CELLULOSE CHEMISTRY AND TECHNOLOGY

FUNCTIONAL CELLULOSIC FILTER PAPERS PREPARED BY RADIATION-INDUCED GRAFT COPOLYMERIZATION FOR CHELATION OF RARE EARTH ELEMENTS

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Functional cellulosic filter papers containing chelating groups were developed by radiation-induced graft copolymerization of acrylonitrile onto cellulosic filter paper, followed by the amidoximation reaction for chelation of rare earth elements (REEs). The obtained functional filter papers were characterized by Fourier transform infrared analysis (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The presence of the functional groups was proven by FTIR spectra analysis. XRD and SEM showed that the grafting process did not break down the orientation and crystallinity of the fibers. TGA indicated the thermal stability of the functional filter paper at temperatures below 200 °C. The functional filter papers were investigated for the chelation of rare earth elements from the monazite mineral prior to qualitative determination by wavelength dispersive X-ray fluorescence (XRF) *via* characteristic L X-ray lines.

Keywords*:* functional filter paper, radiation, graft copolymerization, chelation, X-ray fluorescence

INTRODUCTION

Rare earth elements (REEs) have been increasingly used in the field of chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence and laser materials, high temperature superconductors, secondary batteries and catalysis.[1] Monazite is the most important commercial source of rare earth elements.[2] Many efforts to analyze monazite samples have been reported.[3]

The determination of lanthanides in geological samples, such as monazite, is one of the most difficult and complicated analytical tasks, especially at trace levels, because of their similar chemical properties.[4,5] Naturally occurring high concentrations of certain metals, such as transition metals, alkali metals, and alkaline earth elements, in geological materials usually interfere with the determination of the trace lanthanide metals in these samples.

The disadvantage of ion exchange resins for pre-concentration of rare earth elements is their high affinity for alkali and alkaline earth metals, as well as heavy metals.[6] The development of chelating resins with selective chelating groups covalently attached to different supports has acquired great importance for selective pre-concentration of trace elements, while eliminating alkali and alkaline earth elements.[4,7,8]

Filter papers containing functional groups were proposed for the enrichment of trace heavy elements with high selectivity prior to quantification with highly sensitive instruments.[9,10] Cellulose was used as matrix over synthetic polymers due to its favorable properties, such as hydrophilicity, porosity, fibrous structure, abundance and cheapness.[11] The incorporation of chelating groups into cellulosic filter papers by the graft polymerization approach presents a means of introducing function groups and modifying the cellulose molecule through the creation of branches that impart to cellulose certain desirable properties, in addition to its favorable properties, such as ion-exchange and dye-adsorption capabilities.[12-15] The properties of the grafted copolymer will be determined by the nature of both cellulose and monomer or polymer grafted onto the cellulose backbone. The resistance of cellulose paper to acids, bases and

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chemicals, and to heat, light and microorganisms was greatly improved by grafting.[15] The mutual irradiation grafting is the most efficient method of grafting since the radicals can react as fast as they are produced. In our previous work, the kinetics of radiation-induced graft polymerization onto filter papers was studied in detail.[16]

In the present work, functional filter papers containing fibers with chemically bonded chelate groups are prepared by grafting of acrylonitrile onto filter papers and subsequent amidoximation of the reactive intermediate nitrile groups. The characteristics of the functional filter papers were studied by FT-IR, XRD, SEM and TGA. The functional filter papers were investigated in the chelation of rare earth elements from a hydrous oxide cake of Egyptian monazite, prior to scanning analysis by wavelength dispersive X-ray fluorescence *via* characteristic L X-ray lines.

EXPERIMENTAL

Synthesis of grafted filter papers with polyacrylonitrile

Radiation-induced grafting was carried out in a Pyrex tube containing Whatman filter paper (W1) and 45% acrylonitrile solution (in DMF), which was exposed to cobalt-60 γ-rays with a dose rate of 4 kGy/h under air atmosphere. A gamma chamber 4000A, India, was used for irradiation at the National Center for Radiation Research and Technology (NCRT), Cairo. The grafted filter papers were simply washed first with DMF and then with water several times to constant weight to remove the homopolymer occluded in the grafted filter paper. The grafted filter papers were then dried at 80 °C for 2 h and weighed. The degree of grafting (G%) was calculated by the following equation:[16-19]

$$G\% = \frac{W_1}{W_2} \times 100\% \qquad (1)$$

where W_1 is the weight of PAN grafts in the grafted filter paper, W_2 is the weight of filter paper in the grafted filter paper.

Synthesis of functional filter papers with amidoxime groups

The preparation of functional filter papers with amidoxime groups is based on the treatment of nitrile with hydroxylamine.[16,20,21] The preparation of the hydroxylamine (NH_2OH) solution was carried out by dissolving about 45 g of hydroxylamine hydrochloride ($NH_2OH.HCl$) in 300 ml methanolic solution (methanol:water 5:1). The HCl of NH_2OH was neutralized by a NaOH solution and the precipitate of NaCl was removed by filtration. The grafted filter paper was placed into a two-neck flask, which was equipped with a magnetic stirrer, a condenser and a thermostat water bath. Then, the above prepared hydroxylamine solution was added to the flask, and the reaction was carried out at 70 °C for 2 h. After completion of the reaction, the functional filter papers were separated from the solution and washed several times with distilled water to remove excess hydroxylamine, and then air dried.

Chelation of rare earth elements

The hydrous oxide cake of Egyptian monazite was obtained from the Nuclear Materials Authority, Egypt, by the alkaline dissolution of monazite mineral, as previously reported.[22,23] 1.0 g of hydrous oxide cake of Egyptian monazite was digested in 30 ml of 4 M HNO_3 and adjusted to a pH of 0.1. Uranium, thorium and lanthanides were chelated from the solution of uranium-thorium cake by functional filter paper using the batch procedure. Functional filter papers of 25 mm diameter were added to the digested monazite solution under magnetic stirring. After 2 hours, the functional filter paper-metal complexes were isolated, washed with distilled water and then dried. The qualitative analysis of the chelating filter paper-metal complex was performed by X-ray fluorescence (XRF).

Measurements

FTIR spectra were measured for the samples in the form of KBr disks, using a Perkin Elmer-1650 FTIR Spectrometer.

Thermogravimetric analysis (TGA) was performed on a TGA-50 (Shimadzu), with a scan rate of 10 ^{o}C/min in N_2 atmosphere.

X-ray diffraction of the samples was recorded within the angle range 2θ = 5-50^{o} on a Shimadzu XRD-610 diffractometer, using CuK_{α} radiation (1.5418°A). The data were collected at a scan speed of 8 deg/min and 1.0 s at each step. The operating voltage and current were 30 kV and 20 mA, respectively. To calculate the crystallinity index (CI) of cellulose from the XRD spectra, peak height methods were used.[24-28] CI was calculated from the height ratio between the intensity of the crystalline peak ($I_{002} - I_{am}$) and total intensity (I_{002}) after subtraction of the background signal:

$$CI\% = [(I_{002} - I_{am}) / I_{002}] \text{ x } 100 \qquad (2)$$

where I_{002} was the intensity of the 002 crystalline peak at 22° and I_{am} the height of the minimum (I_{am}) at 18^{o} between the 002 and the 101 peaks.

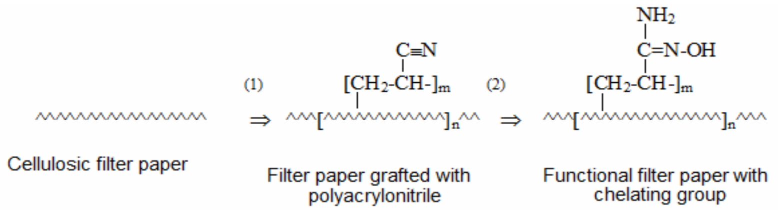
Scanning electron microscopy of the samples was performed on JEOL-SEM 5400. The polymer sample was mounted with adhesive on the specimen holder and then coated under vacuum with a thin layer of gold, scanned by an oscilloscope and monitored *via* a display before being recorded by the JOEL 5400-SEM.

X-ray fluorescence (XRF) analysis was performed with a Philips wavelength dispersive spectrometer (X' Unique II), equipped with flow and scintillation (fs) detectors. The X-ray tube equipped with a Sc-Mo target was operated at 60 kV and 30 mA.

RESULTS AND DISCUSSION

Synthesis of functional filter paper

The synthesis of chelating filter paper with chemically bonded amidoxime groups was carried out in two steps. The first step is the graft polymerization of acrylonitrile onto cellulosic filter paper by the mutual irradiation technique in heterogeneous medium. The mutual irradiation technique involves irradiating the filter papers in the monomer solution with γ-radiation, which results in radical formation on the cellulosic chain; the sites of radical formation become the points of initiation for the side chains. The variation of grafting with irradiation time in graft polymerization of the acrylonitrile solution onto the filter paper at a monomer concentration of 45 vol% (in DMF) and a constant dose rate of 4 kGy/h is shown in Figure 1. Grafting increases with the radiation dose in the range from 0 to 12 kGy and then tends to level off above 12 kGy, *i.e.* the amount of radicals formed by radiation increases linearly with the radiation dose and then reaches a certain limiting value at a higher dose. At higher irradiation doses, the grafting tends to level off due to the recombination of some of the free radicals without initiating graft polymerization. At higher levels of grafting, the reaction becomes a diffusion controlled process.[16] Grafting of acrylonitrile at a concentration of 45% gives considerable grafting yields at a radiation dose of 16 kGy. Above this concentration, the removal of the homopolymer becomes difficult. The kinetics of radiation-induced graft polymerization onto the filter papers was studied in our previous work.[16] The second step is the amidoximation of the grafted filter paper. The synthesis of the functional filter papers with amidoxime groups is based on the treatment of nitrile groups with hydroxylamine. The amidoxime group has both a hydroxyimino (=N–OH) group and an amino (-NH_2) group at the same carbon atom, which offers the fused features of amide, oxime, amidine and hydroxamic acid functionality.[29] The synthesis is shown in Scheme 1.



Scheme 1: Filter papers grafted with polyacrylonitrile (90% grafting ratio) and treated with hydroxylamine ethanol solution at 70 °C for 2 h

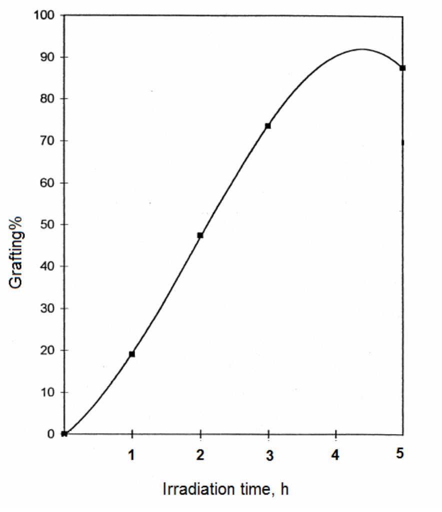


Figure 1: Grafting % *vs* radiation time, h, for grafting of acrylonitrile 45% monomer concentration onto Whatman filter paper (W1) at 4 kGy/h dose rate

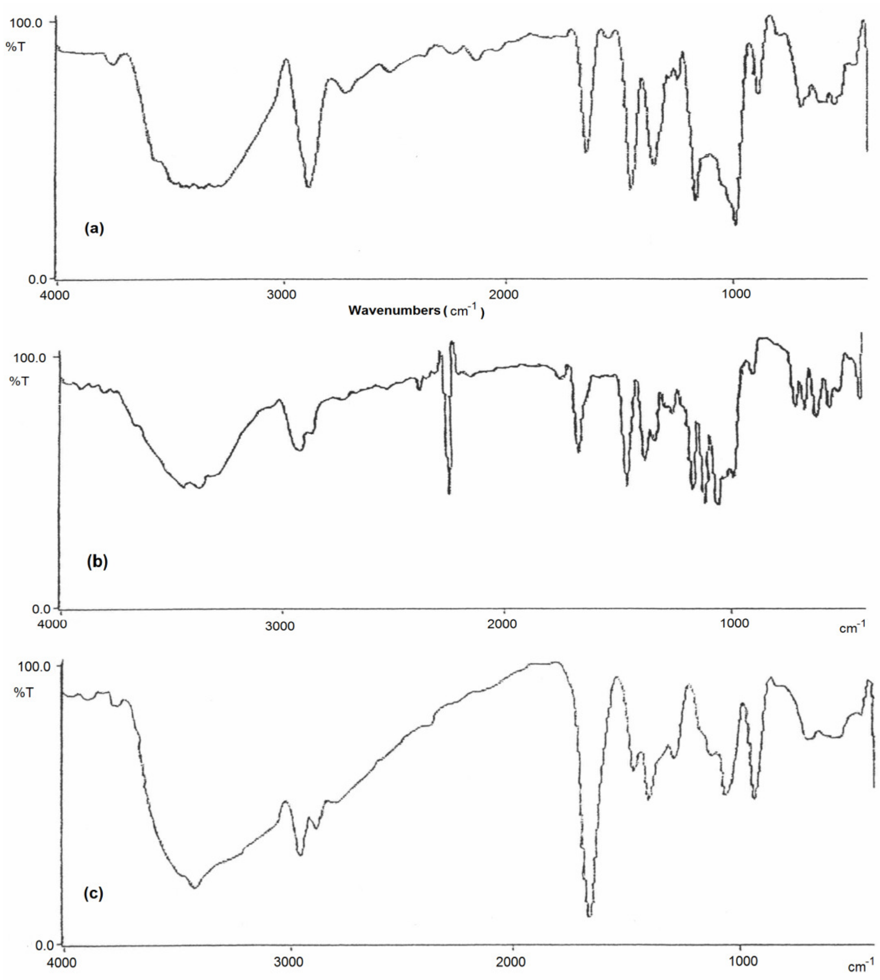


Figure 2: FTIR of (a) filter paper, (b) grafted filter paper and (c) functional filter paper

Figure 2 (a, b and c) shows the infrared spectra of the filter paper, grafted filter paper and functional filter paper, respectively. The grafting with acrylonitrile leads to a decrease of the hydroxyl band intensity around 3450 cm^{-1} and to the creation of a sharp band at 2248 cm^{-1} due to nitrile groups. It confirms that the grafting of polyacrylonitrile took place onto the filter paper. The decrease of the band intensity at 1650 cm^{-1} assigned to OH bending of absorbed water is explained by the hydrophilic nature of nitrile groups. The changes in the infrared spectrum resulting from the amidoximation process show that the band associated with the nitrile group at 2248 cm^{-1} disappears and is replaced by the bands of amidoxime in the region of 3000-3500 cm^{-1} (broad, N-H and O-H stretch vibration) and the strong band at 1650 cm^{-1} (C=N stretch vibration) overlapping with the band due to OH bending of absorbed water.

Characterization of functional filter paper

X-ray diffraction (XRD)

Chemical substitution reactions on the cellulose fibers change the crystallinity and the fiber orientation and destroy the fibrous structure, whereas the graft copolymerization presents a means of modifying the cellulose molecule through the creation of branches that impart certain desirable properties to cellulose, in addition to its favourable properties. Figure 3 (a, b and c) shows the XRD of filter paper, grafted filter paper and functional filter paper, respectively. The diffraction patterns of grafted and functionalized filter paper are similar to that of cellulose filter paper, which is characterized by two main peaks and a broad amorphous background band. Table 1 shows that the crystallinity index% (CI%) of filter paper, grafted filter paper and functional filter paper has been observed to be 94, 80 and 79, respectively. The intensity of the characteristic peak due to the crystalline structure of cellulose decreases. The grafting polymerization does not change basically the XRD pattern of cellulose, it dilutes the crystalline fraction of cellulose in the graft copolymer.[28] This indicates that the acrylonitrile is fitted in the same crystal lattice of cellulose fibers.

The crystallinity index% (CI%) of grafted filter paper (80%) and functional filter paper (79%) indicates that the introduction of the amidoxime groups into the grafted filter paper, by chemical reaction with alkaline solution of hydroxylamine, proceeded without a significant change in the original crystalline arrangement in cellulose nor in the orientation of fibers. The presence of polyacrylonitrile branches protected the cellulose backbone against damage during chemical treatment.

Scanning electron microscopy (SEM)

Figure 4 (a, b and c) shows the SEM of filter paper, grafted filter papers and functional filter paper, respectively. Graft copolymerization covered and thickened the fibers with rough layers of copolymer deposits. The entire fibers are also covered with copolymer as a result of penetration and diffusion of the monomer solution, and consequently, grafting occurred deeply through the fibers. The grafting reactions occur deep within the interior of the cellulose. The grafting starts at the surface of the film, then proceeds inwards by progressive diffusion of monomer through the grafted zones.[30,31] Polymer bridges were formed in some areas, leading to bonding individual fibers together. The fibrous structure and the fibers are not damaged by chemical treatment during the amidoximation reaction as a result of protection by the graft polyacrylonitrile. This is an advantage of graft copolymerization in comparison with substitution methods. It is known that the substitution of cellulose destroys some favorable properties of cellulose, such as porosity, fibrous structure and fiber orientation.

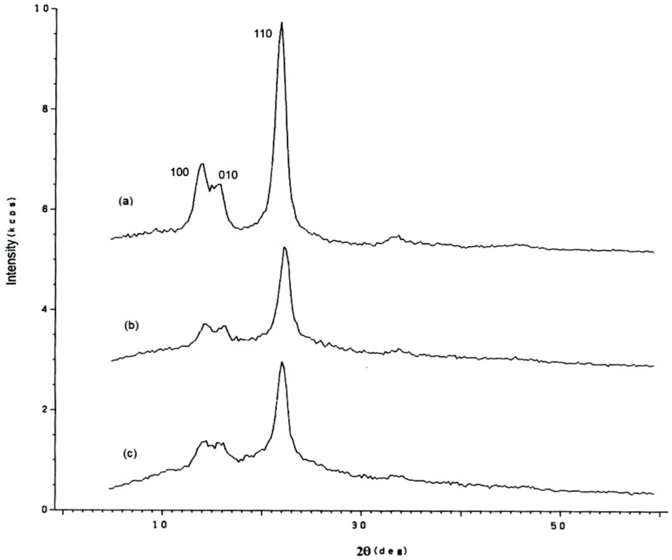


Figure 3: X-ray diffraction of (a) filter paper, (b) grafted filter paper and (c) functional filter paper

Table 1
Crystallinity index% (CI%) of filter paper, grafted filter paper and functional filter paper

Samples	I_{22}	I_{18}	CI%
Filter paper	4.25	0.25	94
Grafted filter paper	2.25	0.45	80
Functional filter paper	2.36	0.5	79

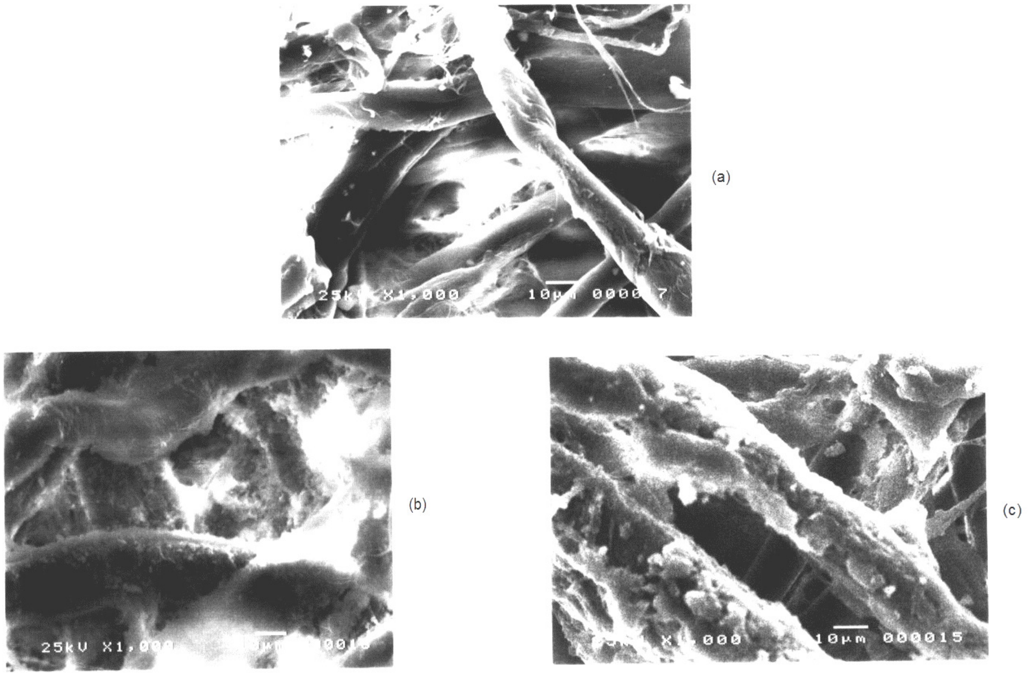


Figure 4: SEM of (a) filter paper, (b) grafted filter paper and (c) functional filter paper

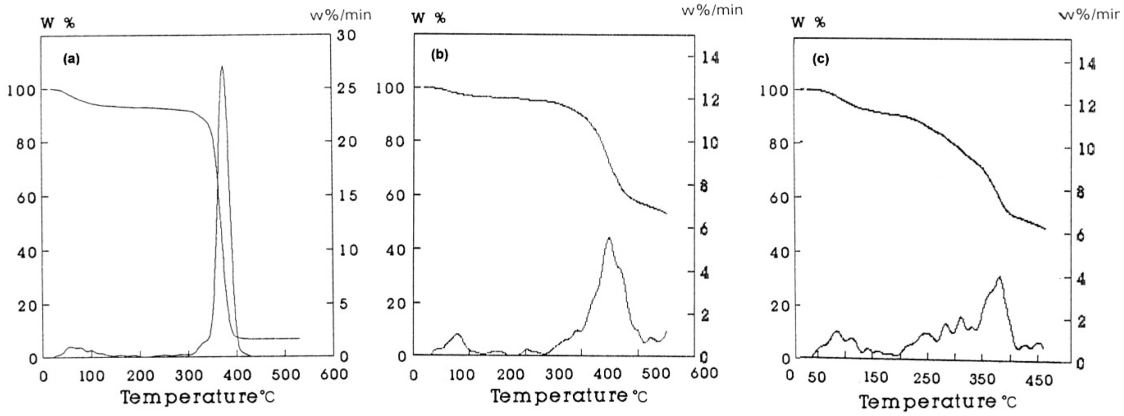
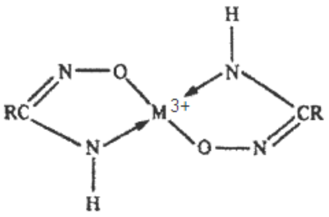


Figure 5: TGA of (a) filter paper, (b) grafted filter paper and (c) functional filter paper

Thermal analysis

The thermogravimetric analysis (TGA) of the filter paper, grafted filter paper and functional filter paper is shown in Figure 5 (a, b and c). The first step of weight loss indicates the hydrophilicity of the filter papers. The water content % of the original filter papers decreased with grafting from 6% to 2% because of the hydrophobicity of the polyacrylonitrile chain. Further treatment of the grafted filter paper with hydroxylamine increases the water content to 9% due to the conversion of the nitrile groups into the hydrophilic amidoxime groups.

In the second step, the decomposition of the filter paper starts at 325 °C and proceeds rapidly. The decomposition of grafted filter paper starts at 225 °C and proceeds gradually. Meanwhile, the decomposition of the functional filter paper starts at 200 °C and is distributed over a broader temperature range. TGA indicated the thermal stability of the functional filter paper at temperatures below 200 °C.



Scheme 2: A possible chelation mechanism for the complexation

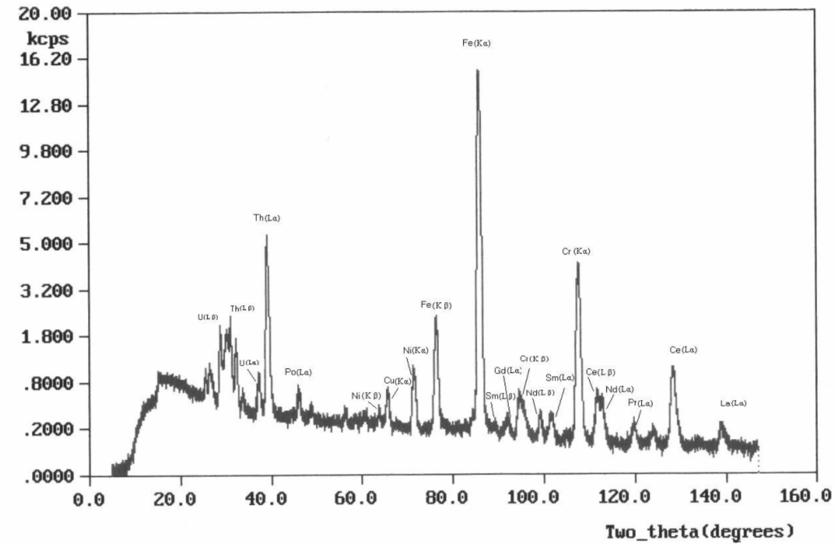


Figure 6: XRF of functional filter paper-REEs complexes

Chelation of rare earth elements for X-ray fluorescence analysis

Spectrophotometric analysis for the determination of uranium, thorium and other rare earth elements shows the difficulties incurred by Egyptian monazite because of the interference with transition elements. The application of functional filter paper with amidoxime groups for chelating the rare earth elements of Egyptian monazite and scanning by XRF were performed in this work.

Amidoxime groups have no affinity for the common metallic cations and do not form chelates with alkali and alkaline earth metal ions, but have a strong tendency to form a chelate complex with a wide range of transition and heavy metal ions in aqueous solution.[29,32-34] A possible chelation mechanism for the complexation is shown in Scheme 2.[32,34]

The low energy L X-ray lines are generally used, because the X-ray tube excitation system does not sufficiently excite the high-energy K X-rays of rare earth elements. The major limitation of using the L X-rays from the lanthanides in the energy-dispersive system is that they are strongly overlapped by the low-energy K X-rays from elements with low atomic numbers. This problem is partly overcome in the wavelength-dispersive system due to its high spectral resolution.[5]

Figure 6 shows the wavelength dispersive XRF of functional filter paper-REEs complexes. Rare earth elements were detected qualitatively at L X-ray lines: U (L_α and L_β), Th (L_α and L_β), Po (L_α), Sm (L_α and L_β), Gd (L_α), Nd (L_α and L_β), Ce (L_α and L_β), Pr (L_α) and La (L_α). Also, other heavy metals with low atomic numbers were detected at K X-ray lines: Ni (K_α and K_β), Cu (K_α and K_β), Fe (K_α and K_β), Cr (K_α and K_β).

The X-ray fluorescence spectra show that the characteristic L X-ray lines of rare earth elements are free of overlapping with any other X-ray emission, as shown in Figure 6. Therefore, functional filter paper-XRF can be used with confidence for evaluating the concentration of rare earth elements.

CONCLUSION

Functional filter papers containing chelating amidoxime groups were synthesized by radiation-induced graft polymerization of acrylonitrile monomer onto filter paper, followed by reaction with hydroxylamine. The presence of the functional groups was proven by FTIR spectra analysis. XRD and SEM showed that the grafting process maintained the orientation of the fibers and the crystallinity of cellulose. The thickness of the individual fibers increased and the fibrous structure was not damaged during chemical treatment due to the protective effect of the graft chain. The functional filter papers were applied in the chelation of rare earth elements from the Egyptian monazite mineral to be analyzed by wavelength dispersive X-ray fluorescence. X-ray fluorescence spectra showed that the characteristic L X-ray lines of rare earth elements are free of overlapping with any other X-ray emission.

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