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Heavy metal removal by ambient-temperature argon plasma modified polyethylene terephthalate (PET) fibers with surface acrylic acid grafting

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This study utilized the capability of ambient-temperature plasma in modifying the surface properties of materials to activate the nonwoven polyethylene terephthalate (PET) fiber surfaces. The effects of different plasma treatment parameters (such as plasma power, treatment time) and grafting parameters (such as grafting temperature, acrylic acid monomer concentration, grafting time) on the activation and grafting of the PET fibers were studied. The feasibility of applying ambient-temperature plasma combined with grafting technology for the preparation of ion exchangers in the wastewater treatment was evaluated. The results showed that the optimal modification effect of PET fibers by Argon plasma and the highest hydrophilicity was achieved at a plasma power of 800 W and treatment time of 10 s. During the grafting procedure, the optimal grafting yield of 4.45% was observed at a grafting temperature of 90°C, an acrylic acid monomer concentration of 6 M, and a reaction time of 5 h. The above surface modification and acrylic acid grafting conditions were used to prepare the ion exchangers for the investigation of subsequent adsorption behaviors. Suitable adsorption performance was achieved at a solution pH of 6, with the adsorption of Copper ion of 0.073 mmole Cu/g-polymer, Lead ion of 0.037 mmole Pb/g-polymer, and Nickel ion of 0.012 mmole Ni/g-polymer. After calculation, the reaction heat was found to be 13.74 kJ/mol, indicating that the adsorption was an endothermic reaction.

Key words: Ambient-temperature plasma, polyethylene terephthalate (PET) fibers, acrylic acid grafting, heavy metal removal.

INTRODUCTION

The electroplating industries have advanced and prospered in recent years. As a result, the release of wastewater containing heavy metals produced in the manufacturing process has increased gradually year after

year. According to the statistical data from the Bureau Industrial Development of the Ministry of Economic Affairs, Taiwan (2007), the discharge of electroplating wastewater was 415,700 m³ per day (CMD). To handle such an enormous quantity of wastewater containing heavy metals, the development of economical and environmentally friendly materials to remove the heavy metals in wastewater has become an important subject worth further investigations.

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The traditional methods for the treatment of wastewater containing heavy metals include chemical precipitation, ion exchange, adsorption, reverse osmosis, and membrane filtration (Bailey et al., 1999). Among these methods, the addition of base reagent with coagulation and precipitation is the most commonly used method. By the addition of an alkaline solution, the metal ion is reacted with hydroxide to form the fairly insoluble metal oxide compound, followed by coagulation and precipitation for metal removal. However, due to the dense urban environment with limited land resources in Taiwan, the traditional precipitation method involving the addition of chemical reagents has become less and less appropriate for dealing with the enormous quantity of wastewater. Moreover, the disposal and treatment of sludge generated by such method have another challenge to overcome. Without proper treatment, the heavy metals may be released (McDonald et al., 2006) and be a secondary environmental hazard. From the perspectives described above, the objective of the present study was focused on the invention of a material capable of adsorbing heavy metals based on the economical, environmental and efficiency-related considerations.

During the last two decades, the literature report many beneficial plastic waste applications such as recycled as fiber reinforced mortar and concrete aggregates (Bayasi and Zeng, 1993; Pereira de Oliveria and Castro-Gomes, 2011; Foti, 2011). The fiber-reinforced concrete performs well in the mechanical properties and makes the possibility of recycling waste plastic materials. Otherwise, an attractive development of plastic material application is surface modification. The most common preparation methods for reactive fiber have induced chemical conversion and grafting of various monomers on the fiber by grafting copolymerization. The adsorption of heavy metals ions from aqueous solution to adsorbents is usually affected by surface functional groups of the adsorbents. The wet surface modification of polyethylene terephthalate (PET), polypropylene (PP) fiber could be done by initiator activation [such as Benzoyl peroxide (BPO) and Ceric ammonium nitrate (CAN)] and then grafted with carboxyl materials. The process is complicated and the initiator is readily active. An alternative to wet chemical processing is plasma activation. Ambient-temperature plasma is easy to operate and possesses the clean way technique with low energy consumption. Therefore, its development is needed from either an economical or an environmental viewpoint, and it has become one of the most enthusiastically studied areas. It can be applied to a wide range of fields such as the improvement of the hydrophilic/hydrophobic property of the surface of material and the adsorption of heavy metals (Lin and Hsieh, 1997; Gupta et al., 2002). Ambient-temperature plasma has many unique features: 1) The plasma surface

modification only works on the surface layer (with a thickness of a few micrometers). Consequently, the properties of the fiber itself will not be destroyed. 2) The plasma device occupies a small area with not much energy required. 3) The plasma modification is a dry method producing very small quantities of hazardous wastes having little harm to the environment. 4) The modification purpose can be achieved within a short period of time with extremely high efficiency. 5) Under different plasma conditions, the organic or inorganic materials of large areas can be modified effectively (Lee et al., 1996; Svorcik et al., 2006). By utilizing the unique properties aforementioned, the economical and environment-friendly objectives for the medication of material are expected to be reached.

In present study, the PET fiber was used and the PET fiber surface was modified by ambient-temperature plasma activation followed by acrylic acid monomer grafting. The formed ion exchanger was capable for heavy metals adsorbing. Moreover, the optimal modification effect of PET fibers by Argon plasma and the highest hydrophilicity, was achieved from various plasma operating conditions. The grafting yield and COOH quantitative method was used to evaluate the grafting effects under different grafting parameters. The adsorption models were investigated to simulate the application for the heavy metal removal in wastewater plants.

MATERIALS AND METHODS

Activation of PET fiber applying ambient-temperature plasma treatment

The nonwoven PET was 30 g/m² with 0.15 mm thickness. The PET was used as the substrate under various ambient-temperature plasma treatment parameters such as plasma power (400, 800, and 1200 W) and plasma treatment time (10, 30, 60, and 120 s). The plasma chamber size is 425 × 350 × 150 mm. The operating characteristics were set at pressure of 200 mtorr (millitorr) in Argon gas with mass flow control (MFC) of 43.8 scc/m (standard cubic centimeter per minute). The plasma excitation was performed by a microwave generator (~2.45 GHz) with 12 × 12 antenna array.

The water loss rate experiment was applied to determine the activation effects of substrates for selecting the optimal plasma treatment parameters. In the water loss rate experiment (MOEA, 2010), the fiber specimen (4 × 4 cm) was put in the moisture analyzer and then 0.2 ml distilled water was added on it. Under the conditions of temperature 20 ± 2°C, relative humidity (RH) 65 ± 2%, the water loss rate was measured by a variety of time for water to be lost on the fiber's surface.

An increasing water loss rate indicated a shorter time for water to be lost on the fiber's surface, and a greater degree of water spread required for a large heating area. This phenomenon illustrated the effect on hydrophilicity increase by plasma modification. Therefore, the comparison of water loss rates using this experiment could reveal the effects on hydrophilicity increase after the treatments under various parameters and the optimal plasma modification conditions were thus investigated.

Modified PET fiber (ion exchanger) preparation applying grafting treatment

The PET fiber after plasma treatment was subjected to grafting treatment under different acrylic acid monomer concentrations (2, 4, and 6 M), grafting times (1, 3, and 5 h), and grafting temperatures (70, 80, and 90°C). The grafting experiments were performed in glass vessels, and the distilled water and the acrylic acid monomer were then added. The plasma-treated PET fiber was immersed in the monomer solution. The grafting reaction was carried out by placing the glass vessel in a water bath which was set at relevant temperature and time. After grafting reaction, the grafted samples were taken out from the monomer solution and washed. The grafting percentage, GP (also known as the degree of grafting) was determined as follows:

$$GP (\%) = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

Where, W_0 and W_1 are the weight of PET fiber samples before and after grafting, respectively.

The titration method was used to analyze the COOH functional group for the determination of grafting effects in order to identify the optimal grafting parameters. This method was based on the reaction between the carboxyl group and NaOH. The weighted PET fiber (grafted) was put in 100 ml beaker, and 25 ml 0.01 N standardized NaOH solution was then added and stirred for 24 h to neutralize the carboxyl group. The excess NaOH was then back titrated by a standardized solution of HCl reagent. Experimental error due to dissolved CO_2 was minimized by performing the titration experiment under a nitrogen atmosphere.

In theory, there is a linear relationship between the amount of COOH and the grafting yield. Assuming one unit of acrylic acid grafted is associated with one unit of COOH, the relationship is as follows:

$$COOH \text{ amount (mmole/g)} = \frac{(W_1 - W_0) \times 1000}{72.06 \times W_0} = \frac{GP \times 10}{72.06} \quad (2)$$

Where, 72.06 is the molecular weight of the acrylic acid monomer. Furthermore, the Fourier-transform infrared-attenuated total reflectance (FTIR-ATR) analysis was taken with Perkin Elmer Spectrum GX model spectrometer and was applied to functional group analysis. The characteristic peak of C=O of COOH in acrylic acid fall at 1720 cm^{-1} (Kormunda and Pavlik, 2010), and the characteristic peak of COO^- of the ion exchanger after alkalization is present at 1650 to 1540 cm^{-1} (Colthup et al., 1990). The presence of these characteristic peaks in FTIR spectra could verify the grafting treatment successfully.

Adsorption experiments

The ion exchangers prepared according to the two points described above were used in the experiments of heavy metal adsorption. Dried grafted PET fiber samples were added into 100 ml beaker containing 50 ml of each metal ion solution (50 mg/L) and adjusted to desired temperature and pH. The mixture solution was stirred and then filtrated. The ion concentration of the filtrates was analyzed with inductive coupled plasma-optical emission spectrometer (ICP-OES) (Perkin Elmer, Optima 2000). The adsorption amount was calculated as follows:

$$Q = \frac{(C_1 - C_0) \times V}{W} \quad (3)$$

Where Q is the adsorption amount (mg/g), W the weight of grafted PET fiber (g), V the volume of solution (L), and C_1 and C_0 are the concentrations of each ion (mg/L) before and after adsorption, respectively. The adsorption behaviors were observed under various adsorption environments. Moreover, liquid and solid phase analyses were conducted to study the adsorption results and properties.

RESULTS AND DISCUSSION

Investigation of the optimal parameters for the plasma modification of PET fiber surface - water loss rate

Under various plasma treatment time and power, the results of the water loss rates are illustrated in Figures 1 and 2. Figure 1 shows that the hydrophilicity increased significantly from 3.2%/min (untreated PET fiber) to 10.5%/min owing to the plasma activation reaction with the optimal treatment time of 10 s. It is considered that, due to the proper treatment time, the fiber's surface reacted with the plasma gas to generate the hydrophilic active sites. Consequently, the resulting hydrophilicity increase was performed. However, longer exposure to plasma may also cause a loss of hydrophilicity, which contributes to the improvement of interfacial adhesion. Thus, the hydrophilic sites were destroyed and consequently the hydrophilicity was reduced compared to that treated for 10 s (Dogue et al., 1995). From Figure 2, the greater hydrophilicity was obtained at the power of 800 W. When the treatment power was raised from 400 to 800 W, the hydrophilic effect improved due to the increase of power provided. On the other hand, a further increase of the power to 1200 W enhanced the collision probability correspondingly due to the higher electron density in the chamber, leading to an etching effect of the active sites on the fiber's surface. Therefore, the hydrophilicity and grafting effect were slightly reduced. Such similar result could be found in the study by Li et al. (2006) who used radio frequency (RF) plasma to modify polyphenylene sulfide (PPS) at the power of 40 to 70 W, with the best grafting result observed at 50 W. To optimize the plasma treatment power and time, application of a plasma power of 800 W for 10 s may be considered as the suitable one in terms of surface modification of PET fibers.

Investigation of the conditions for the acrylic acid grafting of plasma modified PET- grafting yield and COOH quantitative determination

The acrylic acid with a COOH functional group was selected as the grafting monomer for the grafting reaction to form the ion exchangers with the ability of adsorbing heavy metals. The effects of the factors, including grafting temperature, acrylic acid monomer concentration and

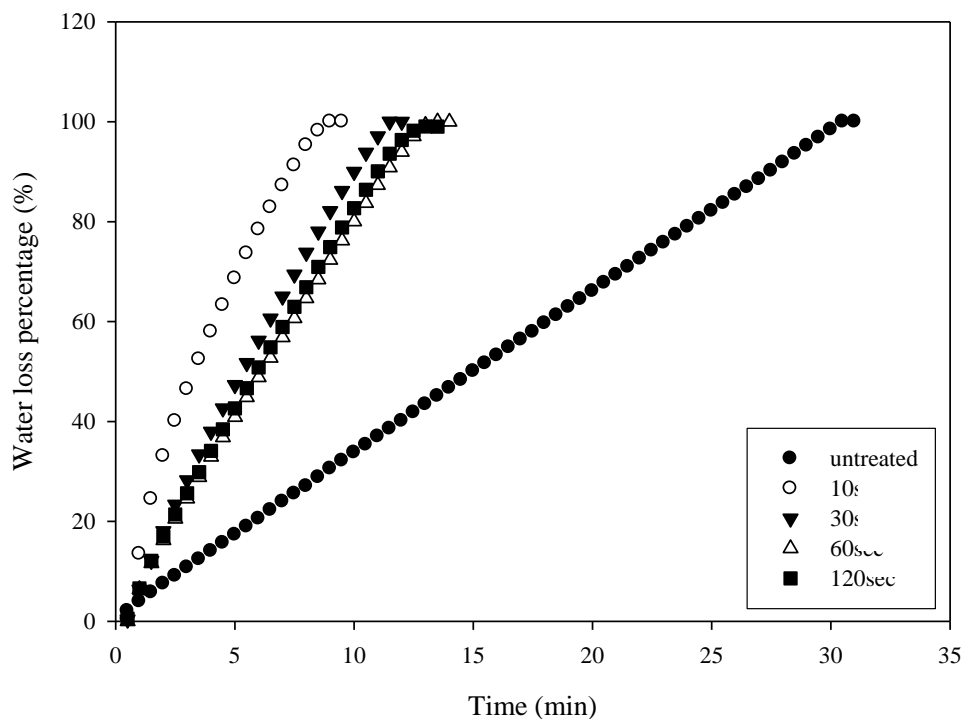


Figure 1. Water loss rates of original (untreated) PET fiber and the fibers treated with argon plasma of 10, 30, 60, and 120 s. The argon plasma power is 800 W and the gas pressure is 200 mtorr.

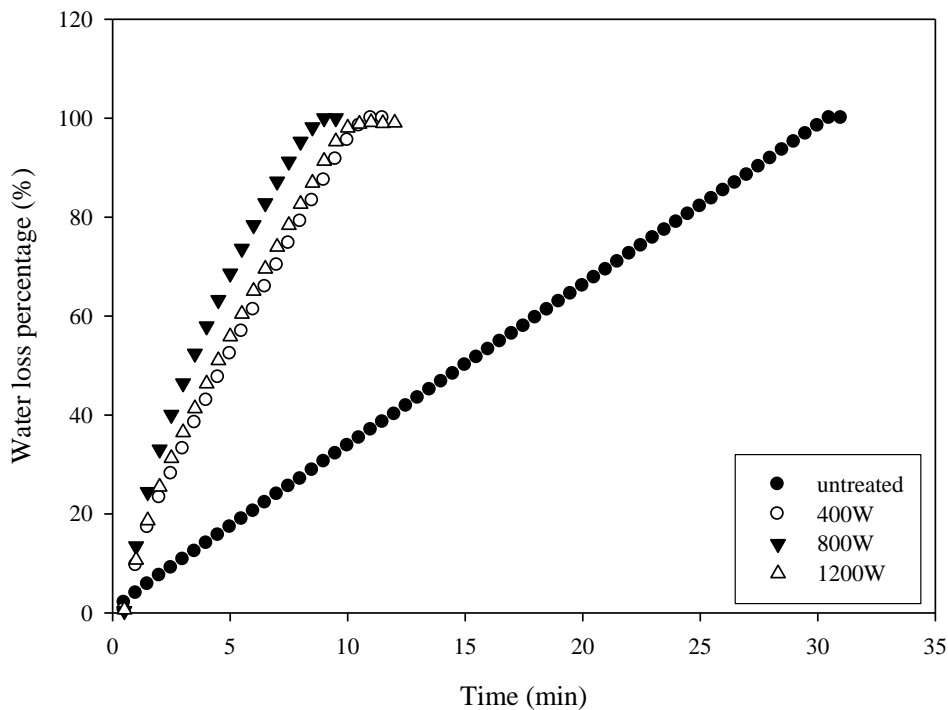


Figure 2. Water loss rates of original (untreated) PET fiber and the fibers treated with argon plasma of 400, 800, and 1200 W. The plasma treatment time is 10 s and the gas pressure is 200 mtorr.

grafting time on the grafting processes were investigated. Figure 3 reveals that the grafting yields altered at different grafting temperatures, with the optimal grafting yield of 4.45% obtained at 90°C. It was believed that, under elevated temperature, the peroxide groups or the initiators on the fiber's surface were easily decomposed thermally to form free radicals leading to a higher grafting probability with a higher grafting yield. Another cause for the increased grafting yield at elevated temperature was that the mobility of the acrylic acid monomer in the solution was enhanced owing to the increase of temperature. As a result, the probability of the monomer to come into contact with the free radicals was raised and giving a higher grafting yields (Xu et al., 2002). It was also found in Figure 3 that the grafting effect at the plasma power of 800 W was superior to that at 400 and 1200 W, thus representing the use of water loss rate for determining the plasma modification effect.

In the experiment of acrylic acid monomer concentrations, various monomer concentrations of 2, 4, and 6 M were used, and the results of the grafting yield were 1.3, 2.8, and 4.0%, respectively. Thus, the concentration of 6 M acrylic acid monomer was used in the experiments. As observed in Figures 4, the grafting yield increased with increasing grafting time. It was thought that the monomers reacted more easily with the free radicals on the fiber's surface as the acrylic acid monomer concentration increased, resulting in a higher grafting probability with an improved grafting yield. This trend was comparable to the result of the study by Guo et al. (1999) who discovered that the grafting yield of acrylic acid increased with increasing time within the grafting time of 150 min.

In addition to the weight method to calculate the grafting yield of acrylic acid monomer, we also used the titration method to analyze the amount of the COOH functional group on the surface. Because COOH can react with metal ions, it was used to remove the metal ions in aqueous solution. Analysis of the amount of COOH on the surface could further verify the relationship of COOH and the grafting yield. Therefore, we used the titration method to measure the amount of COOH on the surface of the PET fibers under various grafting conditions, then compared by the theoretical amount of COOH calculated from the grafting yield (weight method) to observe the difference in the amounts of COOH from the theoretical calculation and the titration method. The amounts of COOH from the analysis of the titration method and those from the calculated theoretical value of the weight method under various grafting parameters are summarized in Table 1.

The graph where the x-axis is the grafting yield and the y-axis is the COOH amount measured by the titration method is illustrated in Figure 5. It was found that there was a close correlation between the grafting yield and the COOH amount, indicating that either the grafting yield or

the COOH amount was a rational option to determine the grafting result.

Figure 6 illustrates the results using FTIR-ATR to analyze the functional groups on the surface of PET fibers before and after the plasma treatment. From Figure 6a, b, and c, it was found that the characteristic peak of C=O (1720 cm^{-1}) appeared in all spectra. It was understood that the acrylic acid contained COOH functional group, yet the PET fibers already contained C=O. As a result, the difference in the position of the characteristic peak was less likely to be observed. Therefore, we further used the ion exchanger in the alkalization process to convert the COOH functional group into COONa by NaOH. Since the degree of ionization of COONa was higher, the characteristic functional group of COO^- would be present. From Figure 6c, it reveals that the characteristic peak of COO^- is present at 1566 and 1580 cm^{-1} . Colthup et al. (1990) demonstrated that the carboxyl salts have a strong asymmetric CO_2 stretching vibration at 1650 to 1540 cm^{-1} . Similar research results from Kondo et al. (2006) also showed the COO^- observed at 1580 cm^{-1} by FTIR spectroscopy. The presence of these characteristic peaks confirmed the grafting of acrylic acid and characteristic functional group of COO^- .

Investigation of the adsorption of heavy metal ions by the modified material

PET fiber with plasma-grafting-alkalization treatment was used in present study. It was prepared prior to the subsequent heavy metal adsorption experiment. Figure 7 shows the effects of different solution pH values on the adsorption of heavy metals. From the trend, we discovered that the adsorption of Cu^{2+} increased significantly with increasing pH values. It was believed that the H^+ ions of higher concentration at a low pH competed with the positively charged heavy metal ions for the adsorption sites (Coskun et al., 2000; Karakisla, 2003) of COO^- on the surface of the ion exchanger, resulting in the observed trend in the figure. From the view of competitiveness, we found that the adsorption effects were $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+}$, demonstrating that the Cu^{2+} ion has more favorable competitiveness in the aqueous solution. This result is similar to that of the study by Gérente et al. (2000) using Cu^{2+} , Ni^{2+} , Pb^{2+} , and consistent with that of the study by Çavuş et al. (2006) who pointed out that Cu^{2+} is less likely to compete with H^+ ions than Pb^{2+} and Cd^{2+} , leading to a higher adsorption effect. The highest adsorption of Cu^{2+} could go as high as $0.073\text{ mmole Cu/g-polymer}$, Pb^{2+} $0.037\text{ mmole Pb/g-polymer}$, and Ni^{2+} $0.012\text{ mmole Ni/g-polymer}$.

The effects of various temperatures on the adsorption of Cu^{2+} were further investigated and the adsorption heat was calculated from the Van't Hoff equation

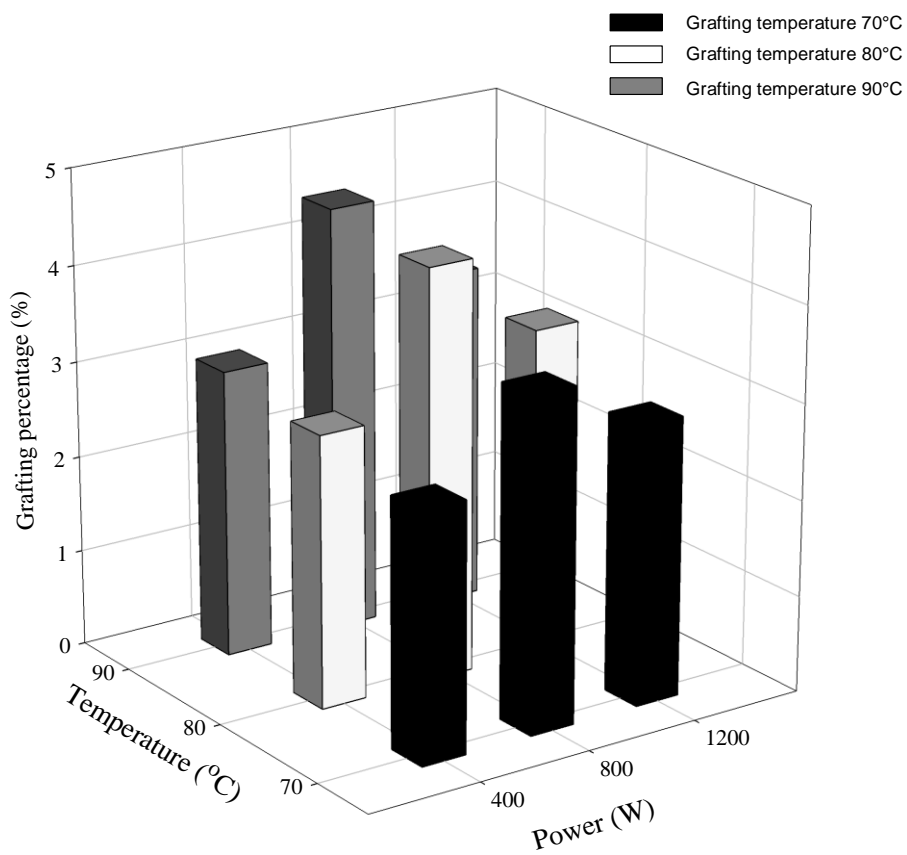


Figure 3. The grafting yields of PET after Argon plasma treatment under various parameters (plasma treatment time: 10 s; gas pressure: 200 mtorr).

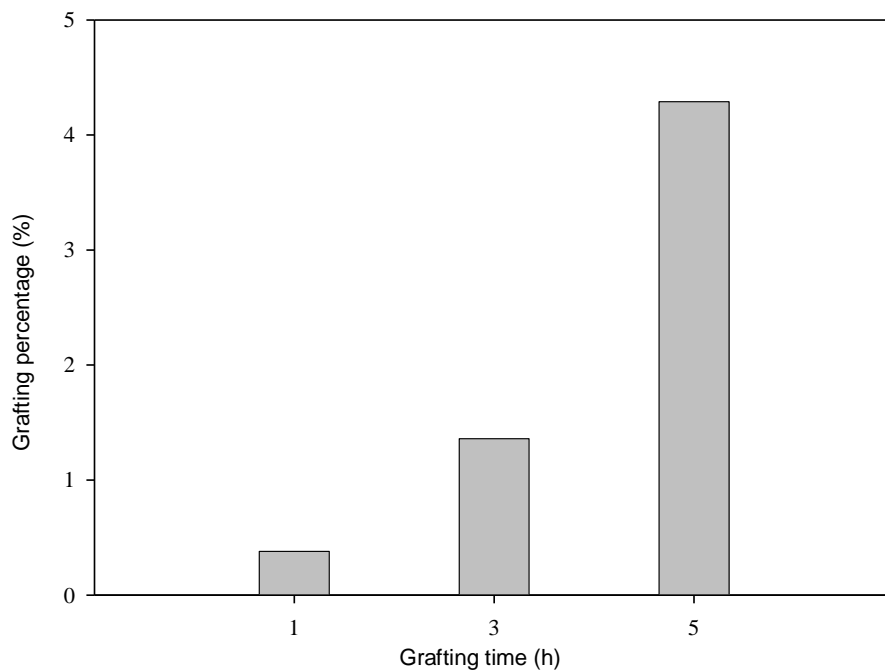
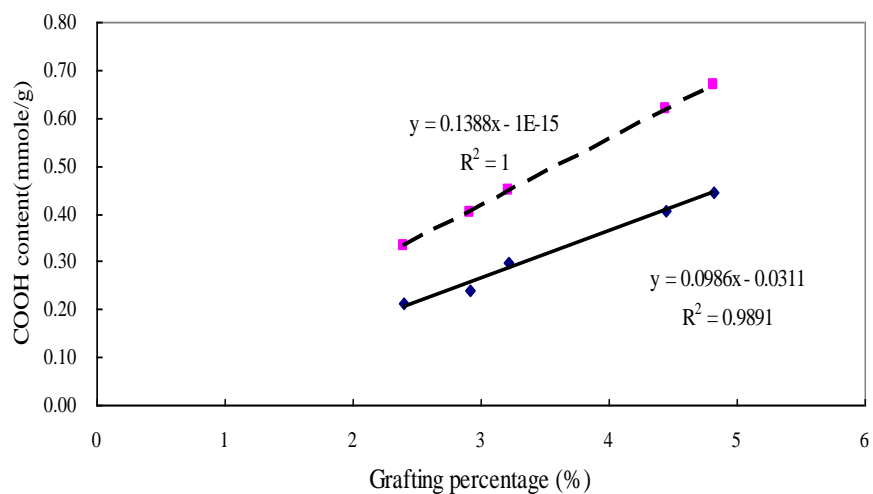
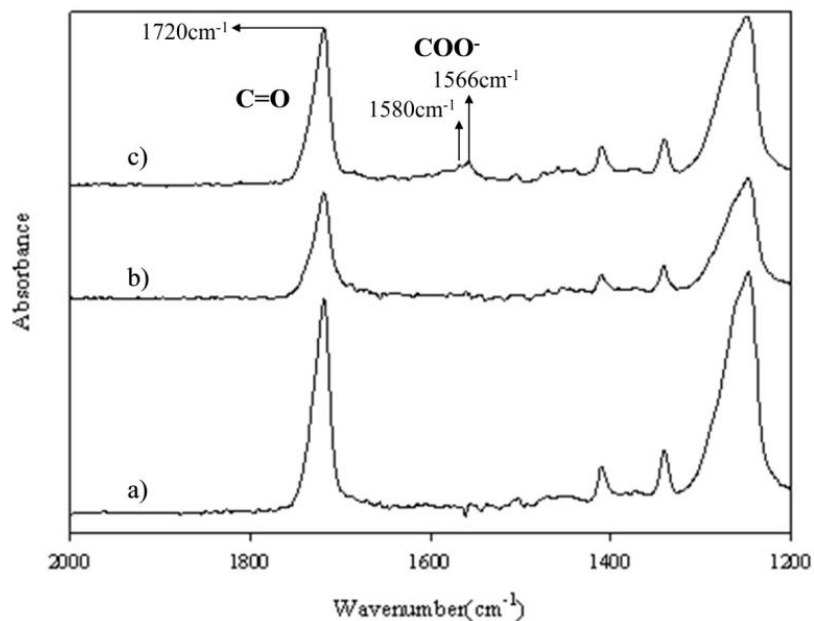


Figure 4. The grafting yields at different grafting time.

Table 1. Acrylic acid grafting yields and COOH amounts on the PET fiber surface.

Grafting parameter	Grafting yields	COOH amount (mmole/g)	
		Titration method	Weight method
800 W, 200 mtorr, 70°C, 10 s	2.40	0.213	0.333
800 W, 200 mtorr, 90°C, 10 s	4.45	0.405	0.618
1200 W, 200 mtorr, 70°C, 10 s	2.91	0.239	0.404
1200 W, 100 mtorr, 80°C, 10 s	3.22	0.296	0.447
1200 W, 200 mtorr, 80°C, 10 s	4.82	0.446	0.669

**Figure 5.** Correlation of COOH amount and grafting yield under various COOH measurement methods (solid line: titration method; broken line: weight method).**Figure 6.** FTIR absorption spectra of PET fibers under various treatments (a, Grafting treatment only; b, plasma treatment and grafting treatment; c, plasma treatment, grafting treatment and followed by alkalization treatment).

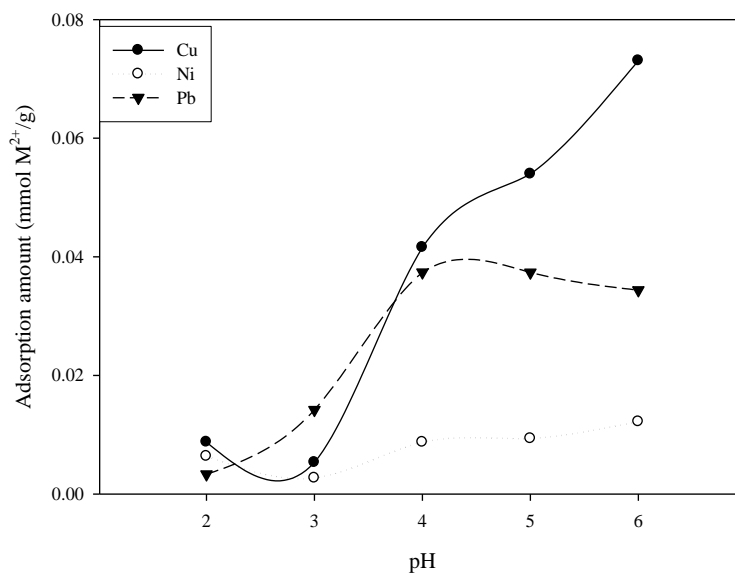


Figure 7. Effects of solution pH on the adsorption of heavy metal ions.

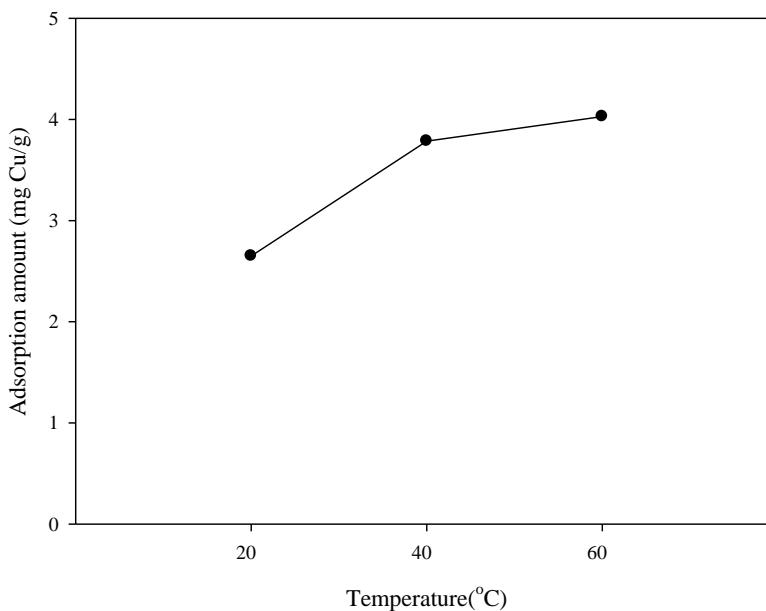


Figure 8. Effects of different reaction temperatures on the adsorption of Cu²⁺.

(Atkins and Paula, 2006) illustrated below:

$$\log \frac{Q}{C_e} = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (4)$$

Where C_e, Concentration of solution at equilibrium (mg/L); Q, concentration of adsorbed solid (mg/L); ΔH, adsorption heat (J/mol); R, 8.314 J/mol K; T, temperature

(K); ΔS, entropy (4.184 J/mol K).

From the equation listed above, a graph was plotted using 1/T as the x-axis and log (Q/C_e) as the y-axis to calculate the adsorption heat ΔH from the slope, which was used to determine the reaction to be endothermic and its adsorption characteristics. Figure 8 illustrates the effects of different temperatures on the adsorption of Cu²⁺. It was observed that the adsorption of Cu²⁺

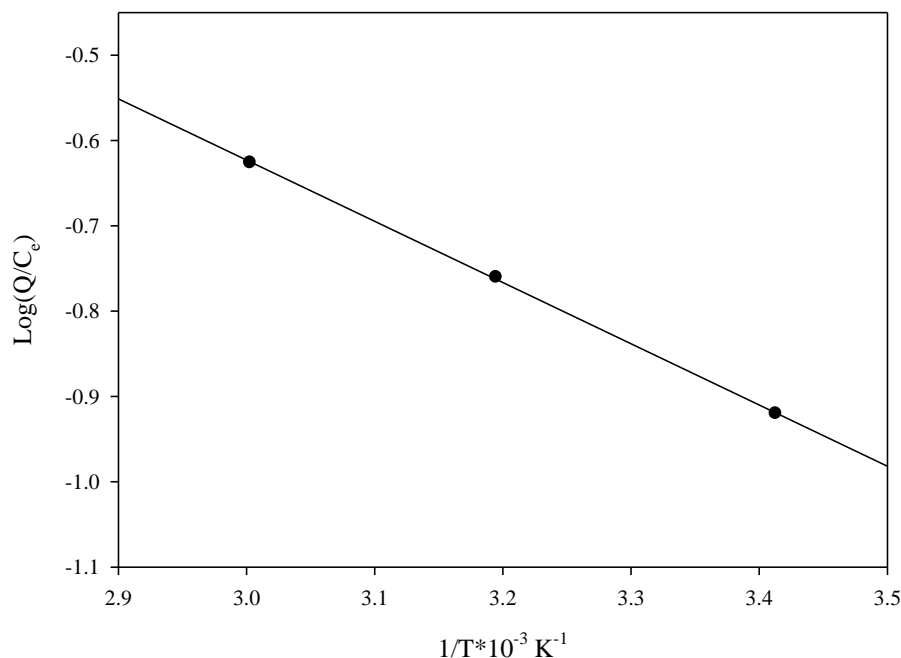


Figure 9. Adsorption curve of Cu^{2+} from Van't Hoff equation.

improved at higher temperatures. Similar observation from Hegazy et al. (2001) demonstrated that this might be attributed to the increase in kinetic energy of metal ions with the temperature and the increase in the flexibility of the grafted chains as well. The result was factored into the Van't Hoff equation to generate Figure 9. From the graph, the slope and the reaction heat ΔH were calculated to be -717.5 and 13.74 kJ/mol, revealing that the reaction was endothermic ($\Delta H > 0$) and the reaction heat was less than 20 kJ/mol. Therefore, the reaction is believed to be a physical adsorption process.

Conclusions

The present study used PET fibers as the substrate and ambient-temperature plasma to modify the surface properties in order to increase the hydrophilicity of the PET fibers. Afterwards, an ion exchanger capable of adsorbing heavy metals was prepared by acrylic acid grafting. Moreover, the ion exchange properties of the COOH functional group were explored to investigate the adsorption behavior of heavy metal ions. The potential of the application of the plasma surface modification combined with an ion exchanger developed by grafting technology was evaluated for wastewater treatment in an actual plant. The results are summarized as follows:

1) After the surface modification and activation of the PET fibers by ambient-temperature plasma, hydrophilicity could be improved to be favorable for acrylic acid

grafting. The optimal modification conditions were a power of 800 W and a modification time of 10 s.

2) The optimal conditions under various environments for the grafting procedure of PET fibers after the plasma treatment were a grafting temperature of 90°C, an acrylic acid monomer concentration of 6 M, and a grafting time of 5 h. The grafting yield could reach 4.45% under such conditions.

3) The pH value of the adsorption environment posed a significant impact on the adsorption effect of the ion exchanger. In the condition pH of 6, Copper, Lead, and Nickel showed more favorable adsorption effects, with the adsorptions of 0.073 mmole Cu/g-polymer, 0.037 mmole Pb/g-polymer, and 0.012 mmole Ni/g-polymer.

4) The use of the Van't Hoff equation to investigate the adsorption model under different adsorption temperatures gave the reaction heat ΔH of 13.74 kJ/mol, indicating that the reaction was endothermic and a physical adsorption reaction.

5) The use of ambient-temperature plasma to modify PET fibers could improve the grafting yield and successfully prepare the ion exchanger to adsorb heavy metals. This technology is unique due to its convenience, quickness, low energy consumption, and environmental friendliness. The adsorption behavior was understood to be favorable for adsorption based on its adsorption model. The process is believed to be a physical adsorption reaction useful for the subsequent desorption and recycling of heavy metals. The developed technology displays a great potential for wastewater treatment in an actual plant and thus requires further advanced study.

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REFERENCES

- Atkins P, Paula JD (2006). Physical Chemistry (8th edition). W.H. Freeman and Company Printing, United States of America. P. 212.
- Bailey SE, Olin TJ, Bricka RM, Adrian DD (1999). Review of potentially low-cost sorbents for heavy metals. *Water Res.* 33(11):2469-2479.
- Bayasi Z, Zeng J (1993). Properties of polypropylene fiber reinforced concrete. *ACI Mater. J.* 90(M61):605-610.
- Bureau of Industrial Development, the Ministry of Economic Affairs (MOEA), Taiwan (2007). www.moeaidb.gov.tw.
- Bureau of Standards, Metrology and Inspection, The Ministry of Economic Affairs (MOEA), Taiwan (2010). CNS 12915-Method of test for fabrics. pp. 1-56.
- Çavuş S, Gurdag G, Yasar M, Guclu K, Gurkaynak MA (2006). The competitive heavy metal removal by hydroxyethyl cellulose-g-poly(acrylic acid) copolymer and its sodium salt: The effect of copper content on the adsorption capacity. *Polym. Bull.* 57(4):445-456.
- Colthup NB, Daly LH, Wiberley SE (1990). Introduction to Infrared and Raman spectroscopy (3rd edition). Academic Press Inc. Publisher, United States of America. pp. 317-318.
- Coskun R, Yigitoglu M, Sacak M (2000). Adsorption behavior of copper(II) ion from aqueous solution on methacrylic acid-grafted poly(ethylene terephthalate) fibers. *J. Appl. Polym. Sci.* 75:766-772.
- Dogue ILJ, Foerch R, Mermilliod N (1995). Plasma-induced hydrogel grafting of vinyl monomers on polypropylene. *J. Adhes. Sci. Technol.* 9(12):1531-1545.
- Foti D (2011). Preliminary analysis of concrete reinforced with waste bottles PET fibers. *Constr. Build. Mater.* 25:1906-1915.
- Gérente C, Couespel du Mesnil P, Andres Y, Thibault JF, Le Cloirec P (2000). Removal of metal ions from aqueous solution on low cost natural polysaccharides. Sorption mechanism approach. *React. Funct. Polym.* 46(2):135-144.
- Guo Y, Zhan J, Shi M (1999). Surface graft copolymerization of acrylic acid onto corona-treated poly(ethylene terephthalate) fabric. *J. Appl. Polym. Sci.* 73(7):1161-1164.
- Gupta B, Plummer C, Bisson I, Frey P, Hilborn J (2002). Plasma-induced graft polymerization of acrylic acid onto poly(ethylene terephthalate) films: Characterization and human smooth muscle cell growth on grafted films. *Biomaterials* 23(3):863-871.
- Hegazy EA, Kamal H, Khalifa NA, Mahmoud GA (2001). Separation and extraction of some heavy and toxic metal ions from their wastes by grafted membranes. *J. Appl. Polym. Sci.* 81:849-860.
- Karakisla M (2003). The adsorption of Cu(II) ion from aqueous solution upon acrylic acid grafted poly(ethylene terephthalate) fibers. *J. Appl. Polym. Sci.* 87(8):1216-1220.
- Kondo Y, Miyazaki K, Takeuchi N, Sakurai K, Kaneko J (2006). Hydrophilization of PET wire mesh in paper manufacture by electron beam irradiation induced graft polymerization (in Japanese). *Sen'i Gakkaishi* 62(5):95-99.
- Kormunda M, Pavlik J (2010). Characterization of oxygen and argon ion flux interaction with PET surfaces by in-situ XPS and *ex-situ* FTIR. *Polym. Degrad. Stabil.* 95:1783-1788.
- Lee SD, Hsiue GH, Kao CY (1996). Preparation and characterization of a homobifunctional silicone rubber membrane grafted with acrylic acid via plasma-induced graft copolymerization. *J. Polym. Sci. Part A: Polym. Chem.* 34(1):141-148.
- Li YN, Sun Y, Deng XH, Yang Q, Bai ZY, Xu ZB (2006). Graft polymerization of acrylic acid onto polyphenylene sulfide nonwoven initiated by low temperature plasma. *J. Appl. Polym. Sci.* 102(6):5884-5889.
- Lin W, Hsieh YL (1997). Ionic Absorption of Polypropylene Functionalized by Surface Grafting and Reactions. *J. Polym. Sci. Part A: Polym. Chem.* 35(4):631-642.
- McDonald DM, Webb JA, Taylor J (2006). Chemical Stability of Acid Rock Drainage Treatment Sludge and Implications for Sludge Management. *Environ. Sci. Technol.* 40(6):1984-1990.
- Pereira de Oliveira LA, Castro-Gomez JP (2011). Physical and Mechanical behaviour of recycled PET fibre reinforced mortar. *Constr. Build. Mater.* 25:1712-1717.
- Svorcik V, Kolarova K, Slepicka P, Mackova A, Novotna M, Hnatowicz V (2006). Modification of surface properties of high and low density polyethylene by Ar plasma discharge. *Polym. Degrad. Stabil.* 91(6):1219-1225.
- Xu Z, Wang J, Shen L, Men D, Xu Y (2002). Microporous polypropylene hollow fiber membrane. Part I. Surface modification by the graft polymerization of acrylic acid. *J. Membr. Sci.* 196(2):221-229.