



CHAPTER V

COMPETITIVE ADSORPTION OF HEAVY-METAL IONS FROM AQUEOUS SOLUTION BY AMINATED POLYCRYLONITRILE NANOFIBER MATS

5.1 Abstract

Aminated polyacrylonitrile (APAN) nanofiber mat was a surface modification of electrospun polyacrylonitrile (e-spun PAN) with diethylenetriamine (DETA). It was developed for the removal of Ag(I), Cu(II), Pb(II) and Fe(II) from aqueous solution. The results showed that adsorbent has the highest adsorption capacity for Ag(I) and Cu(II) in ions mixture system. The parameters of adsorption behavior were also investigated, such as pH-value, initial concentration and contact time. Langmuir and Freundlich isotherm models were applied to analyze the experimental data. Desorption experiments by elution of the adsorbent with a nitric acid show that the APAN nanofiber mats could be reused. APAN nanofiber mat has been shown to have the potential to be used as an effective adsorbent for the removal as well as selective recovery of heavy metal ions in water or wastewater treatment.

(Keywords: electrospinning, amination, nanofiber, heavy-metal ions removal, selective adsorption)

5.2 Introduction

The presence of heavy metals in industrial wastewater has posed many serious environmental problems due to their non-biodegradable properties and toxicity, even at low concentrations [1, 2]. These heavy metals ions are found in various industry sources such as electroplating, textile, metal finishing, chemical manufacturing and storage batteries [3-5]. The most commonly treatment methods are precipitation, membrane processes, electrolytic recovery, liquid-liquid extraction and sorption (adsorption, ion exchange) [6-10]. Among these techniques, adsorption is generally regarded as an effective and economical method for wastewater treatment. A selective property is the main advantages of adsorbent for remove metal ions which depend on the functional group(s) on their surface such as thiol, imimodiacetate, amine, amide, carboxylic acid, hydroxyl and sulfonic acid [11-14]. It has been found that an adsorbent carrying nitrogen-based functional groups was effective in the adsorption or removal of heavy metal ions [15-18].

Recently, nano-materials are very interesting in their development as adsorbent due to their high surface area to unit mass ratios. Nano-adsorbents, including nanobeads [19], nanocomposites [18, 20], magnetic-nano adsorbents [21], and nanofiber mats [22-25], have been widely explored. Nanofiber mats have attracted a great deal of attention because of their many advantages, such as high porosity, high gas permeability, and high specific surface area per unit mass, which should lead to a high adsorption capacity. For example, the adsorption data of for Cu(II) ions onthe chitosan electrospun nanofiber were ~6 and ~11 times higher than the reported highest values of chitosan microsphere and the plain chitosan [24].

Numerous techniques for nanofiber production are available such as: template synthesis, self-assembly, solution blow spinning, drawing spinning, and electrospinning methods. Electrospinning technique is reported in several articles as method to produce nanofibers. In this process, a continuous strand of a polymer liquid (i.e., solution or melt) is ejected through a nozzle by a high electrostatic force onto a grounded collector as a non-woven fiber mat [26]. The morphology of the electrospun fibers depends on a number of factors, such as solution properties,

processing conditions, and ambient conditions [27, 28]. These fibers exhibit several interesting characteristics, e.g., a high surface area to mass or volume ratio, small inter-fibrous pore size with high porosity, vast possibilities for surface functionalization, etc. [23, 29-31]. These advantages render electrospun (e-spun) polymeric fibers good candidates for a wide variety of applications, including composite reinforcements [32], carriers for topical or transdermal delivery of drugs [33], and scaffolds for cell and tissue culture [34]. Furthermore, the introduction of appropriate functional groups onto the surface of an electrospun nanofiber mat allows it to be used as an adsorbent in waste water treatment [22, 23, 31]. Polyacrylonitrile (PAN) microfibers have been widely modified to contain a proper functional group(s) and used as adsorbent for metal ion removal [15, 16, 35], because it is an inexpensive and common commercial product. Additionally, PAN can easily be prepared into nanofiber mats by electrospinning process.

In this study, aminated polyacrylonitrile nanofiber mats were investigated for the removal of silver, copper, iron, and lead ions in aqueous solution under competitive adsorption conditions. The effects of initial pH, contact time, initial ion concentration on adsorption of those ions were studied.

5.3 Experimental Details

5.3.1 Materials

Polyacrylonitrile (PAN), which contained 91.4 wt% acrylonitrile monomer ($\text{CH}_2=\text{CHCN}$) and 8.6 wt% methylacrylate comonomer ($\text{CH}_2=\text{CHCOOHCH}_3$), was received from Thai Acrylic Fibre Co., Ltd. (Thailand). The weight-average molecular weight of polymer was about 55,500 Da. Dimethylformamide (DMF; ~99.98% purity) and ethanol (Lab-scan Asia Co., Ltd., Thailand) were analytical reagent grade. Diethylenetriamine (DETA; ~99% purity) and aluminium chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$; ~99% purity) were purchased from Sigma-Aldrich (USA). Stock solutions of metal ions were prepared from the

nitrate salts of Ag(I), Cu(II), Pb(II), and Fe(II). pH of solutions were adjusted by using $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ and NaOH solutions.

5.3.2 Preparation of PAN Nanofiber Mat Modified with Diethylenetriamine

Aminated polyacrylonitrile (APAN) nanofiber mats were prepared in a similar method that reported in previous research conducted in our group [23]. Briefly, electrospun PAN fiber mats were fabricated from 10 wt% PAN in DMF by electrospinning process, under a fixed electric field of 15 kV/20 cm. The fiber mats of $125 \pm 10 \mu\text{m}$ in thickness were obtained by collecting continuously for 48 h. After that, the electrospun PAN fiber mats (0.6 g) were placed into a 50 mL of DETA and 2.0 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. The reaction temperature and time were 90°C and 4 h. The obtained fiber mats were washed with distilled water and ethanol, and were then dried *in vacuo* at room temperature ($25 \pm 1^\circ\text{C}$).

5.3.3 Characterization

Morphologies of both of the PAN and the APAN nanofiber mats were observed by a JEOL JSM-6400 scanning electron microscope (SEM). Each specimen was coated with a thin layer of gold using a JEOL JFC-1100E sputtering device prior to the SEM observation. The diameters of the individual fiber segments within each specimen were measured directly from the SEM images using SemAphore 4.0 software. No less than fifty diameters were determined on different fiber segments and the average value was calculated. A Thermo-Nicolet Nexus 670 Fourier-transform infrared spectroscope (FT-IR) from KBr pellets, operating at a resolution of 4 cm^{-1} and a wavenumber range of 4000 to 400 cm^{-1} , was used to characterize the neat and the modified electrospun PAN fiber mats. Perkin-Elmer Optima/4300DV inductively coupled plasma spectrometer was used throughout the measurement.

5.3.4 Adsorption Behavior

The adsorption of metal ions by APAN nanofiber mat was studied by batch method. A 0.05 g adsorbent was placed in 20 mL solution of mixture of 10 mg L^{-1} of each Ag(I), Cu(II), Pb(II) and Fe(II) at pH 5. The samples were equilibrated in shaker bath, operating at 30°C and 100 rpm. After a period of time, the supernatants

were collected and quantified for the amount of metal by ICP. The effects of the pH, the contact time, and the initial metal ion concentration on the adsorption capacity of the APAN nanofiber mats were examined.

The adsorption capacity and percent of removed metal ions by adsorbent was calculated by the following equations [22]:

$$q_t = \frac{(C_0 - C_t)V}{M}, \quad (1)$$

$$\text{and} \quad R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where C_0 and C_t are the initial and the concentrations at period of time of the metal ions in the testing solution ($\text{mg}\cdot\text{L}^{-1}$), V is the volume of the testing solution (L), and M is the weight of the adsorbent (i.e., 0.05 g).

5.3.5 Desorption and Reusability of APAN Nanofiber Mat

When adsorption equilibrium was reached, the fiber mats were rinsed with distilled water to remove any residual solution and were then dried *in vacuo* at room temperature (25 ± 1 °C). Desorption of metal ions was carried out by using 1M HNO_3 or HCl aqueous solutions. The contents of the flasks were shaken at 100 rpm and 30°C for 1 h. The ion concentrations in the solutions were analyzed by ICP. The desorption ratio (D , in %) was calculated as follows [36]:

$$D\% = \frac{(\text{mg of metal ion desorbed} \times 100)}{\text{mg of metal ion adsorbed onto fiber mats}}, \quad (3)$$

5.4 Results and Discussions

5.4.1 Adsorbent Characterizations

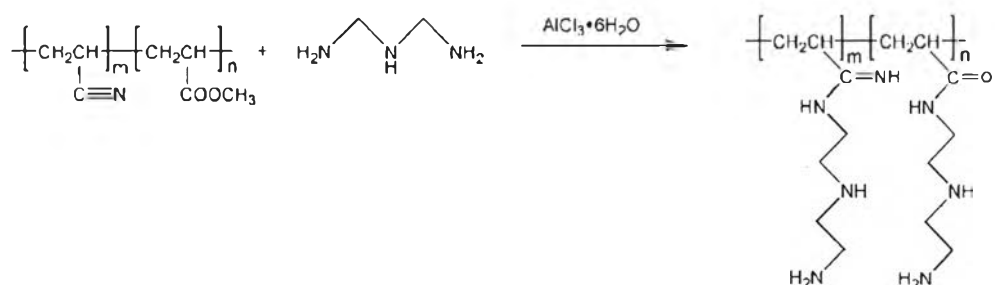
Morphologies of the neat and the aminated PAN nanofiber mats by SEM image are shown in Figure 5.1. The neat PAN nanofiber mats had individual diameters of 218 ± 45 nm with smooth surface and uniform. After modification process, the aminated PAN nanofiber mats obtained are 226 ± 40 nm of diameters which was similar to that of the neat PAN fibers [23, 27]. There was evidence of some adjacent fiber segments conglutinating to each other at touching points. The reaction time of 4 hours is the optimum condition that prevent of changing in

morphology of fiber mat. The percentage conversion of the nitrile group into the amidinodiethylenediamine group (C_n , in %) on the surface the modified PAN fiber mats is $54.1\% \pm 2.7\%$, estimated from follow equation [22]:

$$C_n = \frac{W_1 - W_0}{W_0} \times \frac{M_0}{M_1} \times 100, \quad (4)$$

where W_1 and W_0 (i.e., 0.6 g) are the weights of the PAN fiber mat after and before the reaction, M_0 is the molecular weight of the acrylonitrile monomer (i.e., 53 g.mol⁻¹) and M_1 is the molecular weight of DETA (i.e., 103 g.mol⁻¹). The weights of the samples after the reaction were measured using a Sartorius BS 224S digital balance, which has a measurement resolution of 0.1 mg.

Figure 5.2 show the FT-IR spectra of the neat and the aminated PAN nanofiber mats. After modification process, the adsorption peaks of the neat PAN nanofiber mat at 2244 and 1735cm⁻¹ decreased. These peaks are corresponding to the stretching vibrations of the nitrile group and the carbonyl group of the ester of the methylacrylate co-monomer [23], respectively. On the other hand, the spectra of the APAN fiber mats showed new absorption bands at 3339, 1656, 1600, and 1480 cm⁻¹. These can be assigned to the stretching vibrations of the secondary amine (N-H), the amidine group (N-C=N), and the primary amine (NH₂) and the bending vibrations of the methyl group of DETA, respectively[15, 37]. As result, it can be indicated that both of nitrile and carbonyl group are converted to amidine and amide group, respectively, which is shown in Scheme 5.1.



Scheme 5.1. Chemical reaction between PAN and DETA.

5.4.2 Effect of pH

The pH plays an important role in metal adsorption which is related to both the metal species and the availability of binding site which depends on the

functional group of the sorbent [38]. The metal species, M(II); Cu(II), Pb(II) and Fe(II), are present in forms of M^{2+} , $M(OH)^+$, $M(OH)_{2(S)}$, etc. in water [39]. The solubility of the $M(OH)_{2(S)}$ is very high at $pH \approx 5.0$, so a large amount of the M^{2+} presents as main species. When pH is increased the solubility of $M(OH)_{2(S)}$ decrease resulting in the main species in the solution is $M(OH)_{2(S)}$ instead. It can be told that the M^{2+} must be much more reduce at higher pH, but the major process for removing the M^{2+} is the precipitation, not adsorption. To avoid the precipitation of metal ions, no adsorption experiments were done at a pH greater than 7.

The adsorption of metal ionson the APAN nanofiber mats was first investigated as a function of the initial pH of the 10mg L^{-1} mixed metal ions solution. The results are shown in Figure 5.3. The initial pH of them was varied in the range of 2.0 to 7.0 by, using either 0.1M NaOH or 0.1M HNO_3 for pH adjustment. Removal of Ag(I), Cu(II), Pb(II), and Fe(II) increases with increasing solution pH and a maximum value was reached at an equilibrium pH of around 5.0. Acid conditions are not favorable due to a competitive adsorption between the H^+ and the metal ions. The protonation of the primary and the secondary amines of the DETA ligands giving a strong electrostatic repulsive force to the positively-charged metal ions could thus explain this weak adsorption [23]. On further increase of pH adsorption decreases probably due to the formation of metal hydroxide lead to chemical precipitation.

There are many research studied the effect of pH on metal ions removal by different adsorbents [38-41]. The adsorptions were observed in pH between 5 and 6, gave the highest adsorption capacities for these metal ions in all case. At the initial concentration of the metal ions in the testing solutions of 10 mg L^{-1} , a pH of 5.0 was selected for subsequent work, as 97.35, 73.90, 54.69, and 26.76% of Ag(I), Cu(II), Pb(II), and Fe(II) ions could be removed from the testing solutions.

5.4.3 Effect of Contact Time

Figure 5.4 shows the effect of t on the uptake of Ag(I), Cu(II), Pb(II) and Fe(II) ions from aqueous metal ion solutions. The adsorption of the metal ions on the APAN nanofiber mats increased rapidly with an initial increase in the contact time (i.e., high adsorption rate) to finally reach the maximal, plateau value after the

substrate had been in contact with the Cu(II) and Fe(II) ions for about 5 h and with Ag(I) and Pb(II) ions for about 10h. The residual concentrations at those contact time were found to be higher by maximum less than 1%. The adsorption of metal ions onto surface of the APAN nanofiber mats occurred in two steps. Initially, the adsorption was very fast because a large number of vacant surface sites are available for adsorption. In the second step, adsorption rates decreased and finally reached equilibria. This result from the reduction of available sites which are difficult to be occupied due to repulsive forces between the solute molecules adsorbed on the solid surface and the bulk phase[38, 41, 42].

The maximal adsorbed amounts at 24 h of Ag(I) ions were $4.53 \pm 0.2 \text{ mg}\cdot\text{g}^{-1}$ (92.8%), Cu(II) ions were $3.64 \pm 0.3 \text{ mg}\cdot\text{g}^{-1}$ (74.6%), Pb(II) ions were $2.04 \pm 0.3 \text{ mg}\cdot\text{g}^{-1}$ (41.8%), and Fe(II) ions were $0.95 \pm 0.2 \text{ mg}\cdot\text{g}^{-1}$ (19.5%).

5.4.4 Adsorption Isotherm

The effect of the initial concentration (C_0) of metal ions in the testing solutions on the adsorbed amounts of them on the APAN nanofiber mats was investigated by varying initial concentrations (5-100 mg L^{-1}) of mixed metal ions solutions with the initial pH of 5.0 and the results are reported in Figure 5.5. The adsorption isotherm is the relationship between the amounts of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solutions. Various isotherm models have been developed for describe how solutes interact with the sorbent, including Langmuir and Freundlich [43, 44].

The Langmuir model was derived to describe monolayer adsorption of an adsorbate on a homogenous, flat surface of an adsorbent and each adsorptive site can be only occupied once in a one-on-one manner, is given by [21, 22]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{K}{q_m}, \quad (3)$$

where C_e is the equilibrium concentration of metal ions in the testing solution ($\text{mg}\cdot\text{L}^{-1}$), q_e and q_m are the equilibrium and the maximal adsorption capacities of the metal ions on the adsorbent ($\text{mg}\cdot\text{g}^{-1}$), and K is the Langmuir constant related to the affinity of binding sites ($\text{mg}\cdot\text{L}^{-1}$). The results are graphically

shown Figure 5.6, the value of q_m is taken as the slope of the plot of C_e/q_e versus C_e , while that of K_L can be calculated from the values of the slope and the y -intercept of the plot (i.e., slope/ y -intercept). The values of these parameters are summarized in Table 5.1.

The Freundlich model is used to describe the adsorption of an adsorbate on a heterogeneous surface of an adsorbent. The mathematical expression of the model is given as follows [21]:

$$q_e = K_F C_e^{1/n}, \quad (4)$$

where K_F [$\text{mg}^{(1-1/n)} \cdot \text{L}^{1/n} \cdot \text{g}^{-1}$] and n are Freundlich constants. By plotting $\log q_e$ as a function of $\log C_e$, as a linear equation;

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (5)$$

the value of K_F is taken as the anti-logarithmic value of the y -intercept and n is the inverse value of the slope, which were analyzed from the plots shown in Figure 5.7. The values of these parameters are summarized in Table 5.1.

According to the obtained results, the adsorption data of the four metal ions on the APAN nanofiber mats were fitted well with the Langmuir model, as indicated by the very high values of the correlation coefficient (r^2) in range of 0.95-0.99. As shown in Table 5.2, using the Langmuir model, the maximum adsorption capacity for the metals can be estimated as: 53.48, 30.40, 15.75, and 5.42 $\text{mg} \cdot \text{g}^{-1}$ of Ag(I), Cu(II), Pb(II), and Fe(II), ions respectively.

5.4.5 Desorption and Repeated Use

Desorption of Ag(I), Cu(II), Pb(II) and Fe(II) ions from the surface of the APAN nanofiber mats was carried out in 0.1 M HCl or 0.1 M HNO₃ aqueous solution and the amount of metal ions desorbed in 1 h was measured. As the results in Table 5.3, the metals adsorbed in batch experiments were high effectively desorption, over 90%, when 0.1 M HNO₃ served as desorbent.

In order to obtain the reusability of APAN nanofiber mat, adsorption-desorption cycle was repeated three times by using the same adsorbent in batch experiment. From Figure 5.6 it can be seen that after 3 cycles reused, the adsorption

capacities reduced about 6.5, 11.4, 35.3 and 23.6% of Ag(I), Cu(II), Pb(II) and Fe(II), respectively.

5.5 Conclusions

The present study proves the capability and effectiveness of APAN nanofiber mat as an adsorbent for heavy metals removal. Adsorption behavior of Ag(I), Cu(II), Pb(II), and Fe(II) were affected by experimental parameters such as pH, contact time, and initial concentration of ions solution. It was found that adsorption isotherms were better described by Langmuir model for all of those metal ions. The maximum adsorption capacity values of Ag(I) and Cu(II) ions in a mixture of four ion metals with APAN nanofiber mat, estimated from Langmuir model, were 53.48 and 30.40 mg g^{-1} , respectively.

5.6 Acknowledgements

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5.7 References

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Table 5.1. Langmuir and Freundlich isotherm constants and correlation coefficients for the adsorption of Ag(I), Cu(II), Pb(II), and Fe(II) ions onto APAN nanofiber mats

Metal	Langmuir model			Freundlich model		
	q_m (mg g^{-1})	K (mgL^{-1})	R^2	K_F (mg g^{-1})	n	R^2
Ag(I)	53.48	2.7540	0.9951	12.23	1.3305	0.9869
Cu(II)	30.40	23.7052	0.9806	1.61	1.4637	0.9588
Pb(II)	15.75	22.9039	0.9935	0.99	1.6292	0.9737
Fe(II)	5.42	38.9246	0.9927	0.90	1.5291	0.9654

Table 5.2 Effect of different eluants on desorption recovery (%) for metal ions adsorbed on APAN nanofiber mats (N= 3).

Eluant	Recovery (%)			
	Ag(I)	Cu(II)	Pb(II)	Fe(II)
1 mol L ⁻¹ HCl	88± 2	98 ± 2	81 ± 2	94 ± 2
1 mol L ⁻¹ HNO ₃	92± 2	99 ± 1	99 ± 1	99 ± 1

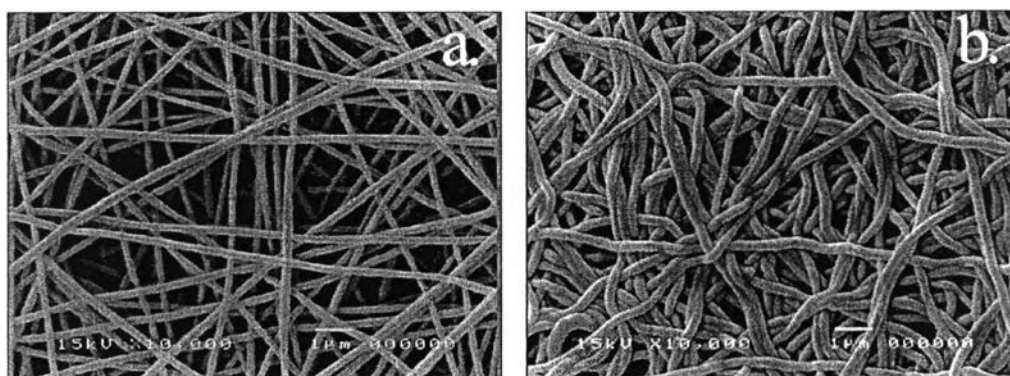


Figure 5.1 Selected SEM images of (a) the neat PAN and (b) APAN nanofiber mat synthesized at 90 °C with reaction time of 4 hours.

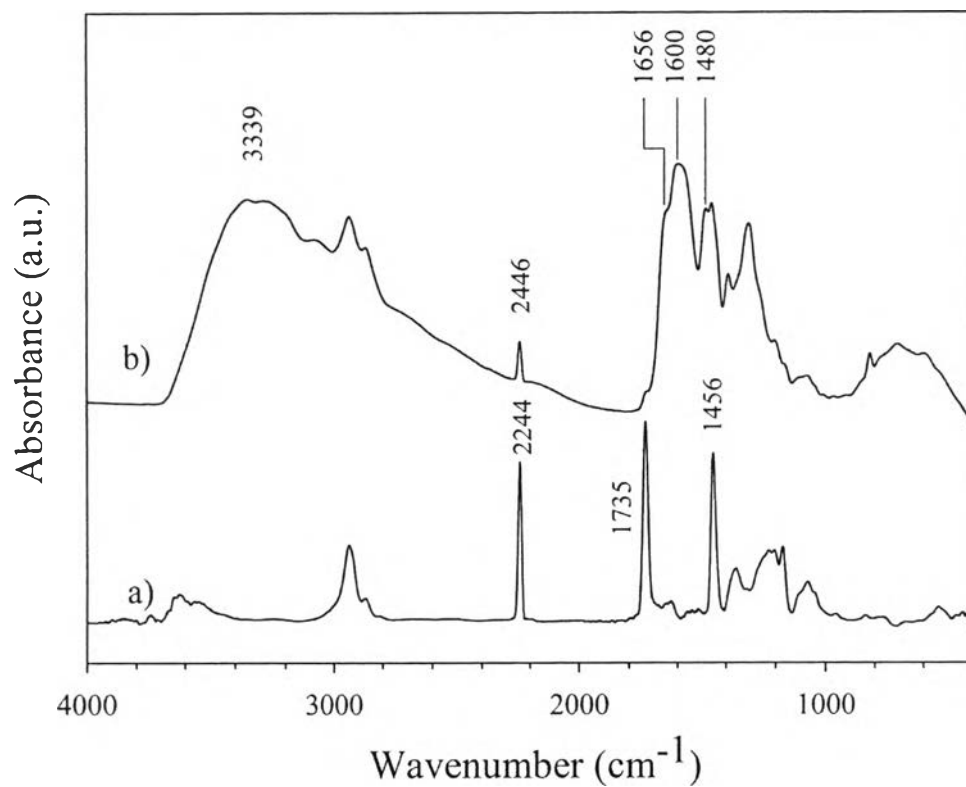


Figure 5.2 FTIR spectra of (a) the neat PAN and (b) APAN nanofiber mat synthesized at 90 °C after reaction for 4 hours.

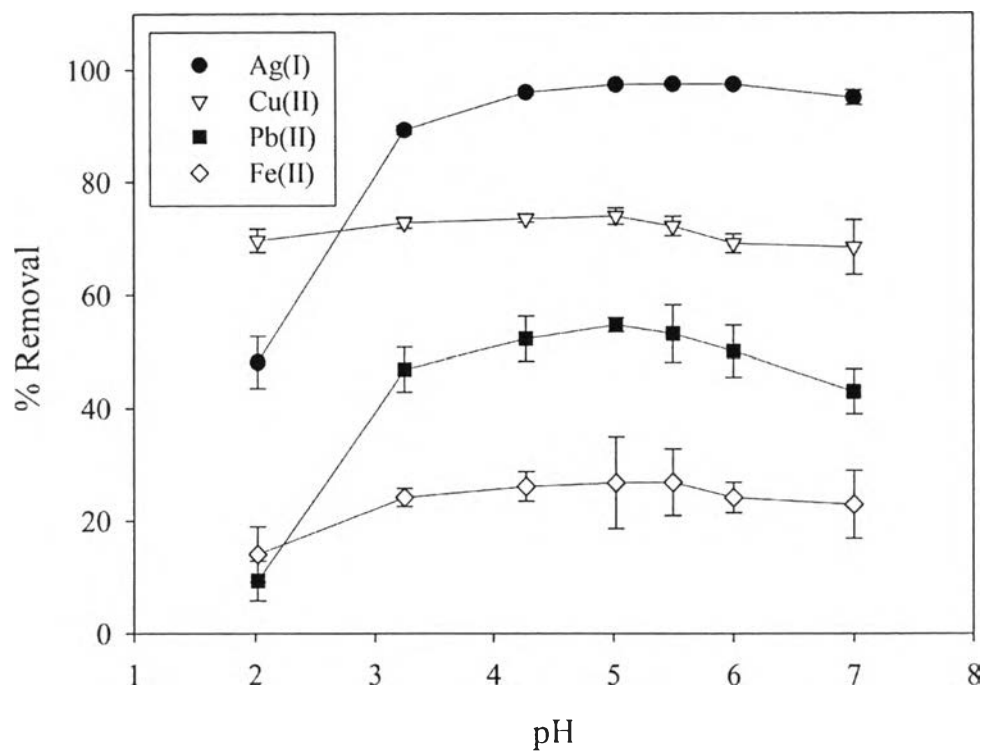


Figure 5.3 Percentage of metal ions removal at different pHs. Conditions: 0.05 g adsorbent, 20 mL of 10 mgL^{-1} of heavy-metal ions, contact time = 24 hours.

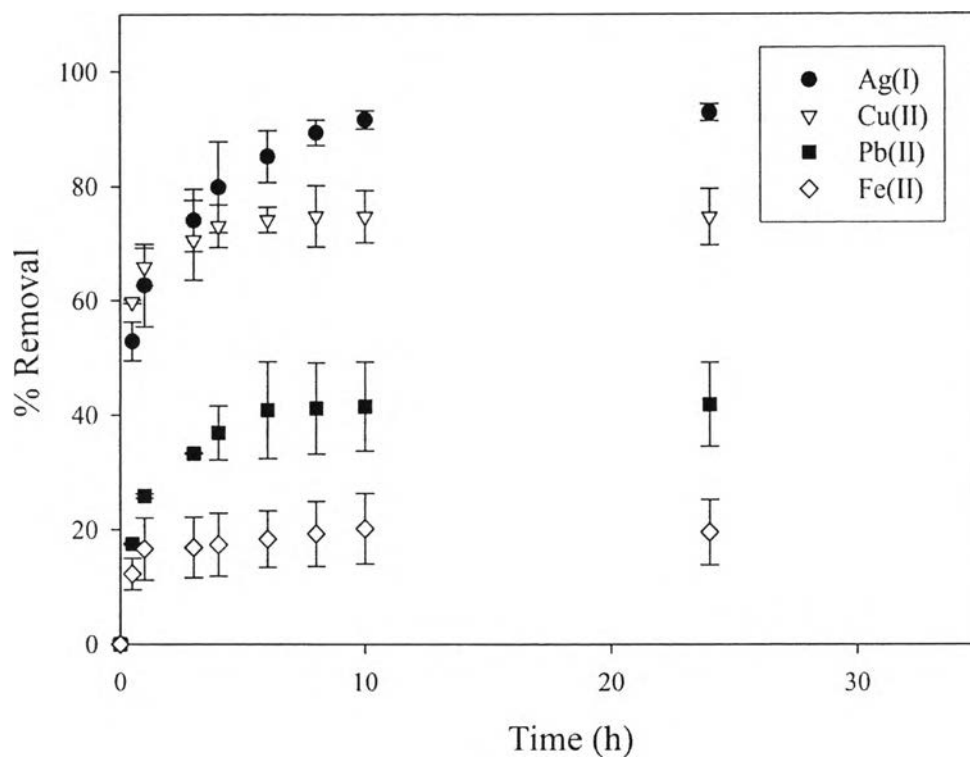


Figure 5.4 Percentage removal of heavy metals at different times. Conditions: 0.05 g adsorbent, 20 mL of 10 mgL^{-1} of heavy-metal ions, pH 5.0

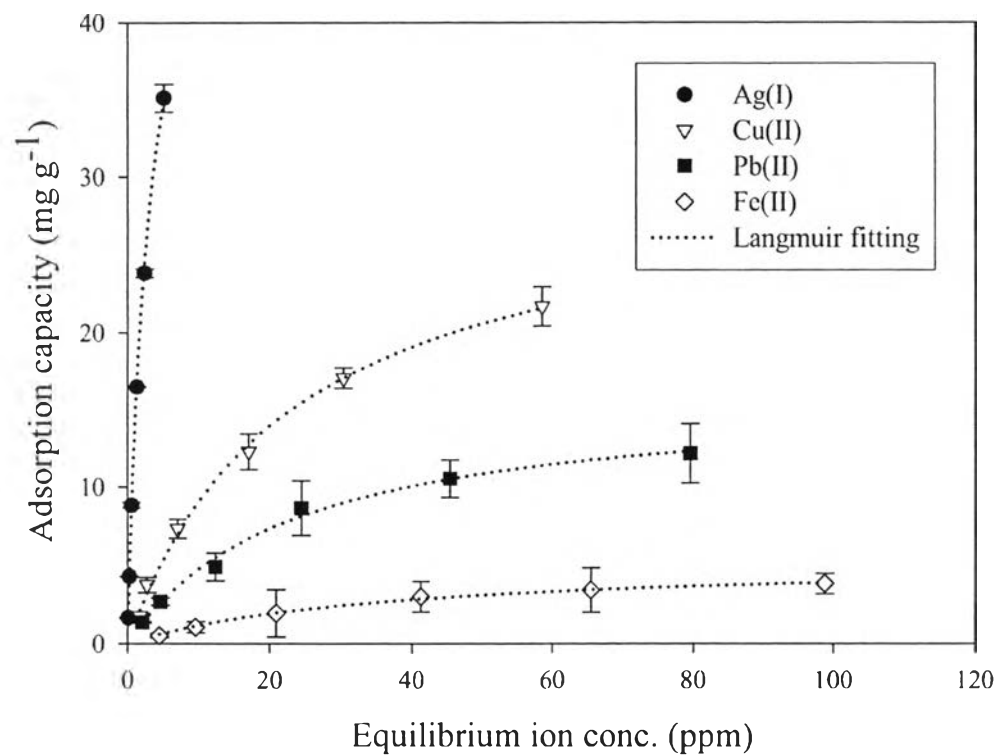


Figure 5.5 Langmuir adsorption isotherm of metal ions for APAN nanofiber mats.

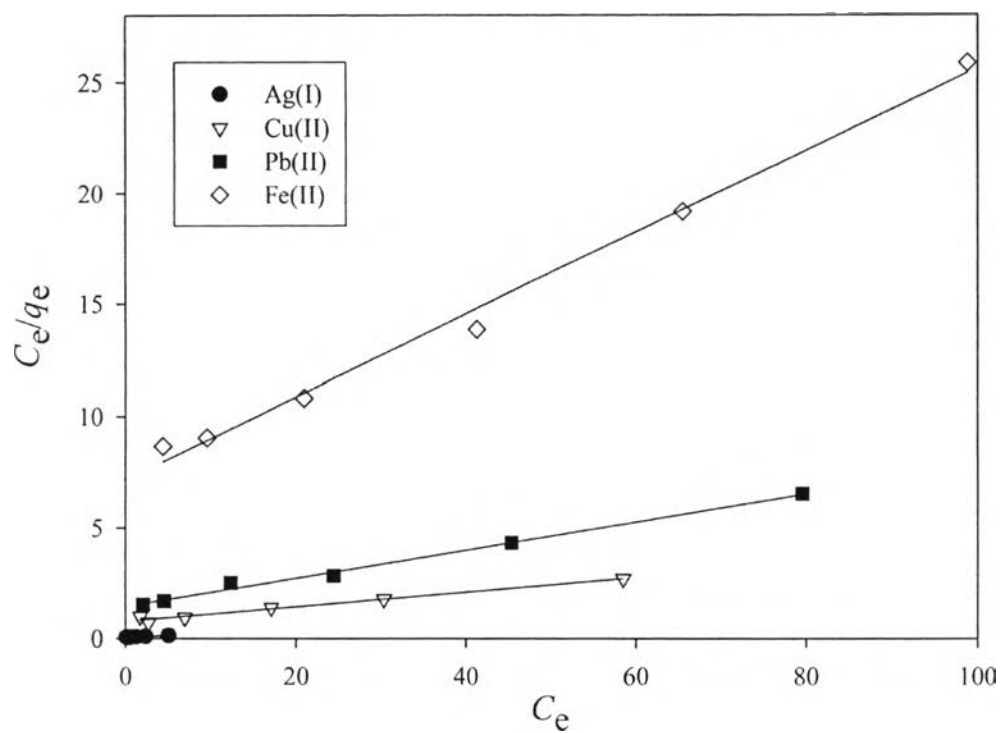


Figure 5.6 Langmuir plot of Ag(I), Cu(II), Pb(II), and Fe(II) ions onto APAN nanofiber mat (pH5), at 30°C

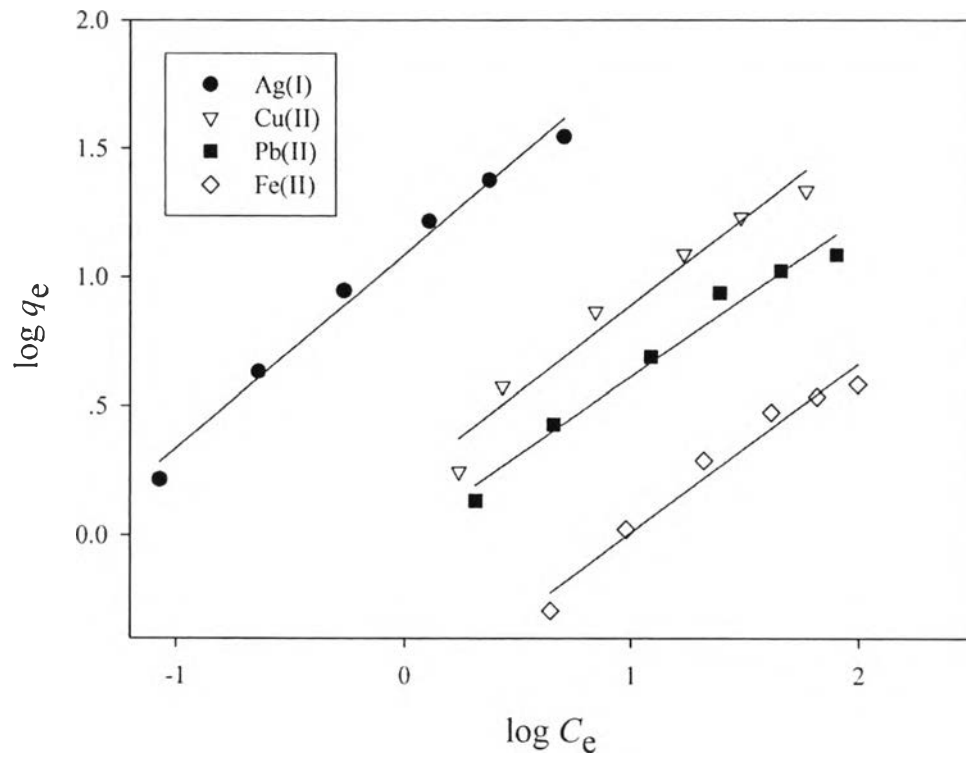


Figure 5.7 Freundlich plot of Ag(I), Cu(II), Pb(II), and Fe(II) ions onto APAN nanofiber mat (pH5), at 30°C

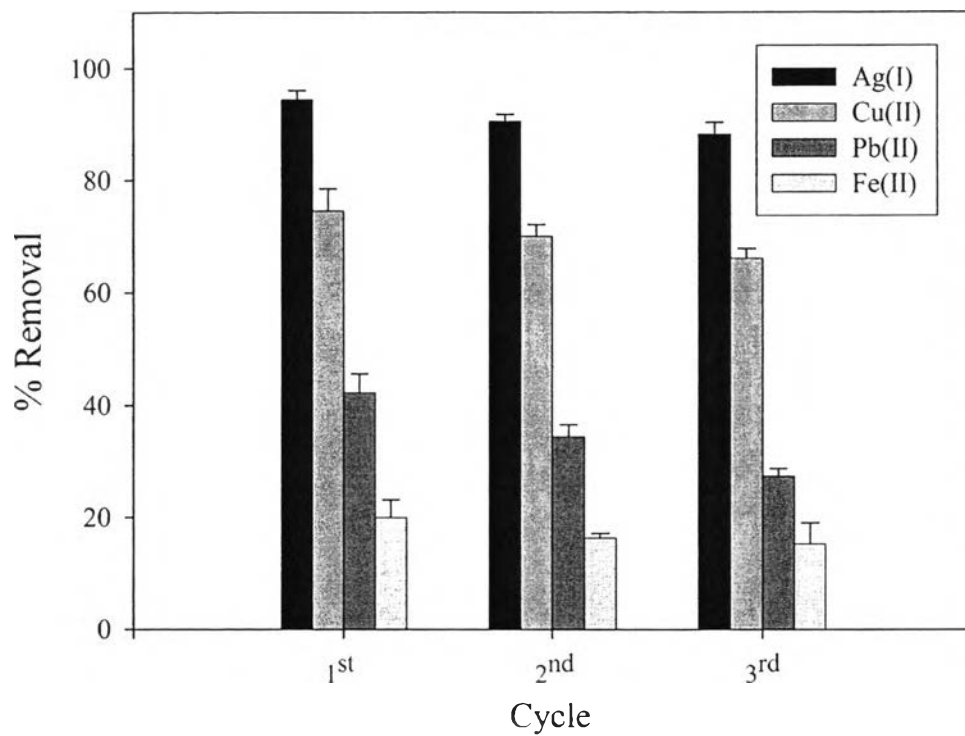


Figure 5.8 Adsorption capacity of heavy metal ions onto APAN nanofiber mats after repeated adsorption cycle.