CHAPTER IV

RESULT AND DISCUSSION

The investigation was carried out to assess the efficiency of the removing of heavy metal ions by formaldehyde treated water hyacinth (FTWH) at the optimum concentration. Heavy metal ions in the study is Cu^{2+}, Ni^{2+} and Zn^{2+}. Batch experiment was conducted at high concentration of heavy metal ions ; ranging from 25 to 100 ppm, to allow the determination by complexometric method while column experiment was conducted at low concentration for atomic absorption spectrophotometry method. The possible mechanism of removing and some physical properties have been investigated. In addition, the 5 % FTWH was applied to the electroplating wastewater for treatment and recycling.

Concentration of some heavy metals in original water hyacinth

It is evidently that water hyacinth accumulates a variety of heavy metal ions in its tissue (Gobal, 1987). This experimental section was designed to determine the concentration of heavy metal ions in both of tissue and leaching solutions, carried out by agitating with 0.4 N H_2SO_4. The concentrations of original water hyacinth were shown in Table 4.1. It was found that the concentration of zinc ion had greater than those of copper and nickel ions. In agreement with Haider et al. (1984), it is possible that the zinc ion might be accumulated by its environment and is one of the trace components in water hyacinth.

Other factors such as location and sampling method may also associate with the result.

Table 4.1 : Concentration (mg/kg) of some heavy metal ions in untreated
water hyacinth (*Eichhornia crassipes*)

Heavy metal ions	Amount	
	Solid	Liquid
Cu	0.244	0.421
Ni	0.187	0.705
Zn	1.301	5.003

Note : The concentration obtained by nitric and sulfuric digestion (two replications)

Batch experiments

Effect of contact time

Figure 4.1 shows the adsorption of Cu^{2+}, Ni^{2+} and Zn^{2+} at pH 5.0, respectively. The rate of adsorption by pretreated water hyacinth (PWH) was depended on the time intervals ; the uptake was very rapid in the first 5 minutes followed by slower uptake. This could be due to the two different sorption processes as possible, a fast ion exchange followed by a chemisorption (Low et al, 1993). In case of Cu^{2+}, the uptake was drastically decreased after 20 mins and the pH of the solution was 5 to 3. The possibility of this mechanism was a desorption theory. The theory needs to be considered because of the pH value significantly decreased at every of time interval. This result is partially inconsistents with a previous study by Low et al., 1992, in which the results of the desorption process had not occurred in batch experiment; the used substrate was oil-palm fibres (Appendix B; table B1).
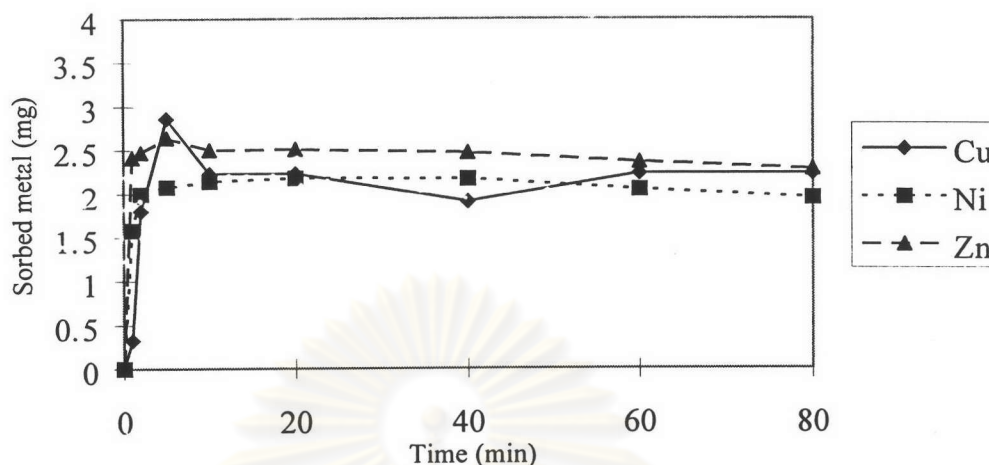
Figure 4.1 : Effect of contact time for the sorption of various metal ions by pretreated W.H. at pH 5

Effect of formaldehyde treatment

All of substrate samples were carried out by using a 20 mins interval for continuous shaking. Results from varying percentages of formaldehyde treament on water hyacinth substrate, 5 % FTWH, were not fitted to a modified Langmiur isotherm, especially for Cu^{2+} (Figure 4.2a)

$$C/N \quad = \quad 1/N*b + C/N*$$

Where **N** is the amount of heavy metal sorbed per gram of substrate at concentration **C, N*** is the maximum sorption capacity and **b** is a constant. The plots of **C/N** against C are shown in Figure 4.2 a, b and c, respectively. The result showed that some metal ions might have been leached slightly on batch process by desorption mechanism.
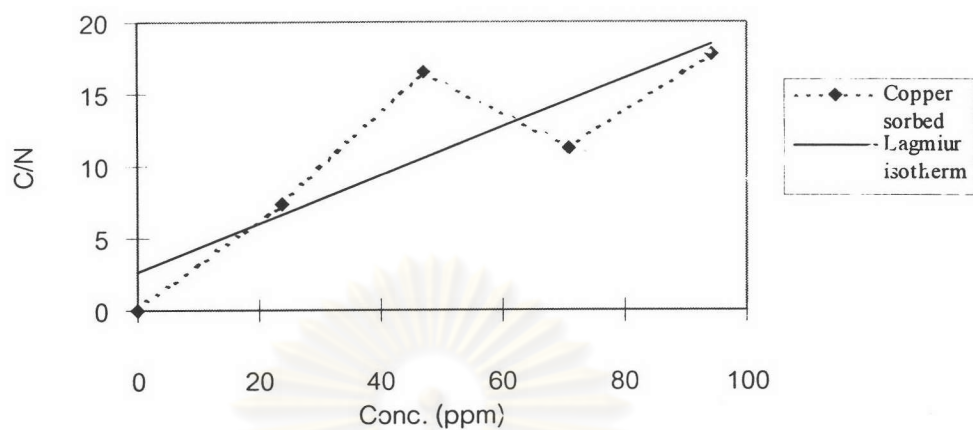
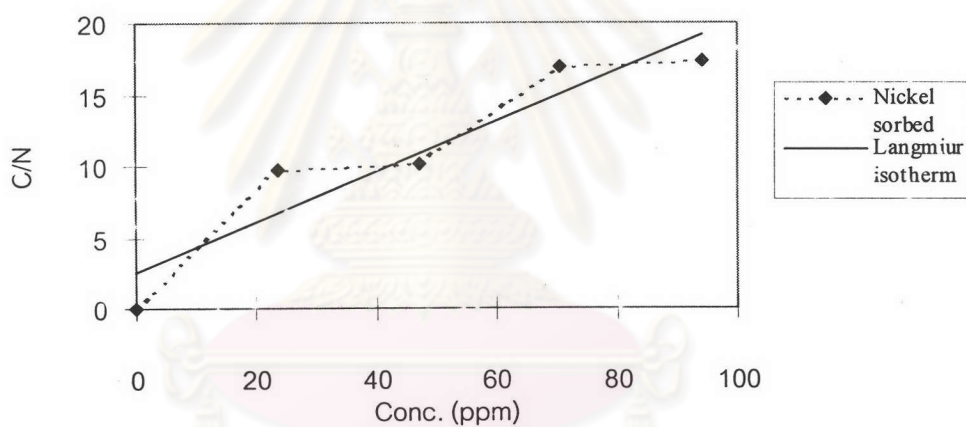Figure 4.2a : Sorption isotherm of cu^{2+} ions on 5% FTWH

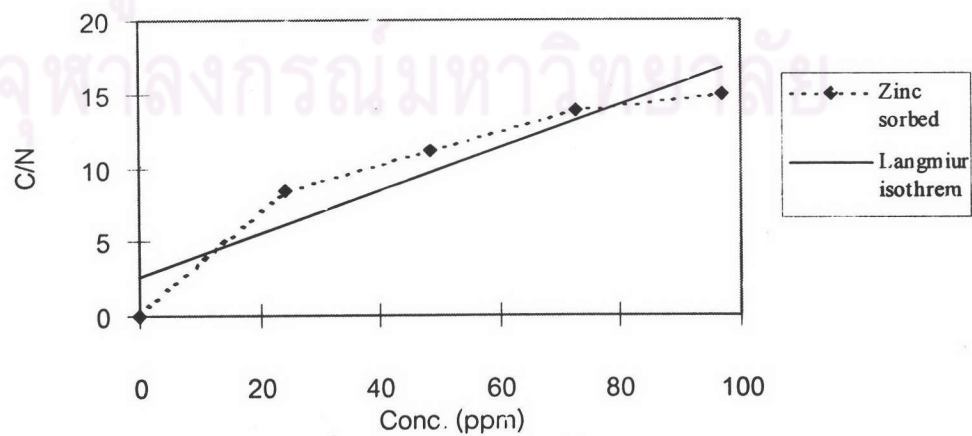Figure 4.2b : Sorption isotherm of Ni^{2+} ions on 5%TWH.

Figure 4.2c : Sorption isotherm of Zn^{2+} on 5% FTWH

According to the results from the analysis of varian-one way classification using SPSS program, considering with cost-benefit and pollutant discharge. Most of the treatments, in particular for 50 ppm of synthetic solution, indicated that the substrate capacities were not significantly difference after increasing more than 20 % concentration of formaldehyde (F.prob<0.05) and slightly increasing for their capacities were observed, compared to 5 % concentration of formaldehyde. It showed at the concentration of formaldehyde should be considered for optimum condition of water hyacinth treatment (Appendix D; table D1) and was, therefore, selected for this experiment (Figure 4.3a-c). As can be expected, for two ways-ANOVA analysis, both of concentration and the percentage of formaldehyde had significantly affected on the capacity of water hyacinth substrate (Appendix D; table D2a-c).
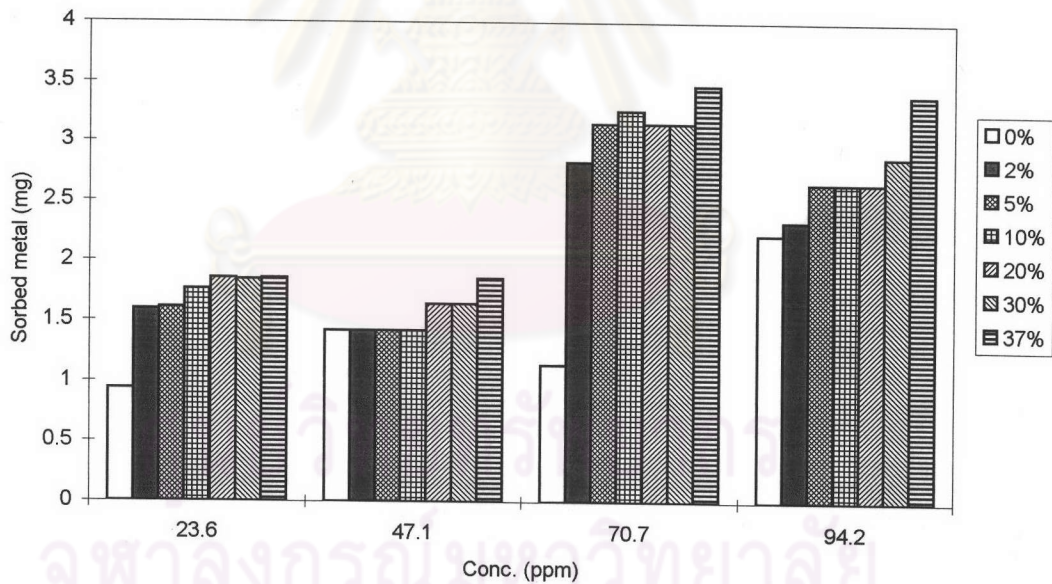

Figure 4.3a : Removal of Cu (II) ions by various treated formaldehyde
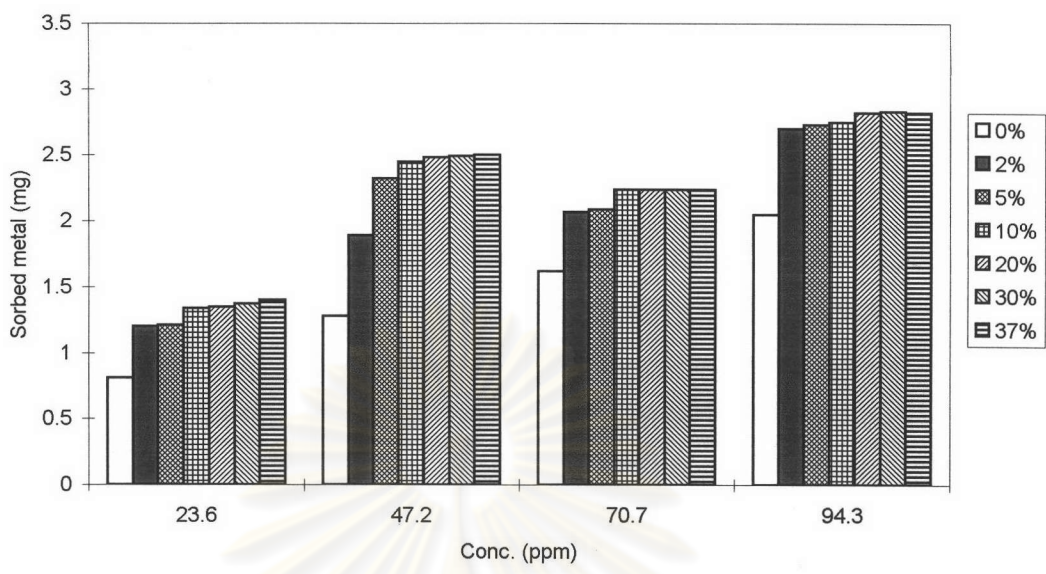W.H. on a batch test

Figure 4.3b : Removal of Ni (II) ions by various treated formaldehyde
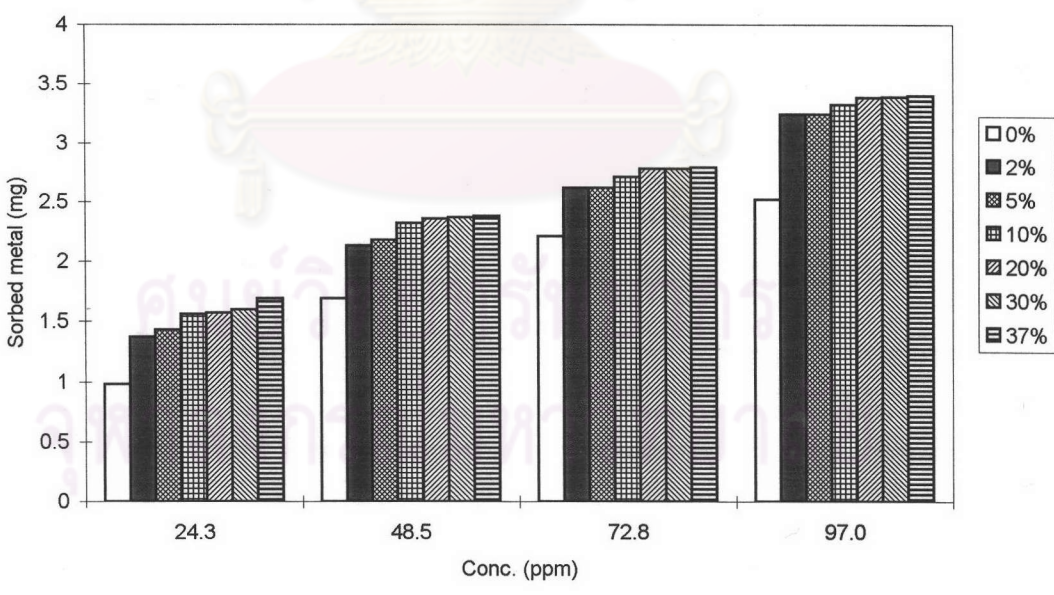W.H. on a batch test

Figure 4.3c : Removal of Zn (II) ions by various treated formaldehyde
W.H. on a batch test

These great increasing of capacity might due to the crosslinked reaction by acidic formaldehyde which reacted between the methylene ether and the secondary hydroxyl groups of cellulose in water hyacinth. Other supports of the result are the physical property tests. The swelling and moisture values were decreased simultaneously when this substrate was treated to improve capacity (Appendix A; table A1-3). Concerning with theory, the result is consistent with a fundamental of ion exchange properties that related the crosslink effect and hydration value; as the crosslink is increased, the amount of water that substrate retain will decrease (Simon, 1991).

Scanning Electron Microscope (SEM) Analysis

A cellular structure of lignocellulosic material from water hyacinth substrate was obtained by microscopic examination (Figure 4.4a,b). Under high magnification (x200) using an electron microscope, the microfibril cellulose look like a frabric having a surface area larger than those of other agricultural wastes such as bagasse, which increased assessibility to other materials (Chawakitchareon et al., 1995). Because of the morphology of this substrate, therefore the specific sorption for dissolved solids such as transition metal ions and polar organic molecules is quite high (Coupal and Latancete, 1976). From this reason, the water hyacinth could be effectively used for removing heavy metal ions by sorption mechanism.
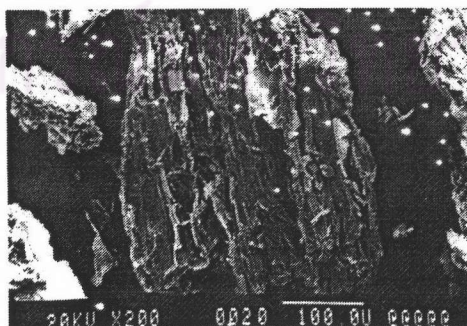

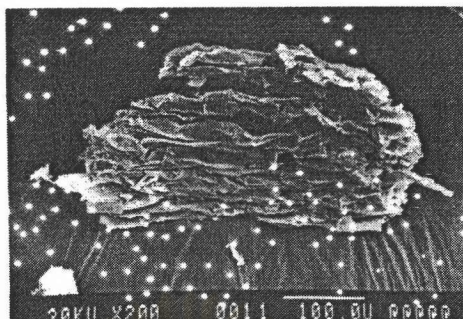Figure 4.4a : SEM photograph of untreated water hyacinth

Figure 4.4b : SEM photograph of 5 % FTWH

IR spectroscopy

In agreement with Odozi, 1985, this study found that all the water hyacinth substrate had a broad peak and another sharp one in the range of 3400-3200 cm^{-1} show the presence of OH groups (Appendix E1-E8). Thus, the substrate is basically monofunctional, with phenolic groups, participating in the exchange reaction with metal ions. A peak in the range of 1540-1405 cm^{-1} is that due to C-C multiple bond stretching. In addition broad signal occurring at about 1204-1041 cm^{-1} points to the presence of the C-O-C band (Appendix E). It is possible that the cross-linked reaction between microfibril of cellulose and formaldehyde may be obtained in the chemical treatment stage because only the C-O-C band from lignin would not show a great peak; some parts of lignin may be decomposed by this condition. The assignment of the significant peaks are showed in table 4.2

Table 4.2 : Main IR bands of various water hyacinth substrates

Assignments	Position of bands (cm^{-1})
O-H strectching (H-bonding)	4000-3000
C-H strectching in methylene groups	2942-2819
C-O-C stretching	1204-1041
C-C multiple bond stretching	1540-1405

Column experiments

Total capacity

The total capacities of the water hyacinth substrate are showed in Table 4.2. The values were very low in the original substrate but a considerable increase was obtained when the substrate was treated with 5 % formaldehyde. The selected percentage of formaldehyde was achieved from analysis of variance-one way classification by using SPSS program.

Table 4.3 : Total capacity of untreated W.H. and 5 % CH_2O treated W.H.

Metal ions	Samples	Untreated W.H.			5 % CH_2O treated W.H.		
		D.W. of substrate	Conc. (ppm)	Meq/g	D.W. of substrate	Conc. (ppm)	Meq/g
Cu^{2+}	1	05688	198.21	0.8987	0.5630	160.80	1.0965
	2	05683	198.51	0.8985	0.5642	161.10	1.0991
	3	05689	197.59	0.8958	0.5634	160.39	1.0929
			Average	0.8977		Average	1.0962
Ni^{2+}	1	0.5649	115.98	0.4978	0.5633	82.30	0.6995
	2	0.5637	115.20	0.5021	0.5637	83.07	0.6963
	3	0.5642	115.77	0.4973	0.5630	82.17	0.6991
			Average	0.4991		Average	0.6983
Zn^{2+}	1	0.5639	191.20	0.7182	0.5639	132.39	1.0372
	2	0.5638	191.31	0.7179	0.5631	132.15	1.0380
	3	0.5633	191.03	0.7173	0.5633	132.09	1.0374
			Average	0.7178		Average	1.0375

Calculation : $Meq/g = \dfrac{Conc. \times 100}{Eq.\ wt. \times 1000 \times wt.\ of\ sample}$

As given in table 4.2, the total capacities of 5 % FTWH were 1.0962, 0.6983 and 1.0375 meq/g for Cu^{2+}, Ni^{2+} and Zn^{2+}, respectively. It was found that the formaldehyde treated water hyacinth (FTWH) showed total capacity values of up to 1.0 meq/g for Cu^{2+} and Zn^{2+} when comparing with purolite synthetic resin (up to 3.0 meq/g). It notices that the values found for Cu^{2+} were always higher than those of Ni^{2+} and Zn^{2+}. This result is consistent with previous study by Chawakitchareon et al. (1995), which used acid treated water hyacinth, carboxymethyl water hyacinth, acid treated bagasse and carboxymethyl bagasse as substrates (Table 4.4).

Table 4.4 : Total capacities of various substrates

Substrates	Total capacities		
	Cu^{2+}	Ni^{2+}	Zn^{2+}
Acid treated W.H.*	0.809	0.686	0.705
Carboxymethyl W.H.*	0.496	0.346	0.330
Acid treated Bagasse*	0.086	0.065	0.069
Carboxymethyl Bagasse*	0.069	0.052	0.056
PWH	0.8977	0.4991	0.7178
5 % FTWH	1.0962	0.6983	1.0375

Remark : *Chawakitchareon and et al., 1995

Ion exchange capacity

As regard other possible sorption mechanisms, the experiment section was proposed to determine the main mechanism of removing some transition metal ions. However, the mechanism of sorption of water hyacinth is far as to conclude or indicate exactly. Thus, only the ion exchange mechanism was proposed instead. Ion exchange capacities of various substrates are showed in table 4.3, the capacities of

these substrates were measured according to the conventional method using ordinary acid-base titration. The capacities of synthetic Purolite resin, 5 % FTWH and unmodified water hyacinth were 3.367, 0.4094 and 0.3858 meq/g respectively. From this result, however, a capacity from other mechanisms can be computed by common equation as follow.

Other sorption capacity	=	Total capacity - Ion exchange capacity

Other sorption capacity may be associated with the adsorption and chelate formation (Chaney, 1979 ; Basta et al., 1996) due to obtaining data of this section that indicated certainly. However, it is not probable to compute the certainty of value. By almost of reasons relating with quite different methods, are all of average values of both capacities could not related precisely, especially for varying in species of transition metal ions (see table 4.3 and 4.4).

Table 4.5 : Ion exchange capacities of various substrate

Samples	Weight of substrates	Volume of 0.0989 N NaOH	Meq/g
Purolite resin			
1	0.5612	19.1	3.3660
2	0.5608	19.1	3.3684
3	0.5611	19.1	3.3666
		Average value	3.3670
5 % CH2O treated W.H.			
1	0.5636	2.3	0.4036
2	0.5638	2.4	0.4210
3	0.5635	2.3	0.4037
		Average value	0.4094
Untreated W.H.			
1	0.5639	2.2	0.3858
2	0.5640	2.2	0.3858
3	0.5382	2.1	0.3859
		Average value	0.3858

Calculation : Meq/g $=$ $\dfrac{\text{Normality of NaOH x } V_{\text{NaOH (ml)}}}{\text{Wt. of substrate}}$

Heavy metal ion removal

From the results obtained in the batch experiments, several experiments were conducted with the various heavy metal ion synthetic solutions using packed bed column of FTWH packed beds column (Appendix C; experiment no. C1-12). Also, continuous sorption on a packed bed column is often more economical to operate than a batch process.

As can be expected, a decrease in concentration of synthetic solution led to an increase in the dynamic capacities (Figure 4.5 a-l). The correlation coefficient for Cu^{2+}, Ni^{2+} and Zn^{2+}, indicating perfect negative relationship, are -0.85, -1.00 and -0.78, respectively. These values were computed by Pearson product - moment method (Appendix D-3). Concerning affinity of heavy metal ions, it was found that the greatest apparent capacity of FTWH for removal of heavy metal ions was for Cu^{2+}. The result is similar to the results from batch experiments of this study and may be due to the presence of lignin and other chelating substances that involved in chemical bonding (Coupal and Lalancette, 1976 ; Chaney, 1979). In addition, the result is consistent with a previous study by Randall (1978) using peanut skins as a substrate.
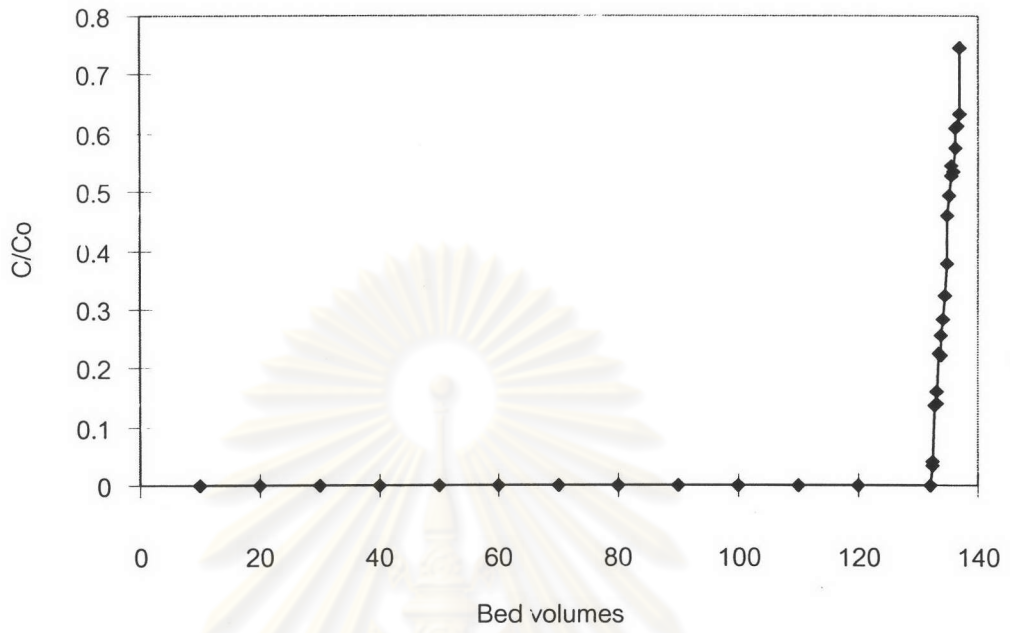
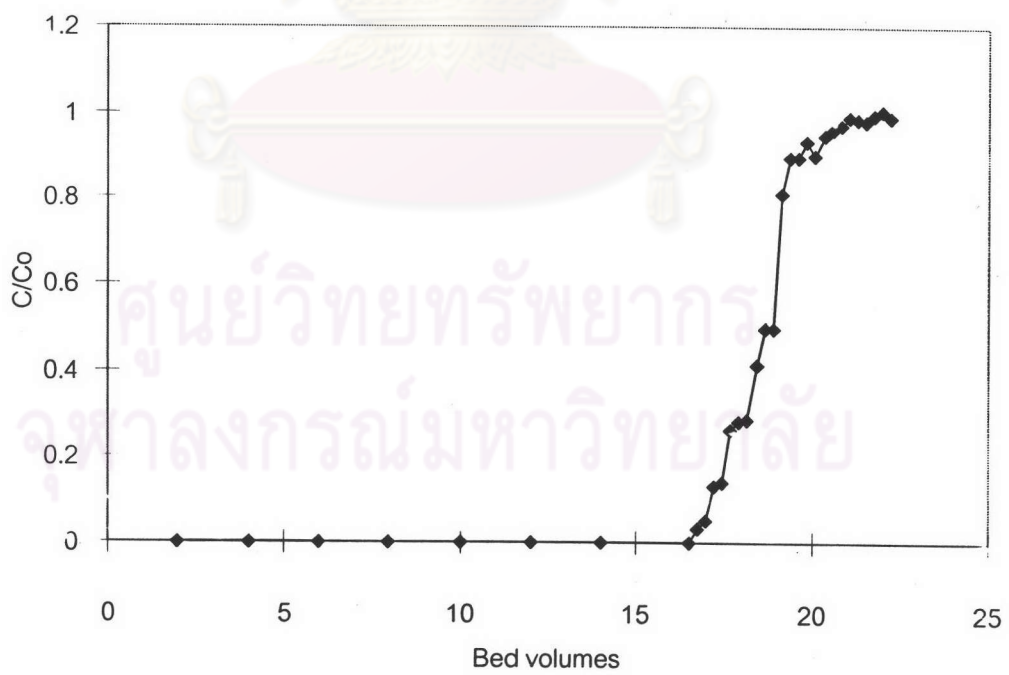Figure 4.5a : Heavy metal ion removal for 5.16 ppm Cu^{2+}
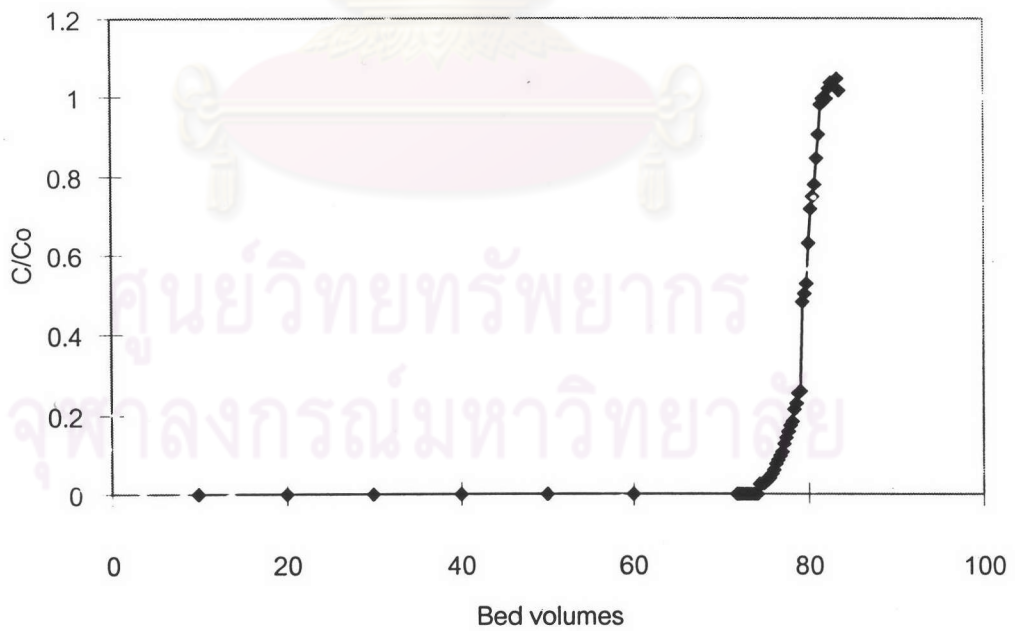
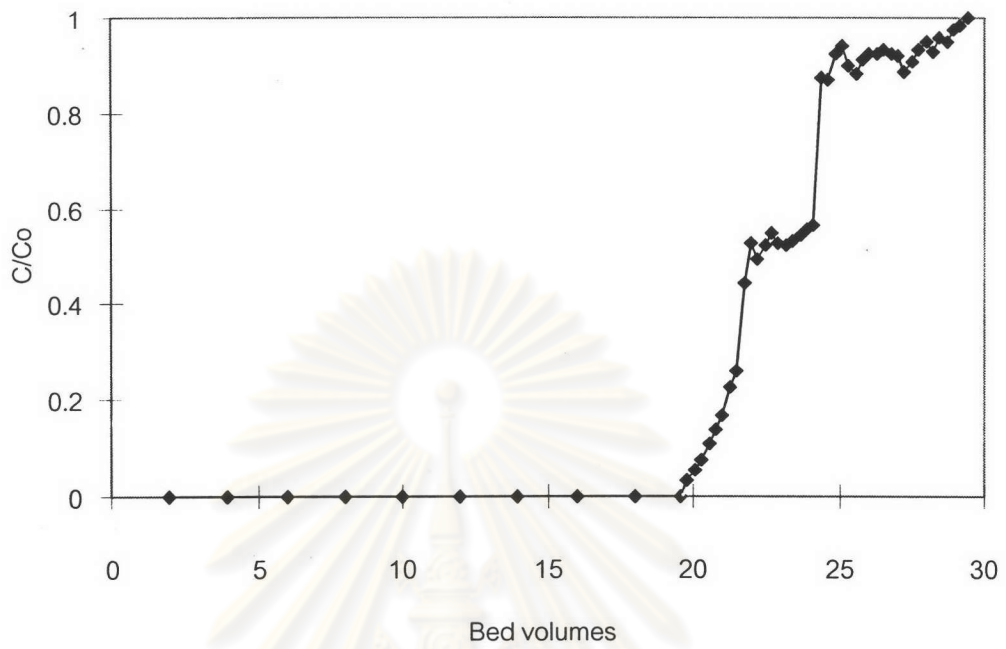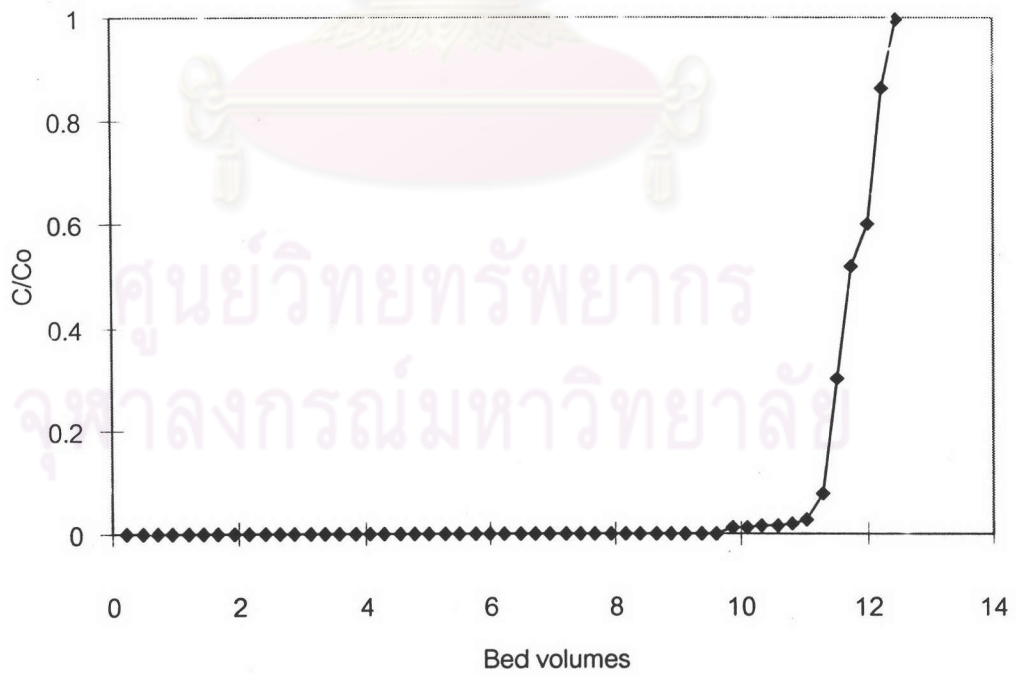Figure 4.5b : Heavy metal ion removal for 5.12 ppm of Ni^{2+}
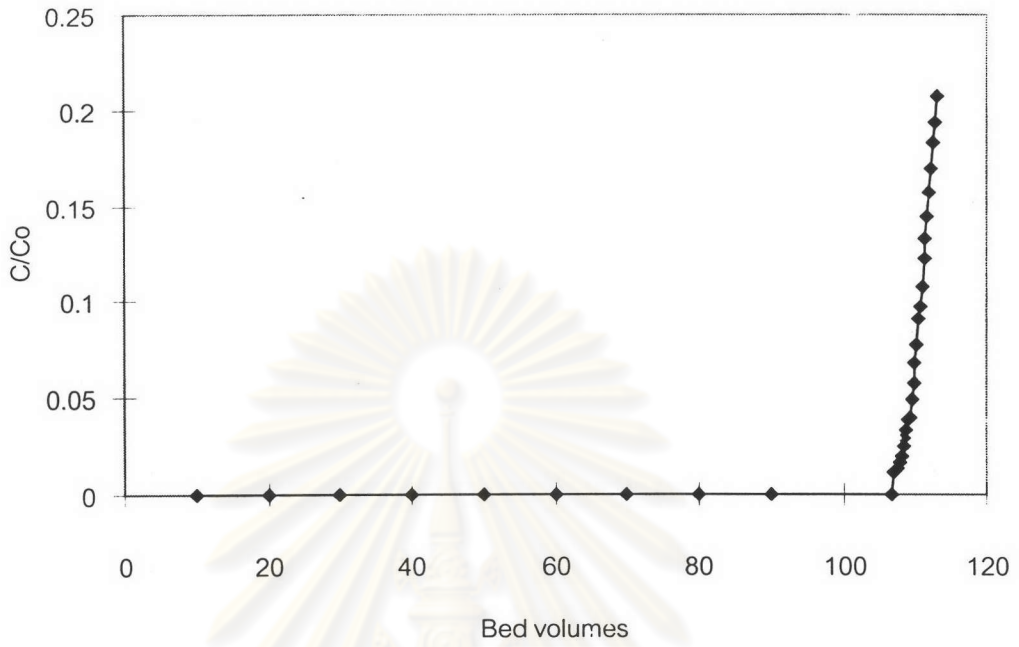
Figure 4.5c : Heavy metal ion removal for 4.92 ppm of Zn^{2+}
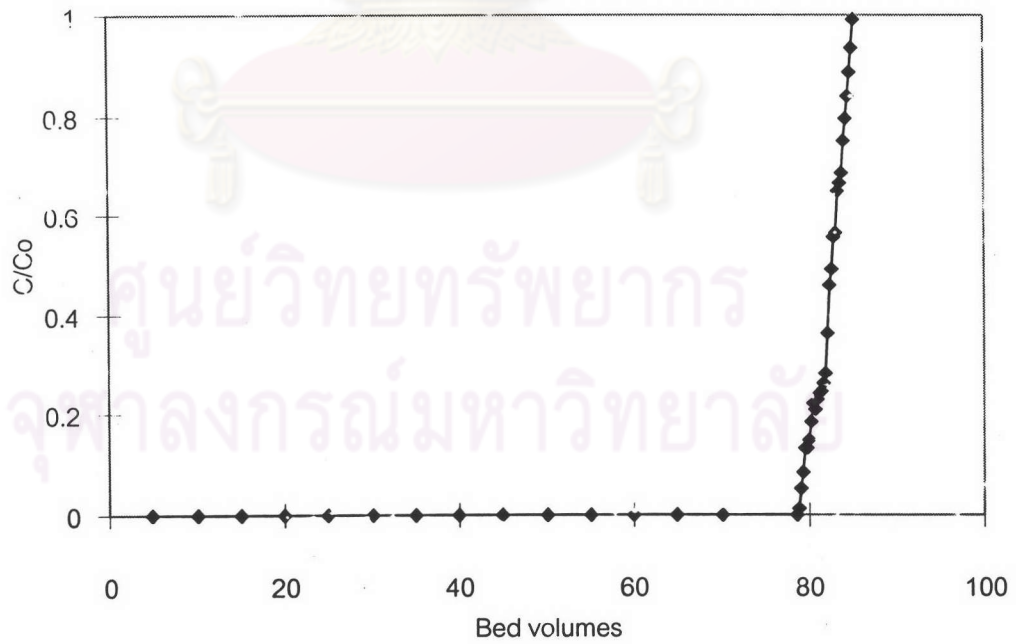
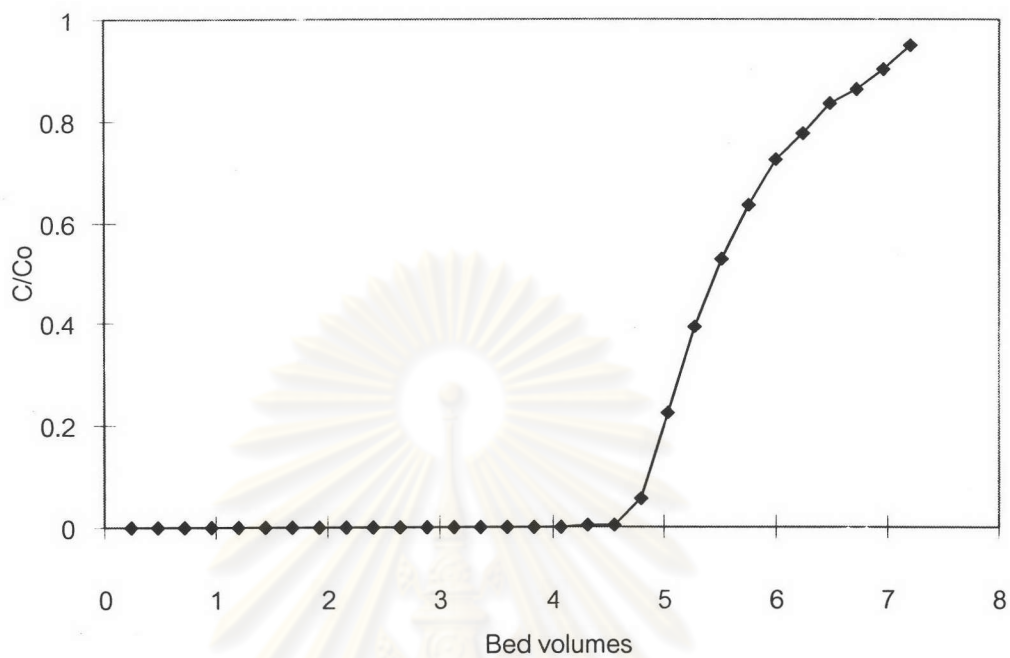Figure 4.5d : Heavy metal ion removal for 10.46 ppm of Cu^{2+}
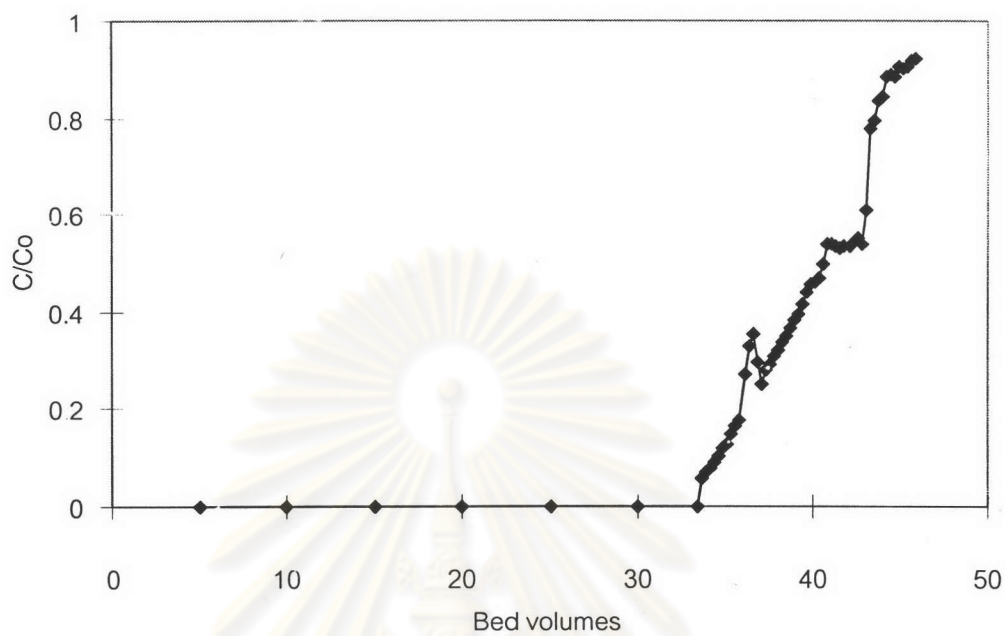
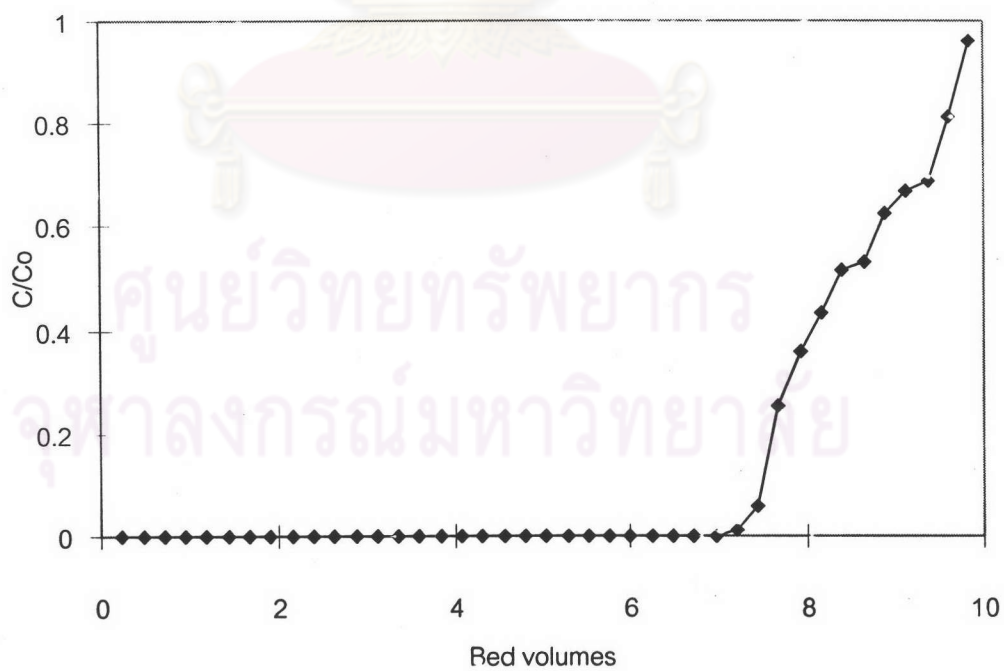Figure 4.5e : Heavy metal ion removal for 10.57 ppm of Ni^{2+}
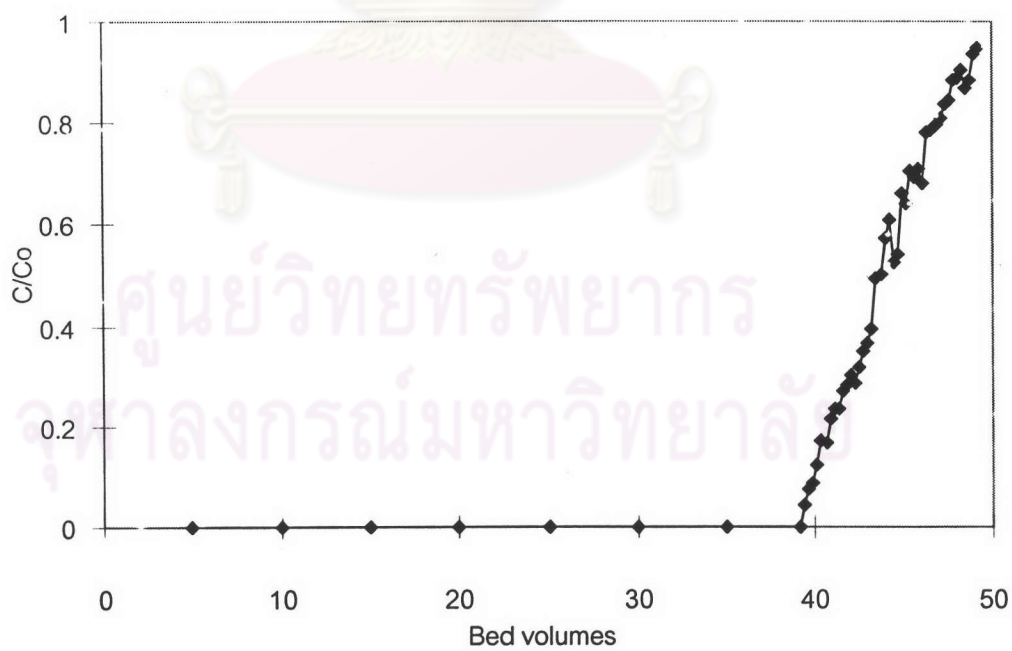
Figure 4.5f : Heavy metal ion removal for 10.49 ppm of Zn^{2+}
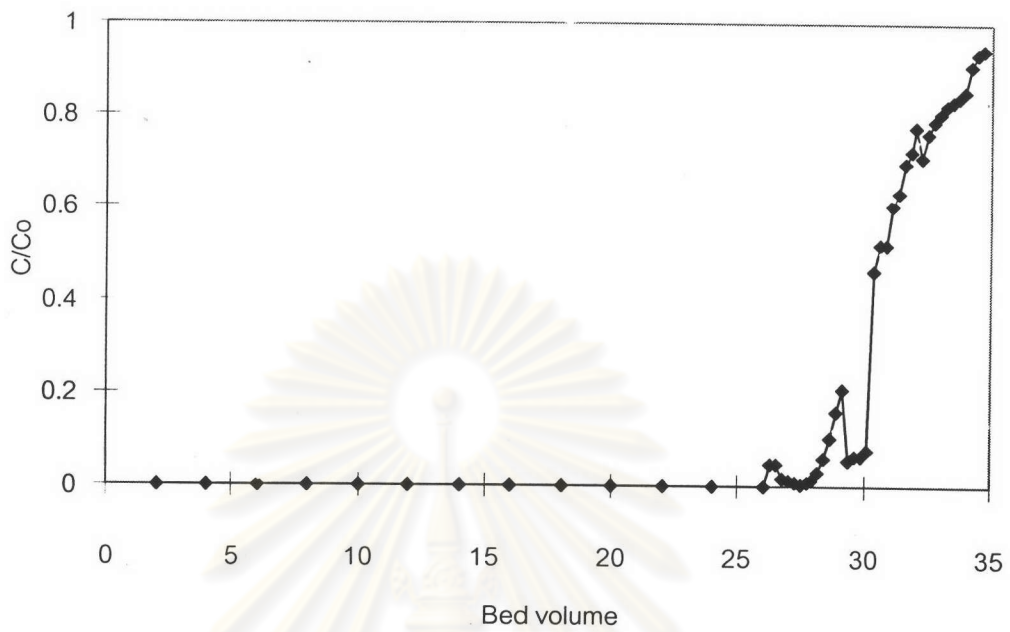
Figure 4.5g : Heavy metal ion removal for 20.86 ppm of Cu^{2+}

Figure 4.5h : Heavy metal ion removal for 18.89 ppm of Ni^{2+}

Figure 4.5i : Heavy metal ion removal for 19.41 ppm of Zn^{2+}

Figure 4.5j : Heavy metal ion removal for 52.65 ppm of Cu^{2+}

Figure 4.5k : Heavy metal ion removal for 51.75 ppm of Ni^{2+}

Figure 4.5l : Heavy metal ion removal for 50.18 ppm of Zn^{2+}

Regeneration

Prior to break through curve, it indicated that the 5 % FTWH packing, which turned brownish black as Cu^{2+} was adsorbed. This result may be partially attributable to the chelating reaction for alternate color of original substrate.

When the experiment was completed, the column was washed with 0.5 N HCl about 1 bed volume until all of heavy metal ions were removed completely (Figure 4.6a-1). To determine the column capacity after regeneration, a small column model was carried out and the result showed that the regenerated substrate has a capacity as same as the original substrate. In the other word, the acid treatment has no apparent effect on the efficiency of the substrate for five times as shown in figure 4.7
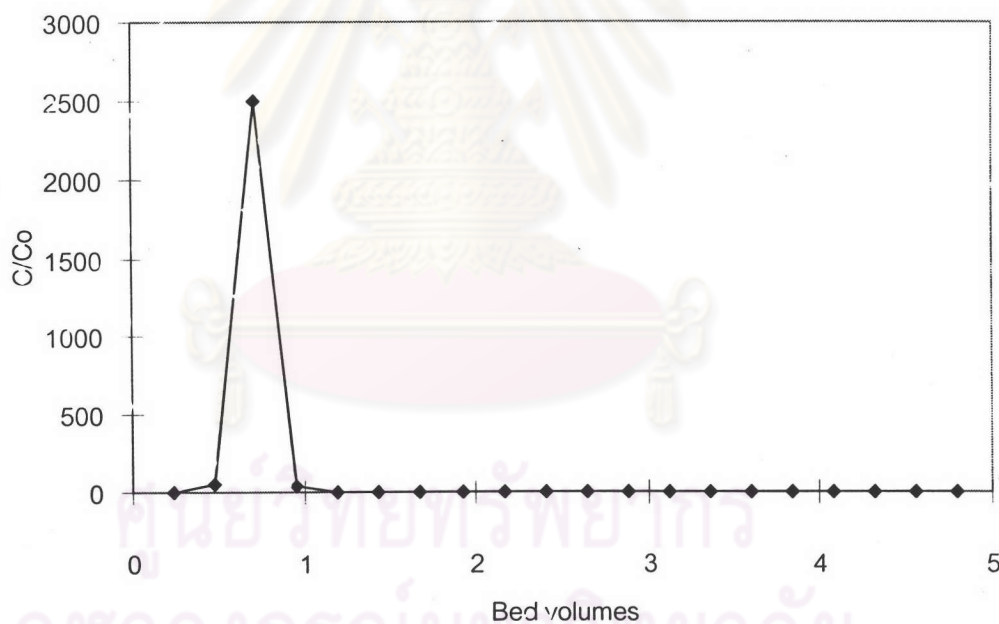
Figure 4.6a : Regeneration for 5.16 ppm of Cu^{2+}
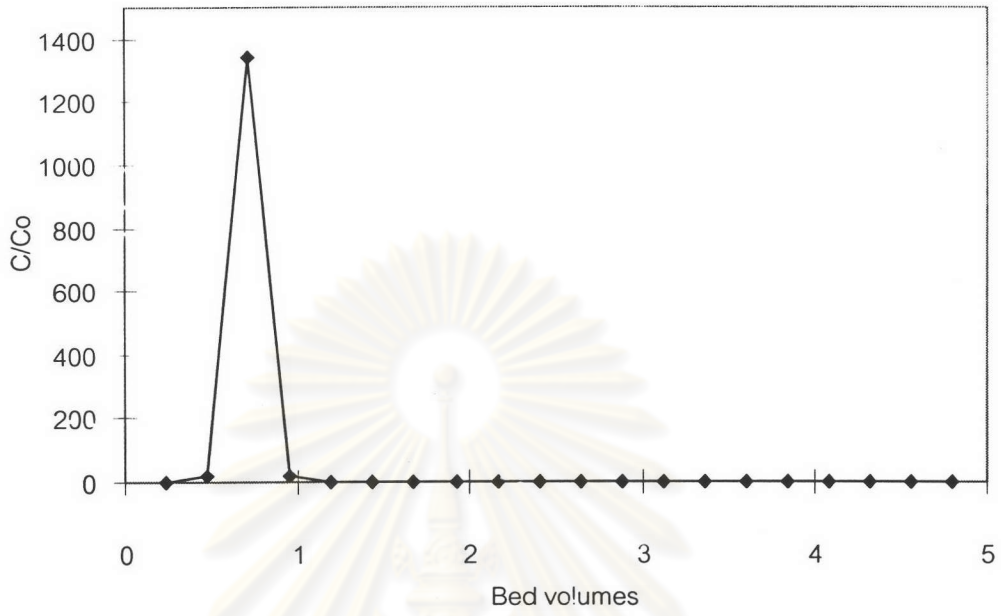
Figure 4.6b : Regeneration for 5.12 ppm of Ni^{2+}
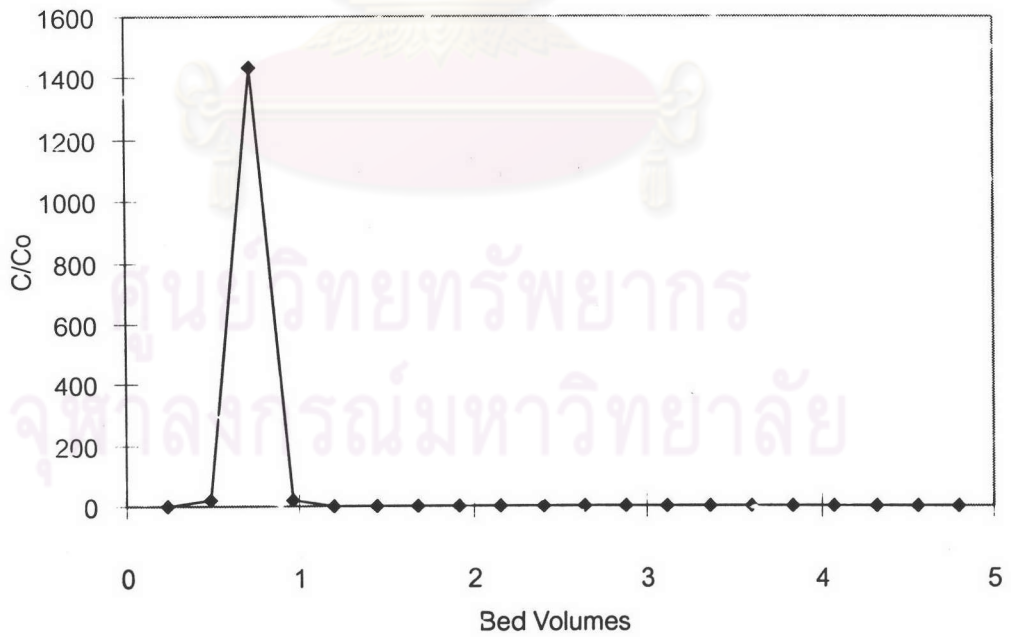
Figure 4.6c : Regeneration for 4.92 ppm of Zn^{2+}
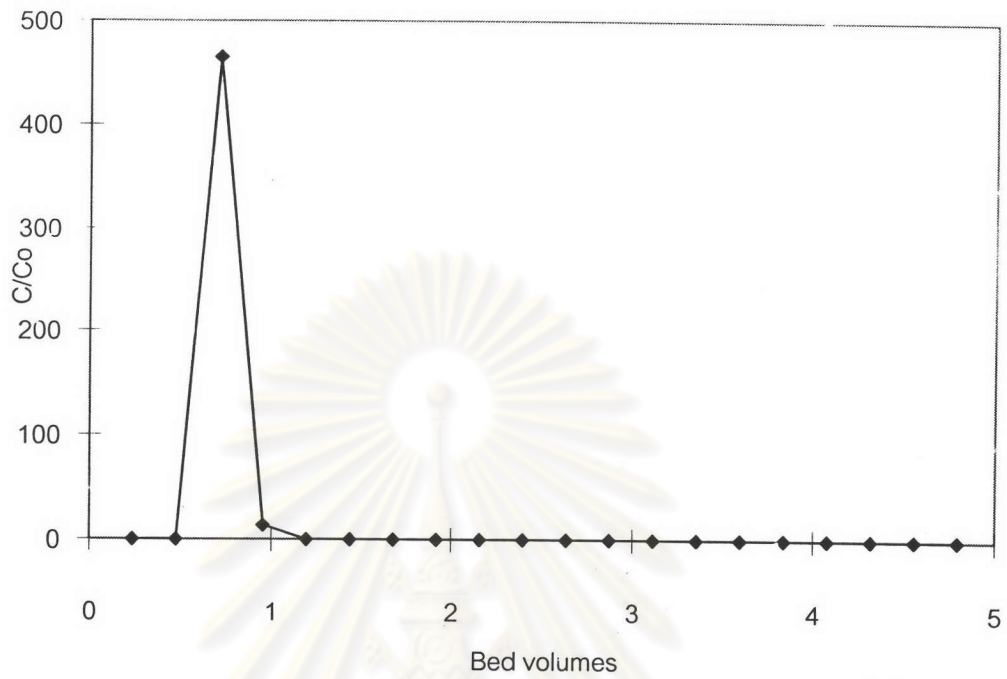
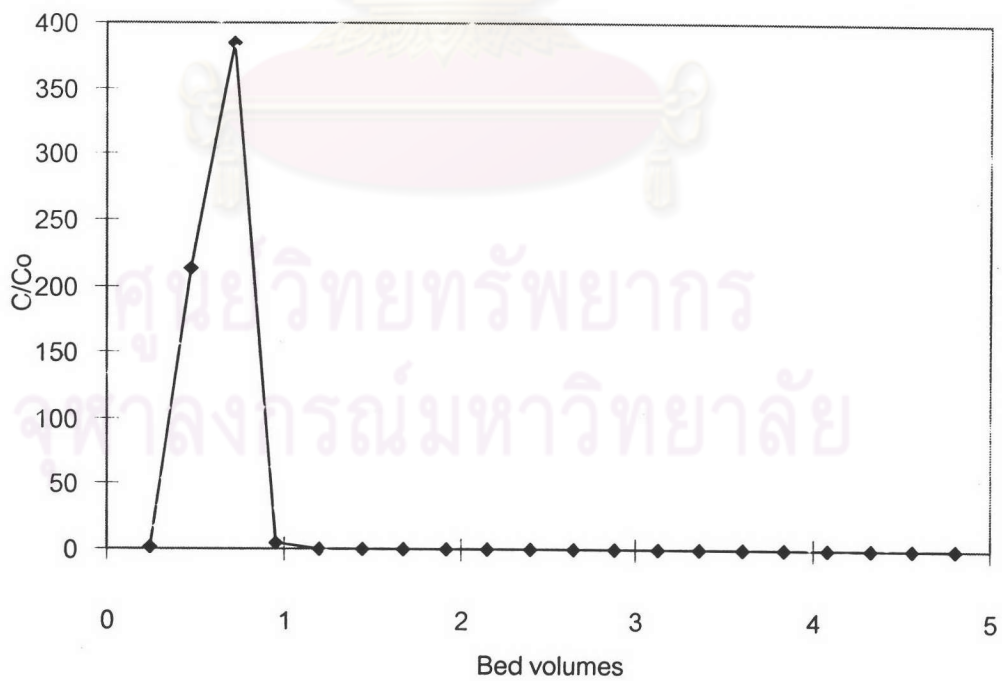Figure 4.6d : Regeneration for 10.46 ppm of Cu^{2+}

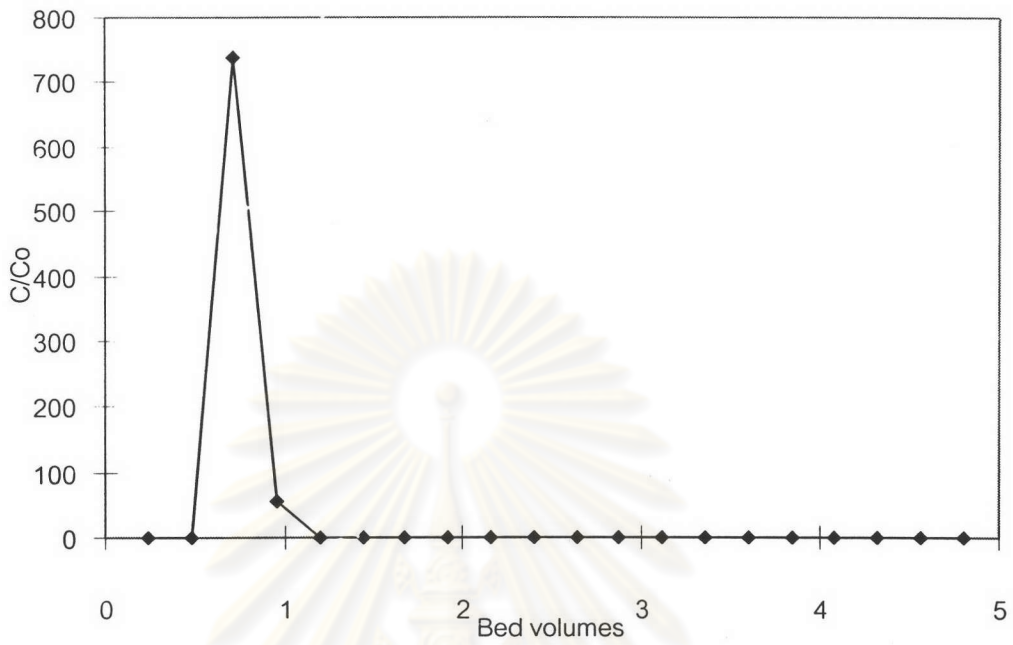Figure 4.6e : Regeneration for 10.57 ppm of Ni^{2+}

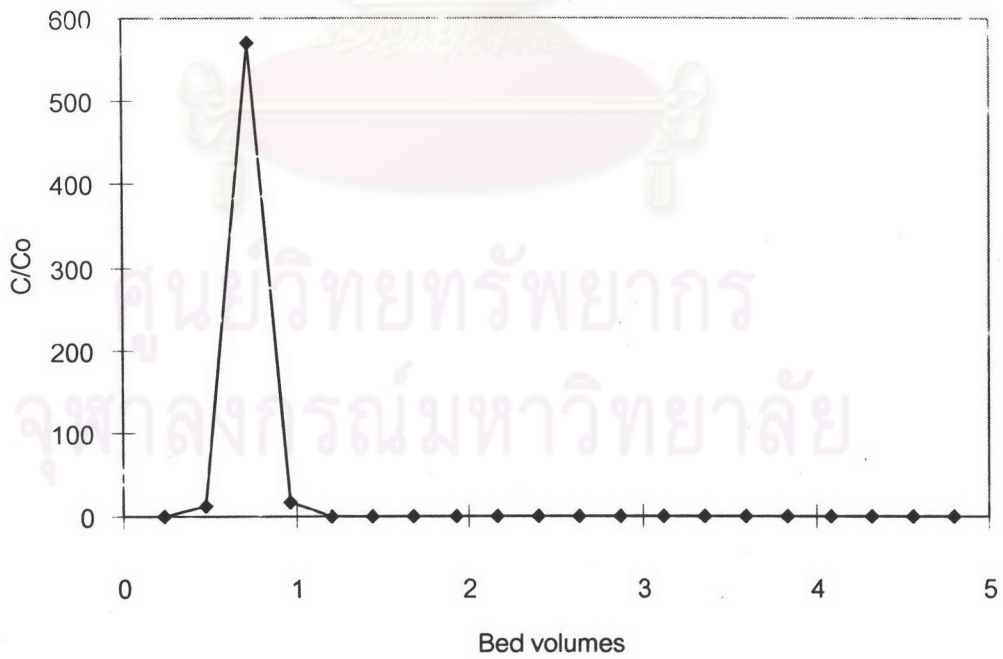Figure 4.6f : Regeneration for 10.49 ppm of Zn^{2+}
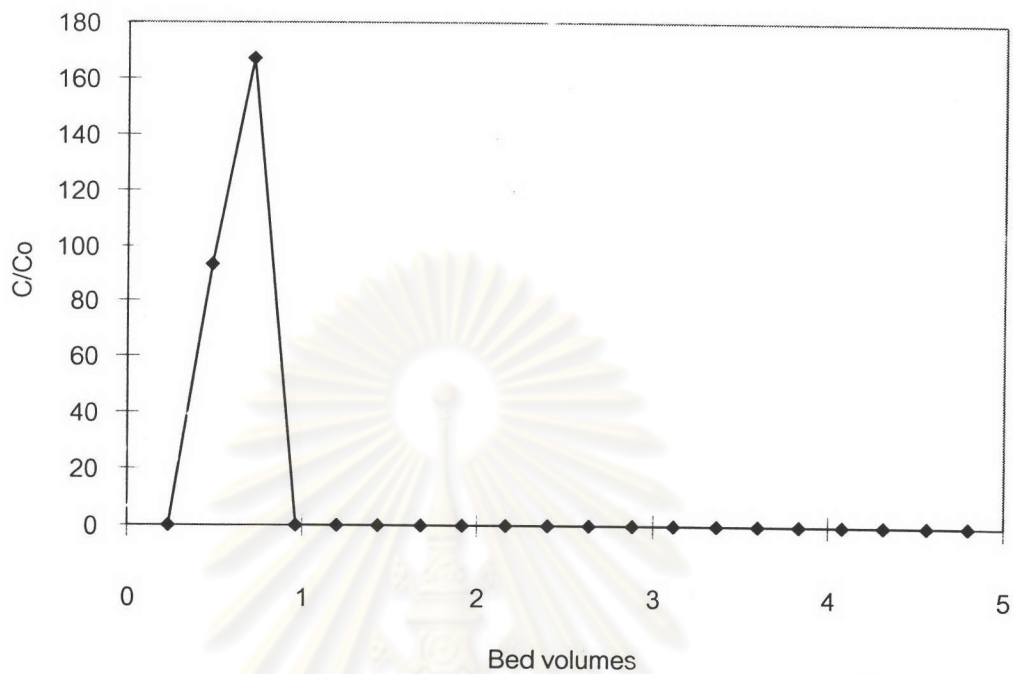

Figure 4.6g : Regeneration for 20.86 ppm of Cu^{2+}

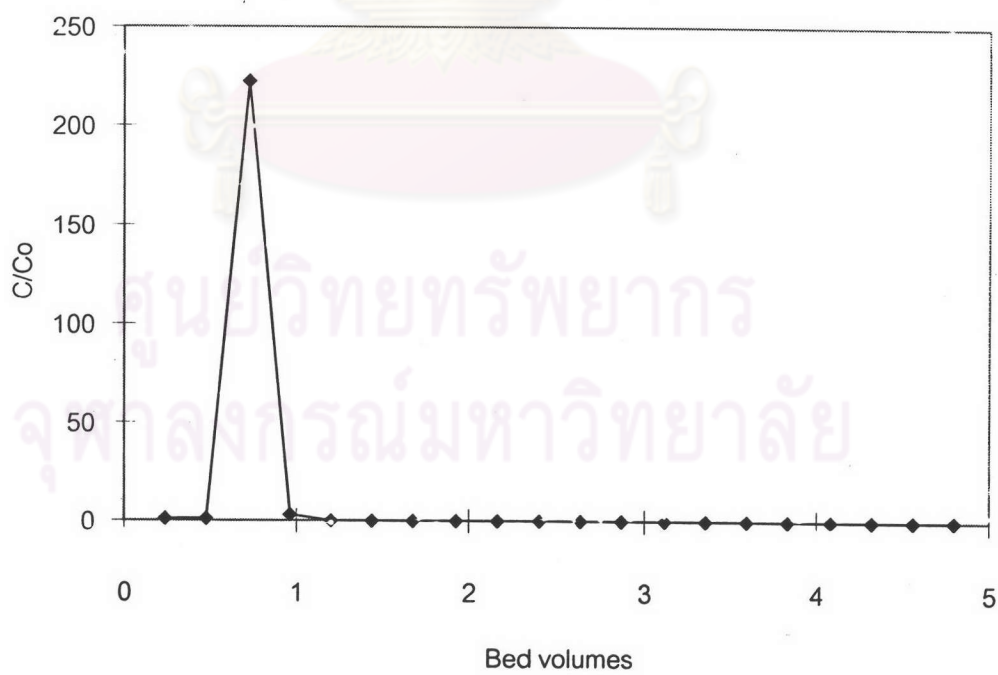Figure 4.6h : Regeneration for 18.89 ppm of Ni^{2+}

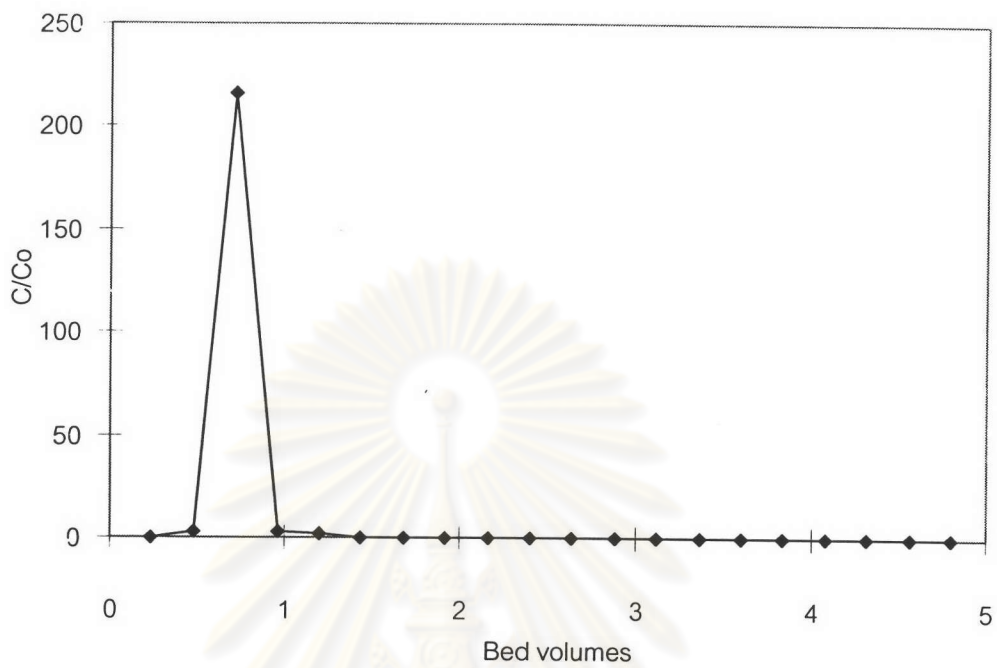Figure 4.6i : Regeneration for 19.41 ppm of Zn^{2+}
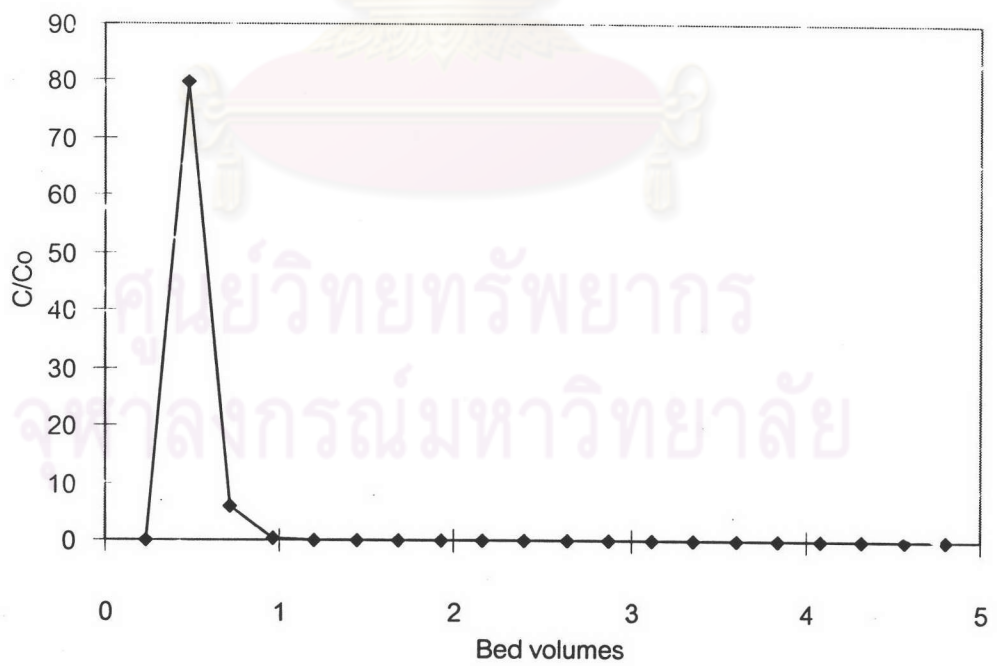
Figure 4.6j : Regeneration for 52.65 ppm of Cu^{2+}
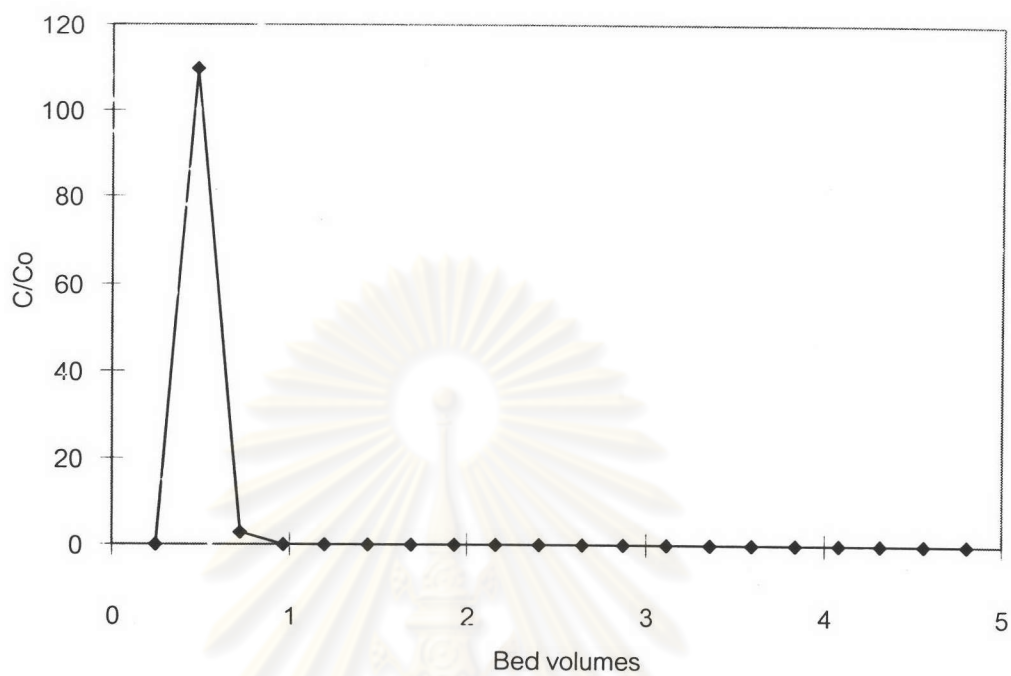

Figure 4.6k : Regeneration for 51.75 ppm of Ni^{2+}

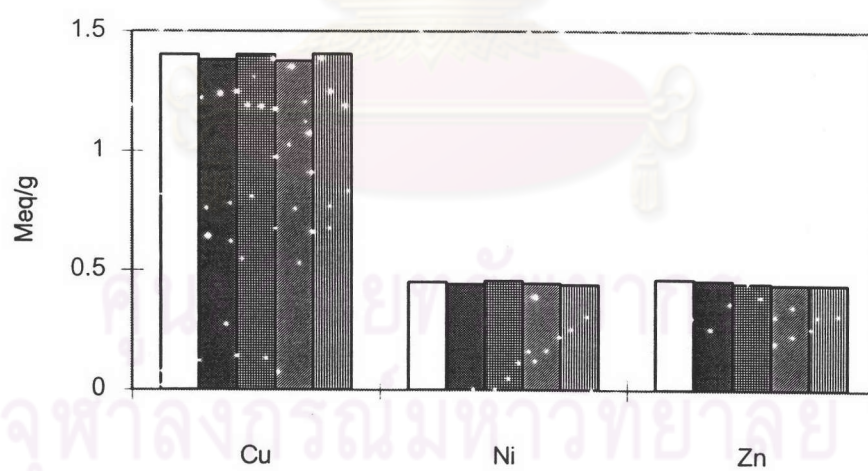Figure 4.6l : Regeneration for 50.18 ppm of Zn^{2+}

Figure 4.7 : Effect of acid treatment for 5 times regeneration

Treatment of Zn-electroplating industrial wastewater

The 5% FTWH could be effectively used for removing heavy metal ions from Zn-electroplating wastewater. Because the remaining of heavy metal ions in effluent, ordinarily treated electroplating effluent showed lower than 0.05 ppm of Zn^{2+} (Table 2.3 : National guideline, 1992), which is a level below local water quality limits (5 ppm) and also acceptable concentratins of toxicants for marine and estuarine waters (see Table 2.2). For amount of substrate used, it found that 0.1357 m^3 of the wastewater could be treated by using a kilogram of 5 % FTWH. The dynamic capacity, however, was slightly decreased when comparing with synthetic solution. It might be partially attributable to other metal ions such as Fe^{2+}, Fe^{3+} and Cu^{2+} that affected the dynamic capacity (Appendix C; experiment no. C13).
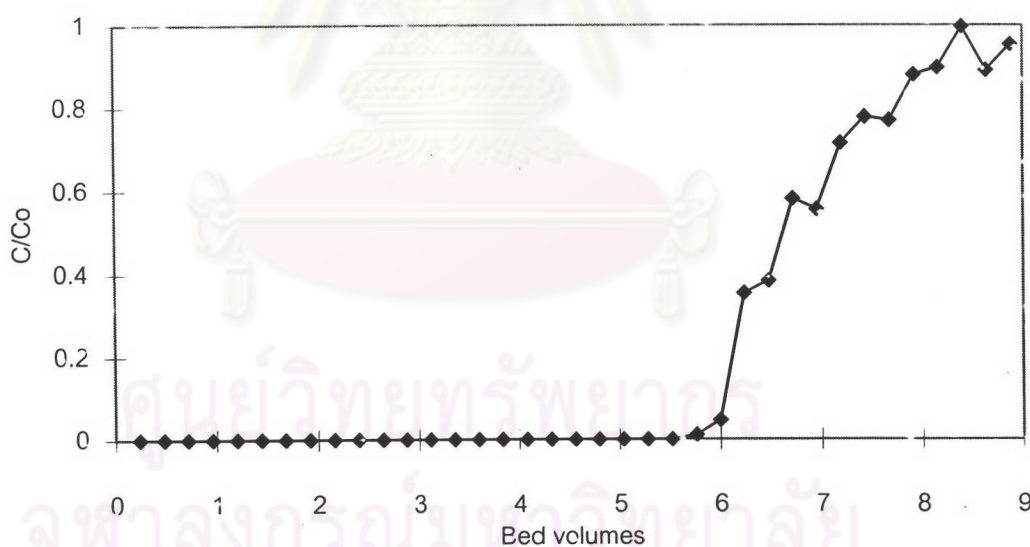

Figure 4.8a : Heavy metal removal for 48.88 ppm of Zn^{2+} ions
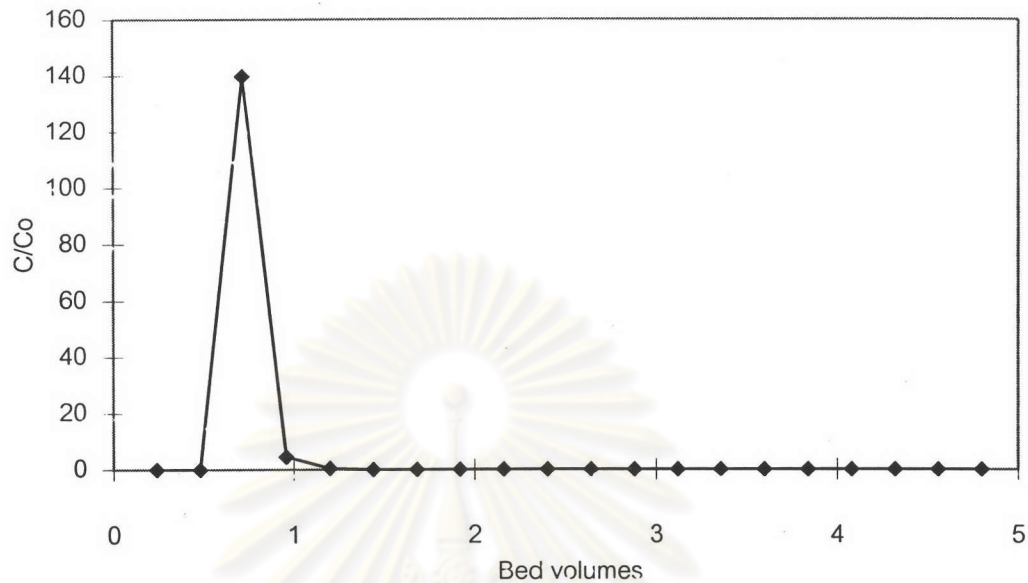
from electroplating wastewater

Figure 4.8b : Regeneration for 48.88 ppm of Zn2+ ions from

electroplating wastewater

Effect of deprotonation on pH value

Almost of pH different ranging between influent and effluent solutions, obtained by column experiments, it was found that there was a significant difference between influent pH value (pH = 5) and effluent pH value (pH varying = 3.0-4.0). After brokethrough curve had obtained, the pH value of effluent had increased gradually because the protons were replaced partly from the packed column. This result is probably due to the ion exchange process, including some of chelate forming process. Because the fundamental of ion exchange mechanism is the releasing of counter-ions such proton (H^+) as some of transition metal ions are replaced (Appendix C; experiment no. C1-12).