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博士論文

**Development of Low-Cost Adsorbents Based on Solid Waste  
Materials to Remove Heavy Metal Ions in Water**

(水中の重金属イオンの除去のための固形廃棄物に基づく安価な吸着剤の開発)



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## Summary

### **Development of low-cost adsorbents based on solid waste materials to remove heavy metal ions in water**

(水中の重金属イオンの除去のための固形廃棄物に基づく安価な吸着剤の開発)

The environmental contaminations with heavy metals such as cadmium (Cd) and lead (Pb) have been considered as one of the serious environmental problems because of the potential damage to human health and ecosystem. Even the low concentration of cadmium and lead in water is still potential for kidney and bone damage, cancer, disturbing the respiratory and reproduction system due to the accumulation effect. Many technologies have been employed in order to minimize the pollution with heavy metals, i.e. membrane technology, ion exchange, phytoremediation and adsorption. Adsorption is one of the common methods that have been widely used for water and wastewater treatment. As adsorbent, activated carbon has been often utilized in many countries, however, this material is quite expensive. The high cost of activated carbon has inspired many researchers into the development of alternative low-cost adsorbent materials. However, the studies on sludge of drinking water treatment plant (DWTP), sludge of paper industry and leaves of *Platanus* as a low-cost adsorbent have been still limited.

In the present study, I developed a low-cost adsorbent based on solid waste materials, sludge of DWTP, sludge of paper industry and leaves of *Platanus*, to remove cadmium and lead ions in water. In order to improve the adsorption capacity of these adsorbents, the chemical modification using phosphoric acid and citric acid was employed for sludge of paper industry and leaves of *Platanus*, respectively. Furthermore, the encapsulation with agar was applied to the adsorbent based on *Platanus* leaf aiming the easy separation of adsorbent materials from solution after an adsorption process.

Some parameters such as the dose of the adsorbent, pH of solution and shaking time were investigated in the batch system in order to know the optimum condition and the adsorption ability of the adsorbent. In order to know the economic value of the adsorbents, I tried to calculate the cost of each adsorbent and compare with a commercial activated carbon as the most common adsorbent.

This doctoral thesis consists of six chapters. The background of this study is described in Chapter 1. In Chapter 2, a low-cost adsorbent based on sludge of DWTP, solid waste by-product of sedimentation process in the DWTP, was studied for adsorption of cadmium ion in water. Artificial sludge was also prepared by the similar process to the DWTP using kaolin, humic acid and iron, which are the major components of the DWTP sludge and then the adsorption ability was examined in order to clarify the key components for the adsorption. When humic acid and iron were removed completely from the DWTP sludge, the adsorption capacity of this sludge for cadmium ion was decreased significantly. The low adsorption capacity of the artificial sludge without the humic acid and iron proved that the humic acid and iron oxide were the key components of the adsorbent material for adsorption of cadmium ion in water. The favorable pH of solution to remove cadmium ion was in the range of pH 6 to 8. From Langmuir isotherm adsorption model, the adsorption capacities of the adsorbent based on sludge of Miyamachi and Nishino DWTP for cadmium ion were 5.3 and 9.2 mg/g, respectively.

In Chapter 3, I described the development of a low-cost adsorbent based on sludge of paper industry. The adsorption capacity of the adsorbent based on sludge of paper industry for cadmium ion was 5.2 mg/g. After modification with phosphoric acid, its adsorption capacity for Cd and Pb determined by Langmuir isotherm model was 29

and 139 mg/g, respectively. The increase of adsorption capacity after modification with phosphoric acid may be due to two possible reasons. First, after treatment with phosphoric acid, it was found from FTIR spectra that the adsorbent had phosphate functional group which contributed to the adsorption of Cd and Pb ions. Second, calcium in the paper sludge reacted with phosphoric acid to form calcium phosphate which also had a binding ability with some metal ions such as Cd and Pb.

The development of low-cost adsorbent based on leaves of *Platanus* was described in Chapter 4. The adsorption capacity of leaves of as a low-cost and environmentally friendly adsorbent was very high compared to the other materials such as sludge of DWTP and paper industry. Based on the Langmuir isotherm adsorption model, the adsorption capacity of raw leaves of *Platanus* was 25 mg/g. Modification of the leaves with citric acid increased its adsorption capacity to 83 mg/g. However, the adsorption capacity of the encapsulated adsorbent in agar was 23 mg/g. The high adsorption capacity after treatment with citric acid may be due to the introduction of carboxylic groups into the adsorbent and also the increase in the surface area and pore volume of the adsorbent.

In Chapter 5, the cost of these adsorbents was derived on the basis of cost analysis as comparing the cost with commercial activated carbon. Finally, in Chapter 6, I concluded that DWTP sludge, sludge of paper industry and leaves of *Platanus* were able to be considered as low-cost adsorbent materials for removal of cadmium and lead ions in water. The chemical modification with phosphoric acid on sludge of paper industry and citric acid on leaves of *Platanus* improved the adsorption capacity of adsorbents significantly. Moreover, the encapsulation with agar led to the easy separation of the adsorbent materials from solution after an adsorption process. The

development of low-cost adsorbent based on solid waste materials brings the double benefits, one is to be able to decrease the amount of solid waste materials if the adsorbent based on the material will be used in large scale. Another is the decrease the cost if the adsorbent will be used instead of the activated carbon.



**CHAPTER 1**  
**General Introduction**

## 1.1 Background

The environmental contaminations with heavy metals such as cadmium (Cd) and lead (Pb) have been considered as one of the serious environmental problems and attracted public concern because of the potential damage to human health and ecosystem. Even the low concentration of cadmium and lead in water is still potential for kidney and bone damage, cancer, disturbing the respiratory and reproduction system due to the accumulation. Contamination with cadmium, one of the most toxic metal ions, is a worldwide environmental concern, since it is a toxic heavy metal and does not have a clear function for living organisms (Clabeaux et al., 2011).

The presence of cadmium in the environment sometimes causes a serious problem for human beings and an ecosystem. Cadmium can be released to the environments by many kinds of industrial activities such as ceramics, metal plating and textile (Rao et al., 2006; Wang et al., 2009). It adversely affects several important enzymes to cause bone disease and kidney damage (Manahan 2010).

Itai-itai disease, which was caused by cadmium poisoning and resulted in softening of the bone and kidney failure in the Jinzu river area of Toyama prefecture, was one of the most severe environmental problems in Japan. The rate of death among the patients was 72.6% and it was considered that itai-itai disease has a long-lasting negative effect on the patient's life span (Kawano S, et al., 1986). In the Watarase river water near Ashio mine in Gunma prefecture, the concentration of cadmium was 0.02-0.34  $\mu$ g/l (Ohmichi K, et al., 2006). Generally, the concentration of cadmium in aquatic environment of Japan is much lower in comparison with those of developing countries such as Indonesia. The concentration of Cd in the water area of Jakarta, the capital city of Indonesia, was sometimes up to 0.47 mg/l, higher than the standard of

Indonesian government (0.03 mg/l) (Rochyatun E, 2007). The concentration of Pb and Cu in the sediment taken from Jakarta bay is up to 6.9 and 4.1 ppm, respectively (Takahiro H, et al., 2011). The concentration of Cd in some freshwater fishes in Keuretoe river (Aceh province, Indonesia) is in the ranges between 0.0064 ppm and 0.0260ppm (Sarong M. A, et al., 2013). It is known that heavy metals such as Cd and Pb are accumulated in the human body and their influences might be found out after several years. Therefore, even the low concentration of Cd in water is still potential for human damage due to the accumulation effect.

Many methods have been developed to remove heavy metal ions in water, i.e. membrane technology, ion exchange, phytoremediation, adsorption, etc. (Namasivayam and Ranganathan, 1995). Adsorption is one of the most common methods that have been widely used for water and wastewater treatment. As adsorbent, activated carbon has been often utilized in many countries, however, this material is quite expensive (Papandreou et al., 2007). The high cost of activated carbon has inspired many researchers into the development of alternative low-cost adsorbent materials. However, the studies on sludge of drinking water treatment plant (DWTP), sludge of paper industry and leaves of *Platanus* as a low-cost adsorbent have been still limited.

## **1.2 Adsorption and low-cost adsorbent**

There are some terminology of adsorption; enrichment of one or more components in an interfacial layer (Rouquerol F., et al., 1999), the process through which a chemical substance accumulates at the common boundary of two contiguous phases (Garrison S, 2004), a consequence of the field force at the surface of the solid (the adsorbent), which attracts the molecules of the gas or vapour (the adsorbate) (Gregg

S. J. and Sing K. S. W, 1967), the process of interaction between the molecules of gaseous (or liquid) phase with the surface of a solid.

Generally, adsorption is classified into two types of physical and chemical adsorption. Physical adsorption or physisorption, the adsorption without chemical bonding, is adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved. Chemisorption or chemical adsorption is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds or the adsorption involving chemical bonding. Physisorption is a general phenomenon with a relatively low degree of specificity, whereas chemisorption is dependent on the reactivity of the adsorbent and adsorptive (Rouquerol F. et al., 1999).

Since its first introduction for heavy metal removal, activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world. In spite of its prolific use, activated carbon remains an expensive material since the higher quality of activated carbon, the greater its cost. Activated carbon sometimes requires complexing agents such as some acids or bases to improve its removal performance for inorganic matters. Therefore, this situation makes it no longer attractive to be widely used in small-scale industries because of the cost inefficiency (Babel S. and Kurniawan T. A, 2003).

Due to the problems mentioned previously, research interests into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years. Attentions have been focused on the various adsorbents,

which have metal-binding capacities and are able to remove unwanted heavy metals from contaminated water at low cost. Because of their low cost and local availability, natural materials such as chitosan, zeolites, clay, or certain waste products from industrial operations such as fly ash, coal, and oxides are classified as the low-cost adsorbents (Babel S. and Kurniawan T. A, 2003).

The terminology of the low-cost adsorbents is still not clearly described for the present. An adsorbent which has a high adsorption capacity and can be prepared cheaply may be considered as a low-cost adsorbent. There are some low-cost adsorbents have been utilized for the removal of heavy metal ions such as waste slurry (Lee and Davis, 2001), Fly ash pellet (Papandreou A. et al., 2007), dried activated sludge (Khosravan & Lashkari, 2011), Cushew nut shells (Tangjuannk et al., 2009) and bagasse fly ash (Gupta V. K., et al., 2003).

### **1.3 Objectives and advantages of this study**

In the present study we intended to develop low-cost adsorbents based on DWTP sludge, sludge of paper industry and *Platanus* leaf. This study has three general objectives. The first is to clarify the key components, to determine adsorption mechanism and adsorption capacity of low cost adsorbent based on each adsorbent material. The second is to improve the adsorption efficiency by chemical modification using phosphoric acid on sludge of paper industry and citric acid on *Platanus* leaf. The third is to investigate the effect of agar encapsulation on *Platanus* leaf and to estimate the feasibility of these adsorbent materials for the removal of heavy metal ions based on a simple cost analysis.

The findings of this study can be considered as the basic information for the

further development of low-cost adsorbents based on solid waste materials. It was clear that DWTP sludge, paper sludge and *Platanus* leaf had a good capacity as an adsorbent to remove heavy metal ions such as cadmium and lead in water. Furthermore, the agar encapsulation on *Platanus* leaf also showed a good result and this method should be improved in the next study regarding an ease separation between adsorbent and solution in the adsorption process.

All adsorbent materials used in this study are available in many countries in the world including developing countries, therefore this valuable findings on the low-cost adsorbent materials are expected as one of the solutions for the water and wastewater treatment in the near future. For developing countries which are lack of technology and budget, these adsorbent materials may be applied to the removal of heavy metal ions in domestic or industrial wastewater treatment. Therefore, the problems of heavy metal contaminations could be minimized and solved significantly.

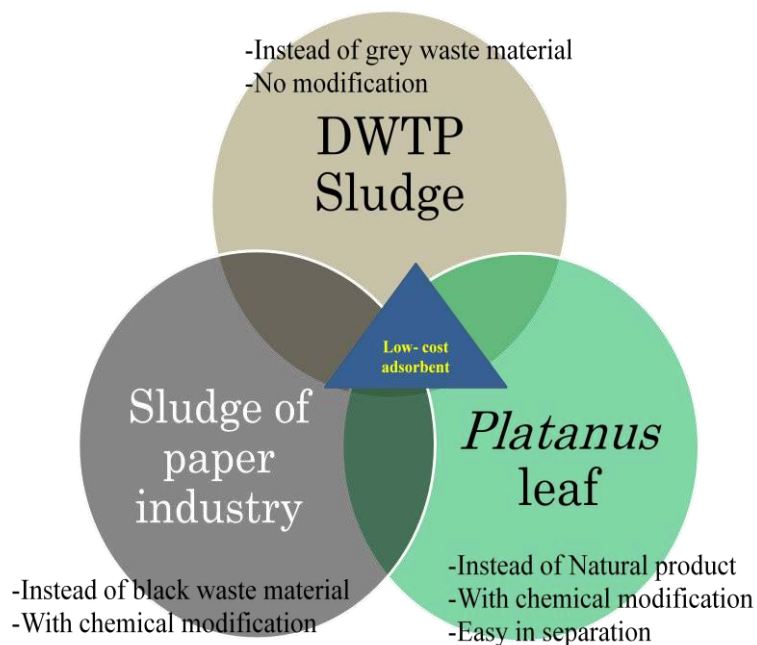
#### **1.4 Organization of the dissertation**

The dissertation entitled “Development of low-cost adsorbents based on solid waste materials to remove heavy metal ions in water” is divided into six chapters. In the present study, three different types of adsorbent materials were developed with or without modification. The structure of the dissertation is based on content and level of study from the simple to the integrated processes. In the first part, we focused on the simple preparation of a low-cost adsorbent, continued with chemical modification and then introduced the separation process by using agar.

Chapter 1, General Introduction, explains about the background of study, general purpose of study, advantage of study and adsorption process including a

description of low-cost adsorbent materials. In the Chapter 2 we determined the key components and adsorption capacity of a low cost adsorbent based on sludge of drinking water treatment plant to adsorb cadmium ion in water. In this chapter we also described the role of the key components of the adsorbent, humic acid and iron oxide in binding cadmium ion. Chapter 3 discusses about the process of chemical modification using phosphoric acid and also the mechanism of its modification and binding with cadmium and lead ions. It was clear that the binding capacity of the adsorbent materials by chemical modification increased significantly. In the Chapter 4, we describe about the modification with citric acid on the adsorbent and then also encapsulation using agar. Chapter 5 describes the consideration of the cost of the adsorbent materials compared to activated carbon used as common adsorbent. Chapter 6, General Conclusion, summarizes the results of each subtopic of the study and then concludes generally.

The correlation between all material of adsorbents employed in the present study is shown in Figure 1.1. We used DWTP sludge instead of grey waste material, paper sludge instead of black waste material and platanus leaf instead of natural product.



**Figure 1.1** Correlation between adsorbent materials

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## **CHAPTER 2**

# **Determination of Key Components and Adsorption Capacity of Low-Cost Adsorbent Based on Sludge of Drinking Water Treatment Plant to Remove Cadmium Ion in Water**

## **Abstract**

A low-cost adsorbent prepared from sludge of drinking water treatment plant (DWTP), solid waste by-product of sedimentation process in the DWTP, was studied for adsorption of cadmium ion in water. Some parameters such as mass of the adsorbent, pH of solution, and shaking time were investigated in the batch system in order to know the optimum condition and adsorption ability of the adsorbent. Artificial sludge was prepared by the similar process to the DWTP and the effect of humic acid extracted from the DWTP sludge was examined in order to clarify the mechanism and key components of the adsorption. This study clarified that humic acid and iron oxide were the key components of the adsorbent material for adsorption of cadmium ion in water. The adsorption capacity of the sludge from Miyamachi and Nishino DWTP based on the Langmuir isotherm adsorption model for Cd(II) was 5.3 and 9.2 mg/g, respectively. The founding of this study is important for further development of a low-cost adsorbent based on the sludge of a drinking water treatment plant in the near future.

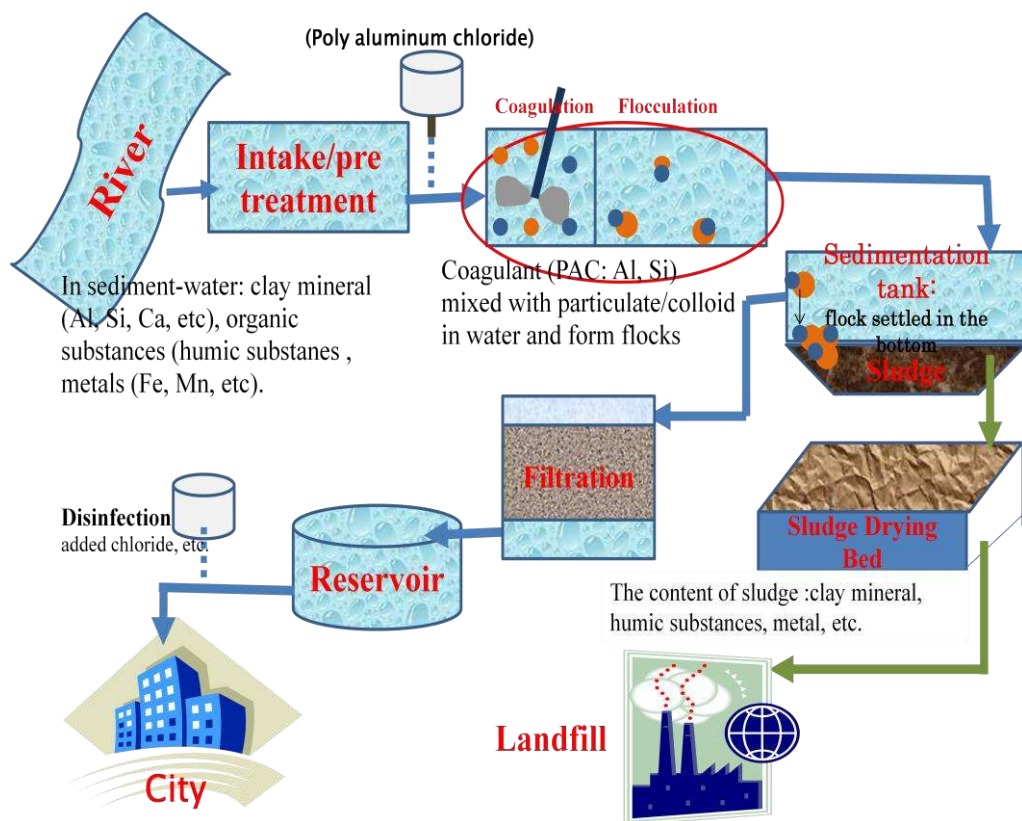
**Keywords:** Cadmium, humic acid, iron oxide, low cost adsorbent, sludge

## 2.1 Introduction

Sludge from DWTP is a sort of by-products in the precipitation process using coagulant, and it is produced daily in large quantities in most municipalities worldwide. The characteristic of the DWTP sludge is influenced by the quality of the source of drinking water, a type of coagulants and the system of treatment plant. The sludge of DWTP is directly disposed to landfill or is recently used as a soil improver (Ishikawa et al., 2007). The quantity of contaminants or hazardous substances in the DWTP sludge is relatively low, since the clean water resources are preferentially used for drinking water production. Therefore, the utilization of the DWTP sludge for an adsorbent material may be favorable. The studies on the reuse and recovery of the DWTP sludge for phosphorus removal have been conducted (Yang et al., 2006; Ishikawa et al., 2007; Razali et al., 2007; Babatunde et al., 2011), however, the study on DWTP sludge as a material of adsorbent for heavy metal ions has been still very limited. Aluminium, silica, iron and humic substances usually exist in the sludge of DWTP. Humic acid, one of the humic substances, can increase the ability of adsorbent if the surface of adsorbent was covered with humic substances to adsorb heavy metal ions such as copper and cadmium ions in water (Santoso 2006). Namasivayam and Ranganathan (1995) mentioned that iron hydroxide produced from waste of fertilizer industry was considered as a low cost adsorbent.

The development of adsorbent using the DWTP sludge is one of potential methods in terms of the cost, preparation of adsorbent, process of adsorption and removal efficiency (Hovsepian and Bonzongo, 2009). The reuse of the sludge will give some benefits, reducing the amount of solid waste from DWTP as well as producing a low cost adsorbent for the removal of heavy metal ions.

The purpose of this study was to investigate the adsorption capacity and to clarify the key components of DWTP sludge for adsorption of cadmium ion in water. The humic acid was extracted from the sludge according to the method of International Humic Substances Society (IHSS) (Stenven 1994) (Fig. 2.3) and several artificial sludges were prepared by following the similar process in DWTP in order to determine the key components due to adsorption of cadmium ion in water. The flowchart of a common DWTP is shown in Fig. 2.1.



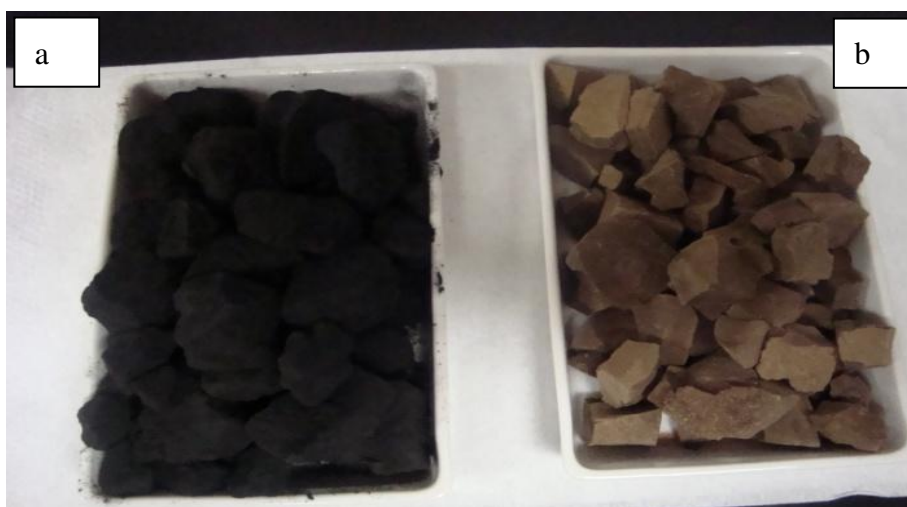
**Figure 2.1** Typical of Drinking Water Treatment Plant

## 2.2 Materials and methods

### 2.2.1 Preparation of adsorbent and stock solutions

Adsorbents were prepared using sludges taken from Miyamachi and Nishino DWTPs in Sapporo city, Hokkaido, Japan (Figure 2.2). Both sludges were collected from a sludge drying bed, a part of the processes in the DWTP to dry the sludge generated from the sedimentation tank, before the disposal to a landfill. Poly aluminum chloride (PAC) is used as a coagulant in Miyamachi and Nishino DWTP. Especially, Nishino DWTP utilizes activated carbon to adsorb metal ions and odor compounds in the raw water so that the color of the sludge from the DWTP is black, which is different from the color of the common sludge.

The sludge was washed with distilled water and dried at 100°C for 24 hours. After cooling it at room temperature, the sludge was crushed into a powder form and then sifted with a 1 mm sieve. The powdery sludge was used as the adsorbent to adsorb cadmium ion in water.



**Figure 2.2** Sludge of DWTP (a) Nishino and (b) Miyamachi

The stock solution of cadmium ion ( $\text{Cd}^{2+}$ ) was prepared with  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  of WAKO Pure Chemical Co (Osaka, Japan). The standard solutions for analysis of  $\text{Cd}^{2+}$  with an atomic adsorption spectrophotometer (AAS HITACHI A-2000) were prepared using a pure standards solution of WAKO Pure Chemical Co (Osaka, Japan).

### **2.2.2 Artificial sludge**

Several artificial sludges were prepared by the following process. Kaolin, a white clay mineral, was used as a basic material of the sludge and it was mixed with other components such as  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$  and humic acids. Aluminium sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ) was employed as a coagulant instead of PAC used in the real drinking water treatment plant in order to form a flock of kaolin. In order to determine the key components of the adsorbent for adsorption of cadmium ion in water, several artificial sludges were prepared by using different kinds and amounts of substances. The amount of each substance was decided according to the composition of the raw waters of DWTPs. Ten g of kaolin, 10 g of  $\text{Al}_2(\text{SO}_4)_3$ , 0.2 mg of  $\text{Fe}^{3+}$ , 0.05 mg of  $\text{Mn}^{2+}$  and 1.2 to 2.4 mg of humic acids were added in 1000 ml of distilled water. A jar test was employed on 150 rpm for 5 minutes and then followed by 40 rpm for 10 minutes. Then the mixed solution was rested around 30 minutes until the sludge was precipitated completely. The sludge was separated from the solution by decantation, dried on  $100^\circ\text{C}$  for 24 hours and then crushed into powder.



### **2.2.3 Characterization of adsorbent**

In order to determine the surface area and main components of sludge such as aluminum, silica and iron as a result of the addition of PAC, Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) (JEOL JSM-6360 LA, Japan) was employed. The amounts of carbon, hydrogen, nitrogen, sulfur, ash and oxygen in the sludge were investigated by using elemental analysis instrument (MICRO CORDER JM10, Yanaco, Japan). In order to identify the metals adsorbed in the sludge, Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (SPQ 6500 Seiko Instrument (SII)) was used according to the following procedure: 200 mg dried sludge was added to 3 ml of 16M HNO<sub>3</sub> and then heated at 120°C for 4 hours. After cooled down at room temperature, the solution was filtered using 0.45 µm of a membrane filter and then diluted to 50 ml with distilled water. This solution was then diluted 10, 20, and 50 times and analyzed using ICP-MS for the measurement of the total concentration of Al, As, Cu, Cr, Hg, Fe, Mn, Pb, Zn, Mg, Co and Cd.

### **2.2.4 Process of cadmium adsorption**

#### **2.2.4.1 Effect of mass of adsorbent**

In order to obtain the optimum adsorbent concentration corresponding to a maximum binding capacity, the adsorbent where mass was varied from 0.1 to 4.0 g was put into 50 ml of cadmium solution with different concentrations (10, 50 and 100 mg/l). After 24 hours of stirring, the solution was centrifuged on 4000 rpm for 10 minutes and then the concentration of Cd<sup>2+</sup> was measured using an atomic adsorption spectrophotometer (AAS HITACHI A-2000).

#### **2.2.4.2 Effect of pH**

The effect of pH on the adsorption of Cd(II) was investigated by using the solution where pH was in the range 2 to 10. Acetic acid, HNO<sub>3</sub> and NaOH were utilized to adjust the desired pH values of the sample solutions. The initial Cd<sup>2+</sup> solutions at 10, 50 and 100 mg/l were prepared to investigate the influence of pH on different concentrations of Cd(II) solutions. The duration of the adsorption process for the adsorbents generated from sludge taken from Miyamachi and Nishino DWTPs was 24 hours with a constant stirring rate.

#### **2.2.4.3 Effect of shaking time**

Shaking time is one of the important factors in the process of adsorption to achieve the equilibrium. In order to know the influence of shaking time on adsorption capacity, the study was conducted in various shaking time from 30 to 1440 minutes. A shaker (EYELA CUTE MIXER CM-1000) was employed at 1000 rpm. The phase in which the adsorption capacity becomes stable was considered as an optimum shaking time and implemented for further experiments.

### **2.3 Results and discussion**

#### **2.3.1 Properties of adsorbent**

The results of the elemental analysis are shown in Table 2.1. The results showed that the sludge from Nishino DWTP contained higher amount of carbon (42%) than that of the sludge from Miyamachi (9%). The high amount of carbon in Nishino sludge was due to the addition of activated carbon in the process of drinking water treatment plant.

**Table 2.1** Elemental analysis of the sludge from Miyamachi and Nishino DWTP.

Element (% w/w)	Sludge	
	Miyamachi DWTP	Nishino DWTP
C	8.81	42.4
H	2.96	2.42
O	26.3	19.8
N	0.48	0.3
S	0.49	0.29
Ash	61.4	35.1

According to the analysis using ICP-MS as shown in Table 2.2, Cd concentrations in both sludges were below the detection limit of the ICP-MS. The other heavy metals such as Hg and As were very low and less than the environmental standard of soil in Japan which are 0.5 mg/kg, and 15 mg/kg in soil for agricultural land.

The photograph of scanning electron microscopy of both sludges and activated carbon shown in Fig. 2.4 reveals the surface texture and porosity of these samples. The surface structure of sludge of Nishino was similar to that of activated carbon because the Nishino drinking water treatment plant used activated carbon in their treatment plant. The availability of the pores and internal surface is requisite for an effective adsorbent to remove heavy metal ions in water (Rao et al., 2006).

The surface area of sludge of Miyamachi and Nishino determined by Brunauer-Emmet-Teller (BET) instrument (BELSORP-mini, BEL Japan INC, Osaka Japan) was 50 and 413 m<sup>2</sup>g<sup>-1</sup>, respectively. The large surface area of Nishino sludge was due to the addition of activated carbon in Nishino DWTP.

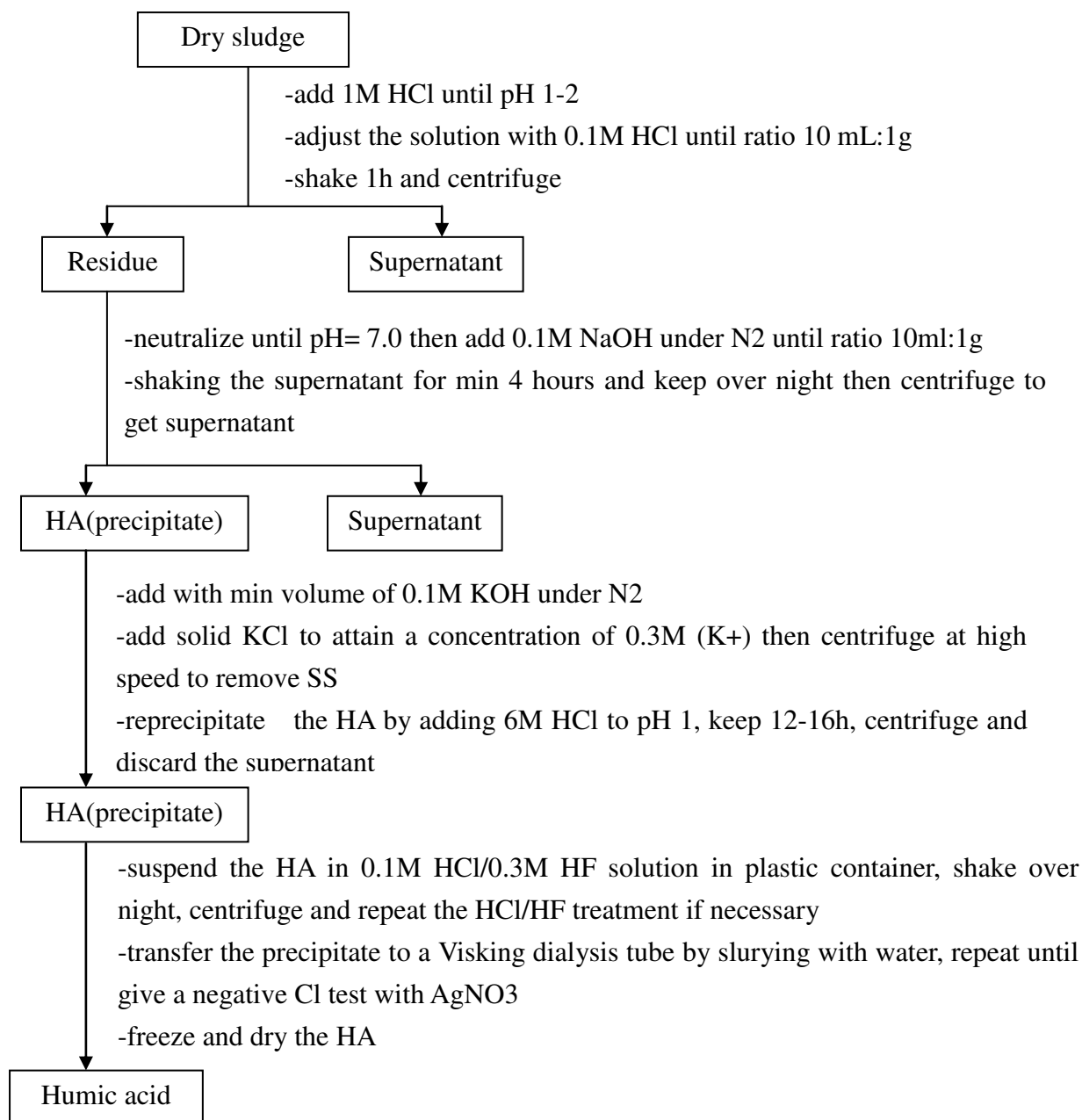
**Table 2.2** The concentration of metals in the sludge.

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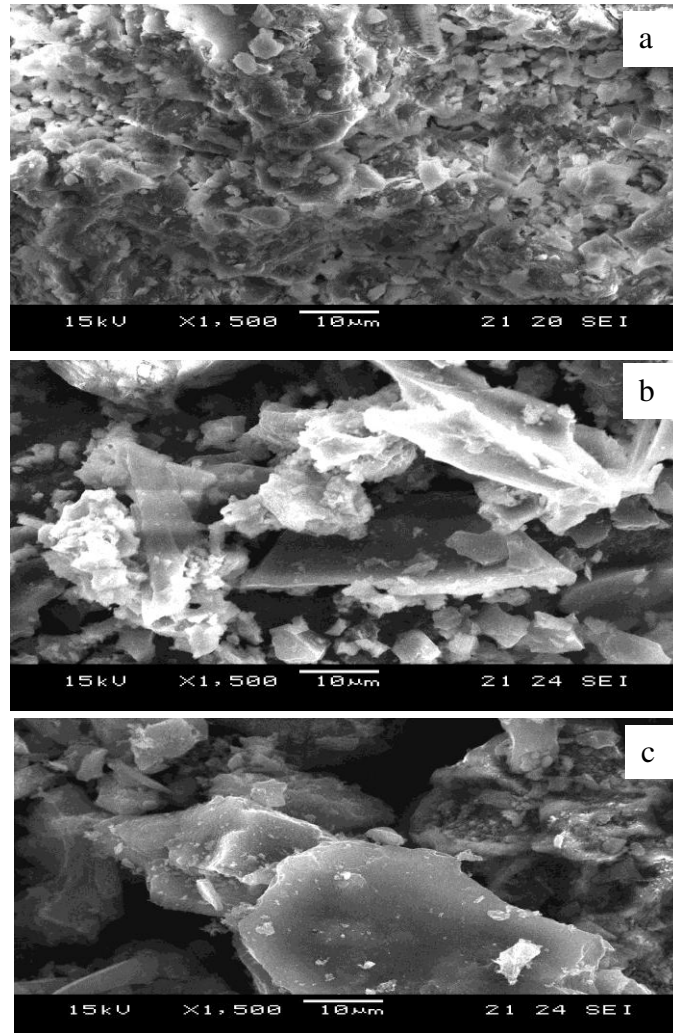
<b>Parameter</b>	<b>Unit</b>	<b>Sludge of Miyamachi DWTP</b>	<b>Sludge of Nishino DWTP</b>
pH		5.6	5.6
Al	mg/kg	63600	53250
As	mg/kg	8.89	0.76
Cd	mg/kg	nd	nd
Co	mg/kg	6.20	4.83
Cr	mg/kg	nd	nd
Cu	mg/kg	110	13.6
Fe	mg/kg	17450	11475
Hg	mg/kg	nd	nd
Mg	mg/kg	1775	2342
Mn	mg/kg	1176	1407
Pb	mg/kg	nd	nd
Zn	mg/kg	178	156

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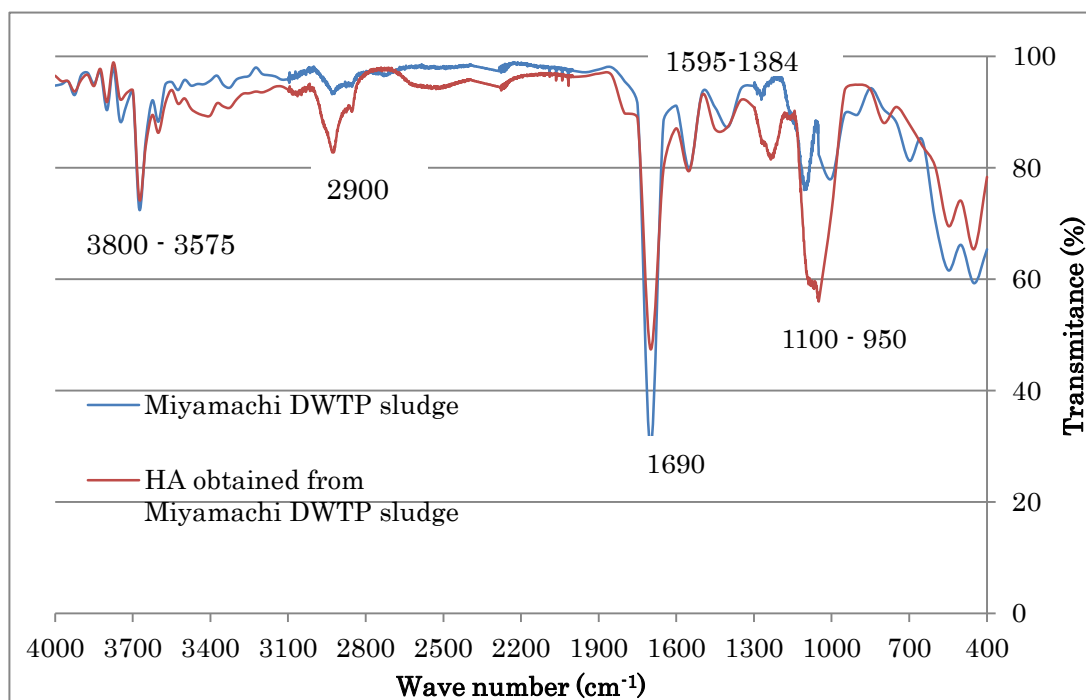
nd: under the detection limit of instrument



**Figure 2.3** Purification of humic acid from the DWTP sludge



**Figure 2.4** SEM photographs of adsorbents prepared from Miyamachi DWTP sludge (a), Nishino DWTP sludge (b) and activated carbon (c).



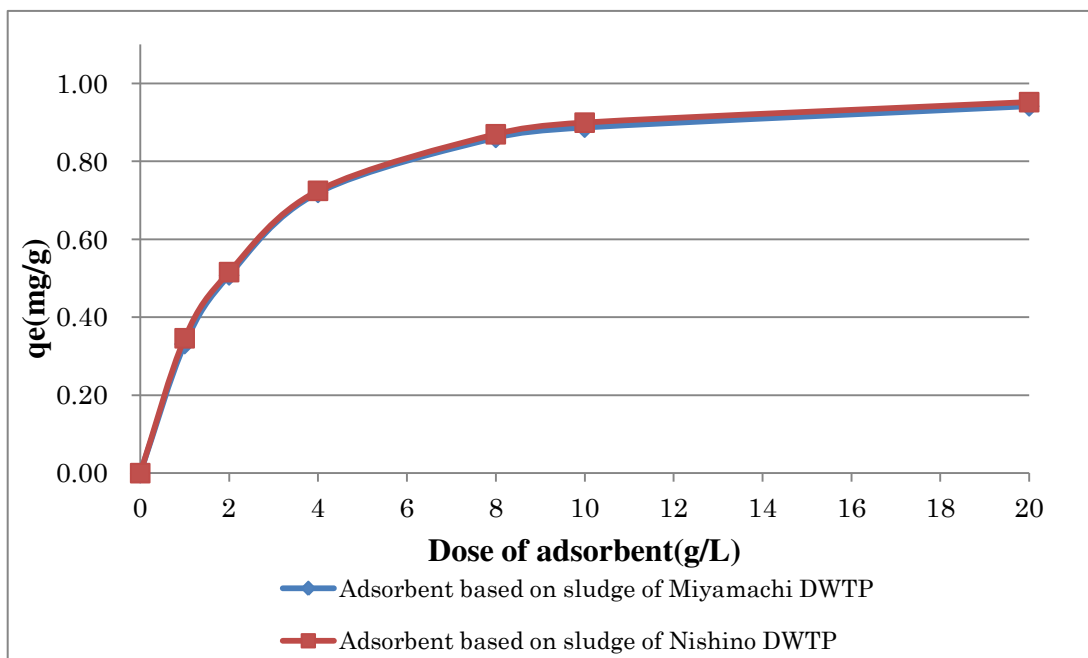
**Figure 2.5** FT-IR spectra of adsorbent (sludge from Miyamachi DWTP). HA represents humic acid.

Fig. 2.5 shows FT-IR spectra of the adsorbent based on the sludge of Miyamachi DWTP. The FT-IR spectrum showed some absorption peaks, indicating the complex nature of the adsorbent material. It was clear that the adsorbents have strong bands at 3800-3575  $\text{cm}^{-1}$  indicating  $-\text{OH}$  in the carboxyl group (Choi and Yun, 2006), the bands appearing at 1384-1595  $\text{cm}^{-1}$  indicated the formation of oxygen functional groups like a highly conjugated  $\text{C}=\text{O}$  stretching in carboxylic groups (Rao et al., 2006). The band at around 1690  $\text{cm}^{-1}$  indicating  $\text{N}-\text{H}$  in the amine group and some absorption bands at around 950-1100  $\text{cm}^{-1}$  can be considered the presence of phosphonate group (Choi and Yun, 2006; Won et al., 2006). It was clearly shown in the figure of FTIR spectra that the absorption peak of humic acid obtained from the sludge of Miyamachi DWTP was

similar to the sludge of Miyamachi DWTP. This data proved that the functional groups in the adsorbents were strongly influenced by humic acid in the sludge.

### 2.3.2 Effect of dosage of the adsorbent on Cd(II) ion adsorption

Fig. 2.6 shows the adsorption capacity of adsorbents on cadmium ion in water in the different mass of the adsorbents. The adsorption capacity for cadmium ion increased with increasing of the adsorbent dose and gradually became almost constant over 10 g/L of adsorbent. The increase in the adsorption efficiency with increase in the adsorbent mass was due to the greater availability of the binding sites or surface area (Rao et al., 2006; Wang et al., 2009; Tangjuannk et al., 2009; Khosravan and Lashkari, 2011).



**Figure 2.6** Effect of adsorbent mass on adsorption of cadmium ion (the pH of solution was 6.0, shaking time 2 hours for 50 ml of 10 mg/l Cd(II)).

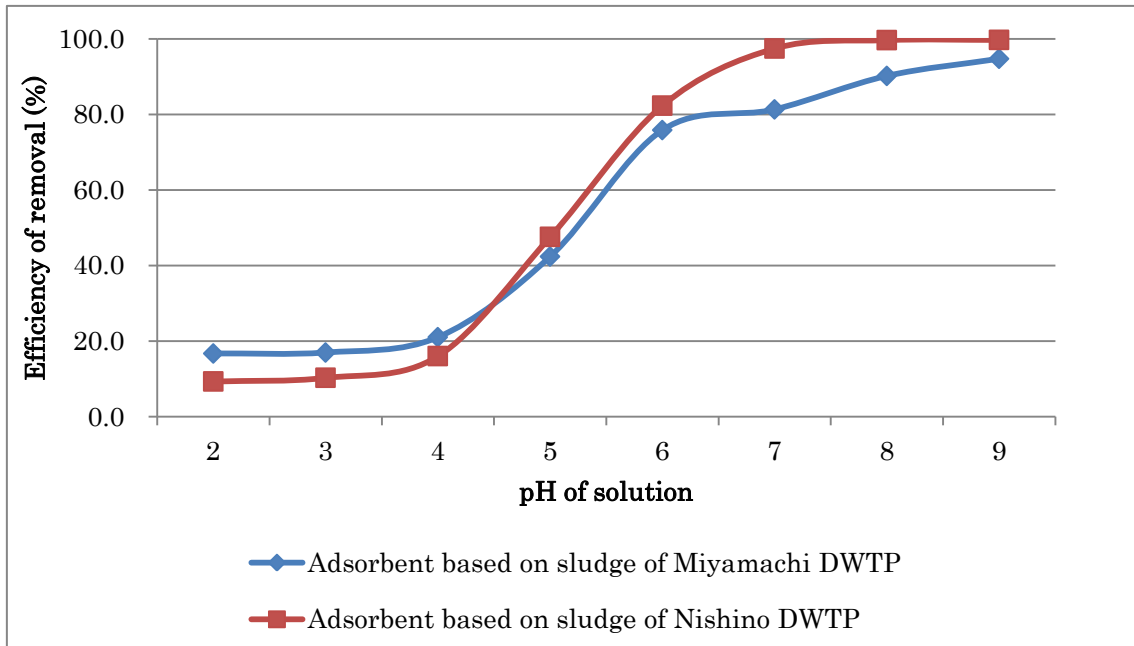


### 2.3.3 Effect of pH

The binding of cadmium ion with the surface functional groups of adsorbent strongly depended on the pH of solution. Fig. 2.7 shows the influence of pH on the adsorption of 10 mg/l cadmium ion in water, where both of the adsorbents showed the similar result. The removal efficiency of cadmium ion increased with pH of the solution because cadmium ion formed complex with some acidic functional groups in the adsorbent (Khalifa and Bagane, 2011). Adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and the distribution of metal species also depends on the pH of the solution. The removal efficiency of cadmium decreased with the decrease in pH, because protons compete with metal ion for the binding sites on the adsorbent surface as well as the protons decrease the negative charges by association of the functional group with protons. The increase in the removal of metal ions as pH increases can be explained on the basis of the decrease in  $H^+$  on the surface, which results in the less repulsion with metal ions (Namasivayam and Ranganathan, 1995; Kadirvelu and Namasivayam, 2003). Under pH 5, the surface of adsorbent was positively charged and adsorption of metal ion was low due to the electrostatic repulsion (Rao et al., 2006). In the highly acidic medium, the dissolution of Miyamachi and Nishino DWTP sludges occurred and consequently the active sites of the sludges decreased. Under this condition, the adsorbent surface is highly protonated, which is not favorable for the uptake of cadmium ion because of the electrostatic repulsion (Sing et al., 1998; Papandreou et al., 2007).

It is known that cadmium ion in the solution is precipitated above pH of about 8.5 (Lee and Davis, 2001; Ishikawa et al., 2007; Wang et al., 2009; Khosravan and

Lashkari, 2011). The recent study confirmed that cadmium ions were precipitated at the higher pH than 8. The ideal pH for adsorption of 10 mg/l of cadmium solution for both adsorbents was within the range of 6 to 8.

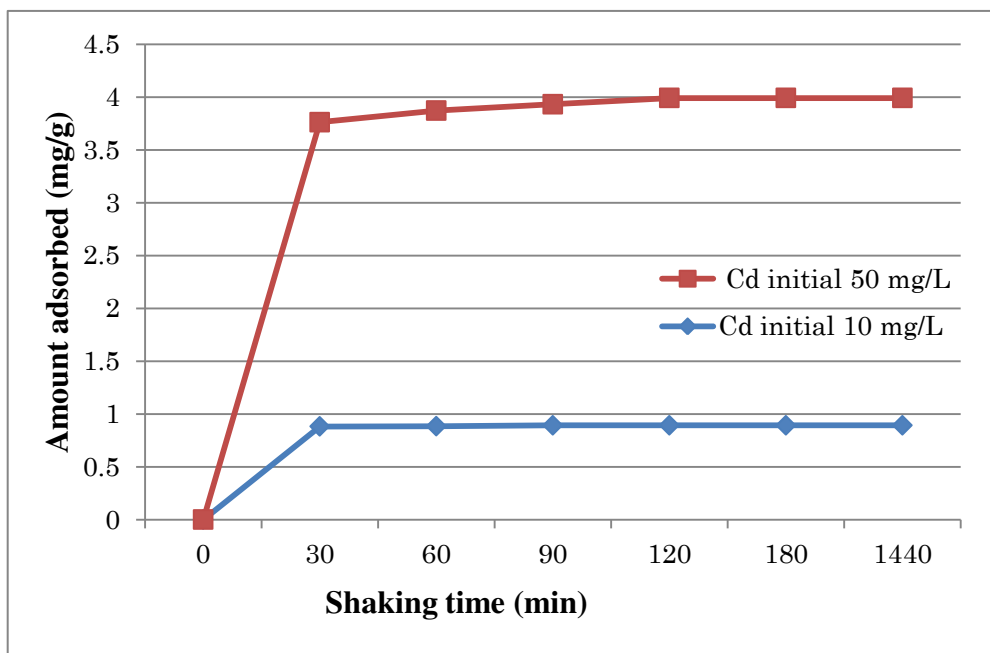


**Figure 2.7** The influence of pH of buffer solution on the Cd adsorption. Adsorbent mass was 0.5g and shaking was time 24 hours for 50 ml of 10 mg/l Cd(II).

### 2.3.4 Effect of shaking time

The capacity of adsorption for 10 and 50 mg/l of Cd(II) solution increased rapidly until around 30 minutes and then became constant after 24 hours of shaking. It was clear from the result of this study presented in Figure 2.8 that the required shaking time for the maximum adsorption of Cd<sup>2+</sup> ion by this adsorbent was dependent on the initial cadmium concentration. The removal efficiency of cadmium ion was higher for

the solution with low concentration of cadmium ion than the solution with high concentration of cadmium ion at the same time. This result is important because the time required to reach equilibrium is one of the considerations for the application of this adsorbents to economical wastewater treatment plant (Rao et al., 2006; Khalifa and Bagane, 2011).



**Figure 2.8** The influence of stirring time on the Cd adsorption. Mass of Sludge of Miyamachi DWTP was 0.5 g, pH of solution was 6, volume of Cd solution was 50 ml.

### 2.3.5 Adsorption isotherm

The Langmuir isotherm model was applied to obtain the equilibrium constant of adsorption by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L \cdot q_m} \quad (2.1)$$

where  $C_e$  is the equilibrium concentration (mg/l),  $q_e$  is the adsorbed amount of cadmium

at equilibrium (mg/g),  $q_m$  and  $K_L$  are the constants of Langmuir isotherm related to the adsorption capacity and energy of adsorption, respectively. From the equation, a plot of  $C_e/q_e$  versus  $C_e$  will be used to determine the values of  $q_m$  and  $K_L$  as the tangent of approximate straight line and its intercept of the vertical axis.

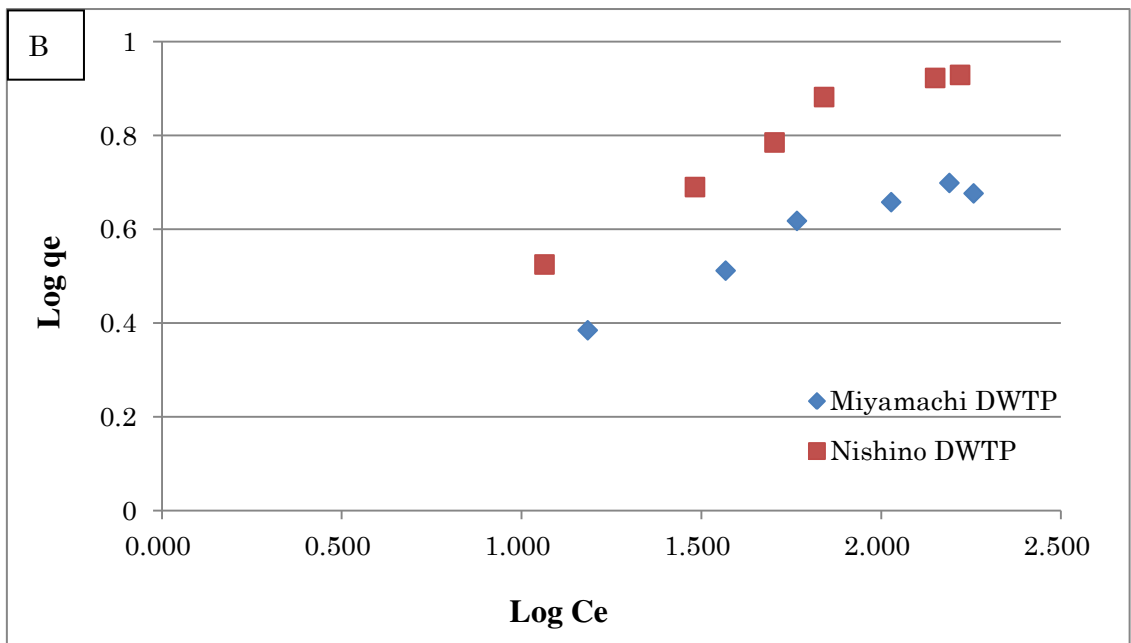
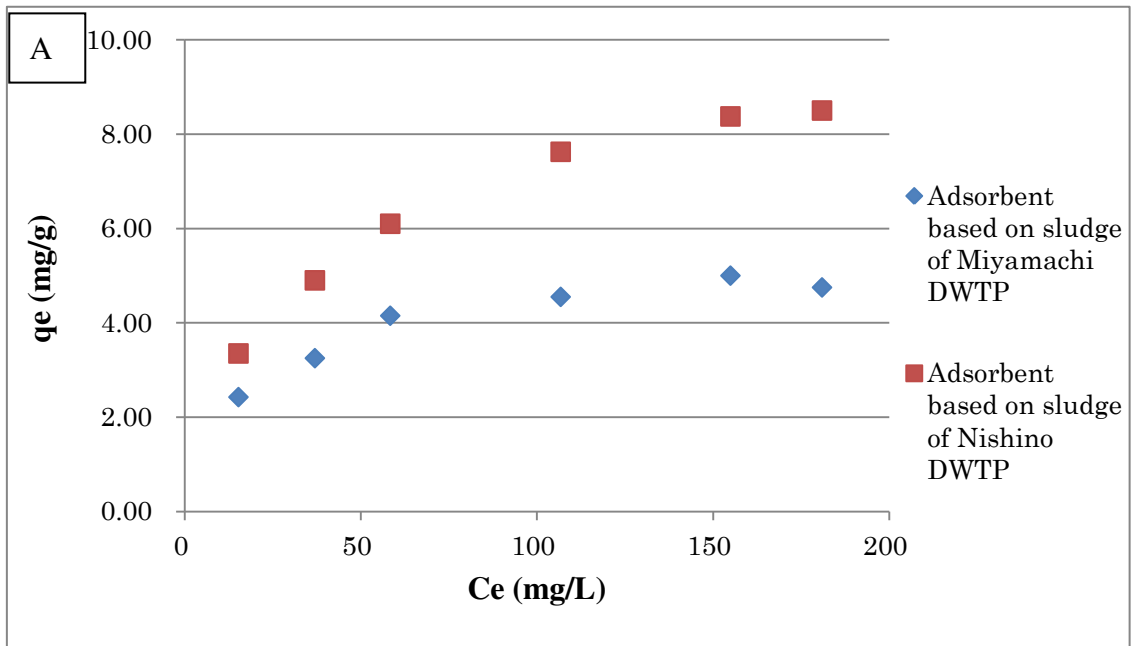
The Freundlich isotherm model was also used to evaluate the isotherm process in this study. The equation of this model is:

$$q_e = K_f C_e^{1/n} \quad (2.2)$$

where  $q_e$  is the amount of adsorbed (mg/g),  $C_e$  is the equilibrium concentration (mg/L) and  $K_f$  and  $n$  are constants. To determine the amount of  $K_f$  and  $n$ , plots between  $\log C_e$  and  $\log q_e$ .

$$\log (q_e) = \log (K_f) + 1/n \log (C_e) \quad (2.3)$$

The results of Langmuir and Freundlich adsorption isotherm models are shown in Figure 2.9 and Table 2.3.



**Figure 2.9** Adsorption isotherm of sludge from Miyamachi and Nishino DWTP based on (A) Langmuir and (B) Freundlich adsorption isotherm models.

**Table 2.3** Results from Langmuir and Freundlich model.

Sludge	Langmuir model			Freundlich model		
	$q_m$ (mg/g)	$K_L$ (l/mg)	$R^2$	$K_f$	$n$	$R^2$
Miyamachi DWTP	5.3	0.053	0.976	1.165	3.49	0.945
Nishino DWTP	9.2	0.048	0.971	1.451	2.779	0.960

The essential characteristics of the Langmuir isotherm can be expressed due to a dimensionless constant of the separation factor or equilibrium parameter,  $R_L$ , which is defined as:  $R_L=1/(1+K_L C_0)$ , (2.4)

where  $K_L$  is the Langmuir constant and  $C_0$  is the initial concentration of cadmium ion in the solution. The  $R_L$  value indicates the shape of the isotherm as follows:

$R_L > 1$       Unfavorable

$R_L = 1$       Linear

$0 < R_L < 1$       Favorable

$R_L = 0$       Irreversible

The  $R_L$  value between 0 and 1 is favorable adsorption (McKay et al., 1982). The  $R_L$  values on the concentrations of 10 and 200 mg/l of  $Cd^{2+}$  for Miyamachi and Nishino DWTP were 0.654 to 0.086 and 0.0676 to 0.094, respectively. It means that the adsorbent was favorable adsorption for cadmium ion. The comparison of this adsorbent with some materials can be seen in the Table 2.4. Compared to the other materials, this adsorbent is quite good and could be considered as a low-cost adsorbent.

**Table 2.4** Comparison of adsorption capacity of Cd(II) ion with the other materials.

Adsorbent	$q_m$ (mg/g)	pH	Stirring	Reference
			Time (min)	
Hematite	0.244	9.2	120	(Sing et al., 1998)
Fly ash pellets	4.88	6-7	4320	(Papandreou et al., 2007)
Waste slurry	15.7	6.3	Over night	(Lee and Davis, 2001)
Perlite	0.64	6.0	360	(Mathialagan&Virarag havan, 2002)
Cushew nut shells	14.3	6.5	90-120	(Tangjuannk et al., 2009)
Dried activated sludge	1.28	5.5	180	(Khosravan&Lashkari, 2011)
Bagasse fly ash	1.20	6.0	60	(Gupta et al., 2003)
Activated carbon from coconut coirpith	93.4	5.0-6.2	120	(Kadirvelu&Namasivayam , 2003)
Iron oxide coated sewage sludge	14.7	7.0	60	(Phuengprasop et al., 2011)
Sludge of Miyamachi DWTP	5.3	6.0	120	This study
Sludge of Nishino DWTP	9.2	6.0	120	This study

### 2.3.6 Adsorption kinetics

Adsorption kinetics is one of the important factors in the water and wastewater treatment because it reveals the adsorbate uptake rate, which in turn controls the residence time of adsorbate uptake at solid-liquid interface (Liu et al., 2012). In this study we used pseudo-first order model and pseudo-second order model. The pseudo-first order model can be expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2.5)$$

where  $q_e$  and  $q_t$  are the sorption capacities (mg/g) at equilibrium and at time  $t$ , respectively and  $k_1$  is the pseudo-first order rate constant (L/min). Upon the integration and applying the boundary condition of  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , a simplified linear from the rate equation can be obtained as the equation.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2.6)$$

A plot of  $\log (q_e - q_t)$  versus  $t$  will give a straight line and from the slope and the intercept can be determined the value of  $k_1$  and  $q_e$ .

The pseudo-second order can be described as the equation.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2.7)$$

where  $q_e$  and  $q_t$  are the sorption capacities (mg/g) at equilibrium and at time  $t$ , respectively and  $k_2$  is the pseudo-second order rate constant (g/mg.min).

A plot of  $t/q_t$  versus  $t$  will give a straight line and from the slope and the intercept can be calculated to give the value of  $k_2$  and  $q_e$ .

The results of pseudo-first order and pseudo-second order are shown in Table 2.5. The correlation coefficient ( $R^2$ ) for the pseudo-second order model indicated a



strong correlation, suggesting the adsorption of cadmium by the described stationary phase follows the pseudo-second order kinetic model and the rate limiting step may be chemical adsorption involving sharing or exchanging electrons, in addition adsorption follows Langmuir isotherm.

**Table 2.5** Adsorption kinetics of Miyamachi DWTP Sludge

Type of kinetics	Initial concentration of Cd(II)		
	10 mg/L	50 mg/L	100 mg/L
<b>Pseudo-first order:</b>			
$k_1$ (L/min)	0.080	0.028	0.030
$q_e$ (mg/g)	0.892	3.10	6.268
$R^2$	0.7846	0.7889	0.9477
<b>Pseudo-second order:</b>			
$k_2$ (g/mg.min)	7.00	0.283	0.021
$q_e$ (mg/g)	0.892	3.10	6.30
$R^2$	1	1	0.9998

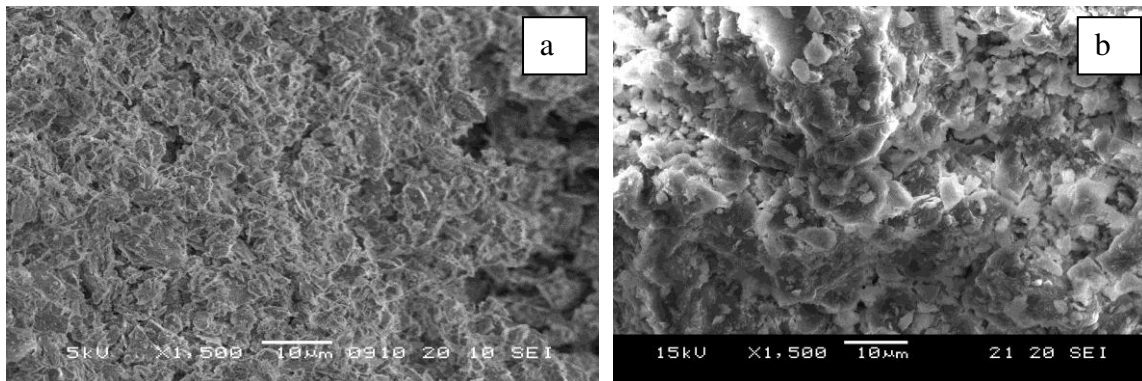
### 2.3.7 Key components of adsorbent

In order to know the mechanism of Cd(II) adsorption and determine key components of the adsorbent in the process of Cd<sup>2+</sup> adsorption, some kinds of artificial sludge were prepared according to the Miyamachi DWTP process. Visually, the characteristics of the artificial sludge were similar to the original sludge of DWTP. Fig. 2.10 shows the surface of artificial sludge based on SEM image where the structure of the surface area was similar to that from Miyamachi DWTP.

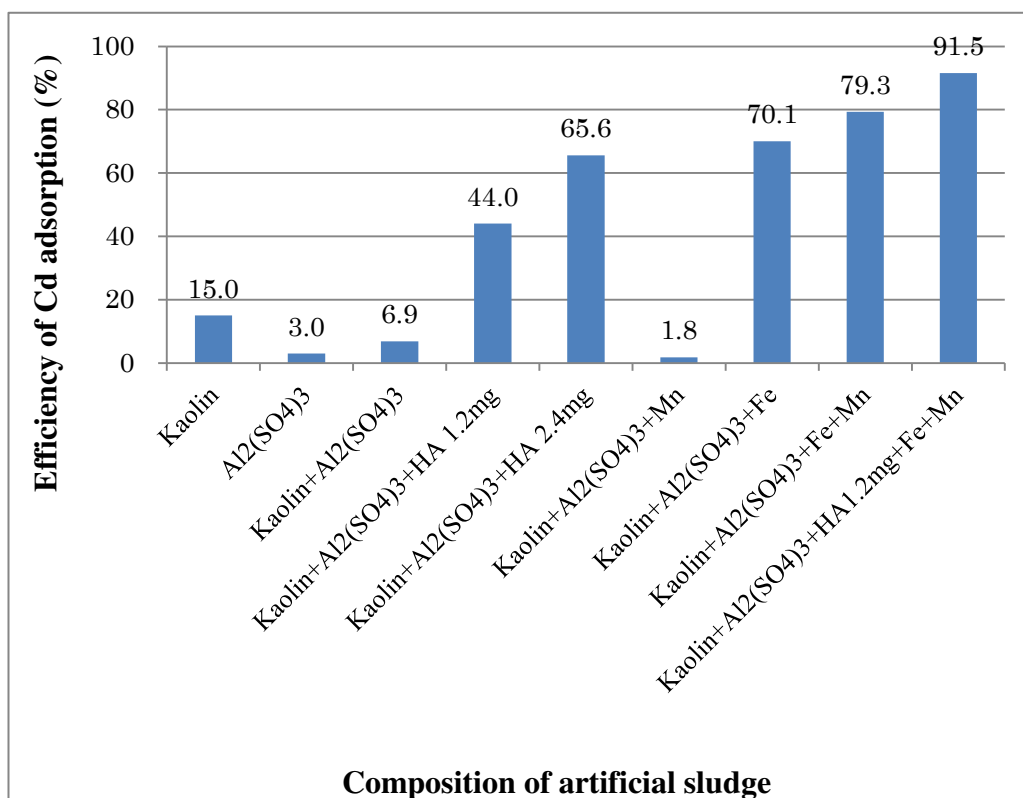
The Cd<sup>2+</sup> adsorption efficiency of the artificial sludge is shown in the Fig. 2.11. Kaolin and aluminium sulphate had a low ability to adsorb Cd<sup>2+</sup> with the removal efficiency of 15 and 3%, respectively. The artificial sludge made of kaolin and humic acid could remove Cd<sup>2+</sup> up to 44% and increased into 66% when amount of humic acid in the sludge was increased to 0.24 mg/g. The adsorption capacity of the artificial sludge with Fe<sup>3+</sup> was 70% and increased into 92% when humic acid was added in the sludge. This result suggested that humic acid and Fe<sup>3+</sup> have an important role in the process of Cd<sup>2+</sup> adsorption in the solution. In order to prove that humic acid and Fe<sup>3+</sup> were main components for Cd<sup>2+</sup> adsorption, these components in the sludge was removed and then the adsorption ability was investigated. The humic acid was extracted from the sludge of Miyamachi DWTP by the following procedure of IHSS and iron in the sludge was removed by washing with 0.1 M HCl. The amount of humic acid extracted from the sludge of Miyamachi DWTP was 0.54%. The adsorption capacity of Cd<sup>2+</sup> by using the sludge, without humic acids and the sludge without iron is shown in the Fig. 2.12.

Humic acids play an important role in the process of adsorption of Cd<sup>2+</sup> because it contains some functional groups (Arias et al., 2002; Khalfa and Bagane, 2011). In the presence of humic acid, the sludge might behave more like a chelating ion-exchanger

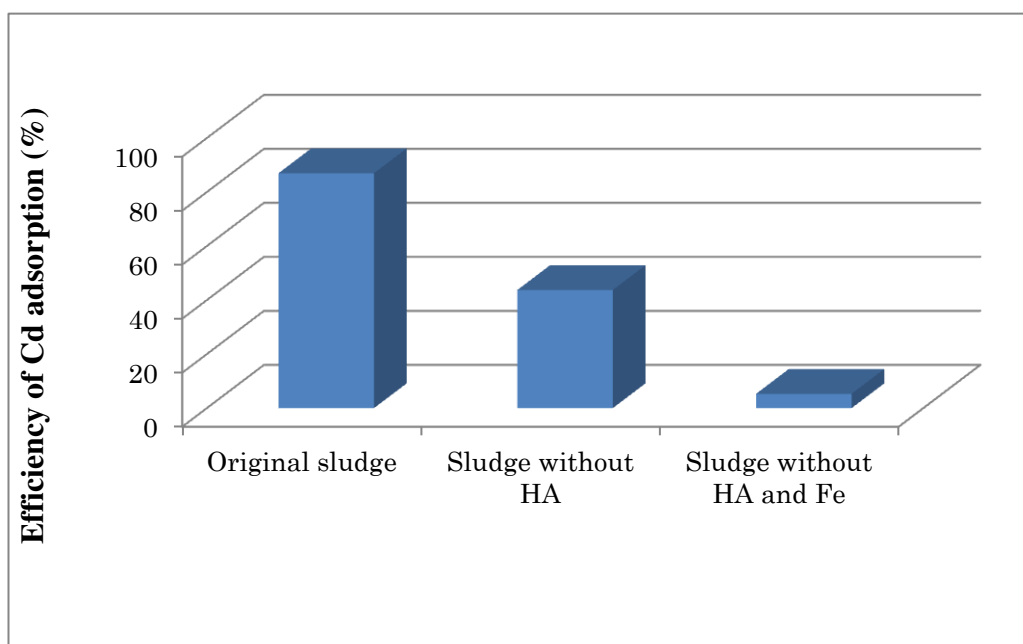
for heavy metal ions than as a simple inorganic ion exchanger (Hizal and Apak, 2010). The possible mechanism of humic substances involved in clay mineral are by Van der Waals forces, bonding by cation bridging, H-bonding, adsorption by association with hydrous oxide and adsorption on interlamellar spaces of clay minerals. The model structure of humic acid is shown in Fig. 2.13. The possibilities of binding of metal ion,  $M^{2+}$ , with humic substances in the sludge are by chelation between carboxyl and phenolic hydroxyl, by chelation between two carboxyl groups and by complexation with a carboxyl group as shown in the Fig. 2.14 (Manahan 2010). The possible mechanism of  $Cd^{2+}$  adsorption on Fe oxides is by ion exchange model (Gupta et al, 2003).



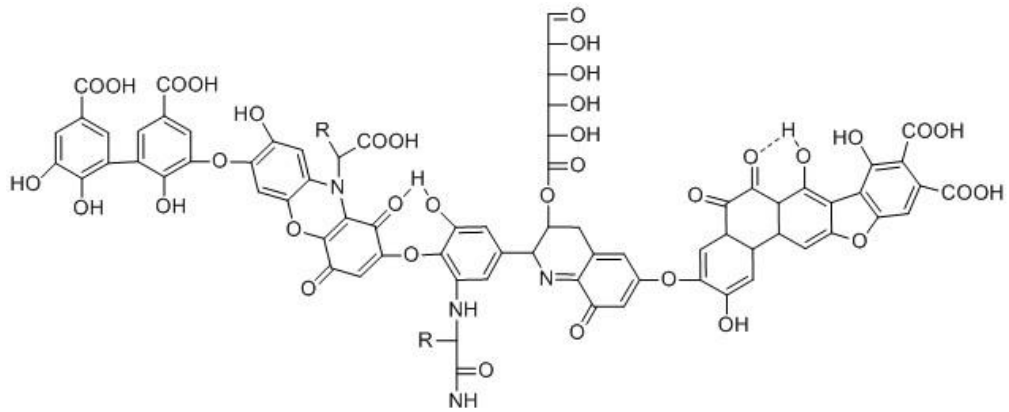
**Figure 2.10** SEM image of artificial sludge (a) and sludge of Miyamachi DWTP (b).



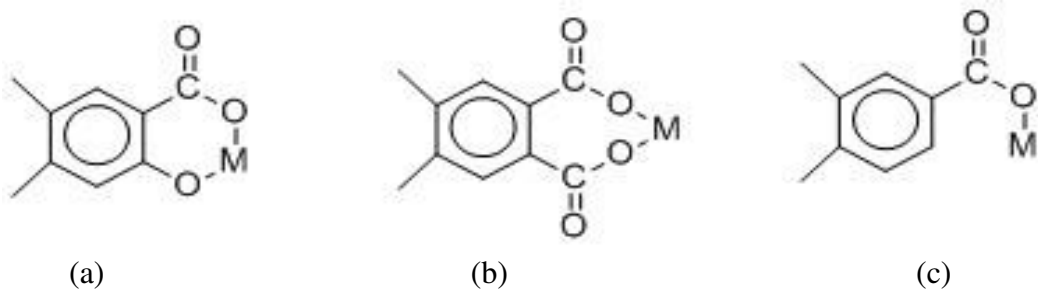
**Figure 2.11** Adsorption capacity of the artificial sludge for cadmium ion.



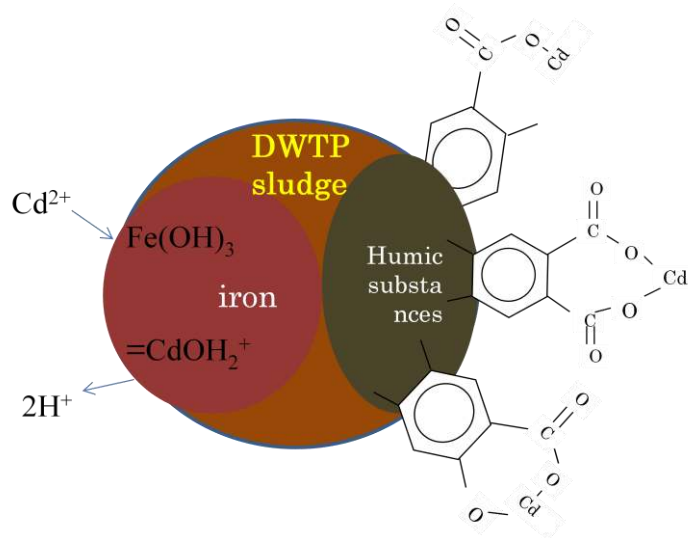
**Figure 2.12** Adsorption capacity of sludge from Miyamachi DWTP, sludge without humic acid and sludge without iron.



**Figure 2.13** model structure of humic acid (Stevenson, 1982)



**Figure 2.14** The binding of metal ion ( $M^{2+}$ ) with humic substances (a) by chelation between carboxyl and phenolic hydroxyl, (b) by chelation between two carboxyl groups and (c) by complexation with a carboxyl group



**Figure 2.15** The possible binding of Cd(II) by DWTP sludge

The illustration of binding of metal ion by DWTP sludge is shown in Fig. 2.15. In the presence of humic substance in the DWTP sludge, when Cd (II) is as Cd(OH)<sup>+</sup> species, the most possible mechanism is complexation with carboxyl group.

## 2.4 Conclusions

This study has proved that the sludge of DWTP could be employed as a raw material of a low-cost adsorbent to remove cadmium ion in the water. The presence of iron oxide and humic substances in the sludge were suggested to be an important factor for the process of cadmium adsorption. The adsorbent material was dependent on the pH of solution, where pH 6-8 was favorable for adsorption of cadmium ion. The concentration of heavy metal ions in the sludge of DWTP is usually very low, therefore utilization this material as a low-cost adsorbent is safe and efficient.

The DWTP sludge also had a high adsorption capacity to remove other heavy metal ions such as Pb(II) and Cr(VI). The application of the DWTP sludge as an adsorbent material in developing country such as Indonesia is recommended because almost all water treatment plant in over the world including Indonesia selects a good quality of raw water from river, lake, spring, deep well, etc.

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## **CHAPTER 3**

# **Phosphoric Acid Modification on Paper Sludge as a Low-Cost Adsorbent Material for Removal of Cadmium and Lead Ions in Water**

## Abstract

In the recent study, a low-cost adsorbent prepared from paper sludge, a solid waste of paper industry, was investigated to adsorb cadmium and lead ions in water. Some parameters such as pH of solution, shaking time and modification with phosphoric acid with the different impregnation ratio were investigated in order to know the optimum condition and adsorption ability of the adsorbent. Before modification with phosphoric acid, it was found that pH 6 to 8 of solution and 60 minutes of shaking time was a suitable condition for the adsorbent in adsorbing cadmium ion. However, for adsorption of lead ion, the adsorption capacity of the adsorbent was very low in the range of pH 2 to 5. The adsorption capacity of the adsorbent based on the sludge of paper industry for cadmium ion was 5.2 mg/g. After modification with phosphoric acid, its adsorption capacity for Cd(II) and Pb(II) determined by Langmuir isotherm model was 29 and 139 mg/g, respectively. The increase in the adsorption capacity after modification with phosphoric acid may be due to two possible reasons. First, after treatment with phosphoric acid, it was found from FTIR spectra that the adsorbent had phosphate functional group which contributed to the adsorption of Cd(II) and Pb(II) ions. Second, calcium in the paper sludge reacted with phosphoric acid to form calcium phosphate which also had a binding ability with some metal ions such as Cd(II) and Pb(II).

**Keywords:** Cadmium ion, low-cost adsorbent, paper sludge, chemical modification, phosphoric acid.

### **3.1 Introduction**

Recently, around 5 million tons of paper sludge is discharged annually as solid waste from paper industry in Japan (Prasetyo J., et al., 2011). The disposal of paper sludge to the landfill or the treatment by incineration is high cost and may cause other environmental problems. Application of the paper sludge as a raw material of adsorbent has multi advantages, reducing amount of solid waste and cost for treatment and also providing a low cost adsorbent for removal of heavy metals. Paper sludge and other organic waste materials from paper industry could be considered as a material of adsorbent due to their high carbon content and cellulose fibres proportion (Mendez A., et al., 2009). The adsorbent from paper sludge has the ability as an adsorbent for the removal of various kinds of heavy metal ions in water (C. Ochola and H. Moo-Young, 2004). However, the application of paper sludge as adsorbent for adsorption of heavy metal ions is still limited. In order to improve the adsorption ability of adsorbent, chemical modification by using phosphoric acid as an effective activated agent for some adsorbent materials was employed by some researchers (V. Fierro, et al, 2010 and Olowoyo, et al, 2012).

The purpose of this study was to investigate the ability of paper sludge as a raw material of adsorbent to adsorb cadmium and lead ions in water and also to investigate the effect of modification with phosphoric acid.

## **3.2 Materials and methods**

### **3.2.1 Preparation of adsorbent**

The eco-adsorbent used in this study was prepared using paper sludge, a solid waste of a paper industry. The paper sludge carbon was provided from Doh-Ei Paper Mfg. Co., Ltd. in Sapporo city, Japan, where paper is produced from the used paper as the main raw material. The paper sludge was produced during the paper production process. After dehydration and dryness of the paper sludge, it was treated at 950°C to form paper sludge carbon. The paper sludge carbon was washed with distilled water and dried at 100°C for 24 hours. After cooling it at room temperature, the paper sludge carbon was crushed into powder form and then sifted with a 1 mm sieve. The powdery paper sludge carbon was used as the adsorbent to adsorb cadmium ion from the water. The phosphoric acid modification was employed for the adsorbent. The impregnation ratio (R) for this modification was from 0.25 (0.25 g adsorbent was added to 1 g adsorbent) to 1.5. The mixed adsorbent and phosphoric acid then dried in oven and continued to be heated at 350°C for 15 minutes. After cooled in room temperature, the modified adsorbent was washed with distilled water until the pH of solution was around neutral, dried in oven for overnight and then crushed into powder form.

### **3.2.2 Characterization of adsorbent**

In order to obtain the surface area of adsorbent, Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS, JEOL JSM-6360 LA, Japan) was employed. Furthermore, the elemental analysis was done using elemental instrument (Micro Corder JM10, Yanaco, Japan) in order to determine the amount of C,

H, N, O, S and ash of adsorbent material. FT-IR Spectrometer (FT/IR-4100) and BET (BELSORP-mini, BEL Japan INC, Osaka Japan) were utilized in order to determine the functional groups, surface area and pore volume of adsorbent materials.

### **3.2.3 Process of adsorption**

Adsorption process in the present study was conducted by the batch system. Parameters such as mass of adsorbent, pH of the solution, stirring time and initial concentration of cadmium ion in the solution were investigated in order to know the ability and the optimum condition for adsorption using this adsorbent. In order to estimate the effect of mass of the adsorbent, 25 to 200 mg of adsorbent were added to 50 ml of cadmium solution and agitated at 1000 rpm for 2 hours using a shaker (EYELA CUTE MIXER CM-1000). The influence of pH on the adsorption of cadmium ion was investigated by using the solution of pH 2 to 8 and pH 2 to 5 for lead ion. Buffer solution, HNO<sub>3</sub> and NaOH were utilized to adjust the desired pHs of solution. Various stirring time from 15 to 1440 minutes was applied in order to know the influence of stirring time on the adsorption of cadmium ion. After equilibrium, the solution was centrifuged at 4000 rpm for 5 minutes using a centrifuge (IEC61010-2-020, KUBOTA, Japan) and then the concentration of cadmium ion in supernatant solution was determined using Flame Atomic Absorption Spectrophotometer (FAAS) (HITACHI A-2000, Japan).

### 3.3 Results and discussion

#### 3.3.1 Properties of adsorbent

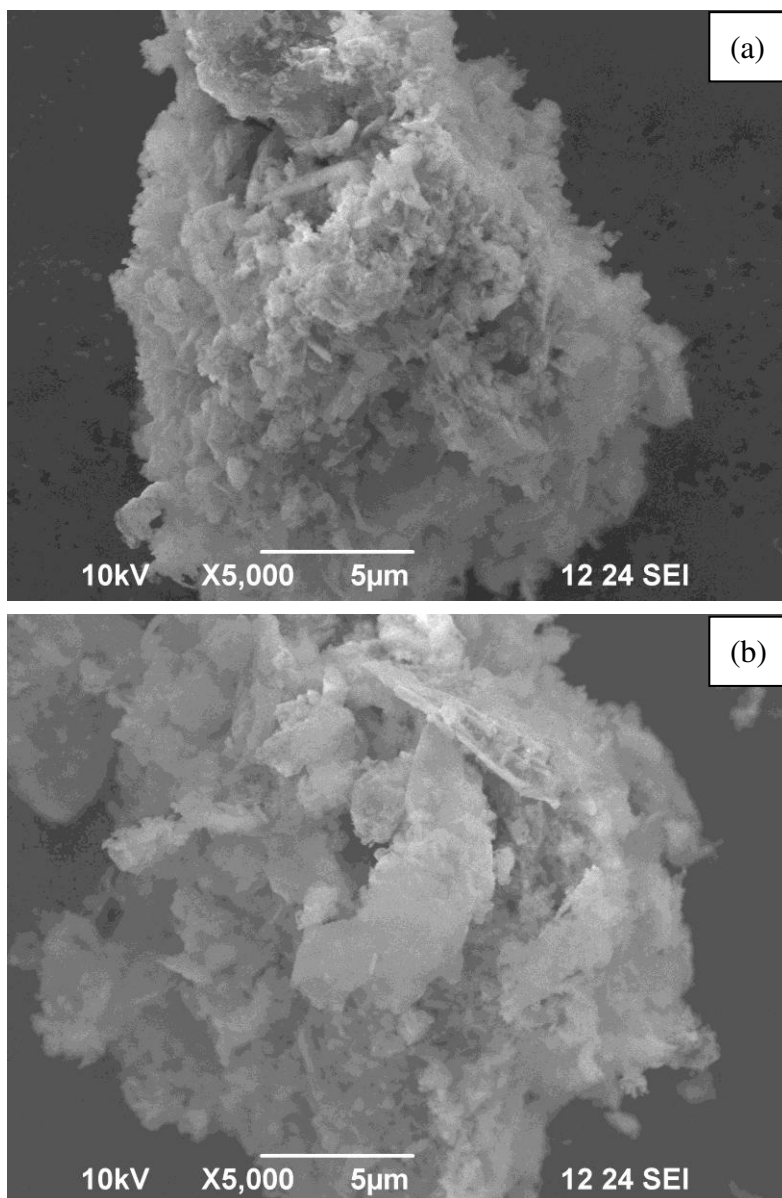
Based on the elemental analysis, the composition of main elements of paper sludge carbon were 19.4, 0.1, 16.3, 0.0, 0.0, and 64.2% for C, H, O, N, S, and ash, respectively. The IR spectra of the paper sludge carbon suggested the presence of some functional groups such as carboxyl and phenolic hydroxyl group. These functional groups might participate in the adsorption of cadmium ion.

Physicals and chemicals properties of the paper sludge carbon are shown in the Table 3.1. According to the result of SEM/EDX, silicate, calcium oxide and carbon were main elements of the paper sludge carbon and with 75.5 m<sup>2</sup>/g of surface area, this adsorbent may have a good performance in adsorbing cadmium ion in water. Fig. 3.1 shows the surface texture and porosity of this adsorbent captured using Analytical Scanning Electron Microscope (SEM) (JEOL JSM-6360 LA, Japan). These high porosity and large surface are essential for the high efficiency of adsorbent.

**Table 3.1** Characteristic of paper sludge

<b>Parameter</b>	<b>Value</b>
pH	10
Alkalinity	0.17
Surface area	50 m <sup>2</sup> /g
Porosity	0.85
Diameter	3.8 nm
Pore capacity	0.14 cm <sup>3</sup> /g
Water adsorbed	1.3 g/g
Density	400 kg/m <sup>3</sup>



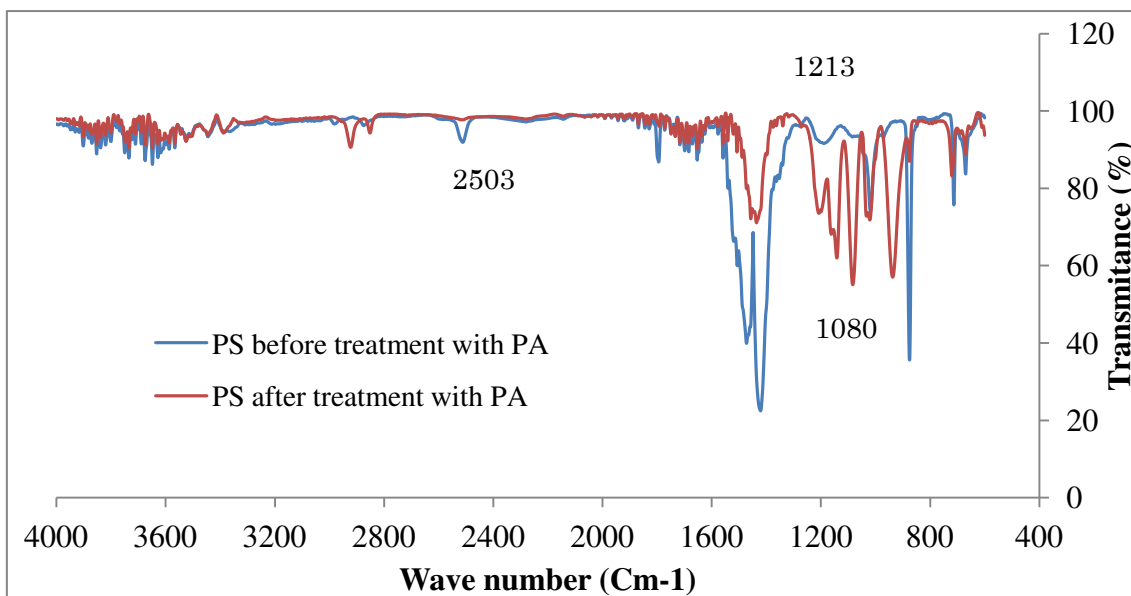


**Figure 3.1** SEM photograph of adsorbent based on sludge of paper industry (a) raw adsorbent, (b) modification with phosphoric acid

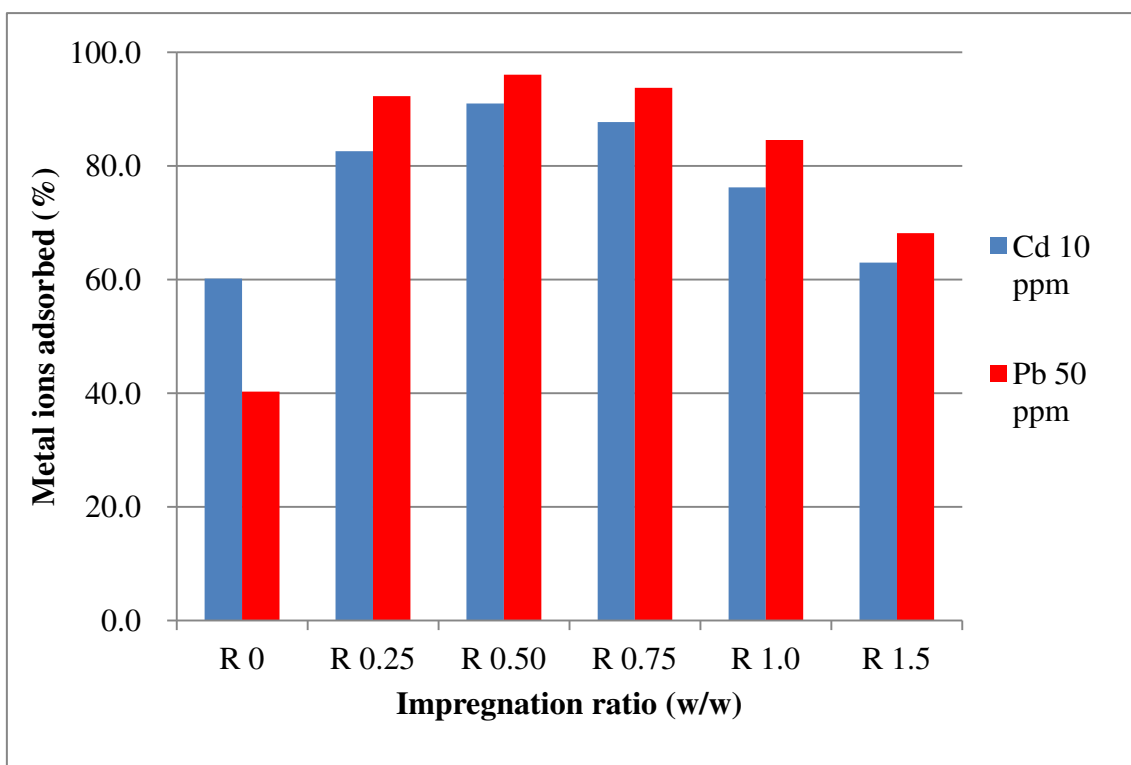
The SEM photograph of adsorbent before and after modification with phosphoric acid is shown in Figure 3.1. It can be seen that the surface of adsorbent after modification with phosphoric acid appears to be physically more porous compared to the raw adsorbent. Treatment with phosphoric acid on the adsorbent material resulted more pore on the surface of adsorbent. Based on the data obtained by BET analysis, the surface area and volume of pore of adsorbents before and after modification with citric acid are  $50 \text{ m}^2.\text{g}^{-1}$  and  $84 \text{ m}^2.\text{g}^{-1}$ , respectively. This data supports the SEM photograph that modification with phosphoric acid resulted more pore on the surface of adsorbent.

Figure 3.2 the FTIR spectra of adsorbent before and after modification with phosphoric acid shows the new peak at 1080 and 1213 on modified adsorbent indicated the presence of phosphate functional group as an effect modification with phosphoric acid. The phosphate functional contributed in the binding of metal ions in water such as Cd(II) and Pb(II), therefore, the adsorption capacity of modified adsorbent increased significantly.

Figure 3.3 shows the effect of impregnation ratio on the adsorbent for removal of cadmium and lead ions. It was clear that impregnation ratio (R) 0.5 was the favorable condition for the adsorbent to remove cadmium and lead ions in water.



**Figure 3.2** FTIR Spectra of adsorbent before and after modification with phosphoric acid



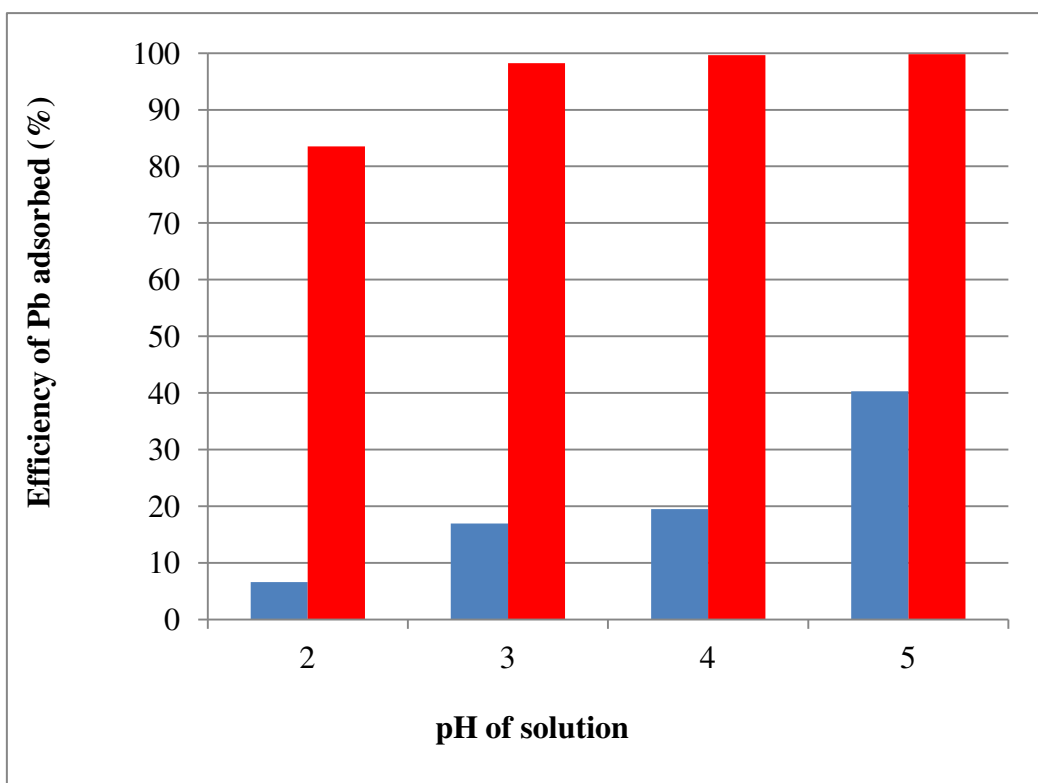
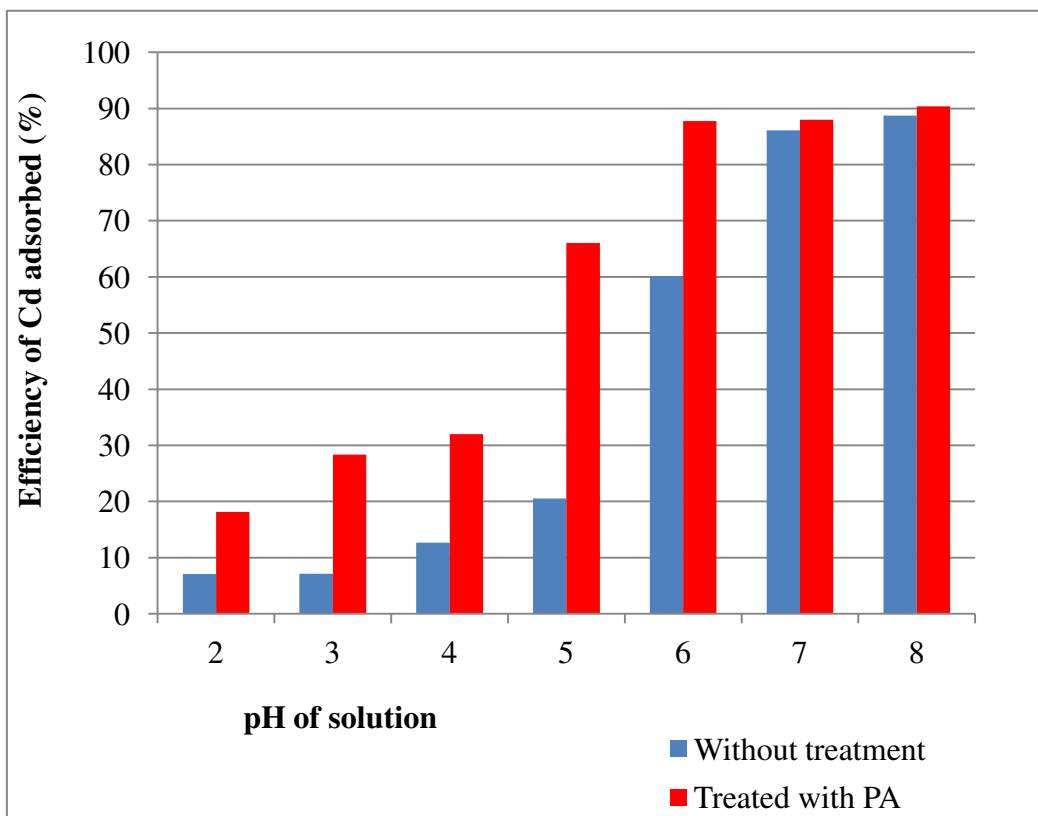
**Figure 3.3** Effect of impregnation ratio of adsorbent on the adsorption of cadmium and lead

### 3.3.2 Effect of pH

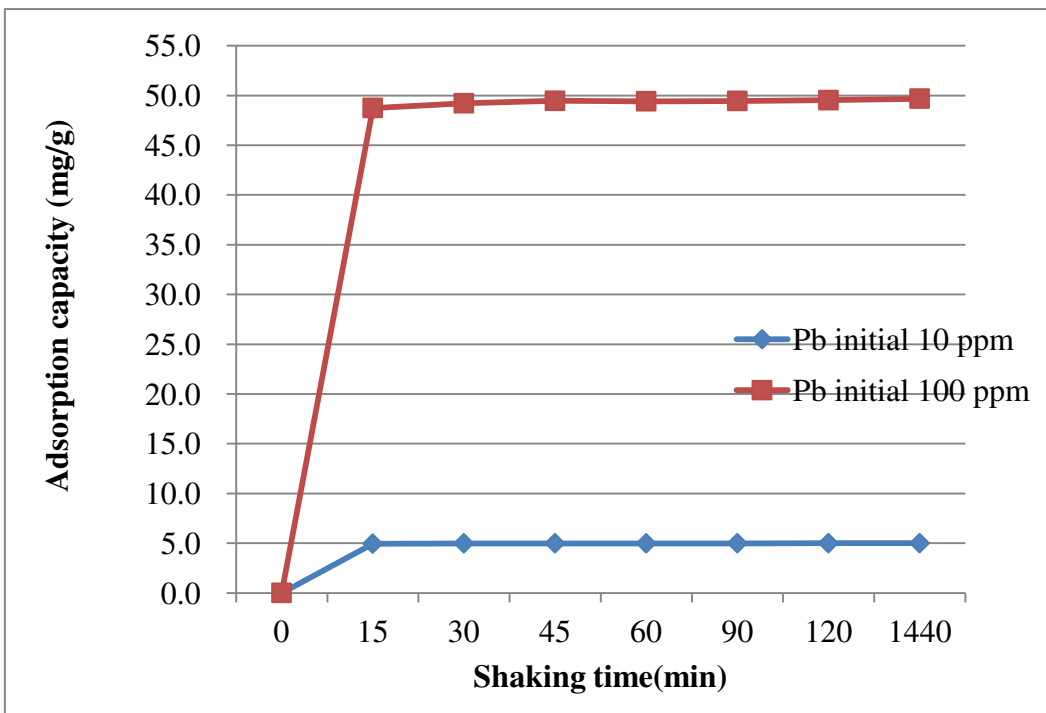
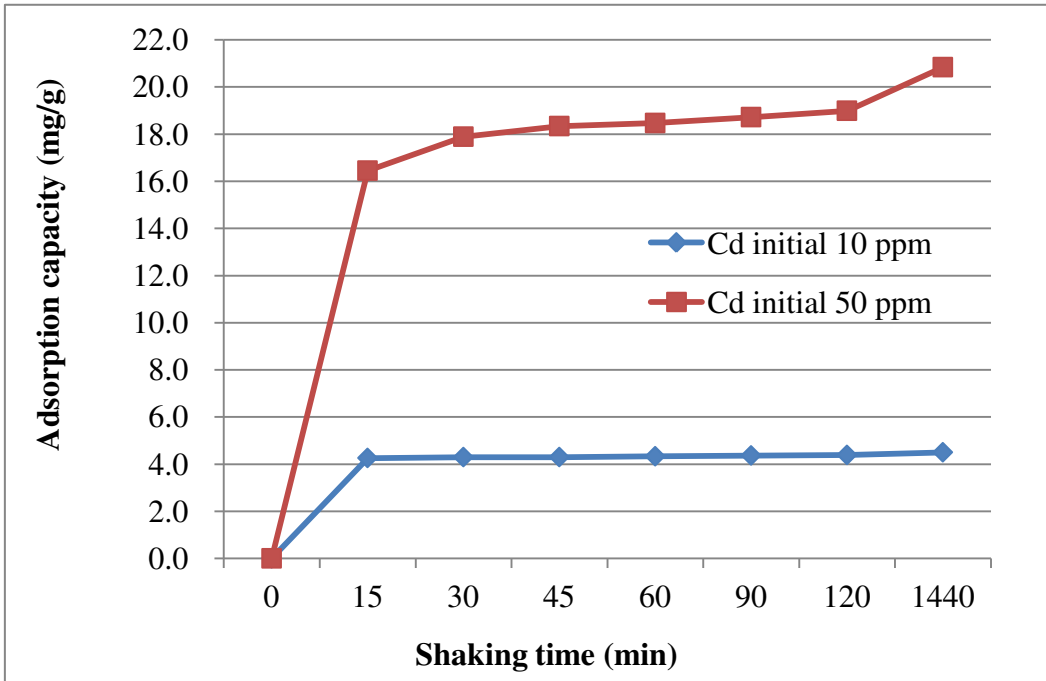
The removal efficiency of raw and modified adsorbents for cadmium and lead ions are shown in Figure. 3.4. The binding of Cd and Pb with surface functional groups strongly depended on the pH of solution. The percent removal of cadmium and lead ions increased with pH of the solution because cadmium and lead ions form complex with some functional groups in the adsorbent. The removal of metal cation at any pH was much greater than that by hydroxide precipitation. Adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and the distribution of metal species which distribution also depends on the pH of the solution. The removal efficiency of cadmium and lead decreased with the decrease of pH, because protons compete with metal ion for the adsorption sites on the adsorbent surface as well as the ion existing decrease of negative charge by association of the functional group with proton. The increase in the removal of metal ions as pH increase can be explained on the basis of the decrease in  $H^+$  on the surface, which results in less repulsion with adsorbing metal ions (C. Namasivayam and K. Ranganathan, 1995) and (Souag R., et al., 2011). Rao M. M, (2006) reported that the point of zero charge of adsorbent was 5.7, where under 5.7 of pH, the surface of adsorbent was positively charged and adsorption of metal ion was low due to the electrostatic repulsion. Another researcher mentioned that in the highly acidic medium, the dissolution of the adsorbent occurs to a consequent decrease in the active sites. In this condition, the adsorbent surface is highly protonated, which is not favorable for the uptake of cadmium and lead ions because of the electrostatic repulsion (Sing D. B., et al., 1998) and (Papandreou A., et al., 2007).

### **3.3.3 Effect of stirring time**

The effect of shaking time on the adsorption of cadmium ion is shown in Figure 3.5. The equilibrium adsorption for 10 mg/l of cadmium and lead ions were achieved after around 15 minute, however, higher initial concentration needs longer stirring time. This result is important because the equilibrium time is one of the considerations for the application of economical wastewater treatment plant (Rao M. M., et al., 2006).



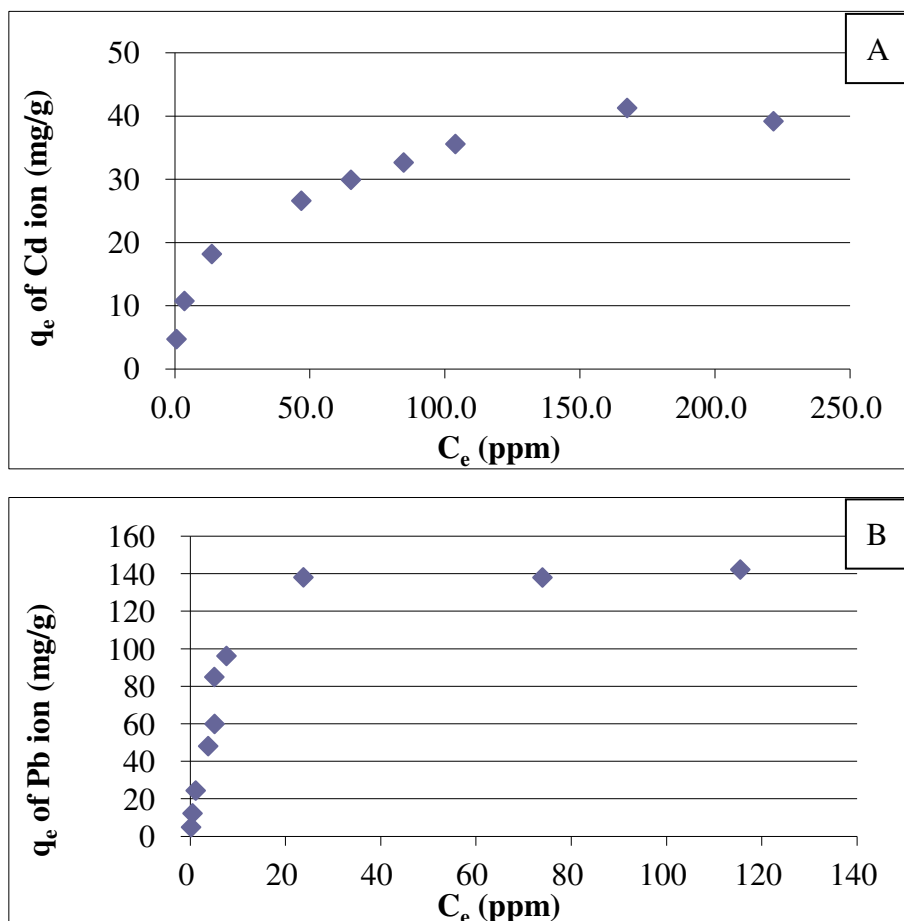
**Figure 3.4** Effect of pH on the adsorption of Cd and Pb



**Figure 3.5** Effect of stirring time on the adsorption of Cd and Pb

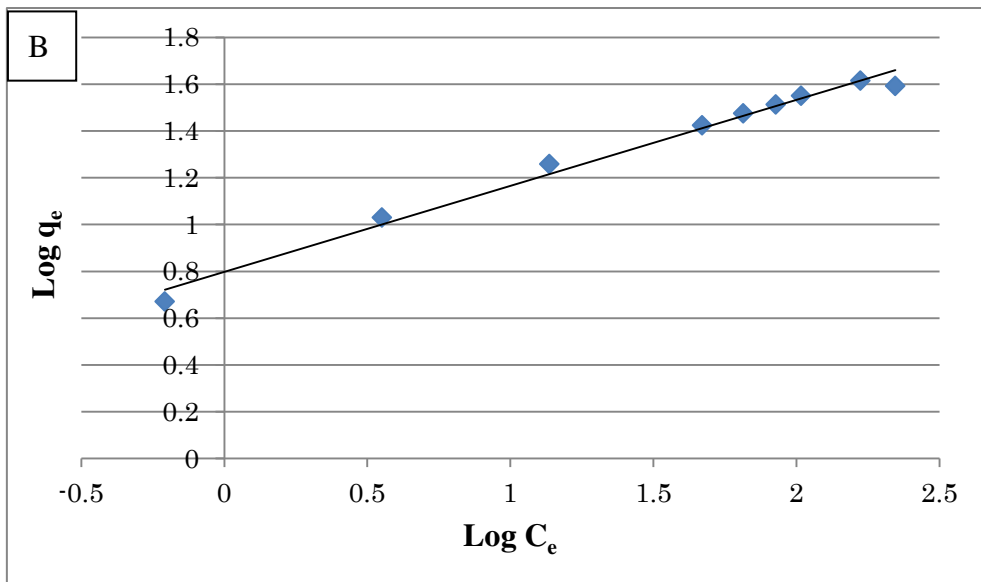
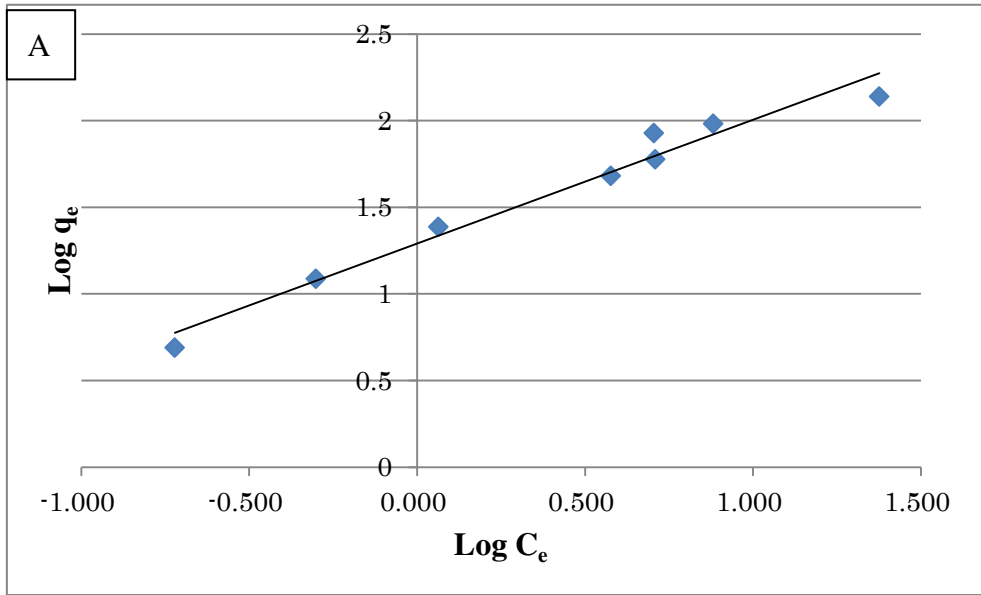
### 3.3.4 Adsorption isotherm

In order to determine the adsorption capacity of adsorbent, the Langmuir and Freundlich isotherm models were applied to the equilibrium constant of adsorption. The adsorption capacity of the modified adsorbent with phosphoric acid for removal of cadmium and lead ions is shown in Figure 3.6, Figure 3.7 and Table 3.2. Based on the result of Langmuir and Freundlich isotherm models, it was clear that sludge of paper industry followed the Langmuir isotherm model rather than Freundlich isotherm model.



**Figure 3.6** Langmuir isotherm model for adsorption of (A) Cd(II) and (B) Pb(II) in water





**Figure 3.7** Freundlich adsorption isotherm model for adsorption of (A) Cd(II) and (B) Pb(II) in water

**Table 3.2** Adsorption isotherm of the adsorbent based on Langmuir and Freundlich models.

Adsorbent	Langmuir model			Freundlich model		
	$q_m$ (mg/g)	$K_L$ (l/mg)	$R^2$	$K_f$	$n$	$R^2$
<b>Cd adsorption</b>	29.2	0.301	0.961	6.275	2.721	0.987
<b>Pb adsorption</b>	138.9	0.193	0.999	0.95	1.691	0.960

### 3.3.5 Adsorption kinetics

In this study we used adsorption kinetics pseudo-first order and pseudo-second order for the adsorption of cadmium and lead ions in water. The results of pseudo-first order and pseudo-second order are shown in Table 3.3. The correlation coefficient ( $R^2$ ) for the pseudo-second order model indicated a strong correlation, suggesting the adsorption of cadmium and lead ion followed the pseudo-second order kinetic model and the rate limiting step may be chemical adsorption.

**Table 3.3** Adsorption kinetics of modified paper sludge on Cd(II) and Pb(II) ions

Type of kinetics	Metal ions	
	Cd initial 50 ppm	Pb initial 100 ppm
<b>Pseudo-first order:</b>		
$k_1$ (L/min)	0.015	0.048
$q_e$ (mg/g)	20.84	49.68
$R^2$	0.5737	0.563
<b>Pseudo-second order:</b>		
$k_2$ (g/mg.min)	0.007	0.072
$q_e$ (mg/g)	20.92	49.75
$R^2$	0.9999	1

### 3.4 Conclusion

It was clear from the present study that sludge of paper industry had a good adsorption capacity to remove cadmium and lead ions in water. The increase of adsorption capacity after modification with phosphoric acid might be due to two possible reasons. First, after treatment with phosphoric acid, it was found from FTIR spectra that the adsorbent had phosphate functional group which contributed in the adsorption of Cd(II) and Pb(II) ions. Second, calcium in the paper sludge reacted with phosphoric acid performing calcium phosphate which also had a contribution in binding of some metal ions such as Cd(II) and Pb(II). Further study is needed to describe the detail mechanism of modification and also effect of some minerals in the solution which may influence the adsorption capacity of the adsorbent.

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## **CHAPTER 4**

### **Encapsulated Bio Adsorbent in Agar Based on Leaves of *Platanus* to Remove Cadmium Ion in Water**

## Abstract

A low-cost and environmentally friendly adsorbent was developed based on leaf of *platanus sp.* to adsorb cadmium ion in water. Adsorbent was modified with citric acid and then also encapsulated in agar for easy separation after process of adsorption. Parameters such as dose of adsorbents, stirring time, pH of solution and modification of the adsorbent with citric acid were investigated on the batch experiment in order to know the optimum condition of Cd (II) adsorption. Based on the Langmuir isotherm adsorption model, the adsorption capacity of cadmium ion for raw adsorbent, modified adsorbent with citric acid and encapsulated adsorbent were 3.69, 15.31 and 6.89 mg/g respectively. The high adsorption capacity after treatment with citric acid might be due to the increase of carboxylic content of the adsorbent surface and also the increase of surface area and pore volume of adsorbent. With this high adsorption capacity of cadmium ion and abundance of raw materials, this bio adsorbent could be considered as a low-cost adsorbent in the near future.

**Keywords:** Cadmium ion, citric acid, encapsulated adsorbent, low cost adsorbent, *platanus* leaf

#### 4.1 Introduction

Recently, the development of bio adsorbents based on leaves of some plants to adsorb heavy metal ions in the solution have been attracted some researchers due to the high removal capacity. *Pinus roxburghii* leaves were utilized to remove heavy metals from the industrial effluent (Tewari and Vivekanand, 2013). In order to increase the adsorption capacity, bio adsorbents were modified with some chemicals. Li *et al.*, (2013) reported that modification of *Imperata cylindrical* leaf powder using sulphuric acid and phosphoric acid resulted in the high adsorption capacity of nickel in the solution. Chemical modification on *Moringa oleifera* leaves powder using NaOH followed with citric acid was applied for the adsorption of Cd (II), Cu (II) and Ni (II) (Reddy *et al.*, 2012), .

In Japan and many other Northern Hemisphere countries, the *platanus* tree is abundant and often used as an ornamental and roadsides trees. The fall leaves of this tree is usually collected and disposed as garbage in Japan. The leaf of this tree has a potential as a low cost and green adsorbent materials, however, the study on the utilization of leaf of *platanus* tree as a material of adsorbents is still limited.

The purpose of this study was to investigate the adsorption capacity of the encapsulated adsorbent in agar based on leaf of *platanus* for the removal of cadmium ion in water. The powder of *platanus* leaf was treated with citric acid and then encapsulated in agar as a binder material for the easy separation of the adsorbent from solution after the process of adsorption of cadmium ion.

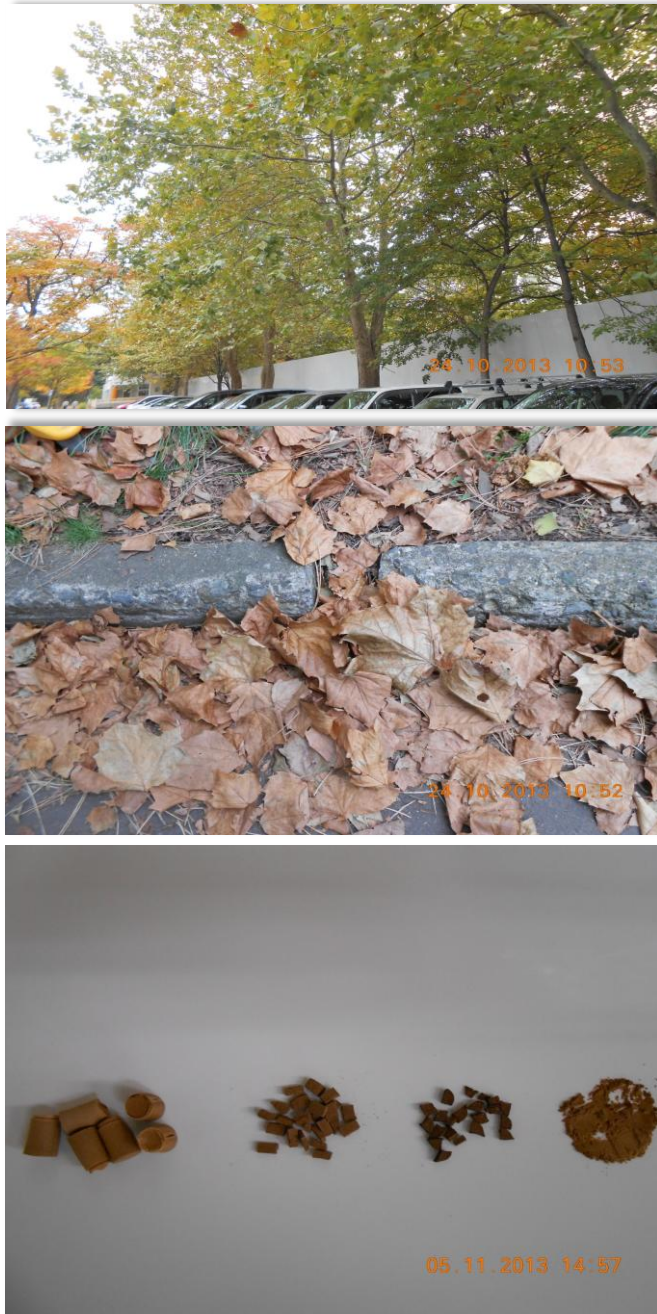


## 4.2 Materials and methods

### 4.2.1 Preparation of adsorbent and stock solution

Adsorbents were prepared based on leaf of *platanus* collected from Hokkaido University campus area. The dry leaf was washed with tap water continued with distilled water to remove dirt and other particulate matters, dried at the 80°C for 24 hours and then crushed into a powder form. In order to increase the adsorption capacity of adsorbent, 1.3 M of citric acid was utilized as activator agent with composition of 1 g (adsorbent) : 4 ml (citric acid) and then heated at 150°C for 30 minutes. The activated adsorbent then was encapsulated in agar with the ratio of 1 g (agar): 2.5 g (activated adsorbent). Figure 4.1 shows the image of Platanus tree, leaf of Platanus and Encapsulated Platanus in agar in different size.

The stock solution of cadmium ion ( $\text{Cd}^{2+}$ ) was prepared with  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  of WAKO Pure Chemical Co (Osaka, Japan). The standard solutions for analysis of  $\text{Cd}^{2+}$  with atomic adsorption spectrophotometer (AAS HITACHI A-2000) were prepared by using a pure standards solution of WAKO Pure Chemical Co (Osaka, Japan).



**Figure 4.1** Platanus leaf and encapsulated platanus

#### **4.2.2 Characterization of adsorbent**

In order to obtain the surface area of adsorbent, Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS, JEOL JSM-6360 LA, Japan) was employed. Furthermore, the elemental analysis was done using elemental instrument (MICRO CORDER JM10, Yanaco, Japan) in order to determine the amount of C, H, N, O, S and ash of adsorbent material. FT-IR Spectrometer (FT/IR-4100) and BET (BELSORP-mini, BEL Japan INC, Osaka Japan) were utilized in order to determine the functional groups, surface area and pore volume of adsorbent materials.

#### **4.2.3 Adsorption process**

Adsorption process in the present study was conducted by the batch system. Parameters such as mass of adsorbent, pH of the solution, stirring time and initial concentration of cadmium ion in the solution were investigated in order to know the ability and the optimum condition for adsorption using this adsorbent. In order to estimate the effect of mass of the adsorbent, 25 to 200 mg of adsorbent were added to 50 ml of cadmium solution and agitated at 1000 rpm for 2 hours using a shaker (EYELA CUTE MIXER CM-1000). The influence of pH on the adsorption of cadmium ion was investigated by using the solution of pH 2 to 8. Acetic buffer, HNO<sub>3</sub> and NaOH were utilized to adjust the desired pHs of solution. Various stirring time from 15 to 1440 minutes was applied in order to know the influence of stirring time on the adsorption of cadmium ion. After equilibrium, the solution was centrifuged at 4000 rpm for 5 minutes using a centrifuge (IEC61010-2-020, KUBOTA, Japan) and then the concentration of cadmium ion in supernatant solution was determined using Flame Atomic Absorption Spectrophotometer (FAAS) (HITACHI A-2000, Japan).

## 4.3 Results and discussion

### 4.3.1 Properties of adsorbent

Table 4.1 shows the composition of C, H, O, N, S and ash of adsorbent materials before and after activated with citric acid. The amount of O in the adsorbent material significantly increased from 23 to 40% and ash decreased from 20 into 1.79% after treatment with citric acid.

The SEM photographs of adsorbent materials before and after activated with citric acid are shown in the Figure 4.2. It can be seen that the surface of adsorbent after modification with citric acid appears to be more porous compared to the raw adsorbent. Treatment with citric acid on the adsorbent material resulted in more pores on the surface of adsorbent.

Based on the data obtained by BET analysis, the surface area and volume of pore of adsorbents before and after modification with citric acid are  $19 \text{ m}^2.\text{g}^{-1}$  and  $4 \text{ cm}^3.\text{g}^{-1}$  and  $32 \text{ m}^2.\text{g}^{-1}$  and  $7 \text{ cm}^3.\text{g}^{-1}$ , respectively. This data supports the SEM photograph that modification with citric acid resulted in more pores on the surface of adsorbent.

The mechanism of citric acid modification on *Platanus* leaf is shown in Figure 4.3. By heating to convert citric acid to citric acid anhydride which can further react with the cellulosic hydroxyl groups in the leaf to form an ester linkage. This reaction introduced carboxyl functional groups to the cellulose of leaf material. The esterification process increases the carboxylic content of the leaf fibre surface leading to a corresponding increase in the sorption of divalent metal ions. In other hand, cellulose has OH functional group which also can interact with metal ions. The possible mechanism is ion exchange and complexation because O in OH has free electron.

The data obtained from SEM/EDS is presented in Table 4.4 and Figure 4.4. It was clear that cadmium ion is not detected in the adsorbent before being used for Cd adsorption. The presence of Cd ion in the adsorbent after process of adsorption indicated that cadmium ion is bound by the adsorbent.

The NMR spectra of raw *platanus* and *platanus* after modification with citric acid are shown in Figure 4.6. The spectra was divided into five chemical regions (Gonzales-Vila et al., 1982; Tanaka et al., 2005). Long-chain aliphatic (0-55 ppm), substituted aliphatic (55-90 ppm), anomeric carbon polysaccharide (90-110 ppm), aromatic (110-160 ppm) and C-carbonyl, carboxyl, amide, ester (160-190)

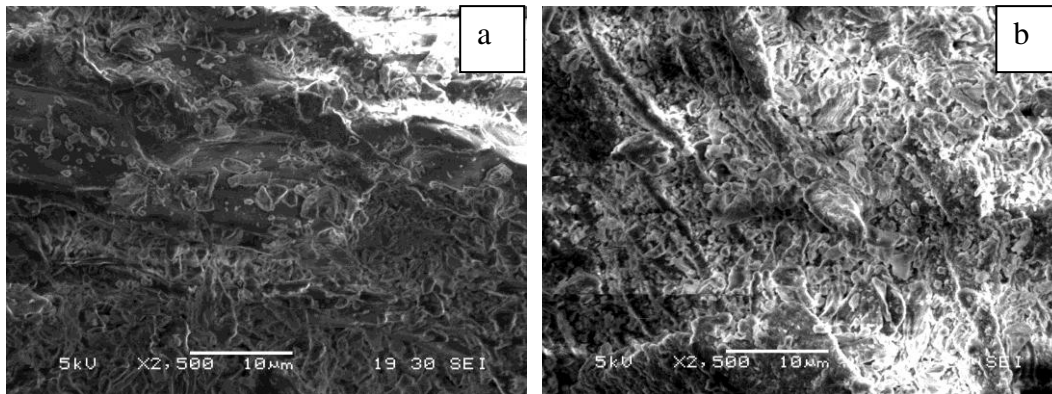
**Table 4.1** Elemental analysis of adsorbent materials before and after treatment with citric acid

Element (% w/w)	Adsorbent	
	Raw adsorbent	After treated with citric acid
Carbon (C)	49.90	49.90
Hydrogen (H)	5.78	6.14
Oxygen (O)	23.03	40.22
Nitrogen (N)	1.10	1.95
Sulphate (S)	0	0
Ash	20.11	1.79

The atomic weight and atomic percent weight of adsorbent before and after modification with citric acid was determined based on data of elemental analysis. Table 4.2 shows the results of atomic weight and percent weight. From the data of atomic percent weight then can be determined the comparison between percent of H/C and O/C to show the effect of activation on the change of the elements. The H/C of adsorbent before and after modification was 1.39 and 1.48 and O/C was 0.35 and 0.61, respectively. The atomic percent weight of citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) used for modification of the adsorbent for C, H, O was 37.50, 4.17, 58.33 % and H/C and O/C was 0.11 and 1.56, respectively. It was clear that composition of H/C and O/C of citric acid was similar to the adsorbent.

**Table 4.2** Atomic percent weight before after modification with citric acid

Parameter	Adsorbents	Elements			
		C	H	O	N
Atomic weight	Raw platanus	4.16	5.78	1.44	0.079
	Platanus activated with CA	4.16	6.14	2.51	0.14
Atomic percent weight	Raw platanus	36.29	50.45	12.56	0.69
	Platanus activated with CA	32.11	47.41	19.41	1.08



**Figure 4.2** SEM photograph of adsorbent a. Raw adsorbent, b. After activated with citric acid

The modification using citric acid increased the amount of carboxylic acid of the adsorbent significantly which is important for binding of metal ions. Table 4.3 shows the amount of carboxylic acid of raw adsorbent, after modification with citric acid and carboxylic acid of citric acid utilized in this study.

**Table 4.3** the amount of carboxylic acid on adsorbent obtained by titration method

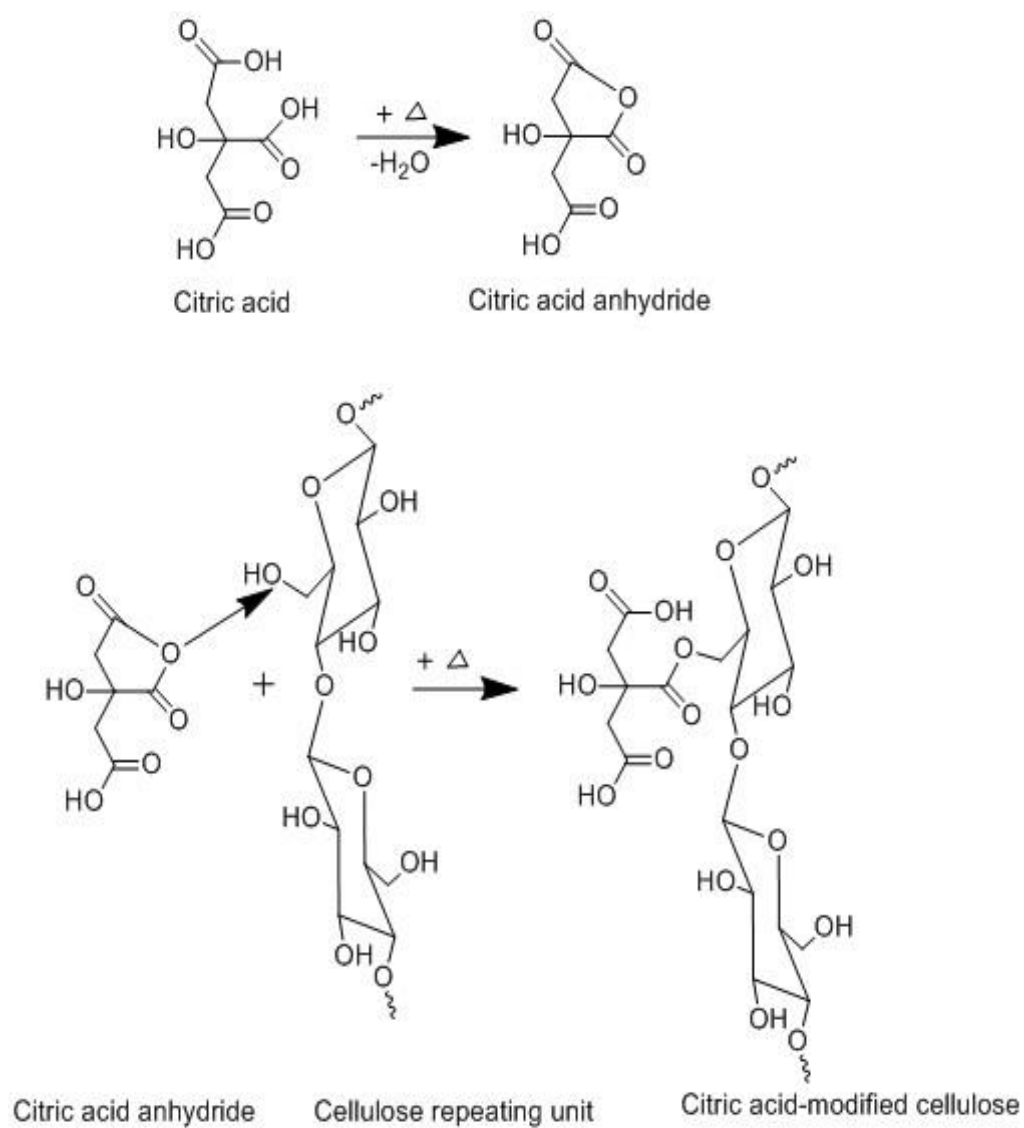
(Adopted from Boehm, 2002)

<b>Sampel</b>	<b>Volume of titran NaOH</b>	<b>Carboxylic acid</b>
	<b>0.1 M</b>	
	<b>(mL)</b>	<b>(mmol/g)</b>
Raw Platanus	1.3	0.26
Platanus modified CA	7	1.4
Citric acid	78	15.6

Carboxylic acid reacted with cellulose =  $1.4 - 0.26 = 1.14$  mmol/g

(Increase of carboxylic acid is around 5 times).

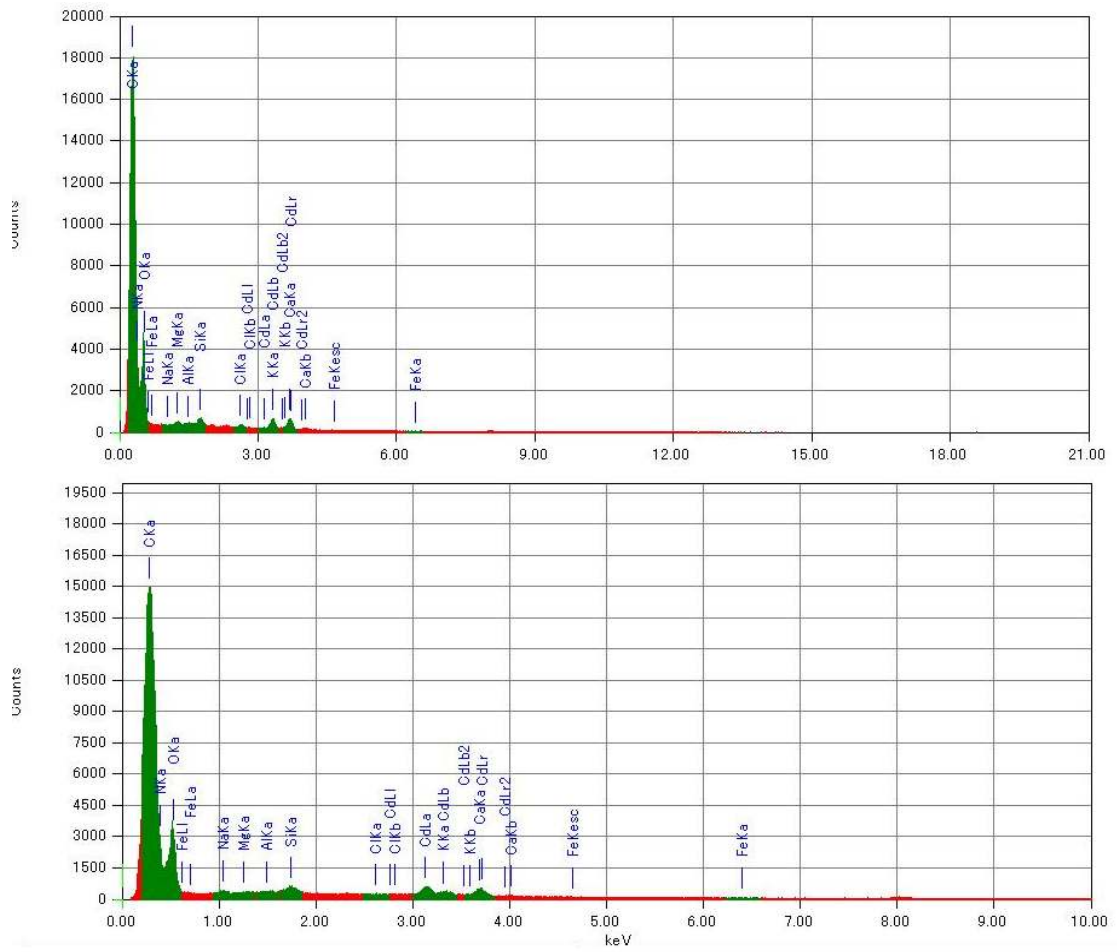




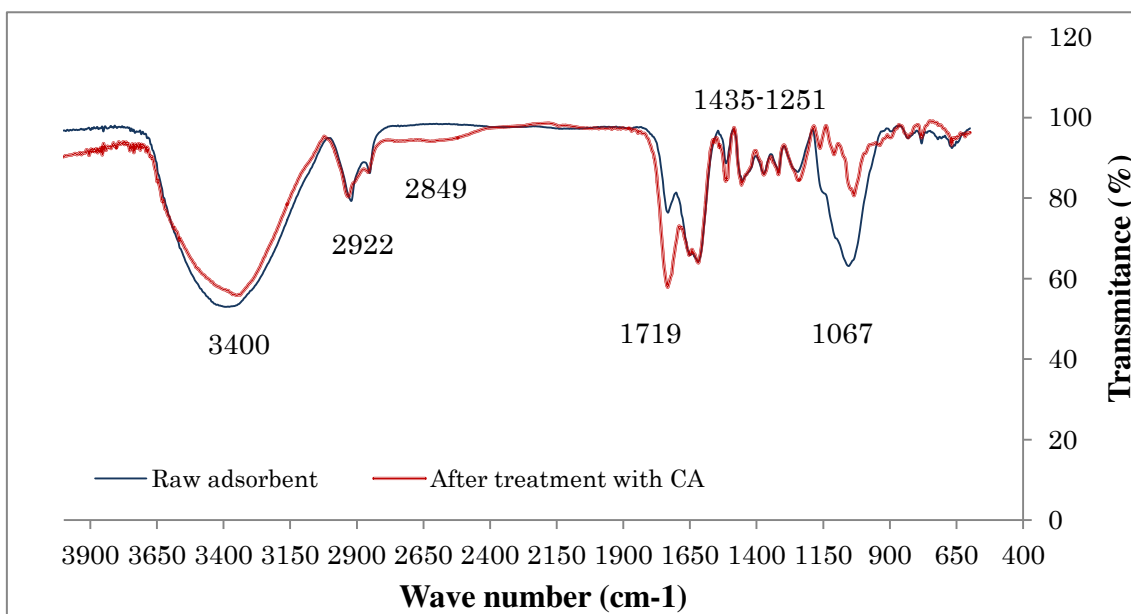
**Figure 4.3** Mechanism of citric acid modification on *Platanus* leaf

**Table 4.4** Concentration of some element in the adsorbent by SEM/EDS

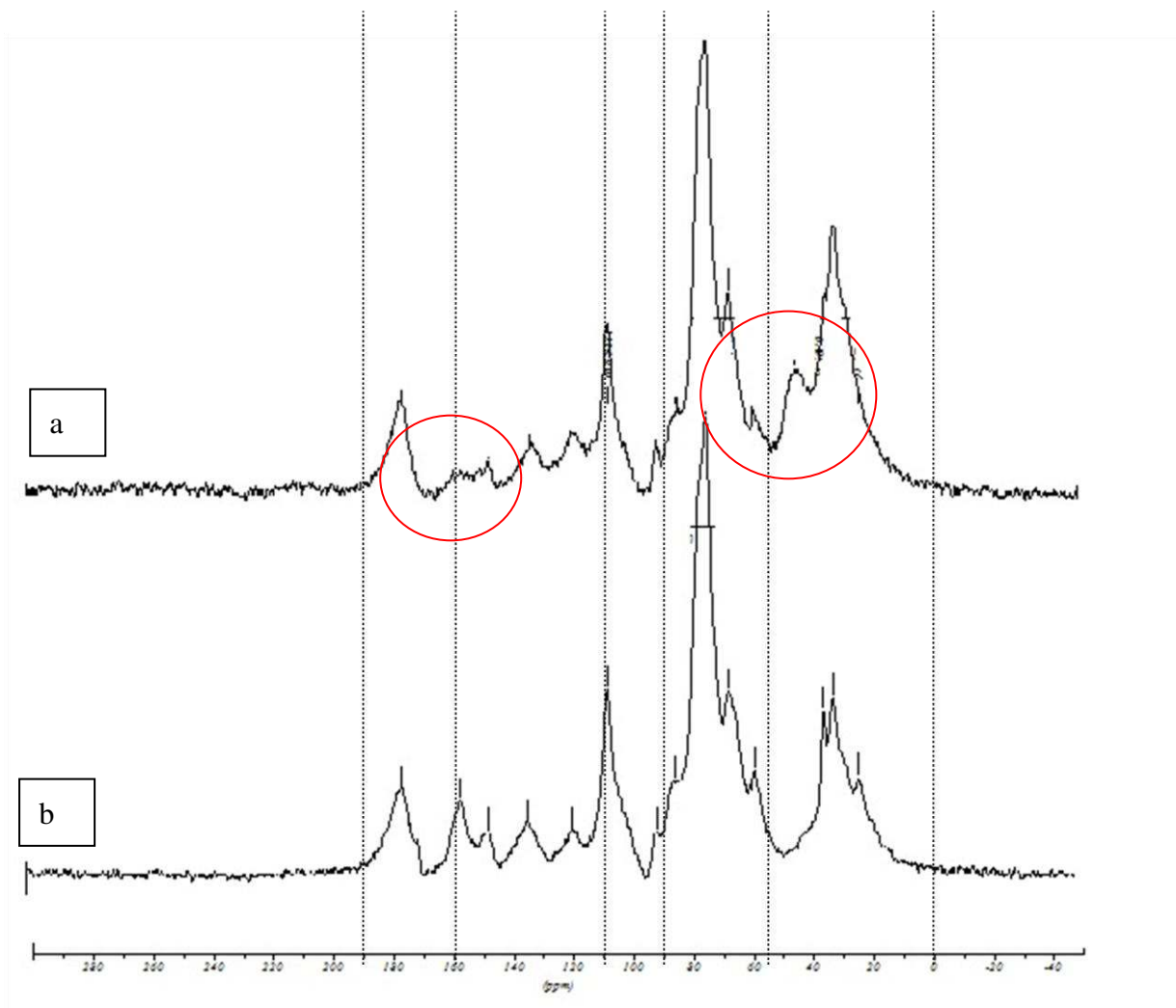
Element	Before adsorption		After adsorption	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	68.65	78.98	65.84	80.91
N	-	-	-	-
O	18.89	16.32	16.19	14.94
Na			0.65	0.42
Mg	0.56	0.32	0.09	0.05
Al	0.03	0.02	0.08	0.04
Si	1.33	0.66	1.09	0.57
Cl	1.06	0.41	0.04	0.02
K	4.29	1.51		
Ca	5.18	1.79	3.84	1.41
Fe	-	-	0.27	0.07
<b>Cd</b>	<b>-</b>	<b>-</b>	<b>11.91</b>	<b>1.56</b>
<b>Total</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>



**Figure 4.4** SEM/EDS of Platanus before and after adsorption process



**Figure 4.5** FTIR spectra of adsorbent before and after treatment with citric acid



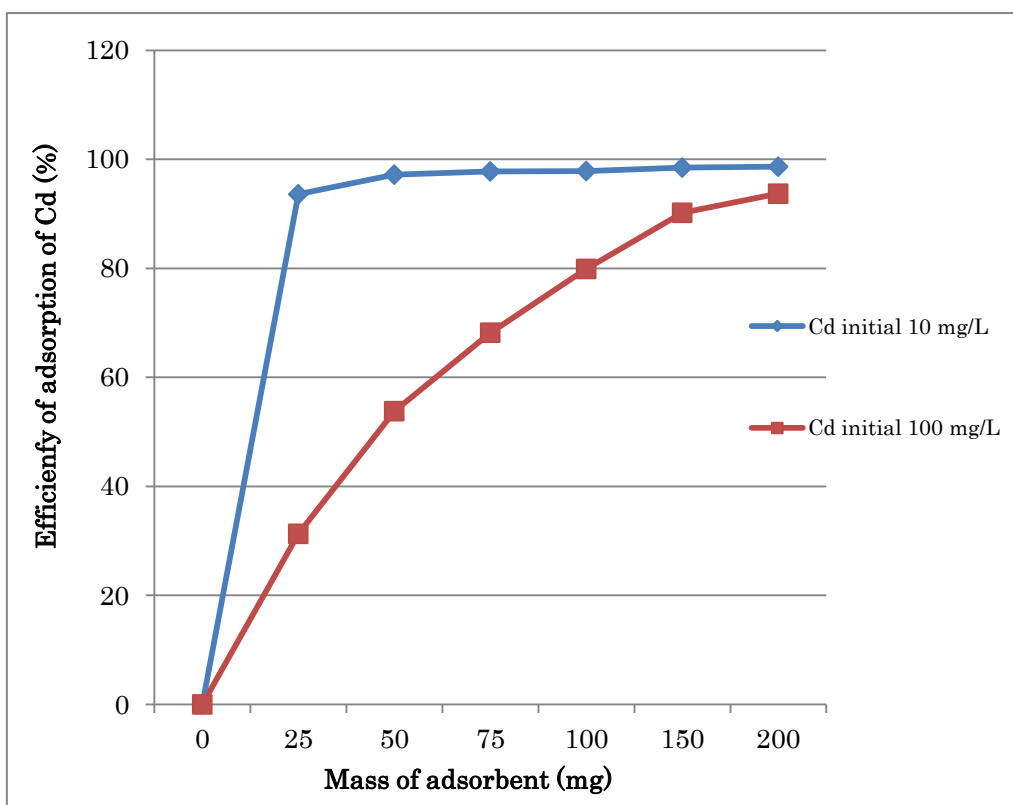
**Figure 4.6** NMR Spectra of (a) modified *Platanus* with CA and (b) raw *Platanus*

FTIR analysis was employed in order to identify the characteristic functional groups on the surface of adsorbents. Fig. 4.5 shows the FTIR spectra of the adsorbents before and after activated with citric acid. The FTIR spectrum of raw adsorbent and activated adsorbent showed a broad peak at  $3400\text{ cm}^{-1}$  indicating the presence of macromolecular such as cellulose, lignin, pectin, etc. The double peaks appeared in both spectra at the wave numbers of  $2922$  and  $2849\text{ cm}^{-1}$  may be due to the asymmetric and symmetric stretch of aliphatic chains (-CH), respectively. The peak around  $1435 - 1251\text{ cm}^{-1}$  indicated the characteristic main skeleton cellulose (Reddy *et al.*, 2012). The peak around  $3371\text{ cm}^{-1}$  indicated the presence of carboxylic O-H groups and the peaks around  $1067\text{ cm}^{-1}$  indicated of C=O group of primary hydroxyl stretching which may be attributed to cellulose structure of *platanus* (Nguyen and Ha, 2009). The activated adsorbent has a strong characteristic stretching vibration absorption band of carboxyl group at  $1719\text{ cm}^{-1}$  as an effect of treatment with citric acid.

Based on the data obtained by SEM, FTIR and BET analysis, it can be concluded that modification with citric acid resulted physical and chemical properties on the surface of adsorbent and increased the adsorption capacity of cadmium in water. The increase of adsorption of metal ions may be due to the esterification process which also increases the carboxylic content of the surface of adsorbents (Low *et al.*, 2004).

### 4.3.2 Effect of dose of adsorbent on the adsorption of cadmium ion

The effect of dose of adsorbent is shown in the Figure 4.7. For 10 mg/L of initial cadmium concentration, the adsorption capacity for all mass of adsorbent from 25 to 200 mg was almost constant; therefore 25 mg was favourable as an ideal mass of adsorbent. When the initial concentration of cadmium increased, the removal efficiency of adsorption increased linearly by the increase of mass of adsorbent and became constant over 150 mg. This result proved that the adsorption of cadmium ion in the water was absolutely due to the presence of the adsorbent.



**Figure 4.7** Effect of dose of adsorbent on cadmium adsorption

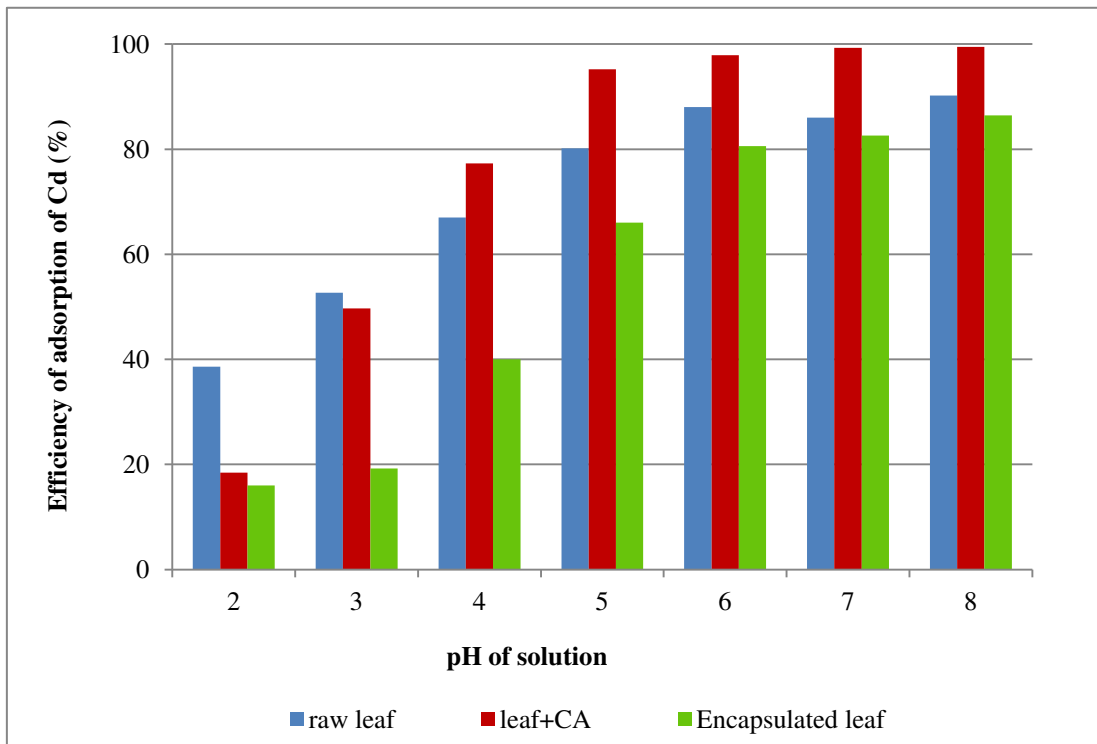
(Volume of Cd soln.: 50 ml, Cd initial.: 10 mg/L, pH of soln.: 6, and stirring time: 2 hours)

### 4.3.3 Effect of pH

The binding of cadmium ion ( $\text{Cd}^{2+}$ ) with the surface functional groups of adsorbent strongly depended on the pH of solution. Fig. 4.8 shows the effect of pH on the adsorption of cadmium ion in water. The removal efficiency of cadmium ion increased with the increase of pH because cadmium ion forms a complex with some acidic functional groups in the adsorbent (Khalifa & Bagane, 2011). The removal of metal cation at any pH was much greater than that by hydroxide precipitation. Adsorption of metal cation on adsorbent was influenced by the nature of adsorbent surface and the distribution of metal species which also depends on the pH of the solution. The removal efficiency of cadmium decreased with the decrease of pH because protons compete with metal ion for the binding sites on the adsorbent surface as well as the protons decrease the negative charges by association of the functional group with protons (Siswoyo and Tanaka, 2013). The increase in the removal of metal ions as pH increase can be explained on the basis of the decrease in  $\text{H}^+$  on the surface, which results in the less repulsion with metal ions (Namasivayam and Ranganathan, 1995; Kadirvelu and Namasivayam, 2003; Souag *et al.*, 2009). In the highly acidic medium, the dissolution of the adsorbent occurs to consequently decrease in the active sites of the adsorbent. The highly protonated adsorbent surface is not favorable for the uptake of cadmium ion because of the electrostatic repulsion (Sing *et al.*, 1998; Papandreou *et al.*, 2007).

It is known that the precipitation of cadmium ion in the solution is started at the pH around 8.5 (Lee and Davis, 2001; Wang *et al.*, 2009; Khosravan and Lashkari, 2011). The recent study confirmed that cadmium ions were precipitated at the pH 9. The pH 6 to 8 was ideal for adsorption of cadmium ion by using this adsorbent.



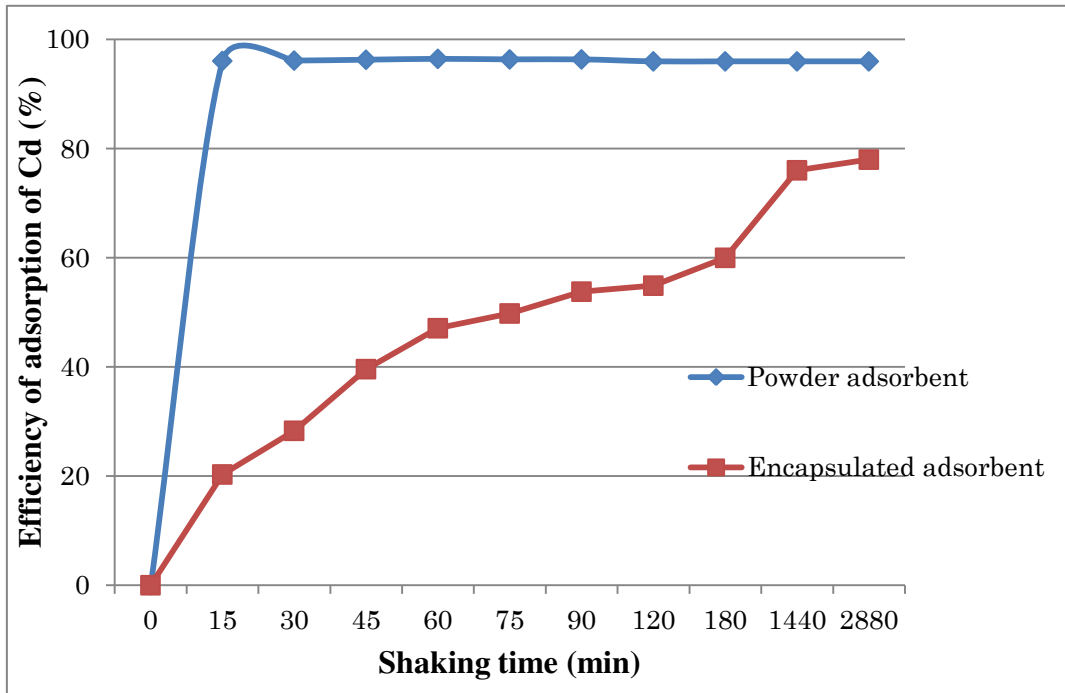


**Figure 4.8** The influence of pH on the adsorption of cadmium

(Mass of adsorbent: 100 mg, volume of Cd soln.: 50 ml, Cd initial.: 10 mg/L, and stirring time: 2 hours)

#### 4.3.4 Effect of stirring time

The effect of stirring time on the adsorption of cadmium ion is shown in the Fig. 4.9. The equilibrium adsorption for powder and encapsulated adsorbent on 10 mg/l of cadmium was achieved after around 30 and 1440 minutes, respectively. The equilibrium time of the encapsulated adsorbent was longer than the powder adsorbent because the binding site of encapsulated adsorbent is covered by agar and the quick equilibrium time is due to the particle size (Messaouda *et al.*, 2012). This result is important because the equilibrium time is one of the considerations for the application of economical wastewater treatment plant (Kadirvelu and Namasivayam, 2003; Rao *et al.*, 2006).



**Figure 4.9** The influence of stirring time on the adsorption of cadmium

(Mass of adsorbent: 100 mg volume of Cd soln.: 50 ml, pH of soln.: 6.0, and Cd initial: 10 mg/L)

#### 4.3.5 Adsorption isotherm

The Langmuir and Freundlich isotherm models were applied to the equilibrium constant of adsorption by the following equations:

The equation of Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L \cdot q_m} \quad (4.1)$$

Where  $C_e$  is the equilibrium concentration (mg/l),  $q_e$  is the adsorbed amount of cadmium at equilibrium (mg/g),  $q_m$  and  $K_L$  are the constants of Langmuir related to the adsorption capacity and energy of adsorption, respectively. From the equation above, a

plot of  $C_e/q_e$  versus  $C_e$  will be used to determine the values of  $q_m$  and  $K_L$  as the tangent and intercept of the curve.

The equation of Freundlich isotherm model:

$$q_e = K_f C_e^{1/n} \quad (4.2)$$

Where  $q_e$  is the amount of adsorbed (mg/g),  $C_e$  is the equilibrium concentration (mg/l) and  $K_f$  and  $n$  are constants. To determine the amount of  $K_f$  and  $n$ , plots between  $\log C_e$  and  $\log q_e$ .

$$\text{Log}(q_e) = \log(K_f) + 1/n \log(C_e) \quad (4.3)$$

The Langmuir and Freundlich adsorption isotherm models are shown in the Fig. 4.10 and the results of Langmuir and Freundlich isotherm models of inactivated, activated and encapsulated adsorbents determined from the above equations are shown in Table 4.5.

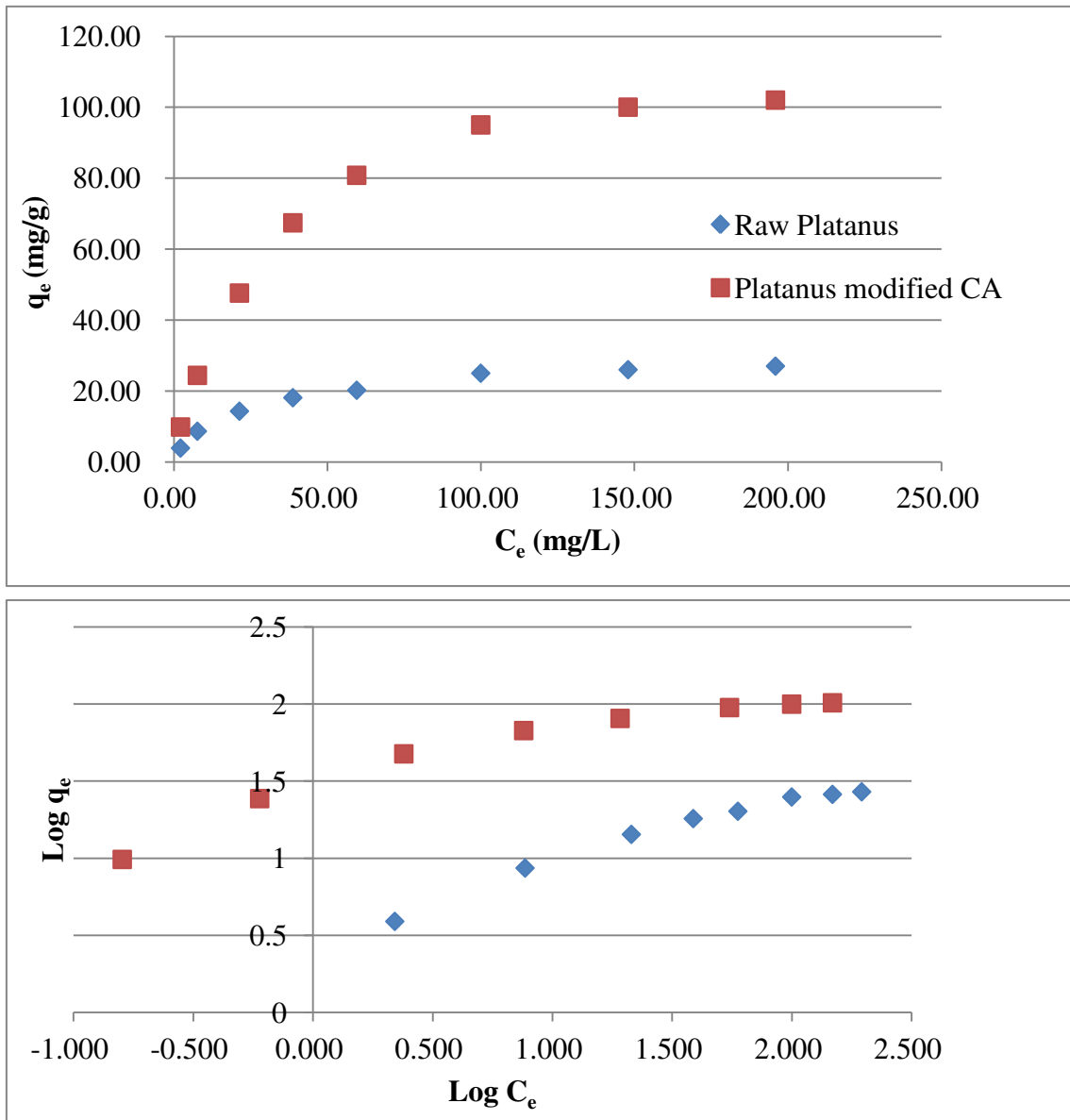
The essential characteristics of the Langmuir isotherm can be expressed due to a dimensionless constant of the separation factor or equilibrium parameter,  $R_L$ , which is defined as:  $R_L=1/(1+K_L C_0)$  (4.4)

Where  $K_L$  is the Langmuir constant and  $C_0$  is the initial concentration of cadmium ion in the solution. The  $R_L$  value indicates the shape of the isotherm as follows:

$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The  $R_L$  value between 0 and 1 is favorable adsorption (McKay et al., 1982). The  $R_L$  values of raw, modified and encapsulated adsorbents for the concentrations of 10 mg/L

$\text{Cd}^{2+}$  were 0.016, 0.069 and 0.039, respectively. It means that the bio adsorbents based on leaf of *platanus* were favorable for the adsorption of cadmium ion in the water.



**Figure 4.10** Langmuir and Freundlich adsorption isotherm models for adsorption of Cd (Mass of adsorbent: 100 mg, volume of Cd soln.: 50 ml, pH of soln.: 6.0, and stirring time: 2 hours and 24 hours for encapsulated adsorbent)

**Table 4.5** The result of Langmuir and Freundlich isotherm models

Adsorbent	Langmuir model			Freundlich model		
	$q_m$ (mg/g)	$K_L$ (l/mg)	$R^2$	$K_f$	$n$	$R^2$
Inactivated	24.51	0.084	0.992	3.35	2.34	0.963
Activated with citric acid	82.65	0.83	0.993	13.29	3.12	0.906
Encapsulated in agar	22.68	0.28	0.915	4.709	2.64	0.991

#### 4.3.6 Adsorption Kinetics

The adsorption kinetics pseudo-first order and pseudo-second order are used in this study. The result of adsorption kinetics based and both kinetic models for *platanus* modified citric acid and encapsulated adsorbent are shown in Table 4.6. The correlation coefficient ( $R^2$ ) for the pseudo-second order model indicated a strong correlation indicated that adsorption of cadmium ion by using this adsorbent followed the pseudo-second order kinetic model.

**Table 4.6** Adsorption kinetics of adsorbents

Type of kinetics	Adsorbent (Cd initial 10 mg/L)	
	Activated with CA	Encapsulated in agar
<b>Pseudo-first order:</b>		
$k_1$ (L/min)	0.112	0.025
$q_e$ (mg/g)	9.64	7.60
$R^2$	0.7515	0.9724
<b>Pseudo-second order:</b>		
$k_2$ (g/mg.min)	3.841	0.003
$q_e$ (mg/g)	9.643	7.8
$R^2$	1	0.9987

#### 4.4 Conclusion

The present study showed that a bio adsorbent based on leaf of *platanus* modified with citric acid had high efficiency on the adsorption of cadmium ion in the water. The batch adsorption experiments have been conducted under the different condition initial cadmium ion concentration, dose of adsorbent, contact time and pH of solutions. The adsorption of cadmium ion was strongly pH-dependent and pH 6 to 8 was favourable for the adsorbent. The encapsulated bio adsorbent in agar decreased the adsorption capacity of cadmium ion, however, the adsorbent material can be separated easily after the process of adsorption. Finally, with this high efficiency, easiness in separation, low cost and environmentally friendly for the removal of cadmium ion in the

water, the adsorbents could be considered as one of a promising solution for water and waste water treatment in the near future.

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# **CHAPTER 5**

## **Cost Analysis**

## **5.1 Determination of unit price of low-cost adsorbents**

Recently, many researchers have been working on the development of low-cost adsorbents, however, a specific cost analysis of the adsorbents has still not been involved in their studies. Most researches in this field only focused on the technical aspect such as finding the new sources of low-cost adsorbents, how to increase the adsorption capacity with physical and chemical modification, how to improve the pH area and how to use the adsorbent materials repeatedly. In order to understand the effectiveness of the low-cost adsorbents, the integrated study including cost analysis is needed.

In this study, we analyzed the effectiveness of some low-cost adsorbents based on the metal uptake capacity and the cost in the preparation of the adsorbent. Moreover, we compared each adsorbent with the commercially available activated carbon as the most common adsorbent material. Some assumptions and simplifications were used in the calculation of the cost for preparation of adsorbent materials because of the limitation of information, especially for the cost of labor. The costs of the adsorbents were determined from the cost of all components in the process of production, raw adsorbent materials, chemicals, water, energy and labor. The cost of adsorbents obtained in this study was calculated for production of 1 kg of adsorbents. The determination of the unit cost of the adsorbents was based on some variables and assumptions:

### **1. Raw adsorbent materials**

-All raw adsorbent materials utilized in the present study are solid waste materials taken from Drinking Water Treatment Plants (DWTP), paper industry and organic garbage, therefore this value is equal to zero.

-The cost for transportation of the adsorbents was influenced by the distance

between the location of raw material and production place. However, the transport cost was neglected in this study.

## 2. Chemicals

-The chemicals were used for modification of sludge of paper industry (phosphoric acid) and *Platanus* leaf (citric acid).

-We used two different prices of chemicals in this analysis, laboratory scale and industrial scale.

-The amount of chemicals needed in this study:

Cost of phosphoric acid (PA):

= 0.25 kg PA was needed for 1 kg of paper sludge

= 0.25 kg/ density of PA

= 0.15 L of PA x price of PA (US\$/L)

Cost of citric acid (CA):

= 4 L CA 1.3 M was needed for 1 kg of *Platanus* leaf

= 0.152 Kg (solid) of CA

= 0.152 Kg CA x price of CA (US\$/kg)

## 3. Water

-Water was used for washing and rinsing of the adsorbents.

-In this analysis, the price of water was based on the price of reverse osmosis (RO) water.

-Water for washing was 5 L for 1 kg of adsorbent

-Water for rinsing after modification with acid was 50 L for 1 kg of adsorbent

Cost of water:

= amount of water ( $M^3$ ) x price of RO water (US\$/ $M^3$ )

#### 4. Energy

-Energy was used for drying and heating

-Type of instruments: Drying (600 watt, capacity 20 kg), heating (850 watt, capacity 1 kg)

-Period of drying and heating was 24 and 1 hours, respectively

-Energy consumption (Kwh)

= Wattage of instrument (watt) x period of drying or heating (hour)/1000 (Kwh)

-Cost for drying:

= Energy consumption (Kwh) x price of energy (US\$/Kwh)

#### 5. Labor

-Working time was determined based on the preparation of 10 kg of adsorbent.

-Variables of working for preparation of the adsorbent without modification were washing, drying and crushing and for adsorbent with modification were chemical preparation, mixing, drying-heating and crushing.

-Cost of labor:

= working hour (hour) x standard fee of labor (US\$/hour/person)

-The labor cost was excluded in the unit price of the adsorbents in the present study, because the fee of labor is different for each country.

## 6. Backward cost

-The company of paper industry has to send their solid waste to landfill and pay for its treatment. The construction and operational cost of landfill is influenced by the volume of landfill. In Japan, the cost per cubic meter decreases from 10,000 to 5,000 yen as a landfill becomes bigger (Tanaka et al., 2004). Utilizing the solid waste of paper industry as adsorbent material will reduce the cost of treatment in the landfill. The amount of the treatment cost of solid waste of paper industry in the landfill was considered as backward cost for the preparation of the adsorbent. The backward cost considered in this analysis only for sludge of paper industry because the information of cost for DWTP sludge and *Platanus* leaf is not available.

-The backward cost of solid waste of paper industry was assumed 100 US\$/ton (based on cost for treatment of hazardous waste in Indonesia). Therefore, the unit price of paper sludge could be reduced up to 0.1 US\$/kg.

The unit price of the adsorbent is shown in Table 5.1 shows the unit price of each adsorbents.

**Table 5.1** Unit price of the adsorbent materials

Adsorbent material	Raw material	Chemical	Unit price	Chemical Needed		Process for 1 kg adsorbent			Unit price/kg**
	(US\$)		(US\$/L or kg)	L or kg	US\$	Water (US\$)	Energy (US\$)	Labor (hour)	(US\$)
DWTP Sludge	0	No		0	0	0.005	0.085	0.06	0.09
Raw paper sludge	0	No		0	0	0.005	0.085	0.06	0.09
Modified paper sludge	0	Phosphoric acid	28.57	0.15	4.29	0.05	0.157	0.13	4.49
Modified paper sludge*	0	Phosphoric acid	0.85	0.15	0.13	0.05	0.157	0.13	0.33
Raw <i>Platanus</i>	0	No		0	0	0.005	0.085	0.09	0.09
Modified <i>Platanus</i>	0	Citric acid	31.43	0.152	4.78	0.05	0.157	0.17	4.98
Modified <i>Platanus</i> *	0	Citric acid	2	0.152	0.3	0.05	0.157	0.17	0.51

Note: - Labor cost is calculated for production of 10 kg of adsorbent

-\*Price of chemical is for industrial scale

-\*\*Cost of labor is not included (depend on the country)

## **5.2 Comparison between low-cost adsorbents and common adsorbent**

The total cost for adsorption of metal ion is depending on the adsorption capacity and unit price of adsorbent. The illustration for treatment of 1000 L of wastewater with 10 mg/L of initial cadmium concentration is shown in Table 5.2.



**Table 5.2** Comparison between low-cost adsorbent and commercial activated carbon

Adsorbent	Adsorption capacity	Adsorbent needed	Unit price	Total cost
	(mg/g)	(kg)	(US\$/kg)	(US\$)
DWTP sludge Miyamachi	5.3	1.89	0.09	0.17
DWTP sludge Nishino	9.2	1.09	0.09	0.10
Raw paper sludge	5.2	1.92	0.09	0.17
Modified paper sludge	29.2	0.34	4.49	1.54
Modified paper sludge (price chemical is for industrial scale)	29.2	0.34	0.33	0.11
Raw <i>Platanus</i>	24.5	0.41	0.09	0.04
Modified <i>Platanus</i>	82.7	0.12	4.98	0.60
Modified <i>Platanus</i> (price of chemical is for industrial scale)	82.7	0.12	0.51	0.06
Commercial activated carbon (GAC)*	11.1	0.90	1.00	0.90

\*Kadirvelu K and Namasivayam C, 2003.

Volume of waste water: 1000 L, Cd concentration: 10 mg.

## References

- Kadirvelu K. and Namasivayam C. 2003 Activated carbon from coconut coirpith as metal adsorbent: adsorption of Cd(II) from aqueous solution, *Advances in Environmental Research*. 7, 471-478.
- Tanaka N., Matsuto T. and Tojo Y. 2004. Landfill engineering for final disposal of solid waste by Japanese style: design, construction, management and scientific knowledge for environmental protection, Faculty of Engineering, Hokkaido University Japan.

## **CHAPTER 6**

### **General Conclusions and Recommendations**

## 6. 1 General conclusions

The study entitled “Development of low-cost adsorbents based on solid waste materials to remove heavy metal ions in water” had the general conclusions as below:

1. Sludge of drinking water treatment plant (DWTP) has a high ability as adsorbent material to remove cadmium ion in water. The presence of humic acid and iron in the sludge was suggested as an important factor on the adsorption of cadmium ion in water.
2. The adsorption capacity of sludge of paper industry for cadmium and lead ions was not so high, however, the modification with phosphoric acid improved its adsorption capacity significantly. The increase of adsorption capacity after modification with phosphoric acid may be due to two possible reasons. First, after treatment with phosphoric acid, it was found from FTIR spectra that the adsorbent had phosphate functional group which contributed to the adsorption of Cd and Pb ions. Second, calcium in the paper sludge reacted with phosphoric acid to form calcium phosphate which also had a binding ability with some metal ions such as Cd and Pb.
3. The adsorption capacity of raw leaves of *Platanus* as a low-cost adsorbent was the highest compared to the other materials such as the sludge of DWTP and paper industry. After modification with citric acid, the high adsorption capacity may be due to the introduction of carboxylic groups into the adsorbent and also the increase in the surface area and pore volume of the adsorbent. Moreover, the encapsulation with agar led to the easy separation of the adsorbent materials from solution after an adsorption process.
4. The development of low-cost adsorbent by using solid waste materials brings a double advantages, one is to be able to decrease the amount of solid waste materials

if the adsorbent based on the material will be used in large scale. Another is the decrease in the cost if the adsorbent will be used instead of the activated carbon.

## **6.2 Recommendations**

The results of this study are important as a basic understanding for the development of low-cost adsorbent in the future. Some recommendations below could be considered for the better results in the development of low-cost adsorbent.

1. The availability of raw material of adsorbent in the local area should be considered in the selection of the raw adsorbent materials.
2. In the chemical modification, the selection of a chemical as an activated agent is very important because it will give different effect on the different raw adsorbent materials. Therefore, several chemicals as activated agent should be tried to get the best results.
3. In order to get the better results in the encapsulation with agar on the adsorbent materials, the process of drying and size of adsorbents should be considered. The adsorbent should be dried immediately at 100° C after cutting into small and uniform sizes.