpm for 20 min. Copper concentration measurement in supernatant was determined by atomic absorption spectroscopy (Hitachi, Z2300). pH was measured before shaking and after equilibrium time.

A similar procedure was applied for pH effect experiments on lead and cadmium adsorption. The amount of absorbents used for lead adsorption examples was 1 g and for cadmium adsorption experiments was 3 g.

Table 7.4. Volume (mL) of acid and base added to adjust pH

HNO_3/NaOH	$Ca(NO_3)_2$	Water
HNO_3 0.1	25	14.9
0.5	25	14.5
1	25	14
1.5	25	15.5
3	25	12
NaOH 0.1	25	14.9
0.2	25	14.8
0.3	25	14.7
0.5	25	14.5
1	25	14

7.2.7 Kinetics of heavy metal adsorption

Experiments were performed at room temperature (25°C) at a metal concentration of 10 mg L^{-1}. Five hundred mL of a metal solution was placed in a 1-L bottle, to which an appropriate amount (10 g for Cu^{2+} and Pb^{2+} experiments, 30 g for Cd^{2+} experiments) of samples was added. The bottles were shaken at 170 rpm without pH adjustment. Several mL of reaction solution was sampled at intervals between 0 and 28 h. The supernatant was immediately filtered through a 0.45 μm membrane filter and then metal concentration was measured.

The percent heavy metal adsorption was calculated using the following equation:

Metal ion adsorption (%) $= (C_0 - C_e) \times 100/C_0$

Where C_0: initial metal ion concentration of test solution in mg L^{-1};
C_e: final equilibrium concentration of test solution in mg L^{-1}.

7.3 RESULTS AND DISCUSSION

7.3.1. Mineralogy and surface charge characteristics

X-ray diffraction patterns of the Mg-saturated and glycerol-solvated clay fractions and fine sand fractions of three laterite samples are shown in Fig. 7.1. The clay fractions of the 1-TT and 2-HL samples showed fairly strong peaks at 0.7, 0.418, 0.35 and 0.269 nm, indicating that these samples contained kaolinite and goethite and hematite. In addition, the 1-TT sample showed weak peak at 1.4 nm, indicating that it contain small amount of non-expandable 2:1 layer silicates. The weak peak at 0.487 nm indicates that all the samples contain gibbsite. The 3-QT sample showed a significantly different mineralogy; it was dominated by quartz and contained much less amount of kaolinite and goethite. The dominance of 0.425 and 0.334 nm peaks in the X-ray diffraction patters for fine sand samples indicate that the major mineral in the fine sand fraction was quartz. The small but distinct peak at 0.418 and 0.269 nm shows that the fine sand fractions also contain goethite and hematite. The silt and coarse sand fractions exhibited similar X-ray patterns.

X-ray diffraction patterns of TRP-Ai sample are also shown in Fig. 7.1. This sample gave faint diffraction peaks only at about 1.4, 0.7 and 0.334 nm after Mg-saturation and glycerol-solvation but the former two peaks disappeared after heating at 550°C (not shown). This suggests that these peaks arose mostly from imogolite but not from layer silicate minerals. The 0.334 nm peak persisted after heating, indicating that the TRP-Ai contained small amount of quartz. The particle size distribution

99

showed that it comprised of 28% of coarse sand (200-2000 μm), 12% of fine sand (20-200 μm), 13% of silt (2-20 μm) and 47% of clay (< 2 μm) by weight.

Fig. 7.2 shows an electron micrograph of the < 2 μm fraction of the TRP-Ai. The aggregates of very fine granules and threads indicate the dominance of allophane and imogolite. Although thread like imogolite is conspicuous in this micrograph, faint peaks in the X-ray diffractogram (Fig. 7.1) and the fact that pure imogolite shows fairly strong diffraction peak at around 1.2-2.0 nm (Wada, 1989) suggest that the relative abundance of imogolite was low.
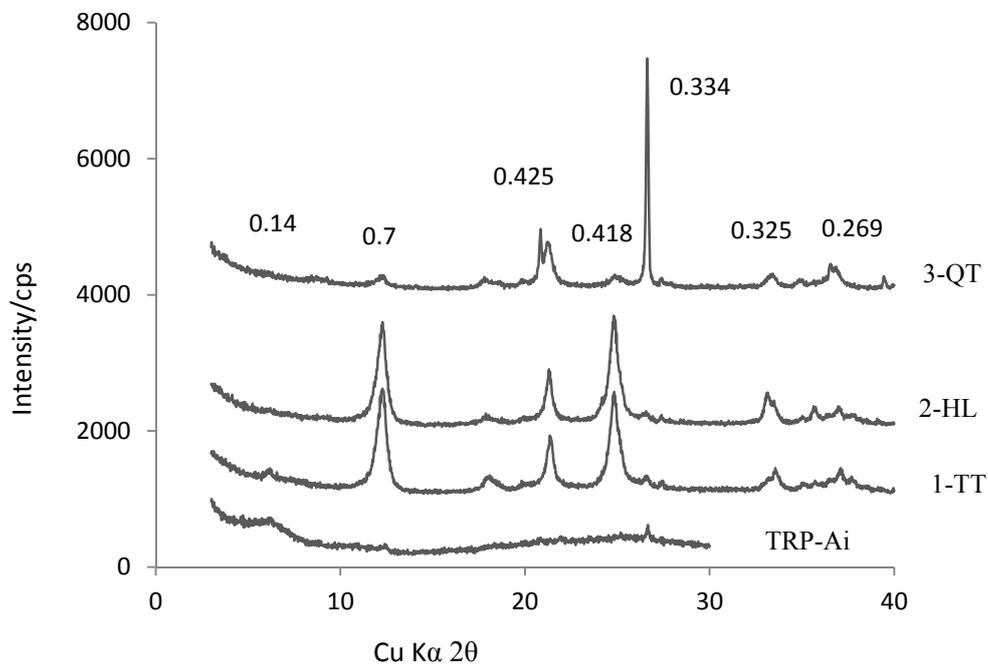

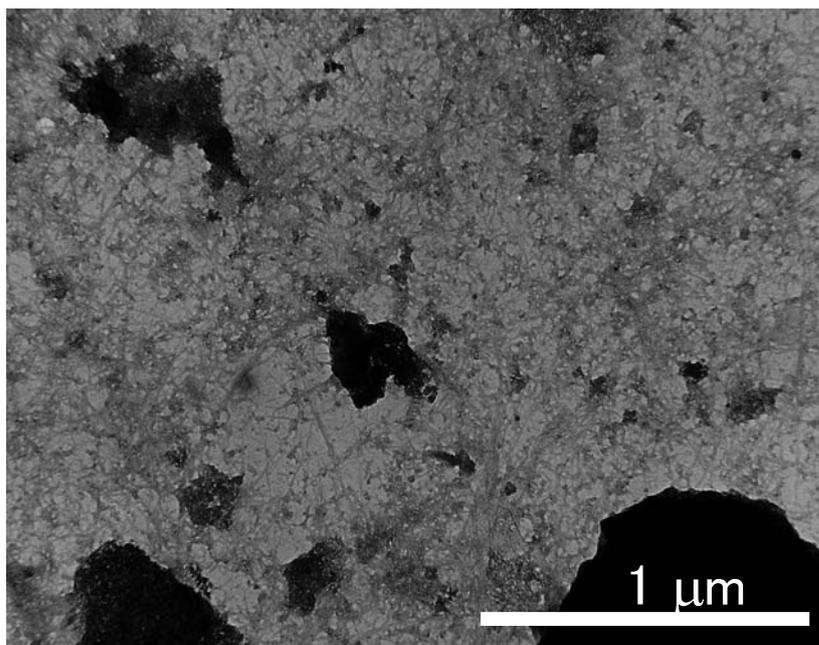**Fig. 7.1**. X-ray diffraction pattern of laterite samples/ Clay fraction

Fig. 7.2. Electron micrograph of < 2 μm fraction of TRP-Ai.

Basic chemical properties of laterite samples are summarized in Table7.1. The pH (H_2O) was in a range from 5.3 to 5.6 and the pH (KCl) was similar, indicating that the samples contained little exchangeable Al. The 1-TT sample showed the highest clay content of 67% followed by the 2-HL and 3-QT samples. The clay content of the 3-QT sample was only 30% and it had fairly high sand content. Although the clay content was high, the effective cation exchange capacity, i.e. the sum of exchangeable cations, was very low. This is a reflection of the virtual lack in 2:1 type layer silicate minerals as indicated by X-ray diffraction (Fig. 7.1).

The results of thermal analyses are shown in Fig.7.3. All the samples showed clear endothermic peaks centered at around 50, 320°C and corresponding weight losses. The 1-TT and 2-HL samples exhibited an additional large endothermic peak at 480°C but the 3-QT sample showed only a faint peak at that temperature. The endothermic peak at 50°C obviously came from desorption of adsorbed water. And the peaks at 320 and 480°C are assigned to dehydration reaction of hydroxide minerals and kaolinite, respectively. Although goethite dehydrates at lower temperature than gibbsite, it is difficult to separate the contribution of these minerals to the endothermic peak centered at around 320°C. These results harmonize with X-ray diffraction patterns shown in Fig. 7.1, particularly in that the 3-QT sample showed very weak diffraction peak at 0.7 nm. The 2-HL and 3-QT samples showed large endothermic peaks at around 840°C but they did not accompany weight loss. The origin of these endothermic peaks was not identified.
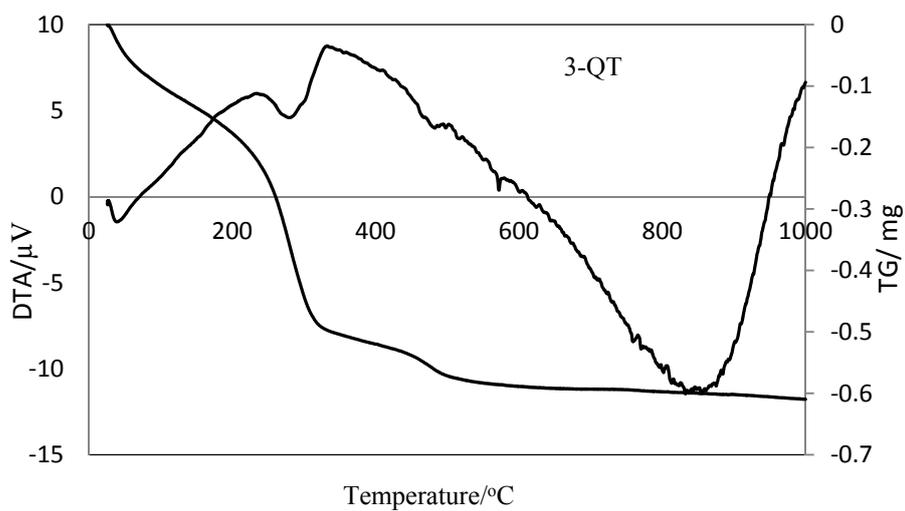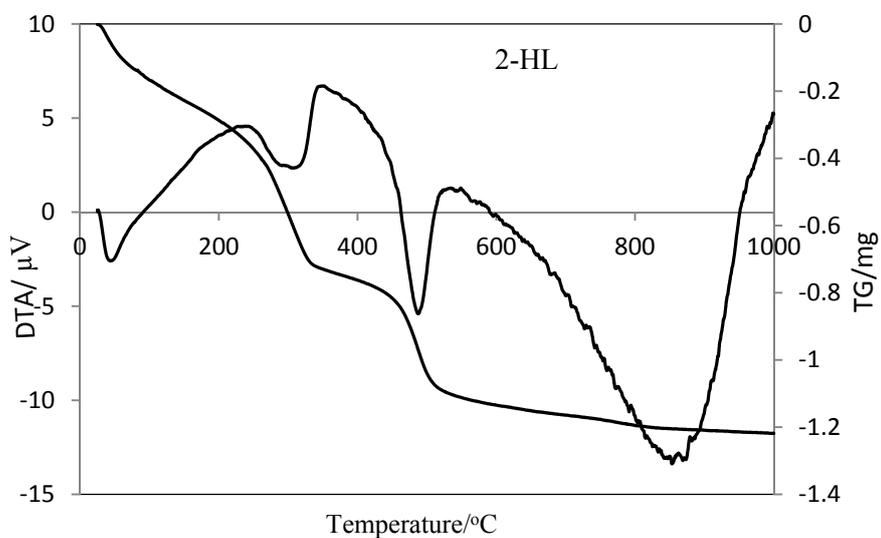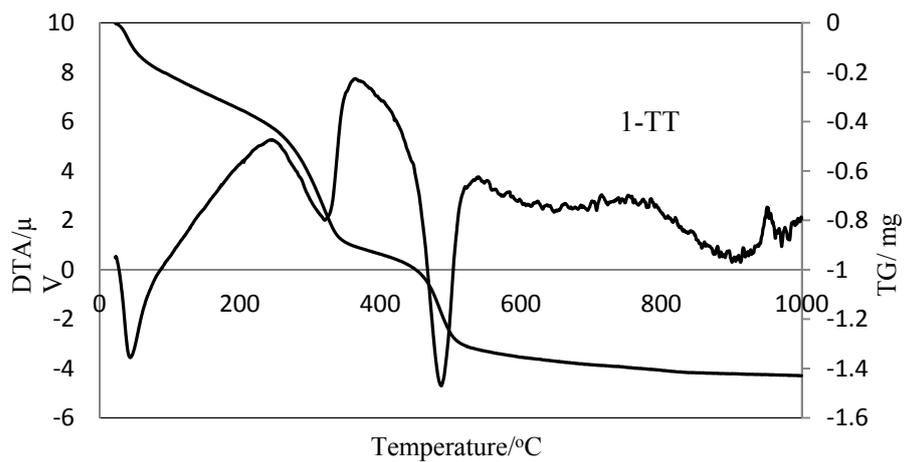
Fig. 7.3. Results of differential thermal analysis and thermogravimetric analysis

The dehydration reaction of gibbsite and kaolinite are expressed as below

$$2Al(OH)_3 = Al_2O_3 + 3H_2O \qquad (7.1)$$

and

$$Si_4Al_4O_{10}(OH)_8 = SiO_2.Al_2O_3 + 4H_2O \qquad (7.2)$$

The weight loss from 200 to 400°C was about 0.5 mg for all three samples. If this came from the dehydration of gibbsite, the stoichiometry in the reaction (1) gives the gibbsite weight of 1.4 mg in 10 mg sample. But this calculation is not convincing enough. Similarly, the weight of kaolinite in is estimated to be 1.4 mg for the 1-TT and 2-HL samples and 0.71 mg for the 3-QT sample.

Fig. 7.4 shows the surface charge characteristics of laterite samples used in the present study, where the net surface charge was plotted against solution pH. The net charge decreased as pH increased and the sign of the net charge reversed at pHs 5.10; 5.00; 5.40 and 6.01 for the 1-TT, 2-HL, 3-QT and TRP-Ai samples, respectively. The net charge of HW sample was not investigated because its characteristics were similar to that of laterites and net charge characteristics can be speculated from that of laterite samples. These pH values, i. e. the point of zero net charge (PZNC) were not much different from pH values measured in water (Table 7.1). Since PZNC for goethite and gibbsite lie around pH 8, the observed lower PZNC values may be due to the presence of kaolinite and quartz.
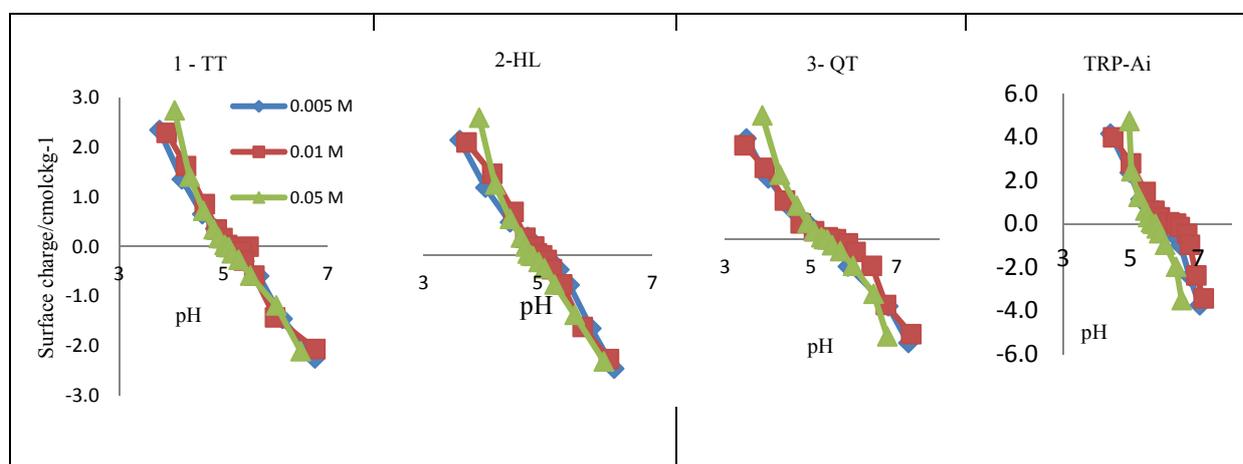

Fig. 7.4. Surface charge diagrams of laterite samples and volcanic ash.

Based on the mineralogical and chemical data, the approximate mineralogical composition of the laterite samples is summarized in Table 7.5. Chemical composition is presented in Table 7.6.

Table 7.5. Mineralogy identification of laterite samples

Sample	Fraction	Identification
1-TT	Clay	Mica; kaolinite; Geothite; feldspars
	Silt	Kaolinite; Geothite; Quazt; Feldspars
	Fine sand	Quazt; Geothite
	Coarse sand	Kaolinite; Geothite; Quazt
2-HL	Clay	Kaolinite; Geothite; Feldspars
	Silt	Kaolinite; Geothite; Quazt; feldspars
	Fine sand	Geothite; Quazt
	Coarse sand	Kaolinite; Geothite; Quazt; hematite, Feldspars
3-QT	Clay	Kaolinite; hematite; Quazt; Feldspars
	Silt	Quazt
	Fine sand	Quazt
	Coarse sand	Geothite; Quazt
HW	Clay	Kaolinite, goethite, feldspars
TRP-Ai	Clay	Allophane and imogolite

Table 7.6. Chemical composition (%) of laterite and volcanic ash samples (XRF analysis)

Composition	1-TT	2-HL	3-QT	HW	TRP-Ai
Al_2O_3	36.684	32.435	12.862	44.718	32.8
SiO_2	34.835	32.001	69.1	9.462	52.8
Fe_2O_3	23.994	31.005	14.871	34.194	7.1
TiO_2	3.184	3.311	0.696	5.654	1.32
K_2O	0.499	0.271	0.394		1.58
P_2O_5	0.292				0.129
SO_3	0.174	0.183	0.154	0.819	0.626
V_2O_5	0.153	0.151			
Cr_2O_3	0.078	0.059		0.284	
ZrO_2	0.061	0.051	0.045	0.063	
MnO	0.045	0.412	1.815	0.435	0.177
CuO		0.075	0.064		
MgO				4.372	0.375
CaO					1.26
Na_2O_3					1.11
Cl^-					0.564

7.3.2. Heavy metal adsorption

7.3.2.1 Effect of contact time

In order to determine equilibrium time of metal adsorption on to materials, the experiment was conducted with a dose of 40 g L^{-1} of adsorbents at pH 4.8-5.0 and initial metal concentration of 10 mg L^{-1}. Copper is selected as a representative metal. A review on copper adsorption by Marc and Alan (1981) showed that it has low adsorption affinity to hydrous metal oxides. Therefore adopting equilibrium time determined for copper will be reasonable. Fig.7.5 shows the variation in the adsorption of copper with contact time. It is evident from the experimental results that absorbance decreased very rapidly in the initial 30 min and gradually afterward until equilibrium was obtained. After 24 h, the absorbance of the reaction solutions for laterite samples (1-TT, 2-HL and 3-QT) reached constant values. Two rest samples (HW and TRP-Ai) required 20 h to reach constant absorbance. For all experiments carried out in the present study, equilibration time was set to 24 h.
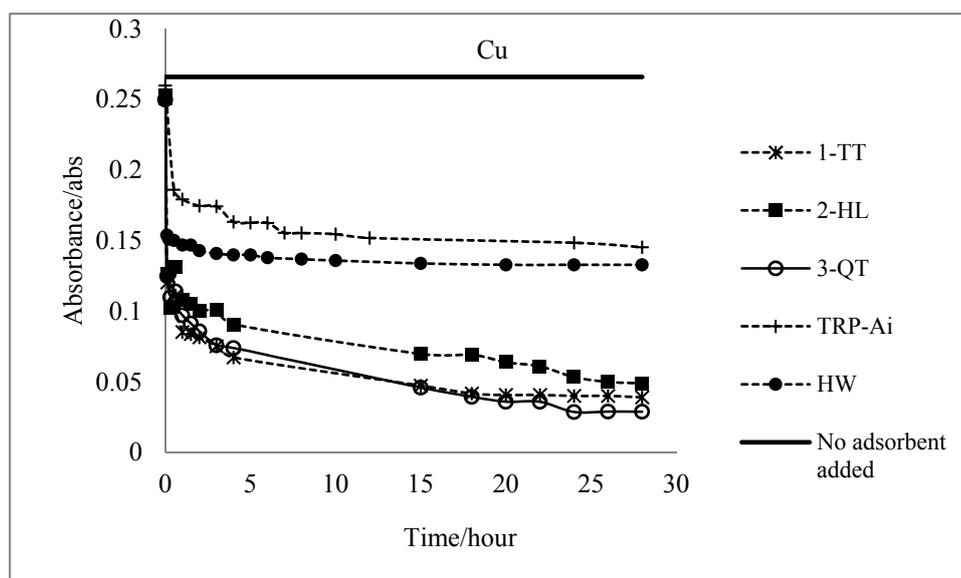

Fig 7. 5. Effect of contact time on metal adsorption by laterite and volcanic samples.

7.3.2.2 Effect of adsorbent dose

The results for removal of heavy metals at different adsorbent doses are shown in Fig 7.6.The experiments were carried out at initial solution pHs from 5.0-5.2. A general trend was that the adsorption of heavy metals increased as dose of adsorbents increased. The possible reasons are that the greater availability of adsorption sites on surfaces of adsorbents. However, the increase was less significant when adsorbents were used with high dose (Fig.7.6). The adsorption seemed to have reached plateau at a dose of 2 g for Cu^{2+}, 1-1.5 g for Pb^{2+} and 3 g for Cd^{2+}. These phenomena were further investigated in other experiments in this study.
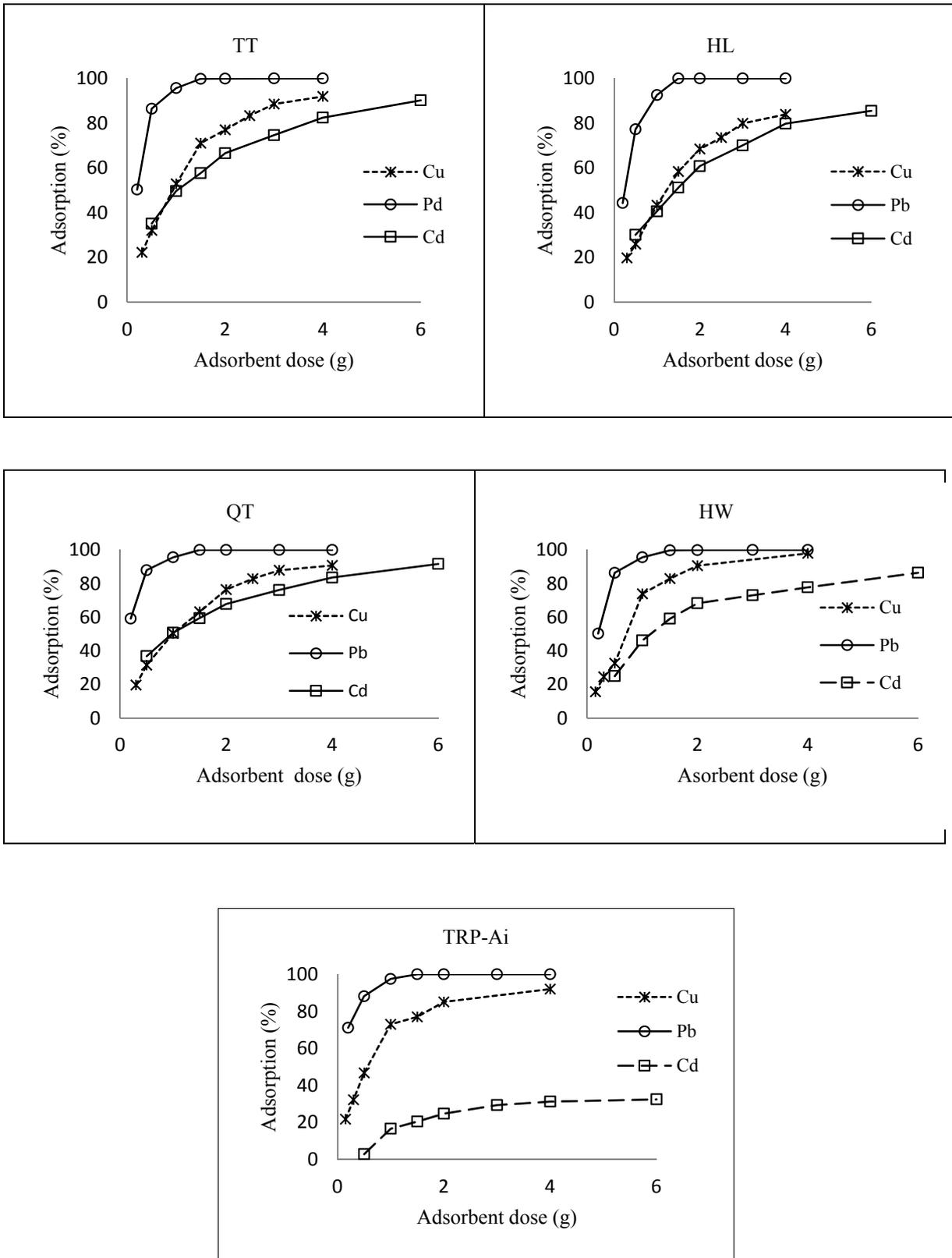
Fig.7.6. Effects of adsorbent dose on metal adsorption by laterite and volcanic samples

Hematite, goethite in (Table7.5) laterite and allophane in TRP-Ai samples are believed to have fairly high metal adsorption capacity. The metal ion adsorption results from surface complexation that is the interaction of surface functional groups (i.e., Fe-OH, Al-OH and Si-OH) with metal cations. Both outer- sphere complexation and inner-sphere complexation are believed to be involved in metal adsorption (Donald, 2003).The metal adsorption occurs on negative surface charges of samples at the pHs over PZNC in which the outer-sphere complexation is dominated. Adsorption of metal ions via the inner-sphere complexation does not depend on surface charge of goethite, hematite and allophane. Surface complexation is described by the reactions;

$$SOH + M^{n+} = SOM^{(n-1)} + H^+$$

$$2SOH + M^{n+} = (SO)_2 M^{(n-2)+} 2H^+$$
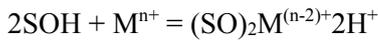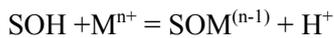
where SOH is the surface functional group. M is the metal ion, having charge number of n.

The adsorbents mostly absorbed 80-90% of heavy metal added, indicating their capability to remove Cu^{2+}, Pb^{2+} and Cd^{2+} from wastewaters. But TRP-Ai (Fig 7.6) which adsorbed less than 40% the added Cd^{2+} was an exception. The poor cadmium adsorption by volcanic ash sample (TRP-Ai) is probably because Cd^{2+} has markedly high affinity for iron oxide minerals (Gadde and Laitinen, 1974; Forbes *et al.*, 1976) but not for aluminum oxide minerals (Kinniburgh *et al.*, 1976). At the same experimental conditions (i.e., pH solution 5-5.2, low ionic strength 0.005M and heavy metal concentration of $10mgL^{-1}$), the difference in required dose of adsorbents to realize maximum removal (i.e., 1-1.5 g for Pb^{2+}; 2 g for Cu^{2+} and 3 g for Cd^{2+}) reveals that the adsorbents adsorbed lead more effectively than copper. Cadmium was absorbed less effectively than copper and lead.

7.3.2.3 Adsorption isotherms

The data for adsorption isotherm were obtained at fixed adsorbent dosage and varying initial concentration of metal ions. The experimental data were analyzed based on the Langmuir and Freundlich isotherm equations.

Langmuir equation is given by

$$Qe = \frac{ka.qm.Ce}{(1 + ka.Ce)}$$

and the Freundlich equation is given by

$$Qe = KeCe^{1/n}$$

Where Q_e is the amount of metal ions adsorbed perunit mass of adsorbent in mg g^{-1},
C_e is the equilibrium concentration of heavy metal ions in mgL^{-1},
K_e and *n* are Freundlich constants,

'q$_m$' is a Langmuir constant which is a measure of adsorption capacity expressed in mgg^{-1},

'K$_a$' is also Langmuir constant which is a measure of energy of adsorption expressed in mg^{-1}.

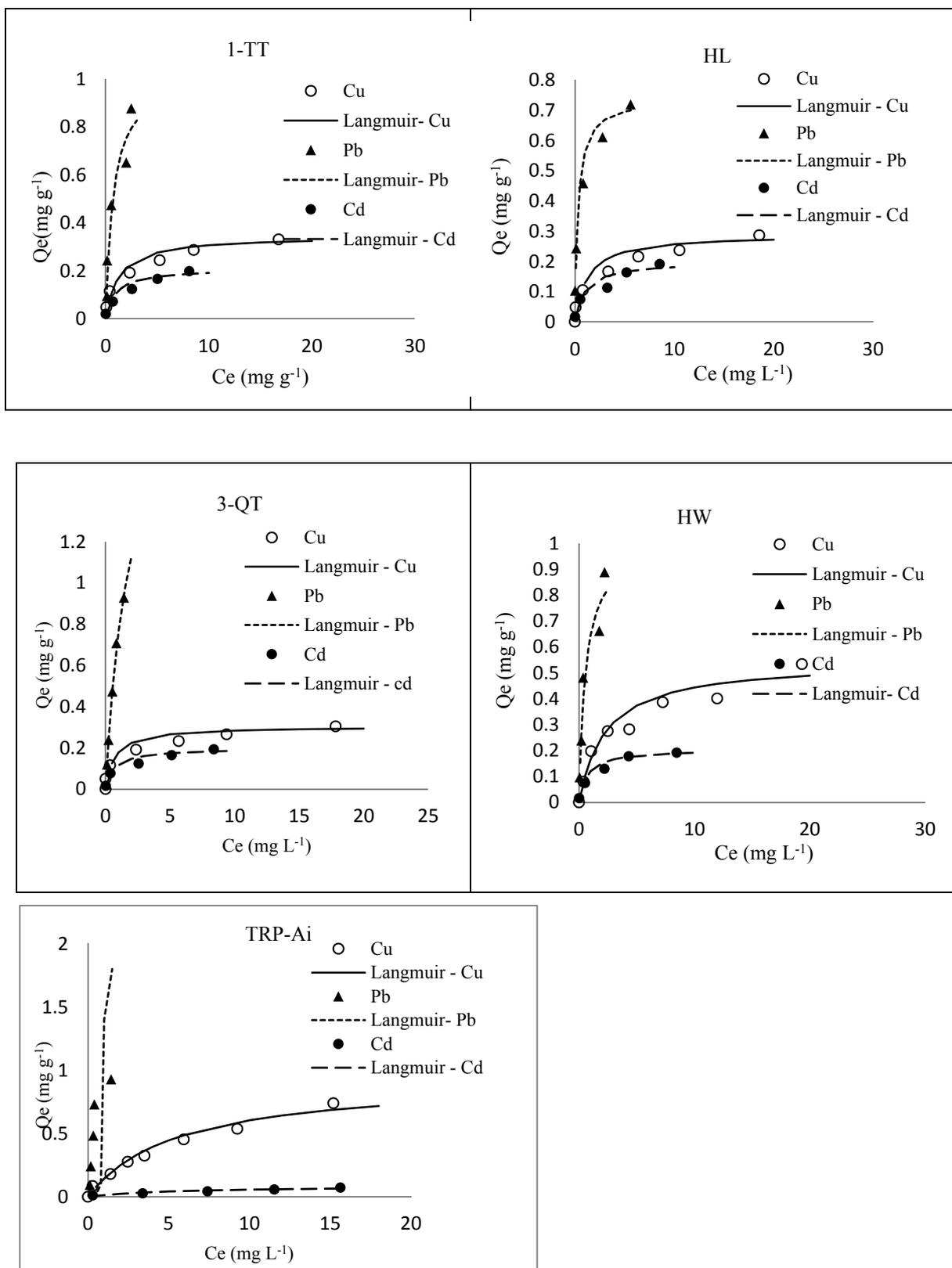The parameters 'q$_m$' and 'Ka' are calculated from the slope and the intercept of the plots.

Fig.7.7. Langmuir isotherm of metal adsorption by laterite and volcanic ash samples.
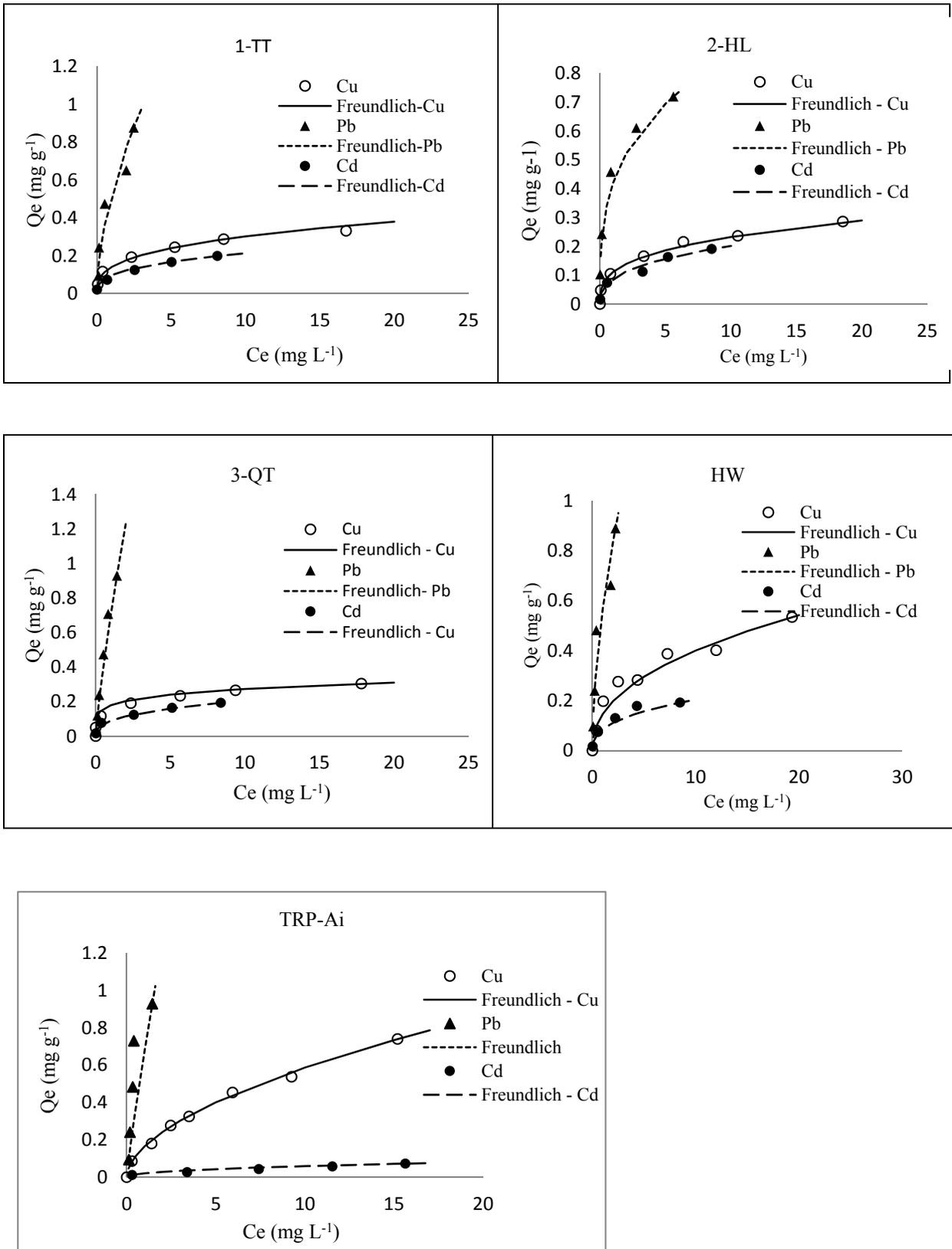
Fig.7.8. Freundlich isotherm metal adsorption by laterite and volcanic ash samples.

Figs. 7.7 and 7.8 present the plots of Langmuir and Freundlich adsorption isotherm where Qe is plotted against Ce. The Langmuir constants and Freundlich constants obtained from intercept and slope of the plot are given in Table. 7.7. Since R^2 values lie between 0.9 and 1 for all adsorbents, the fit of the adsorption data to the Freundlich and Langmuir isotherms are satisfactory. In addition, the fact that the values of n from Freundlich adsorption isotherm plot are in the range from 1 and 10 indicate fairly high affinity of metal ions for materials examined (Slejko, 1985).

Adsorption capacity of metal ions estimated by the value of Qm is found to be in the order Pb (II) > Cu (II) > Cd (II) for all samples. Generally, for three laterite samples from Viet Nam, although there is no much difference in the adsorption capacity, the 1-TT and 3-QT samples performed better adsorption compared to 2-HL sample. The HW sample has similar capacity to the 1-TT sample for Pb (II) and Cd (II), but higher adsorption capacity is observed for Cu (II). This phenomenon is in agreement with the higher iron and aluminum content as determined by XRF analysis for the HW sample (Table 7.6). TRP-Ai was rich in aluminum (see Chapter 3), is potential adsorbent for Cu (II) and Pb (II) because of intensive interaction of aluminum oxide with Cu^{2+} and Pb^{2+} via outer surface complex formation. Cadmium adsorption capacity of TRP-Ai was extremely low (0.0878 mg g^{-1}) from Langmuir adsorption isotherm. The low affinity of Cd (II) for aluminum oxides pointed out earlier is probably a reason for the observed low adsorption capacity.

Table 7.7. Values of Langmuir and Freundlich isotherm constants for the adsorption of heavy metal ions on materials

Samples	Metal ions	Langmuir constants			Freundlich constants		
		Qm (mgg^{-1})	Ka (mg^{-1})	R^2	Ke	n	R^2
TT	Cu (II)	0.3436	0.8120	0.9880	0.1411	3.0211	0.9861
	Pb (II)	1.0225	1.4051	0.9171	0.5688	1.7857	0.9340
	Cd (II)	0.2101	1.0294	0.9561	0.0988	2.9674	0.9933
HL	Cu (II)	0.2883	0.7990	0.9750	0.1122	3.1447	0.9981
	Pb (II)	0.7402	3.1565	0.9912	0.4218	3.2258	0.9952
	Cd (II)	0.1992	1.001	0.9332	0.0893	2.8169	0.9910
QT	Cu (II)	0.3039	1.399	0.9870	0.1791	5.4348	0.9823
	Pb (II)	1.5501	0.8711	0.9612	0.7013	1.2361	0.9921
	Cd (II)	0.1192	1.3973	0.9711	0.0900	2.7778	0.9901
HW	Cu (II)	0.5452	0.4352	0.9501	0.1463	2.2883	0.9251
	Pb (II)	1.0090	1.7759	0.9431	0.7013	1.2361	0.9921
	Cd (II)	0.2052	1.4128	0.9844	0.0860	2.6596	0.9951
TRP-Ai	Cu (II)	0.9372	0.1816	0.9271	0.1652	1.8149	0.9960
	Pb (II)	0.8071	1.0607	0.8950	0.6810	1.1765	0.7978
	Cd (II)	0.0878	0.1883	0.8477	0.0210	2.2173	0.9721

7.3.2.4 Effect of pH

pH is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Fig. 7.9 shows the pH effects on Cu (II), Pb (II) and Cd (II) adsorption on the laterite and volcanic ash adsorbents. The study was conducted at a constant initial metal ion concentration of 10 mg L^{-1}. The adsorbent dose was 1 g of HW, TRP-Ai and 2 g of laterite samples (1-TT, 2-HL, 3-QT) and the reaction time of 24 h was implemented for all of copper, lead and cadmium.
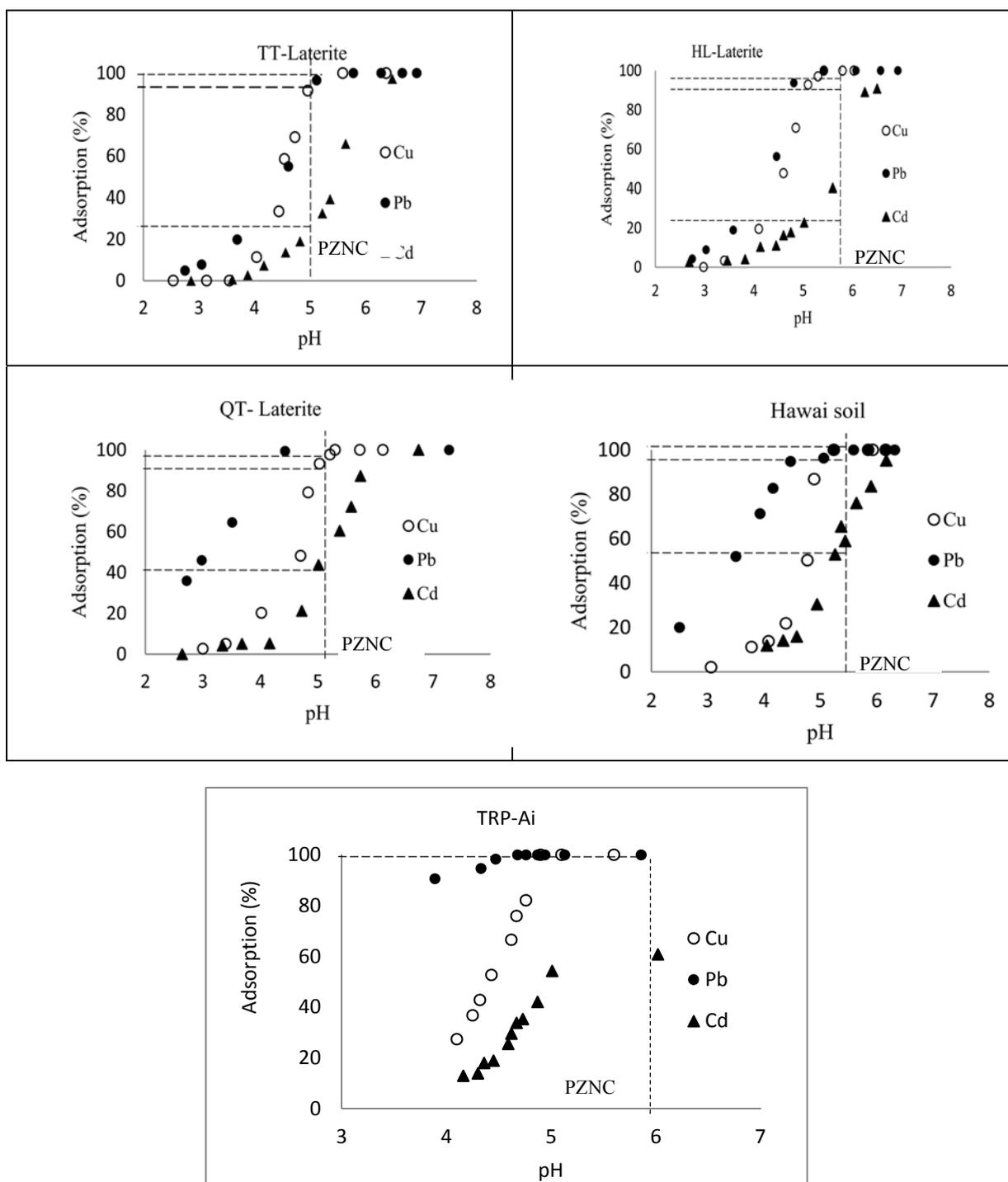

Fig. 7.9. Effect of pH on metal adsorption by laterite and volcanic ash samples.

The experimental data shows that metal ion adsorption on laterite and volcanic ash samples is strongly pH dependent. The percentage of adsorption increased with pH to reach a maximum. The lowest pH value to achieve the maximum adsorption is defined as optimum pH in this study and the estimated optimum pH values are presented in Table.7.7. It is known that a steep increase in metal adsorption occurs in a narrow pH range (Fig. 7.9). For example, percentage of Cu (II) adsorbed by the 1-TT sample was 58.5% at pH 4.54 and it increased to 100% at pH 5.59. The lead adsorption by the 1-TT sample showed a similar trend. Cadmium adsorption by the 1-TT sample was less than copper and lead adsorption, but the adsorption of Cd also increased in a narrow pH range (5.36-6.48) from 39.36% to 97.23%. The adsorption properties of the rest laterites (2-TT, 3-QT and HW) were similar to that of the 1-TT sample. The volcanic ash (TRP-Ai) showed even steeper increase in metal adsorption in over narrower pH range. The copper adsorption increased from 52.66% to 100% as pH increased from 4.43 to 4.90. Remarkably, lead adsorption on to TRP-Ai was not pH dependent as shown in Fig. 7.9. At low pH (3.89), lead adsorption percentage was 90.63% and then it increased to 100% at above pH 4.68.

Table 7.8. Optimum pHs for metal adsorption on to laterite and volcanic ash materials

Samples	Metal ions	Maximum adsorption (%)	Optimal pH
1-TT	Cu (II)	100	5.59
	Pb (II)	100	5.58
	Cd (II)	97.23	6.48
2-HL	Cu (II)	100	5.42
	Pb (II)	100	5.41
	Cd (II)	90.1	6.52
3-QT	Cu (II)	100	5.3
	Pb (II)	100	5.2
	Cd (II)	98.3	6.75
HW	Cu (II)	100	5.25
	Pb (II)	100	5.25
	Cd (II)	95.31	6.17
TRP-Ai	Cu (II)	100	4.9
	Pb (II)	100	4.76
	Cd (II)	72.4	6.02

The observed behavior can be interpreted in terms of dominance of surface complexation reactions. The decrease in metal adsorption in lower pH range can be explained on the basis of competition between proton and metal cations for the same functional groups. In addition, due to protonation of the adsorbent surface at lower pHs turns net surface proton charge, causing electrostatic repulsion between the surface of adsorbents and the metal ions.

The points of zero net charge (PZNC) were pHs 5.10, 5.00, 5.40 and 6.01 for the 1-TT, 2-HL, 3-QT and TRP-Ai samples, respectively, suggesting that thus electrostatic interactions affected the adsorption behavior. Negative surface charges of adsorbents are considered to have favored the attraction of positively charged metal ions at pHs over the PZNC.

7.4 CONCLUSION

Both volcanic and laterite have high lead adsorption capacity (up to 1.0-1.2 mg Pb g^{-1} is recorded at pH5). Adsorption capacity for copper is not as high as that for lead but this is acceptable if they are used in water treatment (about 0.5-0.8 mg Cu g^{-1} at pH5). It is difficult to remove cadmium by laterite and volcanic ash soil. The adsorption capacity is 0.4 mg Cd g^{-1} at initial Cd concentration of 25 mg L^{-1} for laterite and less 0.1 mg Cd g^{-1} for the volcanic ash soil at the same initial concentration. Similar to ferric hydroxides, adsorption of metal cations examined by these materials is strongly pH dependent. At pH lower than 4, these materials are ineffective to adsorb metals. The use of volcanic ash soil and laterite is recommended to remove heavy metals from wastewater when the pH of the target water is over 4 whereas TRP-Ai is not recommended to remove Cd.

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CHAPTER 8. CONCLUSIONS AND GENERAL DISCUSSION ON PRACTICAL APPLICATIONS OF VOLCANIC ASH SOIL AND LATERITE IN WATER TREATMENT

In the following, the results of the previous chapters are discussed to evaluate suitability and limits of these materials in practical applications to wastewater and drinking water treatment.

8. 1. WATER TURBIDITY TREATMENT BY VOLCANIC ASH AND LATERITE

The results obtained from flocculation experiments revealed that mineralogy and surface chemistry characteristics of suspended clay particles significantly affect on their removal efficiency from water by volcanic ash soil and laterite. The volcanic ash soil rich in allophane and imogolite minerals is more effective than laterite containing iron oxide minerals in the removal of suspended clay particles.

Kaolinite, a popular particle type used in ceramic industry, is removed effectively by both volcanic ash soil and laterite. As calculated in the previous chapters, the use of 33 mg of volcanic ash or 60 mg of laterite is necessary to remove 200 mg of kaolinite. The aluminum compounds have high efficiency in environmental treatment, but there is concern about high cost and possible rise in accumulated aluminum concentration. Therefore, in the current context of global climates change, volcanic ash and laterite are suitable agents to use for waste water from ceramic industry or mining activities.

Vermiculite or vermiculite-chlorite particles are widely used in industries as primary materials, e. g., in agriculture as mineral compounds to improve soil hardness, etc,. However, suspension of these minerals discharged from mining industries will pose negatively effects on ecosystem. From this study, it was proven that these minerals can also be removed by using volcanic ash and laterite. It could be concluded that volcanic ash and natural laterite are suitable for the removal of suspended clay particles i.e., kaolinite, vermiculite and vermiculite-chlorite from waste water treatment. The other clay suspended particles such as mica, monmorilinite, smectite, etc., are recommended to use the volcanic ash and laterite with some modifications.

8.2. PHOSPHOROUS REMOVAL FROM CONTAMINATED WATER BY VOLCANIC ASH AND LATERITE

Adsorption of phosphate onto laterite was studied. Laterites had phosphorus adsorption capacity ranging from 1.1 to 1.6 mg P g^{-1} in a pH range of 3-9 and can reduce phosphorus concentration to less 2 mg P L^{-1}. The pH range of contaminated waters is wide, depending on characteristics of sources. Natural water is reported to usually have a pH range from 6-7. The eutrophication water in lake and

river, due to nutrient contamination, is supposed to have higher pH range. Waste waters from detergent industry also have high pH level, but in the pH of waste waters in mining zones are strongly acidic. As is shown, phosphate adsorption onto laterite is slightly pH dependent, an approximately 10% decrease of adsorption capacities was observed when pH increased by 9 units. However, 3-QT sample, which is representative latertie containing high quartz content, had a low adsorption capacity at pH 8- 9. That means the use of laterite to remove phosphorous is reliable for water environment at all pH ranges, but it is not recommended to use laterite containing higher quartz content to remove phosphorous at alkaline pHs. The phosphorous adsorption kinetics was fast in first 8 h, and slowed down afterwards. This characteristic contributes to reduce energy consumption in treatment process. Result on competitive adsorption showed that laterite very much preferred phosphorous over sulfate and carbonate. Many literature reviews reported that the adsorption behavior of phosphorous by volcanic ash agents (Chapter 6) is similar to that by laterite. Allophane and imogolite minerals derived from volcanic ash were considered to be effective to remove contaminants in waste water and landfill. In addition, volcanic ash soil has been known by its strong phosphorous retention characteristics, which sometimes causes phosphorous deficiency. From above interpretation, it can be concluded that laterite and volcanic ash soil can be applied to phosphorous removal from water

8.3. HEAVY METAL REMOVAL FROM WASTE WATER BY VOLCANIC ASH AND LATERITE

In comparison to heavy metal adsorption efficiency of zeolite, paragonite, montmorillonite and kaolinite minerals, both volcanic ash soil and laterite displayed higher adsorption capacity. According to the results of this the lead adsorption capacity ranged from 1.0 to 1.2 mg Pb g^{-1} at pH5. Although adsorption capacity of copper was not as high as that of lead, the capacity of 0.5-0.8 mg Cu g^{-1} at pH5 is acceptable in water treatment.

Cadmium adsorption capacity by laterite was much less than those for lead and copper (0.4 mg Cd g^{-1} at initial Cd concentration of 25 mg L^{-1}), but it is still higher than those of other low cost adsorbents (zeolite, paragosite, montmorilonite and kaolinite minerals). Removal of cadmium has been big challenges in waste water treatment because of its low affinity for aluminum and iron hydroxides as indicated by previous studies. In recent years, cadmium treatment in water has marked remarkable success by new technology application like RO membrane filtration. However, a high treatment cost and energy consumption limit its application in water treatment. Therefore, both laterite and volcanic ash will be promising alternative adsorbents to treat lead and copper in waste waters. For the removal of cadmium, it is recommended to use laterite. The results obtained from the present study show that selective adsorption of metals by laterite and volcanic ash soil is strongly pH dependent. This is typical for the adsorption of heavy metal cations by oxide surfaces at near the

pH_{PZC}. To achieve high removal efficiency in heavy metal treatment, these adsorbents is recommend to use for waste water bodies having pHs over 4.

8.4. USING NATURAL LATERITE AS MEDIUM OF FILTRATION PROCESS

The traditional filtration technology using and gravel as filter media has remarkably improved water quality, especially water turbidity. In the past, when advanced technology had not been devised yet, this technology had been common and chosen by many users as a standard water treatment method. In developing countries, this traditional technology has been still popularly applied until now to purify drinking water. As is indicated by the previous studies, the medium by sand and gravels suffers from many disadvantages including, i) incomplete removal of small particles <1 μm in size, ii) it is difficult to remove anions and cations because sand and gravel have small specific surface area. iii) they are not effective to treat pathogen and microbes.

The laterite is an abundantly available resources in tropical and sub-tropical areas, the use of laterite as a medium replacing sand and gravel will improve water quality e.g., turbidity, concentration of ionic pollutants. This material will be highly appreciated in waste water and drinking water treatment processes.