CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the results are divided into three parts; (i) the characterization of the sorbent, (ii) the extraction of metal ions by batch system, and (iii) the extraction of metal ions by column system. Finally, the method was applied for the extraction of the metal ions in real sample.

4.1 Characterization of humic acids immobilized on aminopropyl silica

The infrared spectra of aminopropyl silica (SiAP), humic acids (HA) and humic acids immobilized on aminopropyl silica (Si-HA) were depicted in Figure 4.1. From Infrared spectrum A, which is aminopropyl silica, the broad absorption band at about 3400 cm^{-1} generally ascribed to N-H stretching of amino groups, and the strong absorption peak at about 1080 cm^{-1} generally attributed to Si-O-Si of the main silica.

From the infrared spectrum B, which is humic acids, the intense broad band at about 3400 cm^{-1} generally ascribed to O-H stretching of carboxyl groups and phenolic hydroxyl groups, and secondarily, to N-H stretching of various functional groups. The two small peaks at about 2920 and 2850 cm^{-1} are C-H stretching of aliphatic groups. The strong two broad peaks at 1720 – 1715 cm^{-1} is preferentially ascribed to C=O stretching of carbonyl, especially carboxyl groups and at 1625 - 1615 cm^{-1}, generally attributed to vibration of various groups, especially the vibration of C=C of aromatic structure of humic acids.

The infrared spectrum C, Si-HA, shows the combination of two spectra mentioned earlier. The strong peak at about 1080 cm^{-1} generally attributed to Si-O-Si of the main silica. The two weak peaks at 1720 cm^{-1} ascribed to C=O stretching of carbonyl, especially

carboxyl groups and at 1615 cm^{-1}, attributed to vibration of C=C of aromatic structure of humic acids and at 3400 cm^{-1} is attributed to N-H and O-H stretching.
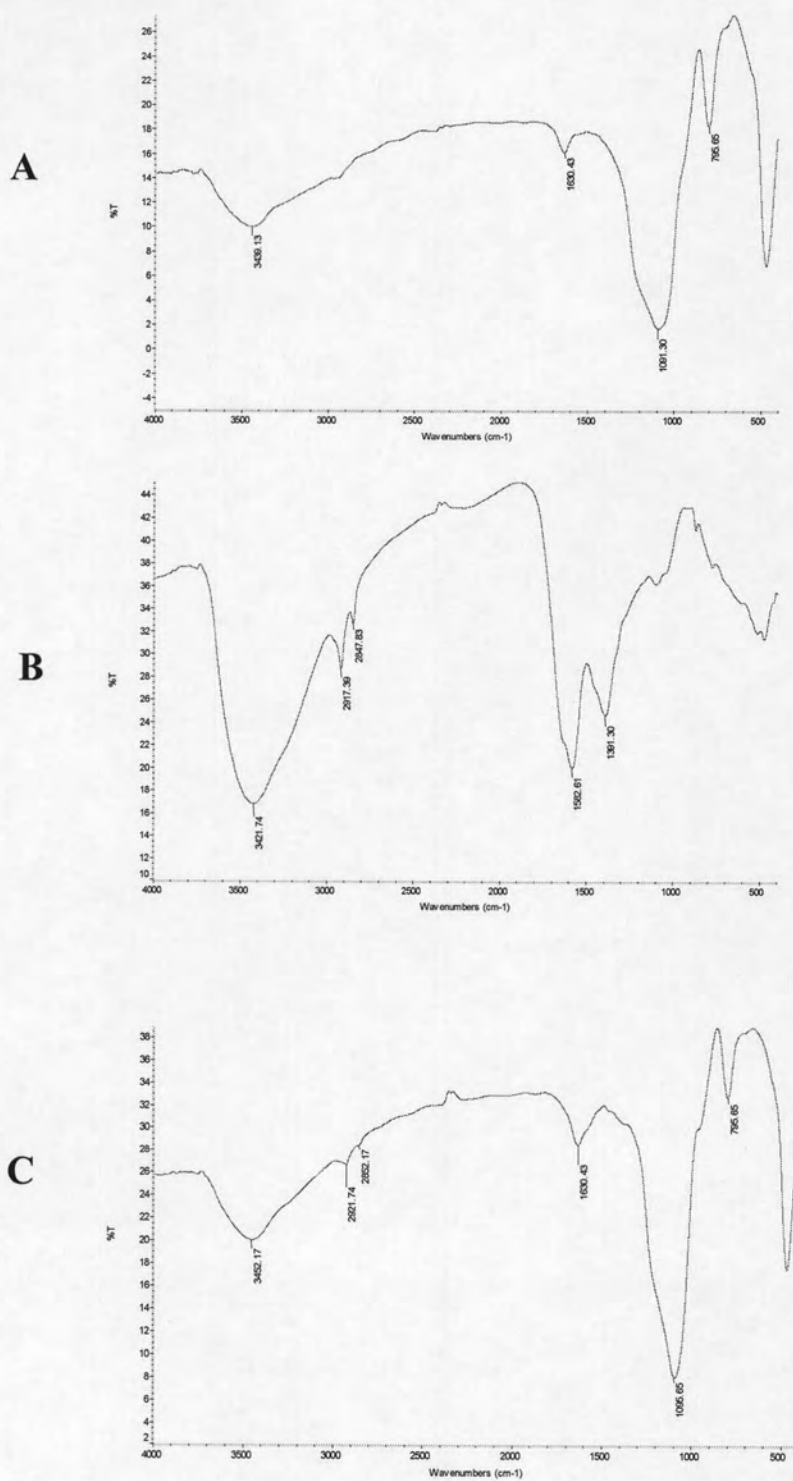
A

B

C

Figure 4.1 Infrared Spectra of A = Aminopropyl silica (SiAP), B = Humic acids (HA) and C = Humic acids immobilized on aminopropyl silica (Si-HA).

This result revealed that humic acids could be successfully coated on aminopropyl silica. The visual color change of the solid support was also observed; SiAP was white, HA was black and Si-HA was brown.

4.2 Extraction study using batch system

The adsorption efficiency is reported in term of percent extraction which is defined as the amount of sorbed metal per initial amount of metal ion according to equation 4.1.

$$\text{Extraction (\%)} = ((n_i - n_f) / n_i) \times 100 \qquad (4.1)$$

where n_i is the initial amount of metal (mg), n_f is the amount of metal in supernatant (mg).

4.2.1 Effect of pH on metal extraction

The adsorption of heavy metals (Au(III), Ag(I), Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II)) onto Si-HA sorbent as a function of pH of aqueous solution was studied using the batch method. The influence of pH on the extraction efficiency is shown in Figure 4.2. The contact time was fixed at 60 minutes in order to ensure the extraction equilibrium.
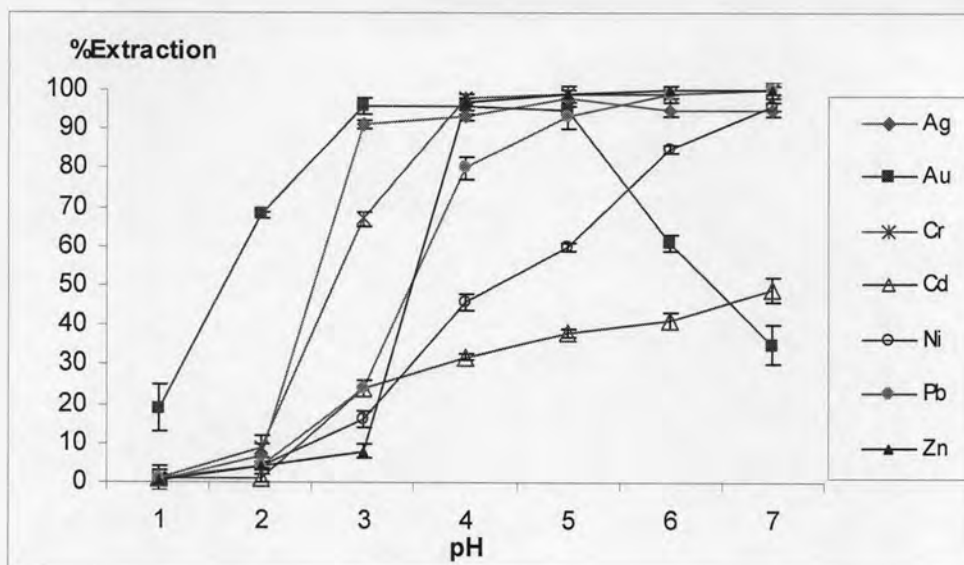
Figure 4.2 Effect of pH of metal solutions on metal adsorption onto Si-HA (contact time 60 min, n=3).

When pH values of solutions increased, the adsorption efficiency of Ag(I), Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) increased. The maximum sorption capacity of these metal ions onto Si-HA was observed at pH ranging from 4.0-7.0 depending on the type of metal ion.

In strongly acidic solutions, Si-HA surface could be positively charged by protonation of amine groups of HA which cannot bind with metal cations. Moreover, at pH lower than 3, the carboxylic groups (-COOH) could not dissociate [1], and as a result, there is no electrostatic interaction with metal ions. Therefore, the adsorption efficiency was low, except Au(III). When the pH values of solution increased, the deprotonation of nitrogen donor atoms as well as the dissociation of –COOH occurred and they became electron donors for metal ions resulting in higher adsorption efficiency.

For Ag(I), Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II), an increase of pH value resulted in the increase of extraction efficiency. It is possible that the adsorption mechanism of these cations with Si-HA was complexation and also ion exchange [38].

On the one hand, the extraction efficiency of Au(III) decreased when pH value was higher than 5. It could be explained that Au(III) was not a free cation but it was in chloride anion form ($AuCl_4^-$). Therefore, the adsorption of Au(III) onto Si-HA may not occur via complexation but ion exchange. At low pH, there were enough protons to protonate the nitrogen atoms in the structure of Si-HA. Therefore, Si-HA showed cationic characteristic on which prefer to adsorb $AuCl_4^-$. On the other hand, the surface of Si-HA became more negative because of proton dissociation of COOH at high pH. As a consequence, there is probably an electrostatic repulsion between $AuCl_4^-$ and COO^- and the adsorption efficiency decreased.

4.2.2 Effect of contact time

In this study, the contact time was varied from 10 to 60 minutes. The extraction efficiencies in function of contact time were shown in Figure 4.3. The contact time required for reaching extraction equilibrium was 30 minutes for all metal ions studied at pH 4.0.
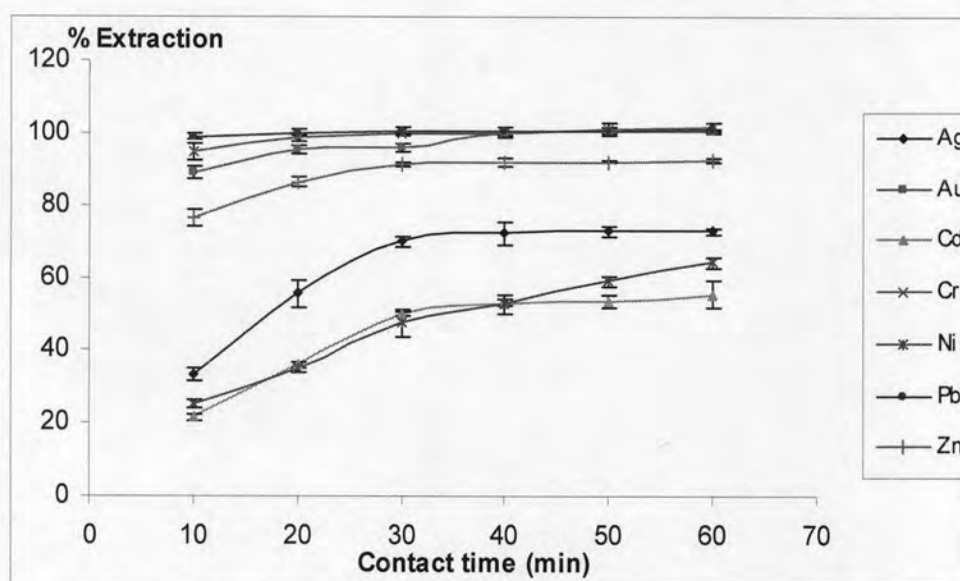

Figure 4.3 Effect of contact time on heavy metal ions adsorption onto Si-HA.

For Ni(II), it does not seem to reach the equilibrium at this condition. An equilibrium time depends on several factors such as an initial concentration and an amount of sorbent used. More experiment was not performed. It seems that the extraction of Ni(II) by batch method is not recommended because of long time required to reach an equilibrium.

4.2.3 Adsorption isotherm

The results showed the linearity of the adsorption isotherm derived from the C/N_f as a function of C plot (Fig. 4.4 – 4.10), indicating that the adsorption isotherm of Ag(I), Au(III), Cr(III), Cd(II), Pb(II), Ni(II) and Zn(II) onto Si-HA obeyed the Langmuir type adsorption model.
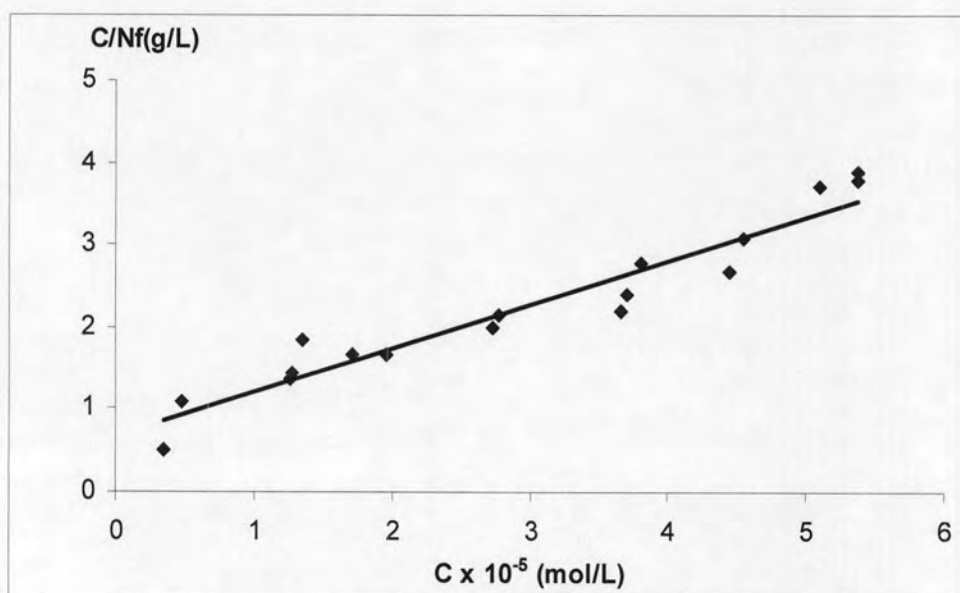

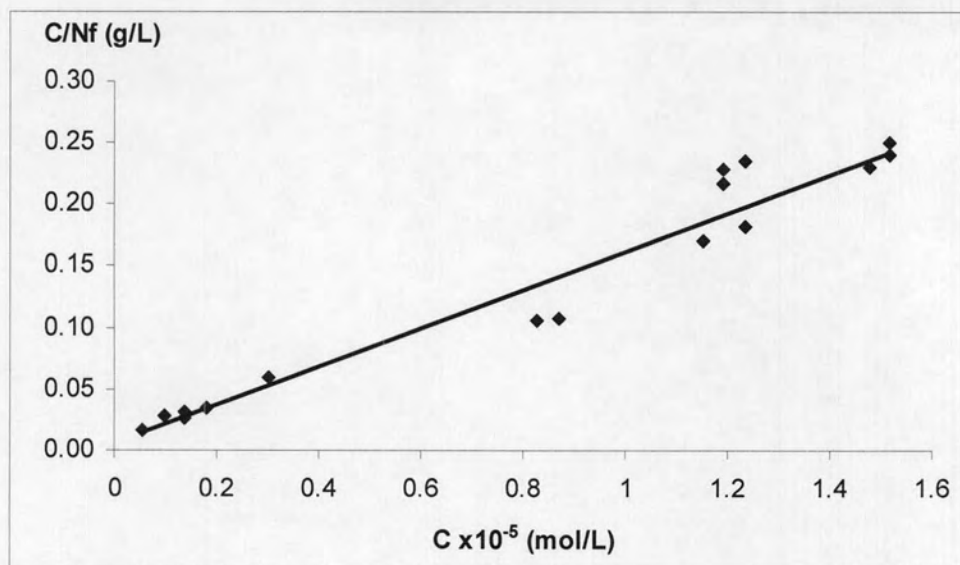**Figure 4.4** Langmuir adsorption model of Ag(I) onto Si-HA at 298 K.

Figure 4.5 Langmuir adsorption model of Au(III) onto Si-HA at 298 K.

Figure 4.6 Langmuir adsorption model of Cr(III) onto Si-HA at 298 K.

Figure 4.7 Langmuir adsorption model of Cd(II) onto Si-HA at 298 K.
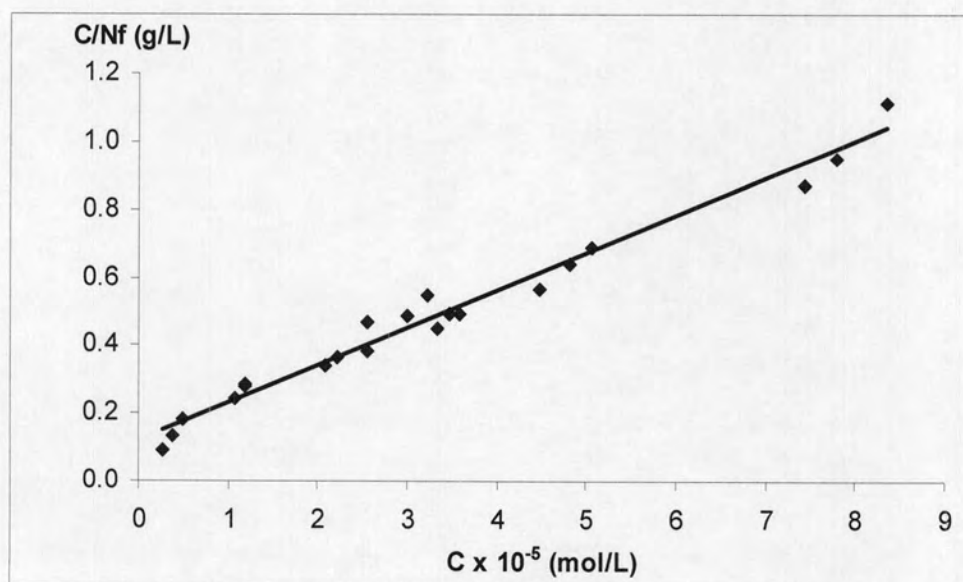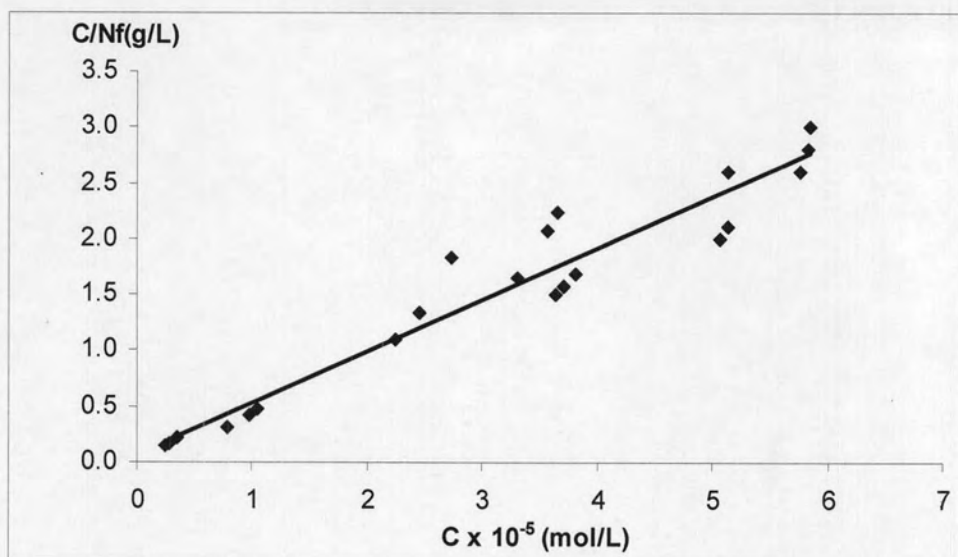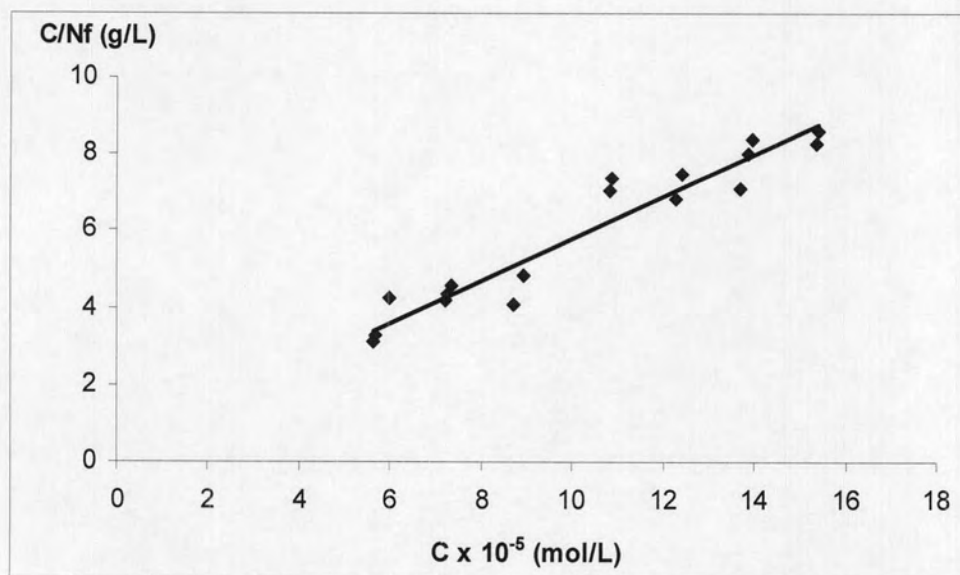

Figure 4.8 Langmuir adsorption model of Ni(II) onto Si-HA at 298 K.
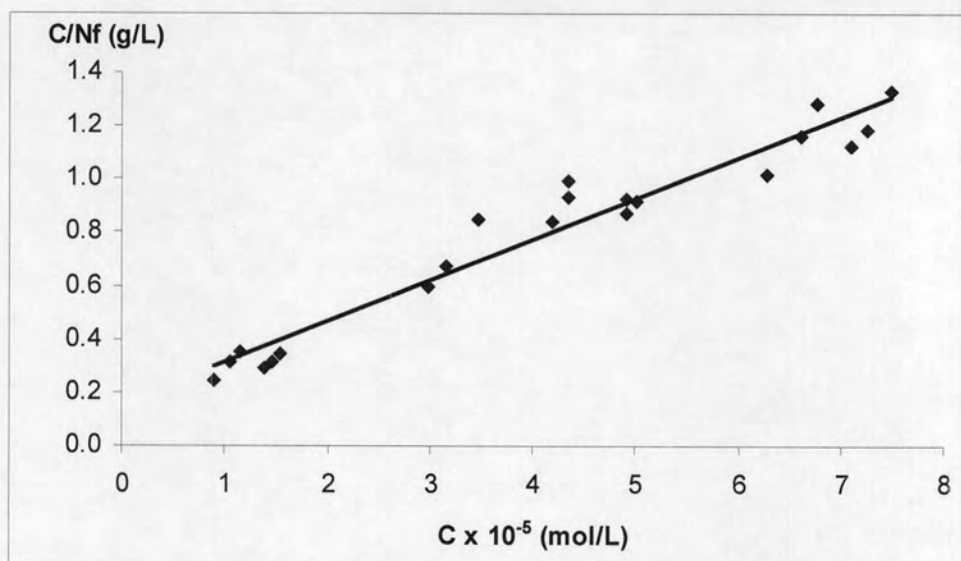
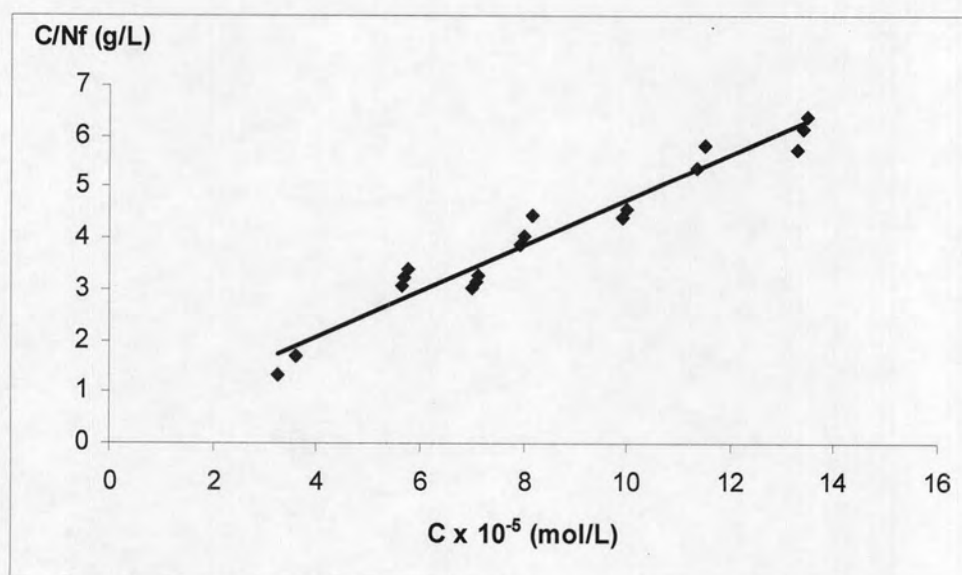**Figure 4.9** Langmuir adsorption model of Pb(II) onto Si-HA at 298 K.

Figure 4.10 Langmuir adsorption model of Zn(II) onto Si-HA at 298 K.

The calculated parameters: maximum sorption capacity (N_f^s), b value and correlation coefficient (r^2) from the Langmuir plots, are reported in Table 4.1.

Table 4.1 Calculated Langmuir constants for metal ion adsorption onto Si-HA at 298 K

	Equation	N_f^s	b	r^2
		$(mol\ g^{-1}) \times 10^{-4}$	$(L\ mol^{-1}) \times 10^4$	
Ag(I)	y = 52896x+0.6828	0.189	7.75	0.9626
Au(III)	y = 15505x+0.0057	0.645	272	0.9768
Cr(III)	y = 10994x+0.1216	0.910	9.04	0.9881
Cd(II)	y = 45963x+0.0796	0.218	57.7	0.9655
Ni(II)	y = 54768x+0.3340	0.182	16.4	0.9141
Pb(II)	y = 15375x+0.1563	0.650	9.84	0.9749
Zn(II)	y = 45044x+0.2523	0.222	17.9	0.9543

The results show that the adsorption of metal ions on Si-HA fitted the Langmuir model with acceptable r^2 values, which means that the adsorption of these metal ions on the surface was monolayer [39].

The calculated maximum sorption capacities order is Cr(III) > Pb(II) $\approx$ Au(III) > Zn(II) $\approx$ Cd(II) > Ag(I) $\approx$ Ni(II).

The observed b values correspond to the strong binding affinity of metal ion onto Si-HA and related to the amount of sorbed metal at equilibrium [41]. The order of b values follows Au(III) >> Cd(II) > Zn(II) $\approx$ Ni(II) > Pb(II) $\approx$ Cr(III) > Ag(I). A large b value of Au(III), differentiated from other metal ions, shows that the adsorption mechanism of Au(III), which is in form of chloroaurate(III) ion, on Si-HA was ion exchange, while that of the other ions is complexation. The previous study reported that the energy of ionic interaction is higher than the energy of complexation [41]. Therefore, Au(III) has a higher b value than the other metal ions, indicating stronger binding affinity.

4.3 Extraction study using column system

A mixed metal ion solution of Ag(I), Cr(III), Cd(II), Ni(II), Pb(II) and Zn(II) was studied in column system. The batch system is the study of the adsorption behavior of an individual metal ion onto Si-HA phase but the column system is the method which will be applied for the extraction of heavy metal ions in real wastewater from a factory. The wastewater probably do not contain only one type of metal ion, so mixed metal ion solution can represent the real wastewater. The extraction of Au(III) was studied separately because the matrix of Au(III) solution was chloride anion, where AgCl could form and precipitated. Moreover, it is hardly to find Au(III) in general wastewater except only from a specific factory.

4.3.1 Effect of sample flow rate

4.3.1.1 Effect of loading flow rate

The loading flow rate of sample should be optimized to ensure quantitative retention along with minimization of the time required for sample processing.

The extraction of metal ions on Si-HA column was studied at 5 flow rates *i.e.* 0.5, 1.3, 2.6, 3.5 and 5.0 mL min^{-1} for the mixture of metal ions, and 0.5, 1.0, 2.5, 4.0 and 5.0 mL min^{-1} for Au(III). The results are illustrated in Figure 4.11 and 4.12.
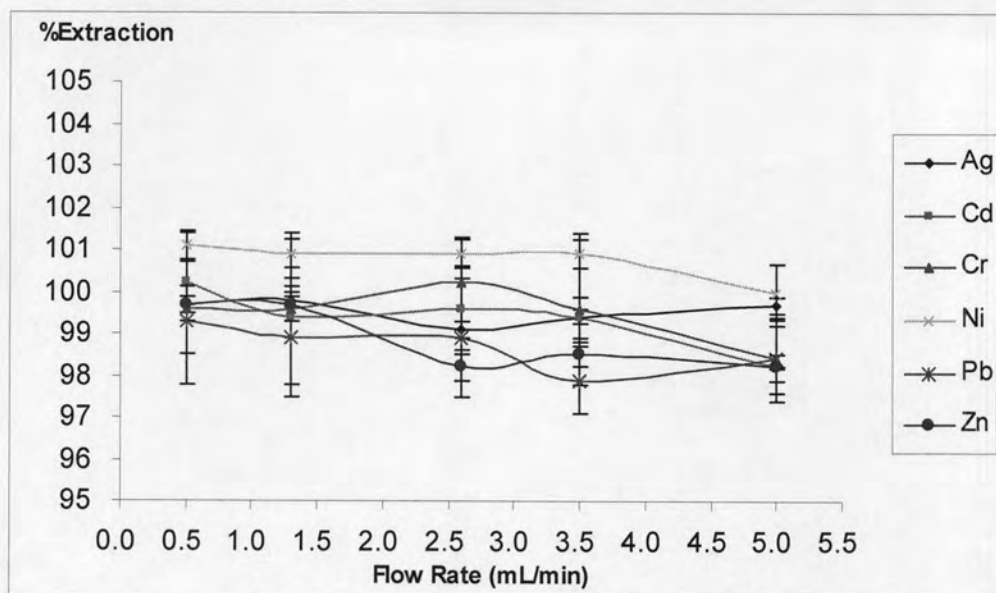
Figure 4.11 Effect of sample loading flow rate on sorption of 10.0 mg L^{-1} of metal ions; Ag(I), Cr(III), Cd(II), Ni(II), Pb(II) and Zn(II) onto Si-HA (1.0 g), pH=5 (n=3).
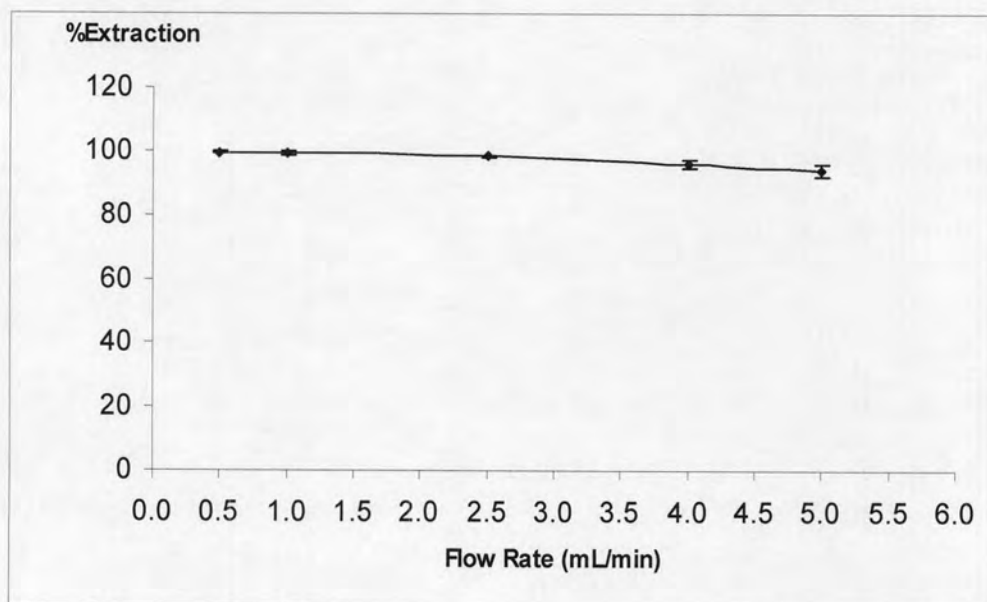

Figure 4.12 Effect of sample loading flow rate on sorption of Au(III) onto Si-HA (1.0 g), pH=4 (n=3).

The flow rate did not affect the percent extraction of Ag(I), Cr(III), Cd(II), Ni(II), Pb(II) and Zn(II). The flow rate within the range of 0.5 – 5.0 mL min^{-1} was recommended

for maximizing sorption efficiency of ions onto Si-HA. However, the optimum flow rate related to the percent extraction depends on the initial concentration of metal ions in a water sample and the amount of the sorbent used. In our case, the initial concentration of the metals ions was 10.0 mg L^{-1} and the amount used of Si-HA was 1 g. The flow rate can be adjusted to the optimum when an extraction of real sample is operated.

4.3.1.2 Effect of elution flow rate

The elution of metal ions from Si-HA column was carried out using 10% nitric acid for Ag(I), Cr(III), Cd(II), Ni(II), Pb(II) and Zn(II) and 10% hydrochloric acid for Au(III). The desorption efficiency, defined as recovery, was evaluated and determined by equation 4.3. The effect of flow rate on elution of metal ions is illustrated in Figure 4.13 and 4.14.

$$\text{Recovery (\%)} = (n_e / n_i) \times 100 \qquad (4.3)$$

where n_e is the amount of metal eluted (mg) from the sorbent and n_i is the initial amount of metal (mg).

The elution was studied at 5 flow rates, 0.5, 1.3, 2.6, 3.5 and 5.0 mL min^{-1}, for Ag(I), Cr(III), Cd(II), Ni(II), Pb(II) and Zn(II) ions and 0.5, 1.0, 2.5, 4.0 and 5.0 mL min^{-1} for Au(III). The loading flow rate of all metal solutions was 2.0 mL min^{-1}.

The type of eluent must be correctly chosen to ensure strong capability of the eluent for metal ions. For this method, the elution was achieved by using an acid that interrupted the chelation and a proton from the acid could displace the adsorbed metal ions. Moreover, by the results shown in section 4.2.1, the retention of metal ions onto Si-HA can only be achieved under the optimum pH range of 4.0-7.0. Nitric acid was chosen for the elution of the sorbed metal ions because it is a suitable matrix for the determination step by

FAAS. The acid concentration was an important factor because a small amount of proton might be not enough to exchange the chelated metal ions. The concentration of 10% (v/v) (pH 0 – 1) of nitric acid solution was chosen.
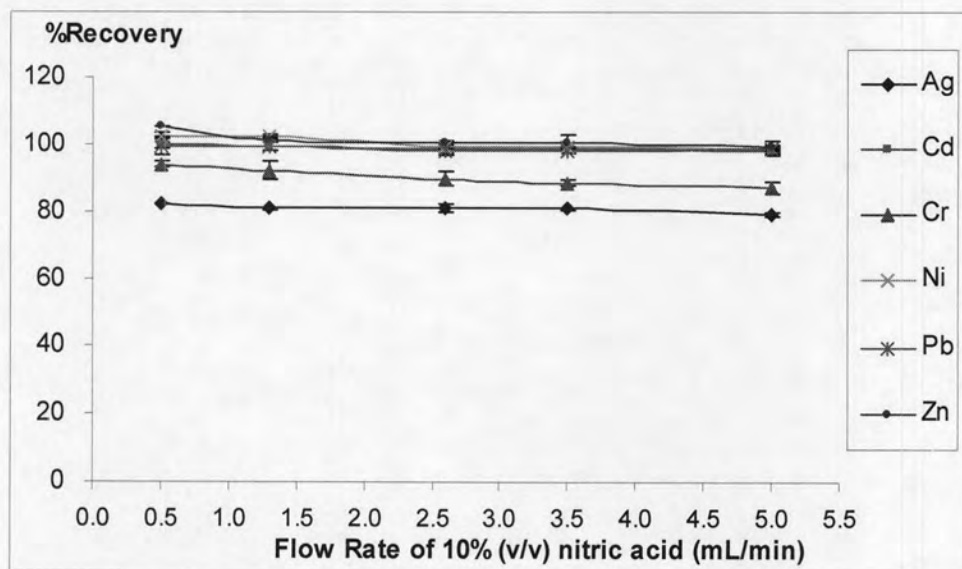

Figure 4.13 Effect of elution flow rate on 10 mg L^{-1} mixed metal ion recoveries from Si-HA column (n=3).
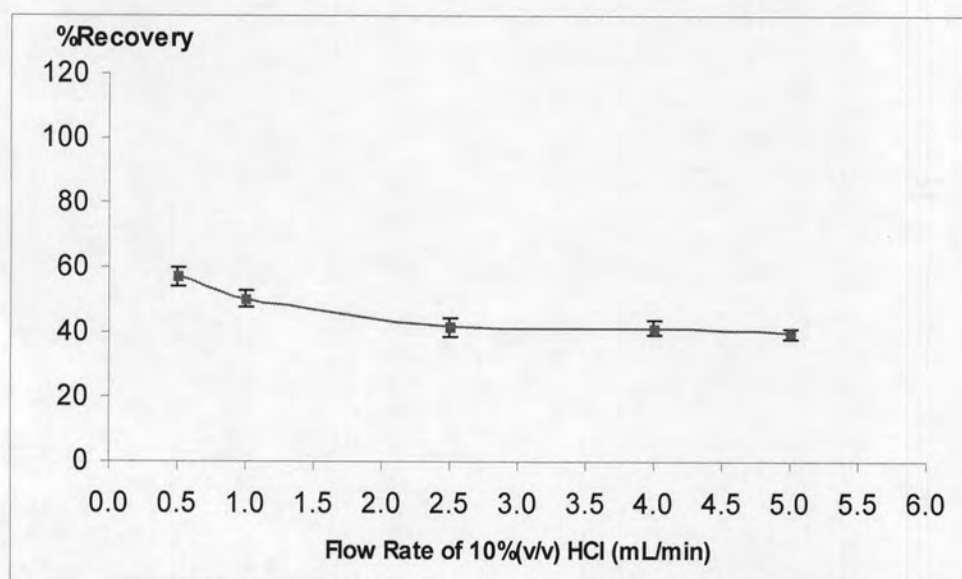

Figure 4.14 Effect of elution flow rate on 10 mg L^{-1} Au(III) recovery from Si-HA column (n=3).

The elution flow rate did not affect the desorption efficiency of Ag(I), Cr(III), Cd(II), Ni(II), Pb(II) and Zn(II) ions from Si-HA. The recovery of divalent ions were close to 100, while the recovery of Ag(I) and Cr(III) was 80 and 90%, respectively. For Au(III), the nitric acid solution was not suitable for the elution because the adsorption type was not chelation, it was probably anion exchange. Thus, chloride might replace $AuCl_4^-$ adsorbed on Si-HA. As Au(III) was in the form of $AuCl_4^-$, certain amount of Au(III) was recovered by hydrochloric acid because of the replacement of chloride ions from the acid solution. However, the recovery of Au(III) was still low (60 – 40%) at every flow rate used. The protons from hydrochloric acid might still protonate the functional group of Si-HA so the surface of Si-HA still show cationic characteristic which prefer to adsorb $AuCl_4^-$. The 10% (v/v) hydrochloric acid solution seems to be an inappropriate for the elution. The thiourea solution was recommended to obtain higher recovery [42].

In conclusion, the elution flow rate recommended for metal ions is 3.5 mL min^{-1}.

4.3.2 Effect of sorbent amount

From the study in 4.3.1, the results showed good column efficiency for both extraction and recovery of 10 mg L^{-1} of Ag(I), Cr(III), Cd(II), Ni(II), Pb(II) and Zn(II) when using Si-HA 1.0 g. In this study, the effect of the sorbent amount was investigated. The amount of Si-HA used was 0.1, 0.3 and 0.6 g. The flow rate was fixed at 3.5 mL min^{-1} for both extraction and desorption steps. As mentioned earlier, the optimum flow rate depends on the initial concentration of metal ions in a water sample and the amount of the sorbent used. This flow rate allowed quick operation and still gave the acceptable efficiency in extraction and recovery, except for Au(III). The elution was performed using 10% (v/v) nitric acid for Ag(I), Cr(III), Cd(II), Ni(II), Pb(II) and Zn(II) and 10% (v/v) hydrochloric acid for Au(III). The results are summarized in Table 4.2 and 4.3.

Table 4.2 Effect of sorbent amount (0.1, 0.3 and 0.6 g) on metal ion sorption at flow rate of 3.5 mL min^{-1} metal ion concentration 10 mgL^{-1} (20 mL), (n=3)

Sorbent Amount (g)	%Extraction ± SD						
	Ag(I)	Cd(II)	Cr(III)	Ni(II)	Pb(II)	Zn(II)	Au(III)
0.100	33.1±1.9	28.6 ±0.2	51.6±0.2	23.4±1.6	72.9±2.6	47.4±0.7	97.9 ±0.6
0.300	95.4±0.3	96.0 ±0.2	99.1±0.2	89.0±1.5	99.6±1.0	95.5±0.7	100.7±0.4
0.600	101.1±0.2	100.2±0.6	100.4±0.2	100.9±1.1	100.2±0.0	100.5±0.4	100.7±0.4

Table 4.3 Effect of sorbent amount (0.1, 0.3 and 0.6 g) on metal ion desorption at flow rate of 3.5 mL min^{-1} desorbed by 20 mL of 10% (v/v) nitric acid for metal ions and 10% (v/v) hydrochloric acid for Au(III)

Sorbent Amount (g)	%Recovery ± SD						
	Ag(I)	Cd(II)	Cr(III)	Ni(II)	Pb(II)	Zn(II)	Au(III)
0.100	102.2±2.7	106.9±2.2	95.3±2.8	101.5±1.9	101.4±2.7	102.2±2.9	36.6±0.5
0.300	101.7±1.4	98.0±0.4	85.9±0.5	96.7±4.6	99.8±1.7	102.4±0.4	46.5±1.1
0.600	102.5±0.4	98.5±0.8	85.8±0.4	96.7±1.3	100.9±1.0	102.7±0.4	47.3±0.3

The sorbent amount of 0.1 g strongly affected the extraction efficiency more than the elution. This could be explained that most of the active sites of Si-HA were bound to the metal ions, called saturation. Comparing to the study of flow rate, 10 times of Si-HA (1.0 g) amount was used and higher percent extraction was obtained. As the result shown in section 4.2.3, the maximum sorption capacities of Cr(III) > Pb(II) > Zn(II) > Cd(II) > Ag(I) , the result in this part is the same, Cr(III), Pb(II) and Zn(II) could be adsorbed on

Si-HA better than Cd(II) and Ag(I) when using 0.1 g of sorbent. The results revealed that a competitive adsorption between metal ions onto the sorbent occurred when the number of active site is limited. On the other hand, an increase of sorbent amount from 0.1 to 0.3 and 0.6 g resulted in an increase in extraction efficiency due to a larger number of active sites.

For the desorption, it can be observed that the amount of sorbent did not affect the elution of Ag(I), Pb(II) and Zn(II) , but slightly affected those of Cd(II), Cr(III) and Ni(II). The desorption should be performed better when using 0.1 g of Si-HA, an decrease in desorption efficiency occurred when using 0.3 and 0.6 g due to a re-adsorption on the sorbent.

The result of Au(III) was different. The amount of Si-HA did not affect the percent extraction. This results were in accordance with the high sorption capacity of Si-HA towards Au(III), as mentioned in section 4.2.3 that the b value from the Langmiur plot was very high. Moreover, There was no competitive adsorption in this single ion extraction. Therefore, the amount of sorbent used in this study is sufficient for Au(III) extraction when using 20 mL of 10 mg L^{-1} solution. The extraction efficiency was still high, but the elution efficiency was low.

4.3.3 Effect of interfering ions

The presence of ions other than the considered species in a sample may cause problems during the extraction. In particular, due to their usually high levels, they may hinder the extraction step by overloading the sorbent. Therefore, their influence should be studied. The cations and anions used in this study were chosen from their major abundance in nature, i.e. Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-}. The salts used for interfering cations and anions studies were nitrate salts and sodium salts, respectively. The experiments were performed with three concentration levels of the interfering ions under the optimum conditions of extraction and elution.

Table 4.4 Effect of interfering ion concentration on metal ion sorption at flow rate of 3.5 mL min^{-1}, sorbent amount 0.6 g and metal ion concentration 10 mgL^{-1} 20 mL (n=3)

Interfering ions (mg L^{-1})		%Extraction ± SD						
		Ag(I)	Cd(II)	Cr(III)	Ni(II)	Pb(II)	Zn(II)	Au(III)
Na$^+$(NO$_3^-$)	10 (26)	100.6±0.1	104.9±0.1	106.4±0.3	102.3±0.1	99.7±0.9	102.7±0.9	77.8±0.4
	100 (260)	100.7±0.1	104.6±0.4	105.9±0.2	102.3±0.1	99.6±0.9	102.6±0.9	78.0±3.9
	1000(2600)	100.7±0.1	104.6±0.4	105.7±0.5	102.2±0.3	100.2±0.1	102.8±0.9	77.4±4.1
K$^+$(NO$_3^-$)	10 (14)	100.8±0.1	105.7±0.1	104.6±1.1	102.4±0.1	100.1±0.1	103.7±0.7	77.8±1.2
	100 (140)	100.6±0.2	105.4±0.4	105.1±0.6	102.2±0.3	99.7±0.9	102.9±0.6	78.2±0.9
	1000(1400)	100.8±0.1	105.4±0.5	106.0±2.9	102.4±0.1	100.2±0.1	103.1±1.5	79.1±3.2
Ca^{2+}(NO$_3^-$)	10 (32)	100.7±0.1	103.6±0.5	104.5±0.8	102.3±0.2	99.7±0.8	102.7±0.9	78.3±0.6
	100 (320)	100.6±0.1	103.8±1.0	105.2±1.2	102.2±0.3	99.7±0.9	102.6±0.9	80.4±1.0
	1000(3200)	100.7±0.1	104.4±1.7	106.8±2.2	102.2±0.3	99.7±0.8	102.8±0.9	78.6±0.5
Mg^{2+}(NO$_3^-$)	10 (50)	100.7±0.1	103.3±0.8	108.8±1.0	102.4±0.1	100.2±0.1	102.7±0.9	77.3±1.1
	100 (500)	100.6±0.1	103.8±0.9	105.5±0.7	102.1±0.3	99.7±0.9	102.6±0.8	78.2±0.7
	1000(5000)	100.7±0.2	104.3±1.7	106.8±2.2	102.2±0.3	99.7±0.9	102.7±0.9	78.0±3.9
Cl$^-$(Na$^+$)	10 (6)	nd	103.3±0.8	105.5±1.5	102.2±0.2	100.6±0.1	102.5±0.6	74.7±1.2
	100 (60)	nd	103.8±0.9	104.4±0.7	102.2±0.2	99.7±0.9	102.4±1.1	75.2±1.0
	1000 (600)	nd	104.6±1.2	105.1±0.8	102.1±0.3	99.6±0.9	102.3±0.5	74.5±1.9
NO$_3^-$(Na$^+$)	10 (3)	100.7±0.4	103.5±0.5	105.5±1.2	102.4±0.1	100.2±1.0	102.6±0.8	74.7±1.0
	100 (30)	100.7±0.2	103.8±0.9	105.8±0.3	102.2±0.3	100.2±0.1	102.6±0.9	70.5±1.6
	1000 (300)	100.6±0.1	104.3±1.7	105.7±0.8	102.1±0.3	100.2±0.1	102.8±0.6	67.1±2.9
SO$_4^{2-}$(Na$^+$)	10 (3)	100.2±0.5	104.9±0.1	105.4±0.8	102.3±0.1	99.6±0.9	102.6±0.9	65.8±1.2
	100 (30)	100.2±0.4	104.6±0.4	104.9±0.5	102.2±0.3	99.6±0.9	102.6±0.6	64.4±0.4
	1000 (300)	100.2±0.5	104.6±0.4	102.9±2.6	102.3±0.1	100.2±0.1	102.7±0.9	61.7±1.8

nd = not detectable.

Table 4.5 Effect of interfering ion concentration on metal ion desorption at flow rate of 3.5 mL min^{-1}, sorbent amount 0.6 g and desorbed by 20 mL (n=3)

Interfering ions			%Recovery ± SD						
			Ag(I)	Cd(II)	Cr(III)	Ni(II)	Pb(II)	Zn(II)	Au(III)
Na$^+$(NO$_3^-$)	10	(26)	94.5±3.1	94.3±1.8	77.7±3.3	96.0±0.5	100.4±0.9	99.5±0.9	40.5±5.3
	100	(260)	93.1±4.0	94.3±1.7	81.0±3.4	95.5±0.5	103.1±1.7	97.4±0.6	36.8±1.6
	1000	(2600)	90.0±4.9	94.4±3.4	80.4±6.4	96.2±2.5	106.0±1.0	96.8±1.4	38.5±1.8
K$^+$(NO$_3^-$)	10	(14)	96.3±2.4	90.4±0.2	81.7±7.9	94.8±7.2	92.6±5.3	98.0±3.7	43.0±1.0
	100	(140)	98.5±2.2	91.9±1.8	80.2±6.7	94.3±3.5	94.6±2.9	98.7±1.5	33.7±0.9
	1000	(1400)	101.4±5.7	92.4±1.3	80.5±8.3	94.5±0.8	96.5±1.7	98.5±0.9	41.8±1.1
Ca^{2+}(NO$_3^-$)	10	(32)	92.0±4.5	92.7±3.1	82.1±7.7	99.0±3.9	93.6±6.9	100.2±0.3	37.2±1.1
	100	(320)	94.5±2.0	94.3±0.9	82.0±4.1	95.9±4.9	94.6±2.9	98.7±2.0	39.8±2.7
	1000	(3200)	94.2±6.0	95.6±0.9	79.1±8.9	94.6±0.5	96.9±1.5	96.6±2.3	36.6±5.9
Mg^{2+}(NO$_3^-$)	10	(50)	96.8±6.7	92.0±1.9	80.8±7.8	97.5±0.2	95.5±6.4	99.6±0.7	32.0±2.0
	100	(500)	96.6±3.5	93.8±0.1	81.5±4.0	94.5±3.7	95.1±4.3	97.6±0.5	35.6±5.2
	1000	(5000)	98.4±6.7	93.9±1.9	79.9±8.8	94.6±0.5	95.6±4.8	94.6±0.8	39.8±6.9
Cl$^-$(Na$^+$)	10	(6)	nd	92.2±2.3	80.9±1.2	95.9±0.7	100.4±0.9	100.2±0.3	39.5±6.5
	100	(60)	nd	93.8±0.1	80.3±5.8	96.2±0.5	103.6±2.0	97.6±0.9	38.8±0.9
	1000	(600)	nd	93.9±1.3	80.8±6.9	96.0±2.3	106.6±0.1	96.3±2.8	38.3±1.2
NO$_3^-$(Na$^+$)	10	(3)	98.0±2.2	91.8±1.6	80.5±1.2	96.9±1.9	95.9±3.6	100.0±0.7	41.3±5.0
	100	(30)	97.4±1.3	93.8±0.1	81.1±3.3	95.6±0.6	99.9±1.6	97.1±0.1	39.3±6.4
	1000	(300)	97.8±0.5	94.1±1.7	80.3±6.2	96.6±2.3	103.7±2.6	99.7±5.0	39.8±3.4
SO$_4^{2-}$(Na$^+$)	10	(3)	96.2±4.7	94.3±1.8	78.5±4.0	95.8±0.5	98.9±1.7	100.1±0.6	37.8±1.9
	100	(30)	104.9±8.9	94.3±1.7	81.8±3.8	95.5±0.8	99.9±4.1	97.4±0.6	39.4±1.9
	1000	(300)	96.5±2.2	94.4±3.4	82.5±6.8	95.9±2.4	107.1±2.5	95.9±2.2	39.8±3.1

nd = not detectable.

It was found that some of the interfering ions slightly affected the efficiency of extraction and recovery of the metal ions, especially for Au(III). Because of its adsorption mechanism is an anion exchange; there was the competition between $AuCl_4^-$ and the anions which come from nitrate salts and other interfering anions resulting in the lowering of the efficiency of the extraction. For the elution of Au(III) which still used 10 %(v/v) HCl as the eluent, so this causes the low recovery that the explanation is the same as the study in 4.3.1.2.

For Ag(I), chloride anion strongly affected the extraction efficiency because it formed AgCl and precipitated.

For Au(III), the result clearly confirmed that the adsorption mechanism was an anion exchange. All anions interfered in the recovery of Au(III).

For other metal ions, from the results, it indicated that all the interfering ions did not influence the adsorption and Si-HA has a potential to apply to a real sample. It could be explained that the studied heavy metal ions were transition metals which have electrons in d-orbital to coordinate with the carboxyl and/or hydroxyl functional groups present on Si-HA. But interfering ions as alkali and alkali-earth can not form complexes with Si-HA, so these interfering ions did not affect the efficiency of extraction and elution.

4.4 Application for real sample

The proposed method was applied to extract heavy metal ions by Si-HA packed in a column with suitable condition selected from the previous results. The wastewater was collected from a factory in Eastern Seaboard Estate. The spike method was used. This procedure was performed under the optimum conditions given in Table 4.6.

Table 4.6 The optimized condition for extraction of metal ions in real sample

Parameters	Optimized condition
Sorbent	0.6 g Si-HA packed column
Sample volume	20 mL
Sample flow rate	2.0 mL min^{-1}
Eluent	20 mL of 10% (v/v) nitric acid
Eluent flow rate	2.0 mL min^{-1}
Spiked level	5 mg L^{-1} of each metal ion

From the previous study, the selected flow rate was 3.5 mL min^{-1} but it could not be operated for the real wastewater probably due to the clogging of the column caused by the dissolved matters in the sample. Together with a very fine particle of Si-HA, so it can not reach this flow rate. However, the flow rate at 2.0 mL min^{-1} was selected from the previous study 4.3.1. The smaller the flow rate, the greater the sorption efficiency.

The limit of detection of the FAAS was calculated by three time of the standard deviation of the blank measurement (n=5). The values are given in Table 4.7.

Table 4.7 Limit of Detection (LOD) of the studied metal ions from this method

Metal ions	LOD (mg L^{-1})
Ag(I)	0.0084
Au(III)	0.0071
Cd(II)	0.0032
Cr(III)	0.0245
Ni(II)	0.0032
Pb(II)	0.1379
Zn(II)	0.0161

The results are shown in Table 4.8

Table 4.8 Recovery of spiked method in wastewater from factory in Eastern Seaboard Estate by Si-HA-column (n=3)

Metal ions	Added, µg (from the spiking)	Found, µg (before passed through the column) ± SD	%Extracted ± SD	%Recovery ± SD
Ag(I)	100	2 ± 0	46 ± 21	41 ± 17
Au(III)	100	100.4 ± 0.7	58 ± 6	27 ± 4
Cd(II)	100	99.6 ± 0.9	101 ± 1	100 ± 2
Cr(III)	100	102 ± 2	101 ± 1	93 ± 2
Ni(II)	100	100 ± 1	101 ± 0	100 ± 2
Pb(II)	100	105 ± 2	99 ± 2	100 ± 6
Zn(II)	100	102 ± 1	100 ± 0	100 ± 2

The extraction and recovery of metal ions in wastewater were nearly 100% for Cr(III), Cd(II), Ni(II), Pb(II) and Zn(II). Ag(I) ion formed AgCl with chloride ions originally contained in wastewater and precipitated. These results show a great potential application of the Si-HA sorbent for metal ion extraction from real wastewater. The detection of all metal ions in real wastewater sample was not detectable.