

# Cobalt Ion Adsorption by the Hydrolyzed AAm Grafted PET Films Prepared by $\gamma$ -ray Irradiation

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## Abstract

Acrylamide (AAm) grafted polyethylene terephthalate (PET) films were prepared by  $\gamma$ -ray induced grafting technique. The partially hydrolyzed AAm grafted PET films were studied for the removal of Co(II) from aqueous solution. The Co(II) adsorbed hydrolyzed grafted films was investigated by SEM, EDS and FTIR. A probable mechanism for the Co(II) adsorption was proposed from the experimental results. In addition, the effects of graft yield, pH, soaking time and initial ion-concentration on the adsorption of Co(II) ions by the hydrolyzed grafted film was studied. The desorption of Co(II) ions from the hydrolyzed grafted films were also investigated, which revealed a high desorption efficiency.

**Keywords:** poly (ethylene terephthalate), acrylamide, radiation grafting, Co (II) adsorption

## 1. Introduction

Ignited by the well-known environmental destruction cases: Minamata disease (organic mercury poisoning), Itai-itai disease (cadmium poisoning) heavy metals have attracted public attention as potential hazards for human life and health and due to the stricter environmental regulations on the discharge of heavy metals it became necessary to develop efficient and low cost technologies for their removal [1]. However the conventional methods used for the treatment of industrial waste water to remove hazardous metal ions such as precipitation, ion exchange, activated carbon adsorption, electrolytic method etc. are not free from demerit like high cost, low removal rate or difficulty for regeneration and reuse. Therefore researches have been conducted to prepare alternative low cost effective adsorbent from sawdust [2], sporopollenin [3, 4], chitosan [5], peat [6], cellulose [7], clay mineral [8] etc.

Considering the excellent chemical and thermal stability and mechanical property of PET (polyethylene terephthalate) we are interested to prepare adsorbent by  $\gamma$ -ray induced grafting of different acrylic monomers on PET films. Most of the adsorbents prepared by grafting of various monomers on PET fibers [9-16] and films [17] studied before were prepared by chemical method. But we adopted  $\gamma$  induced grafting technique to prepare different acrylic monomer grafted PET films for hazardous heavy metal ion recovery to ensure efficient and environment friendly grafting of monomers.  $\gamma$  -induced grafting technique is an important method because of its extensive penetration into the polymer matrix and its rapid and uniform formation of radicals for initiating grafting without using any toxic chemical initiator [18].

We started our journey with the preparation of acrylamide (AAm) grafted PET films by  $\gamma$  irradiation for metal ion

adsorption. In our previous work, we studied Dimethyl sulfoxide (DMSO) assisted grafting of AAm onto PET films by  $\gamma$  irradiation [19]. The work reported the effects of different conditions such as DMSO treatment temperature, presence of inhibitor, monomer concentration, total dose and dose rate on graft yield and confirmed grafting of AAm onto PET films by FTIR, SEM and swelling measurement.

As for the present work, our objective was to study the Co(II) adsorption by the partially hydrolyzed AAm grafted PET films. The adsorption of Co(II) by the hydrolyzed graft films were analyzed with FTIR, SEM and EDS. Besides, the effects of different conditions such as graft yield, pH, soaking time, initial metal ion concentration on the adsorption of Co(II) ions by the hydrolyzed graft films were studied. Desorption of Co(II) from the hydrolyzed grafted films were also investigated.

## 2. Materials and Methods

### 2.1 Materials and Reagents

Commercial PET films (Teijin DuPont films, G2) of thickness 50  $\mu\text{m}$  were kindly provided by Teijin Co. Ltd. These films were cut into small pieces ( $2 \times 2 \text{ cm}^2$ ), washed with acetone, and dried in vacuum oven before use. AAm and  $\text{FeCl}_3$  were procured from Sigma Aldrich. DMSO and KOH were supplied by Wako pure chemical industries Ltd. Cobalt (II) chloride (anhydrous, Chameleon Reagent) and cobalt standard solution (Fluka) were used as a source of the adsorbate and for the calibration of Co(II) concentration, respectively.

### 2.2 Instrument and Apparatus

The PET films were analyzed by a Fourier transform infrared (FTIR) spectrophotometer, Jasco FTIR 620 in the wavenumber range 400 -  $4000 \text{ cm}^{-1}$  to investigate the chemical and/or physical interactions. Scanning electron

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microscopy (SEM) image observations and elemental analyses of the carbon coated PET films were performed using an EDS-analyzer (e-Xpress) equipped SEM (Zeiss Ultra55) operated at 7-10 KeV. The metal-ion concentrations in the solutions were analyzed by an inductively coupled plasma mass spectrometer (ICP MS), Agilent7500ce.

**2.3 Grafting of AAm onto the PET Films by Gamma Radiation**

The dry PET films weighing  $W_{pristine}$  were soaked in DMSO for 0.5 h at different temperatures (from 100 to 160°C). After withdrawing the PET films from DMSO, excess liquid on the surface was removed by blotting between filter paper. The DMSO-treated PET films were taken into glass bottles containing different concentration (25, 40, 50 and 70 wt%) of AAm aqueous solutions with 1 wt% FeCl<sub>3</sub>. FeCl<sub>3</sub> is used to minimize homopolymer formation. The contents of the glass bottles were then irradiated with different doses (20, 50, 70, 100 kGy) of  $\gamma$  rays with a dose rate of 1.0 kGy/h in air ( $\gamma$ -ray irradiation of the PET films was carried out at the <sup>60</sup>Co  $\gamma$ -ray irradiation facility of Research Reactor Institute, Kyoto University). The obtained grafted films were washed in distilled water at 60°C for 24h to remove the homopolymers. Then the films were dried in a vacuum oven at 60°C for 24h and were weighed ( $W_{AAm\text{ grafted}}$ ). The graft yield was determined by the percent increase in the weight as follows:

$$Graft\ Yield\ (\%) = (W_{AAm\text{ grafted}} - W_{pristine}) / W_{pristine} \times 100 \quad (1)$$

**2.4 Adsorption of Co(II) Ion**

The grafted films were partially hydrolyzed by 10% KOH at 60°C for 1h. Then the films were soaked into the aqueous solution of CoCl<sub>2</sub> at Co(II) ion concentration 1 g/L and pH 7 for 15 min. Metal loaded films were washed and dried.

**2.4.1 Determination of Hydrolysis Percent of AAm**

The hydrolysis percent of amide group to carboxylate group was determined by the IR absorbance ratio following the previous study [19] using the equation:

$$Hydrolysis\ (\%) = [(B - C) / (B - A)] \times 100 \quad (2)$$

where the ratio of absorbance at 3200 cm<sup>-1</sup> (assigned for -NH<sub>2</sub> groups of AAm) to 3054 cm<sup>-1</sup> (assigned for aromatic -CH stretching vibration of PET) was designated as *A* in the case of non-grafted PET, *B* in the case of AAm-graft-PET and *C* in the case of hydrolyzed AAm-graft-PET.

**2.4.2 Determination of Co(II) Uptake Capacity**

The Co(II) uptake capacity of the film was calculated as follows:

$$Q = V(C_1 - C_2) / W \quad (3)$$

where *Q* is the adsorption amount (mg/g), *W* the weight of the hydrolyzed grafted film (g), *V* the volume of solution (L), and *C*<sub>1</sub> and *C*<sub>2</sub> are the concentrations (mg/L) of metal ion before and after adsorption respectively.

**2.5 Desorption of Metal Ions**

The desorption of Co(II) ion was carried out by treatment with 10% aqueous solution of HCl for 30 min. The percent desorption was calculated using the following equation.

% Desorption

$$= \frac{\text{Amount of ions (mg) desorbed}}{\text{Adsorbed amount of ions (mg) by adsorbent}} \times 100 \quad (4)$$

After desorption the hydrolyzed grafted film was used repeatedly.

**3. Results and Discussion**

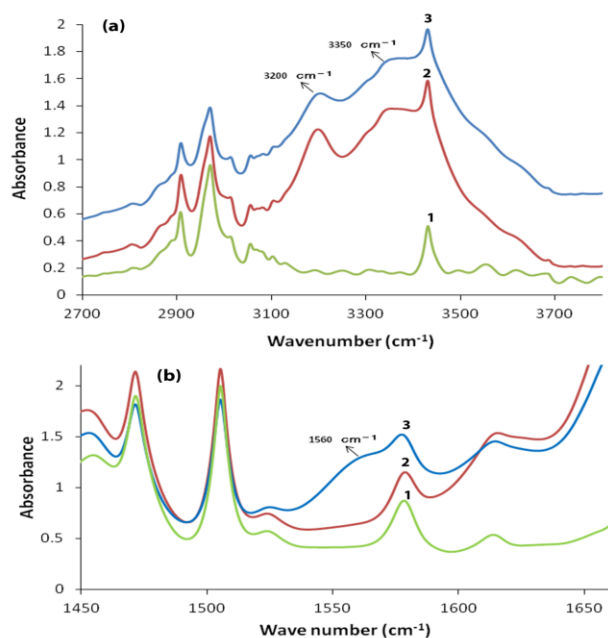
**3.1 Adsorption of Co(II) Ion by Hydrolyzed AAm Graft PET Films**

The grafting of AAm onto PET films was carried out using  $\gamma$ -ray irradiation. As reported in our previous work, the treatment of PET films with DMSO at high temperature (100-160°C) prior to grafting can increase diffusion of AAm solution to the PET films and thereby promote grafting of AAm by  $\gamma$  irradiation [19]. The effects of different conditions such as DMSO treatment temperature, monomer concentration and total dose on graft yield which was discussed in detail in the previous work, are summarized in Table 1.

**Table 1:** Effect of DMSO treatment temperature, monomer concentration and total dose on graft yield

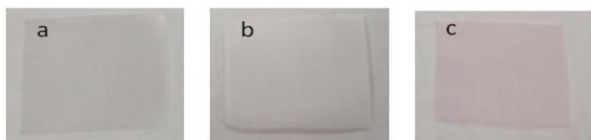
DMSO treatment temperature (°C)	Concentration of AAm (wt %)	Total dose (kGy)	Graft yield (%)
100	50	50	5
140	50	50	14
160	50	50	8
140	25	50	8
140	40	50	12.5
140	70	50	13.5
140	50	20	10
140	50	70	15
140	50	100	15.5

The prepared grafted films were partially hydrolyzed by alkali treatment which increased the accessibility of the metal ions to the amide groups [20] and also converted some of the amide groups to potassium carboxylate (hydrolysis percent was about 30%). The hydrolysis of the amide groups was confirmed by the IR spectra of the films (Fig. 1). The spectrum of the grafted film shows strong peaks at 3200 and 3350cm<sup>-1</sup> assigned for -NH<sub>2</sub> group of AAm which is absent for the ungrafted PET film (Fig. 1a) [13, 21]. The intensity of these peaks is decreased after hydrolysis (Fig. 1a). Again the spectrum of the hydrolyzed grafted film shows a new shoulder peak at 1560cm<sup>-1</sup> that is assigned for asymmetric stretching mode of carboxylate ion which is absent for both the ungrafted and AAm grafted PET film (Fig. 1b) [22].



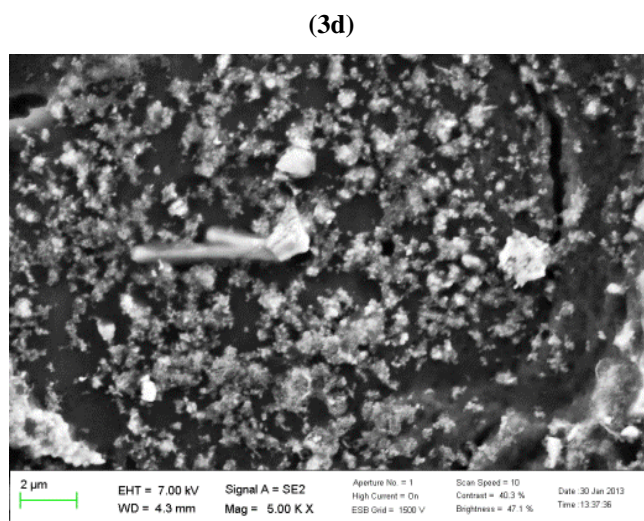
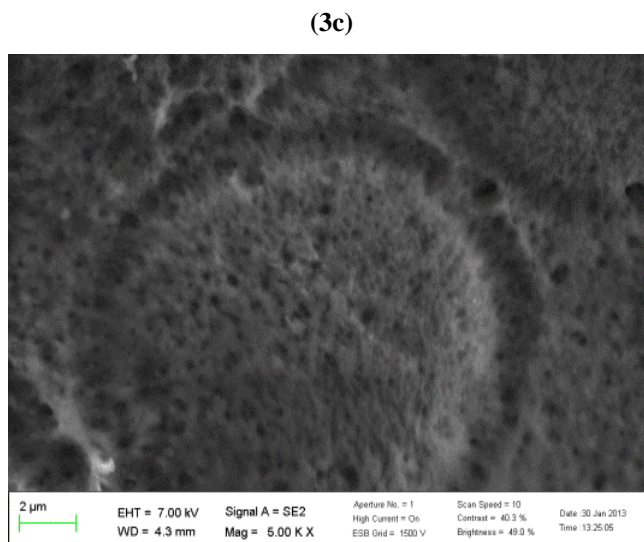
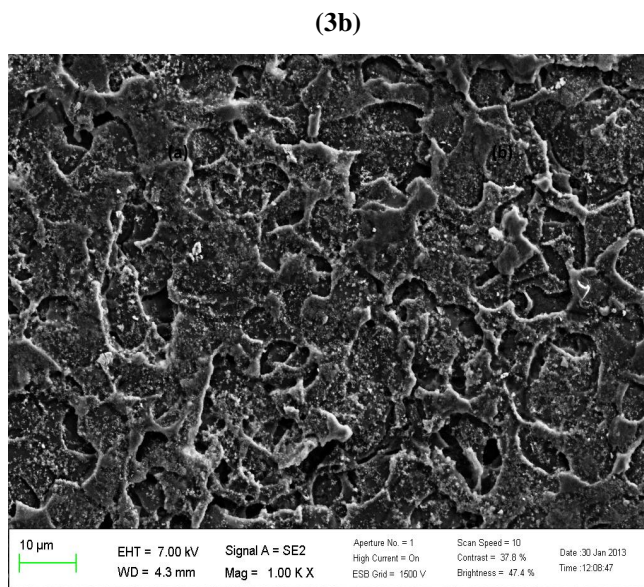
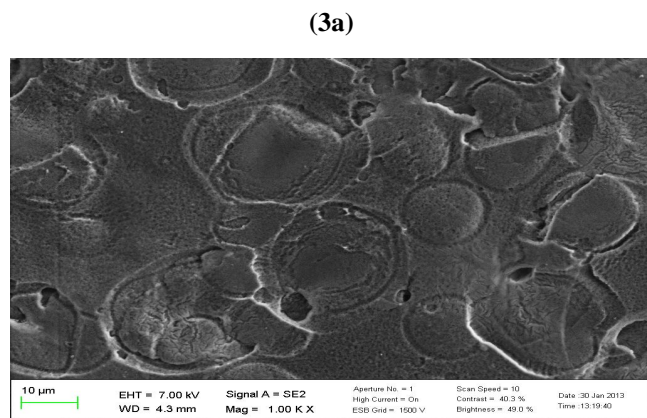
**Fig. 1:** FTIR spectra of (1) ungrafted PET film (2) AAm grafted PET film (3) hydrolyzed AAm graft PET film in the frequency range (a) 2700 to 3800cm<sup>-1</sup> and (b) 1550 to 1660cm<sup>-1</sup>

The hydrolyzed graft films were subjected to Co(II) adsorption from aqueous solution of CoCl<sub>2</sub>. It was observed that the color of the films changed to the color of metal ions within 5 min soaking of the films into the CoCl<sub>2</sub> solutions (Fig. 2). The color of the metal loaded films remained unchanged after washing and drying of the films.



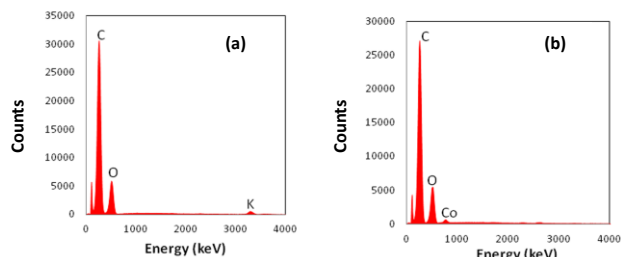
**Fig. 2:** Picture of (a) AAm grafted film, (b) hydrolyzed AAm graft film and (c) Co(II) ion loaded hydrolyzed AAm graft film

The SEM micrographs of the films (Fig. 3) also provide proof of Co(II) adsorption. The surface of the hydrolyzed graft film before Co(II) adsorption is uneven with some cavities. The surface structure of the hydrolyzed grafted film shows clear change after Co(II) ion adsorption.



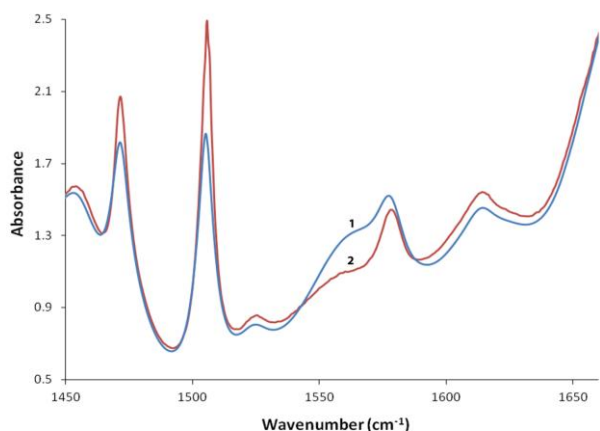
**Fig. 3:** SEM micrographs of the hydrolyzed AAm graft film before Co(II) (a) adsorption ×1000, (c) adsorption ×5000 and after Co(II) (b) adsorption ×1000, (d) adsorption ×5000

To further confirm the presence of Co(II) ions on the film surface and to investigate the mechanism of Co(II) ion adsorption, EDS analysis was employed. The EDS spectrums of the hydrolyzed grafted film before and after Co(II) ion adsorption are shown in Fig. 4.

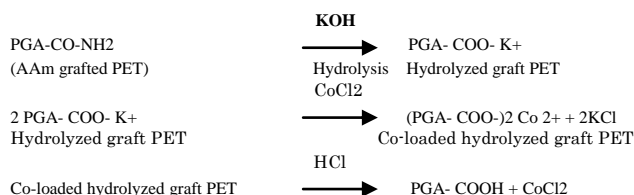


**Fig. 4:** EDS spectra of the hydrolyzed AAm graft PET film (a) before and (b) after Co(II) adsorption

The EDS spectrum of the hydrolyzed grafted film shows the presence of K which is replaced by Co in the spectrum of Co(II) loaded hydrolyzed grafted film. This observation suggests that during the Co(II) ion adsorption  $K^+$  ions are exchanged with  $Co^{2+}$  ions. Again significant decrease of the intensity of the IR peak for carboxylate ion after Co(II) adsorption indicates involvement of carboxylate group in the Co(II) adsorption (Fig. 5).



**Fig. 5:** IR spectra in the frequency range 1450-1660 $cm^{-1}$  of the (1) hydrolyzed AAm graft PET film and (2) the Co(II) loaded hydrolyzed AAm graft film



**Fig. 6:** Principle mechanism of Co(II) ion uptake, PGA refers to (PET-CH<sub>2</sub>-CH<sub>2</sub>-) part of AAm grafted PET

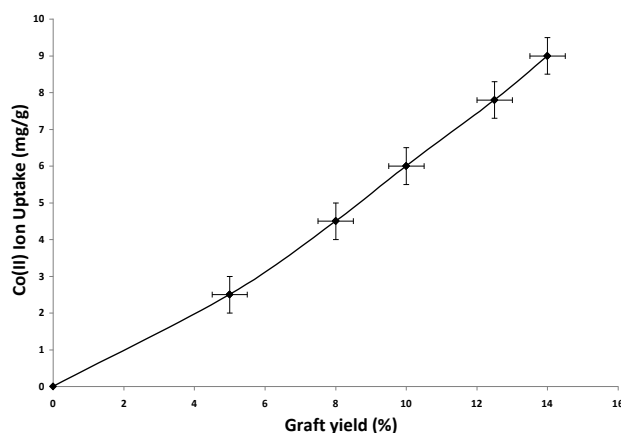
These observations suggest that the main mechanism for the Co(II) uptake was as presented in Fig. 6. On the other hand, some amount of Co(II) adsorption might have occurred through the amide group, but EDS or FTIR

analysis could not provide strong support for the mechanism.

### 3.2 Effect of Different Conditions on Co(II) Adsorption

The effects of graft yield, soaking time, pH and initial concentration on the Co(II) ion uptake by hydrolyzed grafted films were analyzed to find out the optimum condition for maximum ion uptake. The graft yield was varied from 5-14%, the soaking time was varied from 0-15 min, the solution pH was varied from 2-7, and the initial metal ion concentration was varied from 1-6 g/L. The change of concentration of each solution before and after the Co(II) adsorption was analyzed and the metal ion uptake capacity was determined.

The change of Co(II) ion uptake with the graft yield was investigated at the initial Co(II) ion concentration 1g/L, pH 7 and soaking time 15 min. The metal ion uptake is increased with increasing graft yield (Fig. 7). With the increase of graft yield the amount of amide group and carboxylate group present in the hydrolyzed graft film are increased and therefore the Co(II) adsorption is increased.



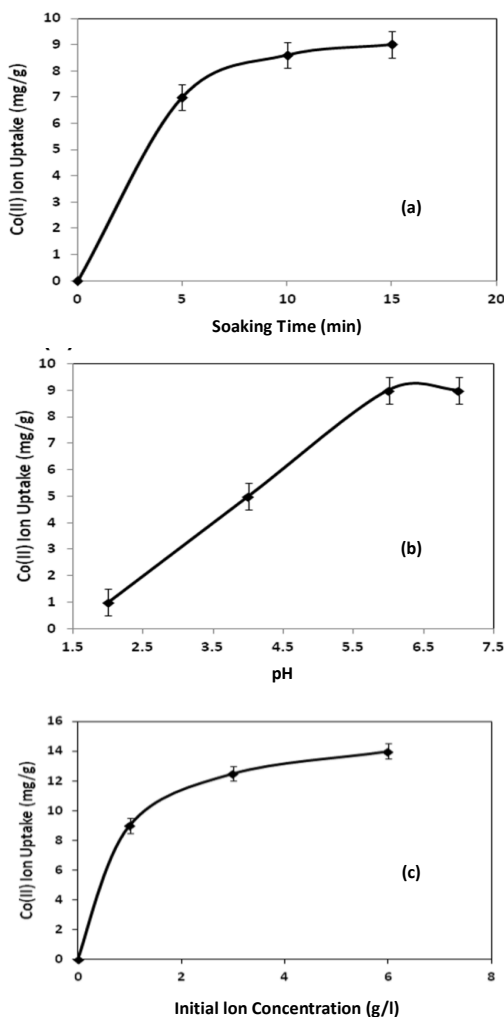
**Fig. 7:** Co(II) ion uptake against graft yield at initial ion concentration 1g/L, pH 7, soaking time 15min

The Co(II) ion uptake against soaking time was studied at the initial Co(II) ion concentration 1g/L, pH 7 and graft yield 14% (Fig. 8(a)). It is observed that the Co(II) ion uptake is very fast and the Co(II) uptake reaches equilibrium after 15 min. The Co(II) ion uptake is 9 mg/g after 15 min. The short equilibrium sorption time also supports that the sorption occurred by an ion exchange mechanism.

To find out the optimum pH value for Co(II) adsorption, the 14% grafted films were subjected to the Co(II) adsorption at the initial ion concentration 1g/L and soaking time 15 min for various pH values (Fig. 8(b)). The increase of the pH of aqueous Co(II) ion solution from 2 to 6 is observed to cause a significant increase in the amount of Co(II) adsorption and reaches the maximum value in the pH range 6 to 7. At low pH values, the hydrogen ions at the interface electrostatically repel the positively charged metal ions and

prevent their approach to the film surface [23]. Therefore, the lower adsorption values are observed at the lower pH values.

The Co(II) ion uptake against initial ion concentration was studied from 1 g/L to 6 g/L at pH 7 and graft yield 14%. The results found are shown in Fig. 8(c). The Co(II) ion uptake increases with increasing initial concentration and then reaches plateau value at higher concentrations. This is attributed to the saturation of the adsorption sites of the reactive film at high concentrations [13].



**Fig. 8:** (a) Co(II) ion uptake against soaking time at initial ion concentration 1 g/L, graft yield 14% and pH 7, (b) Co(II) ion uptake against pH at initial ion concentration 1 g/L, graft yield 14% and soaking time 15 min and (c) Co(II) ion uptake against initial ion concentration at pH 7, graft yield 14% and soaking time 15 min

### 3.3 Desorption of Co(II) Ion from Hydrolyzed Graft Films

The desorption of Co(II) ions from the hydrolyzed graft films was carried out by treating with 10% HCl solution for 30 min. The desorption ratio of Co(II) ions from hydrolyzed graft films is found to be 98%. The regenerated films were found to be effective for the re-adsorption of Co(II) ions.

## 4. Conclusion

In present work, the hydrolyzed AAm grafted PET films were studied for Co(II) adsorption. The hydrolysis of amide group was confirmed by the decrease of intensity of peaks for  $\text{NH}_2$  groups and the appearance of new peak for carboxylate ion in the IR spectrum of the hydrolyzed grafted film. Co (II) adsorption by the hydrolyzed grafted films was analyzed by IR, SEM and EDS which indicated the involvement of carboxylate group in Co(II) adsorption. Present work revealed that the hydrolyzed grafted films can show quick adsorption of considerable amount of Co(II) ions at neutral pH and the adsorbed Co(II) ions can be easily desorbed from the hydrolyzed graft films using 10% HCl solution. These results suggest that the hydrolyzed AAm grafted PET films have potential for the quick removal of Co(II) ions from the industrial waste water.

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