SYNTHESIS OF COUMARIN DERIVATIVES: A GREEN PROCESS

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Keywords: coumarin, solvent free condition; heteropoly acids, bentonite

Coumarins are an important class of organic compounds having biological activities. In the present work coumarin derivatives have been synthesized under solvent free conditions from substituted phenols and ethyl acetoacetate in the presence of catalysts. A catalyst based on clay and heteropoly acid has been synthesized and found to be a potential catalyst for synthesis of coumarin derivatives.

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Introduction

Coumarins are an important class of compounds because a large number of natural product contains this heterocyclic nucleus. They have a wide variety of biological activities i.e. fluorescence sensors,[1] brightening agents,[2] anticoagulants,[3] insecticides[4] etc. coumarins can also be synthesized and the method should be simple, efficient and cheap because of diverse biological activities. There are many ways of synthesizing the coumarin such as knoevengel condensation [5], claisen rearrangement,[6] Perkin reaction,[7] pechmann reaction[8] etc. using a wide variety of reagents like H_2SO_4,[9] $HClO_4$,[10] P_2O_5,[11] ionic liquids[12] and solid acid[13,14] catalysts. Most of the reports are on the synthesis of coumarin derivatives having electron releasing groups and these methods also have the disadvantage of long reaction time and low yield.[15,16]

Using our methodology i.e. phosphotungstic acid (a heteropoly acid) intercalated bentonite coumarin derivatives having electron withdrawing groups can be synthesized with high efficiency and yield in a very short time.

Heteropoly acids are very well known solid acid catalysts. Heteropolyacids (HPAs), also known as polyoxometalates (POMs), are early-transition-metal oxygen anion clusters that exhibit very interesting properties depending on their molecular size, composition, and architecture.[17-19] They are stronger acids than conventional acid catalysts. Being stronger acids, heteropoly acids will have significantly higher catalytic activity than conventional catalysts such as mineral acids, mixed-oxides, zeolites, etc. Their excellent thermal stability[20] also makes HPAs good candidates for application in catalysts and sensors that may require extreme environments. In particular, in organic media, the molar catalytic activity of heteropoly acid is often 100–1000 times higher than that of H_2SO_4.[21-23]. This makes it possible to carry out the catalytic process at a lower catalyst concentration and/or at a lower temperature. Further, heteropoly acid catalysis lacks side reactions. Moreover solid acids offer many advantages by their nature, over soluble counterparts such as aluminium chloride and hydrogen fluoride. The substitution of liquid acids by solids as catalysts for organic synthesis offers a potential for superior effectiveness and environmental integrity. Although they differ in structure from liquid acids, solid acid catalysts work by the same principle. Clays have also been proposed as suitable catalysts for this purpose.[24-26] Today clays are important materials with a large variety of applications such as adsorbents, decoloration agents, ion exchangers, and catalysts.[27] The use of clays, as heterogeneous catalysts, offers many advantages over homogeneous acid catalysts such as ease of separation, mild reaction conditions, better selectivity of the desired product, and elimination of waste disposal problems. In a large number of organic reactions clays have been used as catalysts on laboratory/industrial scales. Properties of clays can be further improved by making pillared clays. Pillared clays are clays with high permanent porosity obtained by separating the clay sheets by a molecular prop or pillaring agent. These pillaring agents can be organic, organometallic, or inorganic complexes. Pillared clay (PILC) possesses several interesting properties, such as large surface area, high pore volume and tunable pore size (from micropore to mesopore), high thermal stability, strong surface acidity and catalytic active substrates/metal oxide pillars. These unique characteristics make PILC an attractive material in catalytic reactions. It can be made either as catalyst support or directly used as catalyst.[28-30]

In the present work we have synthesized the coumarin derivatives using phosphotungstic acid intercalated Bentonite via pechmann condensation of phenols with ethyl acetoacetate using microwave irradiation in excellent yield and high purity.

Experimental

Catalyst preparation

Na-Bentonite. 1.0 g of bentonite clay was added into a 250 ml conical flask containing 50 ml of 1.0 M NaCl this clay suspension was stirred for 16 hours. The residue after centrifugation was washed several times with double distilled water till complete removal of chloride ions. The residue thus obtained after above procedure was dried in an oven at 100°C to generate the Na form of the Bentonite (Na-Ben).

Table 1. Effect of the amount of catalyst on the reaction efficiency

S. No.	Catalyst, mg	Time, s.	Yield of 4-methyl-6-hydroxy coumarin with various catalysts, in %					
			Ben	Al-Ben_2	H^+-Ben	PAAC-Ben_2	PTA	PTA-Ben
1	20	60	33	46	50	55	56	72
2	30	60	40	52	57	62	64	80
3	40	60	50	62	67	72	74	90
4	50	60	58	70	74	78	80	99
5	60	60	58	70	74	78	80	99

Al-Pillared Bentonite (Al-Ben). In a 250 ml conical flask containing 1.0 g of Na-Ben, in 100 ml of double distilled water, 50 ml of the pillaring solution (keggin ion) was gradually added with vigorous stirring for 16 hours. The residue was washed several times with double distilled water till the complete removal of chloride ions was confirmed by $AgNO_3$ test. The residue, thus obtained was dried in an oven at 100°C is referred to as Al-Pillared Bentonite (Al-Ben).[31]

Acid activated Bentonite (H^+-Ben). 5.0 g of Na-Ben was added into a 100 ml beaker containing 50 ml of 3N H_2SO_4, this mixture was exposed to microwave radiation for 30 minutes. The residue was washed several times with double distilled water till the complete removal of SO_4^{2-} ions was confirmed by $BaCl_2$ test. The residue thus obtained was dried in an oven at 100°C to generate the Acid activated Bentonite (H^+-Ben).[32]

Pillared Acid activated Bentonite (PAA-Ben). 1.0 g of H^+ Ben, was added into a 250 ml conical flask containing 100 ml of double distilled water. 50ml of pillaring solution was gradually added with vigorous stirring for 16 hours. The residue was washed several times with double distilled water till the complete removal of chloride ions was confirmed by $AgNO_3$ test. The residue thus obtained was dried in an oven at 100°C and is referred to as Pillared Acid Activated Bentonite (PAA-Ben).

Phosphotungstic intercalated Bentonite (PTA –Ben). In a round bottom flask (250 ml), bentonite (1g) was suspended in double distilled water (50 ml).To this, aqueous solution of 15 mmol % of phosphomolybdic acid (PTA) was added drop wise and then stirred for 16 hrs. After this, the mixture was filtered and washed with double distilled water to remove the excess of Phosphomolybdic acid. Dried the product at 100 ^{0}C.

General procedure for the synthesis of coumarin derivatives

To elucidate the catalytic efficiency of PTA-Ben as catalyst, a controlled reaction was carried out using PTA, bentonite, Al-Ben and PTA-Ben as catalyst with Benzene-1,4-diol as reactant. The best results were obtained with PTA-Ben in microwave. (Table 1).

Under microwave condition: phenols derivatives (10mmol) and ethyl acetoacetate (10 mmol) were mixed with the PTA-Ben (50 mg) (Table 3). The mixture was irradiated in the microwave. After irradiation of the mixture for a specified period, the content was cooled to room temperature. The completion of the reaction was checked by TLC. After the completion of the reaction the catalyst was recovered by filtration and washed with absolute ethanol to remove all the organic impurities. The PTA-Ben was reused for evaluating the performance in the next reaction. The extract was evaporated by rota-vapour under reduced pressure and the product was purified from column chromatography with $CHCl_3$: MeOH with increasing polarity.

Optimization of the Catalysts amount

Reactions have been performed using different amount of various catalysts under uniform conditions. Results of the investigation are presented in the Table 1.

Optimization of Time

The reaction time has been optimized by performing reactions at regular intervals of time. After a certain time period there is not much increase in the yield. That time has been selected as optimum time. Results of the investigation are presented in the Table 2.

Table 2. Optimization of reaction time

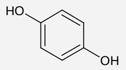
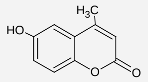
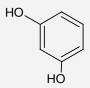
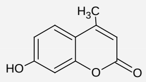
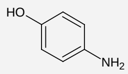
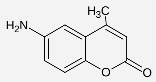
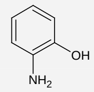
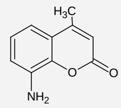
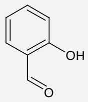
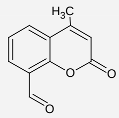
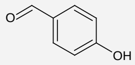
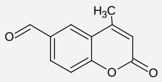
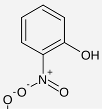
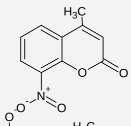
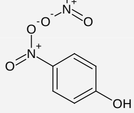
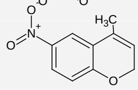
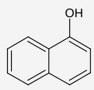
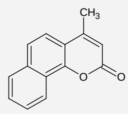
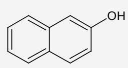
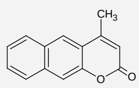
S.No.	Time, s	Yield, %
01	15	65
02	30	80
03	45	90
04	60	99
05	75	99
06	90	99

Results and discussion

Catalyst characterization

X-Ray Diffraction techniques. The XRD pattern of Ben,[33] Na-Ben and H^+-Ben show a sharp peak at 2θ = 5.93, 6.83 and 9.67 respectively corresponding to a d-value of 14.9 Å, 12.9 Å and 9.1 Å. A decrease in the *d*-value of 2 Å and 5.8 Å is observed when interlayer cations (Ca^{2+}) are replaced by the smaller ions, Na^+ and H^+ respectively. PAA-Ben, shows a further shift in the peak position, 2θ =5.30 and a *d*-value of 16.6 Å corresponding to an increase in the interlayer region by 7.5 Å w.r.t H^+-Ben confirms the intercalation of Al Keggin ion into the interlayer region of H^+-Ben.

Table 3. Efficiency of the catalyst (PTA-Ben) for different reactants

S. No.	Reactant	Product	Time, Sec.	Yield, %	Remarks
01			60	99	Single product
02			90	98	Single product
03			120	95	Single product
04			120	92	Single product
05			300	83	Single product
06			300	87	Single product
07			360	76	Single product
08			360	80	Single product
09			420	72	Single product
10			420	75	Single product

The Al-Ben shows a peak at 2θ = 5.20 and a *d*-value of 16.9 Å corresponding to an increase in the d-value of 4 Å w.r.t Na-Ben thus confirming the intercalation of Al Keggin ion in the interlayer region of Na-Ben. PTA-Ben show a peak at 2θ = 5.42 corresponding to a d-value of 16.3 Å respectively. This increase in the *d*-value 3.4 Å w.r.t Na-Ben confirms the intercalation of PTA in the interlayer region of Na-Ben.

Total Surface Area Measurement. Total surface area studies have been performed by EGME method. Surface area values of Ben, Na-Ben, H^+-Ben, Al-Ben, PAAC- Ben and PTA-Ben are represented in the (Table 4). Total surface area of Ben has been found to be 215 m^2 g^{-1}. After conversion to Na-Ben total surface area has been found to be 121 m^2/g which may be due to the decrease in d-spacing as indicated by XRD data. Total surface area of H^+- Ben has been found to be 327 m^2 g^{-1} which is due to replacement of Na ions by H^+ ions. Acid activation also causes the formation of small pores, consequently increasing the surface area.[34,35] Total surface area of Al-Ben has been found to be 295 m^2/g. Due to the intercalation of Al-Keggin ion the inner surface also becomes assessable. PAAC-Ben has been found to have a total surface area of 350 m^2/g which is again due to intercalation of Al-Keggin ion in H^+-Ben. Total surface area of PTA-Ben has been found to be 301 m^2/ g respectively which confirms intercalation of PTA

FT-IR Studies. Vibrational spectra of Ben, Na-Ben, H^+-Ben, Al-Ben and PAA-Ben clays (Figure 1 and 2) indicate two strong absorption bands ~3626 cm^{-1} and ~3436 cm^{-1} corresponding to the stretching vibrations of the O-H group originating from the surface adsorbed and interlayer water. The ~1642 cm^{-1} band in these samples has been assigned to the H–O–H bending vibrations of water.

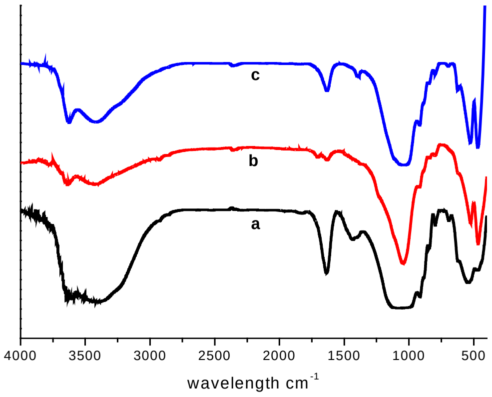


Figure 1. FTIR spectra of (a) Ben, (b) Na-Ben, (c) H^+-Ben

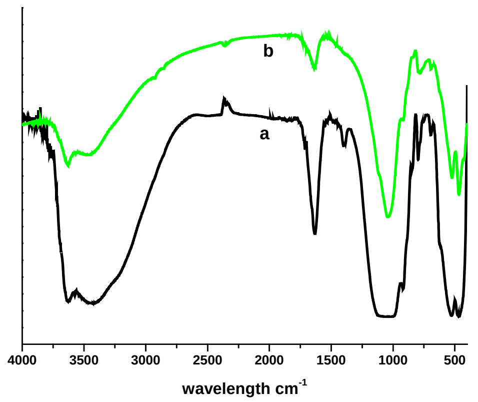


Figure 2. FTIR spectra of (a) Al-Ben, (b) PAA-Ben

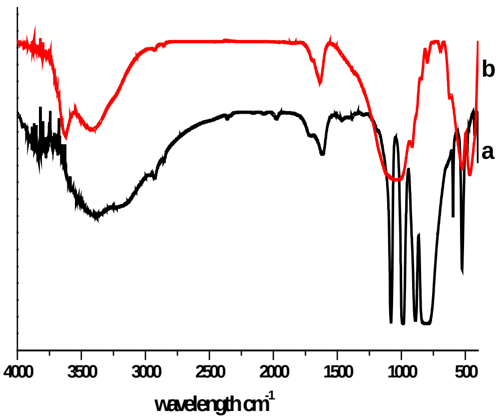


Figure 3. FTIR spectra of (a) PTA, (b) PTA-Ben

The ~1043 cm^{-1} and ~796 cm^{-1} bands are attributed to the stretching vibration of the Si-O bond. The ~522 cm^{-1} and ~466 cm^{-1} bands have been assigned to the Si–O–Al and Si–O–Si deformation vibrations respectively[36,37].The FT-IR spectra of PTA (Figure 3) shows an absorption band at ~3154 cm^{-1} and have been assigned to the stretching vibrations originating from the O-H groups present in the Keggin structure of PTA. The absorption band at ~1699 cm^{-1} have been assigned to the bending vibrations of the O-H group of PTA.

Thermal Method of Analysis. The thermogram (TGA) of Ben, Na-Ben, H^+-Ben (Figure 4) shows four step weight loss pattern. The first step, up to 180^{0}C, corresponds to dehydration of surface adsorbed water. The second step, 180 $^\circ$C to 550 °C, is attributed to dehydration of interlayer water. The third step 550 $^\circ$C to 675 $^\circ$C, is attributed to the gradual dehydroxylation of clay layers. Beyond 675 $^\circ$C the clay loses its structure and practically shows no weight loss.[36]

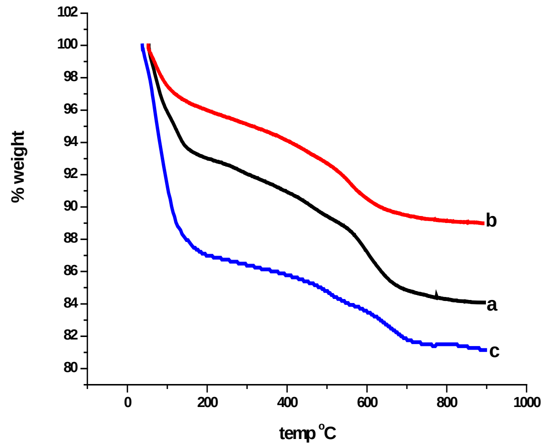


Figure 4. TGA studies of (a) Ben, (b) Na-Ben, (c) H^+-Ben

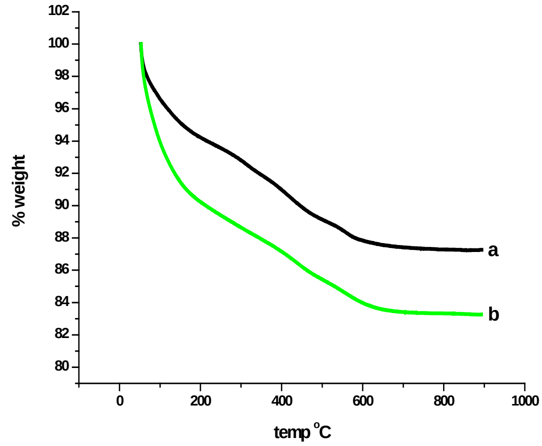


Figure 5. TGA studies of (a) Al-Ben, (b) PAA-Ben

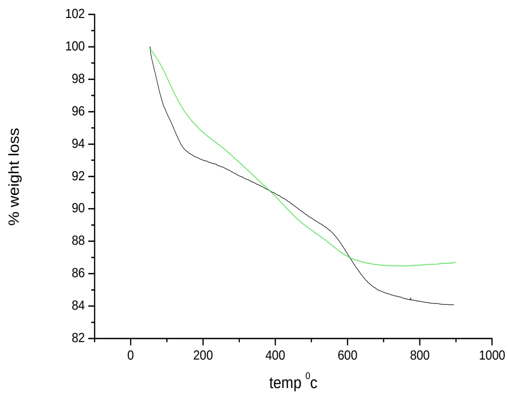


Figure 6. TG-MS curves of (a) PTA, (b) PTA-Ben

The thermogram (TGA) of PAA-Ben, Al-Ben (Figure 5) shows a similar four step weight loss pattern. The first step, up to 200^{0}C, corresponds to dehydration of surface adsorbed water. The second step, 200^{0}C to 350^{0}C, is attributed to dehydration of interlayer water. The third step, 350^{0}C to 600^{0}C, is attributed to the gradual dehydroxylation of clay layers. Beyond 600^{0}C the clay loses its structure and practically shows no weight loss.[36]

The TGA of pure PTA (Figure 6) shows two step weight loss. The first step, up to 200^{0}C corresponds to the loss of water of crystallization. The second step, ~200^{0}C to 600^{0}C corresponding to the decomposition of keggin unit of PTA.

The TGA of PTA-Ben (Figure 6) shows four step weight loss pattern, the first step, up to 150^{0}C, corresponds to dehydration of surface water. The second step, 150^{0}C to 500^{0}C, is attributed to dehydration of interlayer water. The third step, 500^{0}C to 700^{0}C, is attributed to the dehydroxylation of clay layers and the loss of keggin ion structure. The heteropoly acids are stable up to 600^{0}C but after intercalation the catalyst becomes stable up to 800^{0}C.

SEM Studies with EDX analysis. The SEM pictures (magnification of 832X) of Ben, PTA-Ben are represented in Figure 7 a and b respectively. The SEM pictures of Ben and PTA-Ben show no distinct change in the surface morphology and appears to have the layered structure. Therefore, it appears that PTA is not adsorbed on the surface of the clay but is intercalated in the layers of the clay. This fact is also supported by the XRD and IR studies.

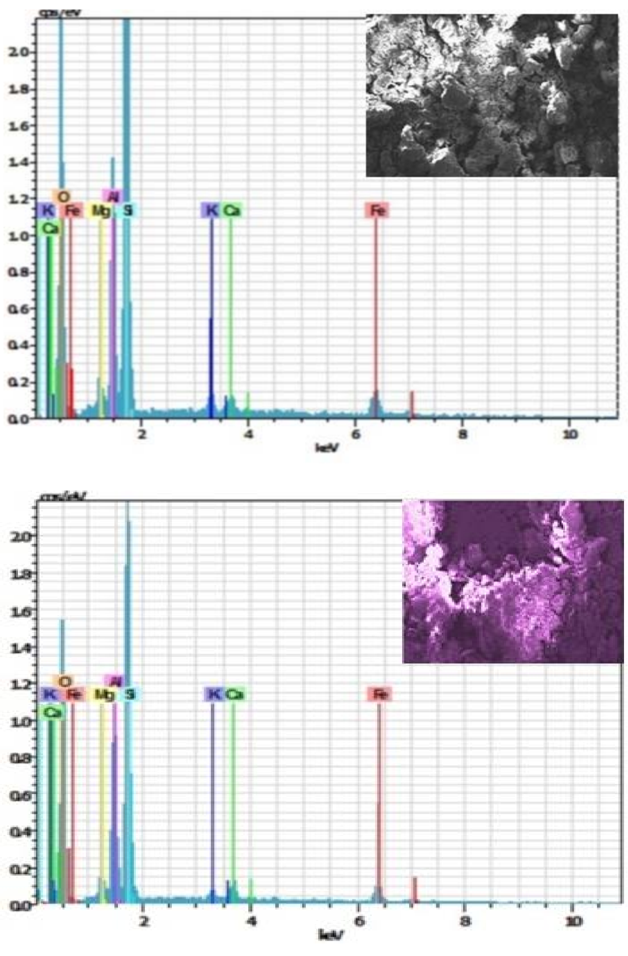


Figure 7. SEM-EDX of (a) Ben, (b) PTA-Ben

The SEM results are also supported by the EDX analysis (Figure 7a and 7b). In all the cases surface composition consist of Al, Si, O, Mg, Fe, Ca & K. No signal corresponding to P and W was supported by the EDX data which further confirms intercalation of PTA in to the layers of Bentonite.

Reusability of PTA-Ben for the Synthesis of 6-OH-4-Me-coumarin

The reusability of PTA-Ben has been investigated up to six repeated cycles using synthesis of 6-OH-4-Me-Coumarin. The catalyst, PTA-Ben, was washed with MeOH after every cycle and was characterized using FT-IR, TGA, DSC, XRD, SEM and EDX etc. techniques. No noticeable changes were observed even after six cycles, which not only indicates the stability of the catalyst but also indicates that none of the reactants/products remain with the catalyst. The product/s, after separation and isolation, was characterized by the earlier described methods and the yield in each case was calculated (Figure 8). The variation in the yield was found to be in the range of ~ 99% to 75%.

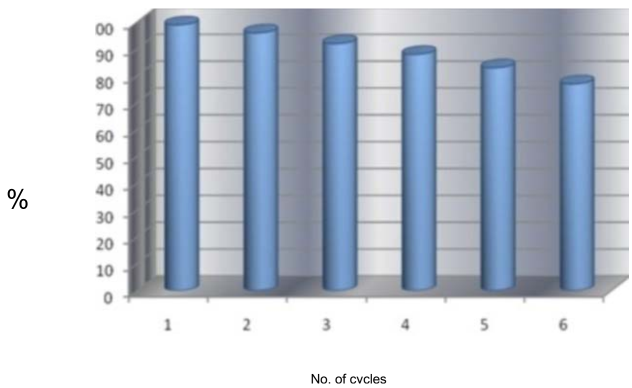


Figure 8. Reusability of PTA-Ben up to 6 repeated cycles

The catalyst characterization was performed on the catalyst after the 6th cycle of reaction was performed on the catalyst and following observations was made. The SEM picture (Figure 9) does not show any change in the surface morphology, the layered structure is maintained. The EDX data indicates the same elemental composition as earlier, i.e. Al, Si, O, Mg, Fe, Ca, K and Na.

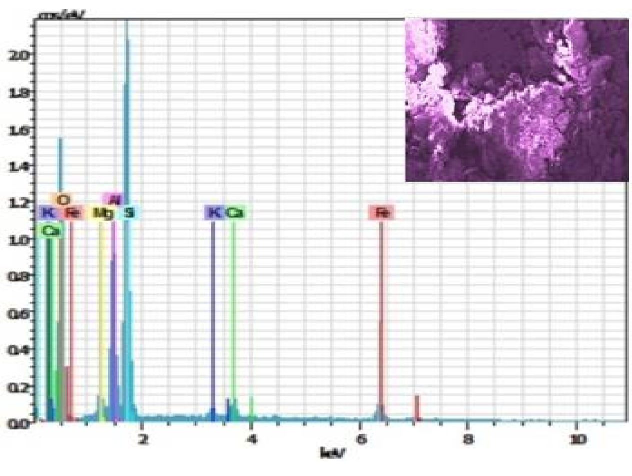


Figure 9. SEM and EDX of PTA-Ben after 6th cycle

The thermal stability of the catalyst was found to be unaffected after reuse except a slight change in the weight loss (from 11.7 % to 14%) which may be due to the presence of small quantity of adsorbed organic matter after the 6th cycle (Figure 10).

XRD and FTIR data (Figure 11) of PTA-Ben has been found to have no significant change.

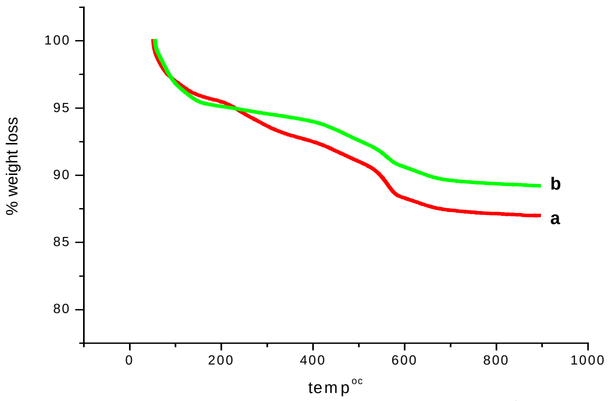


Figure 10. TGA studies of (a) PTA-Ben after 1st cycle, (c) PTA-Ben after 6th cycle

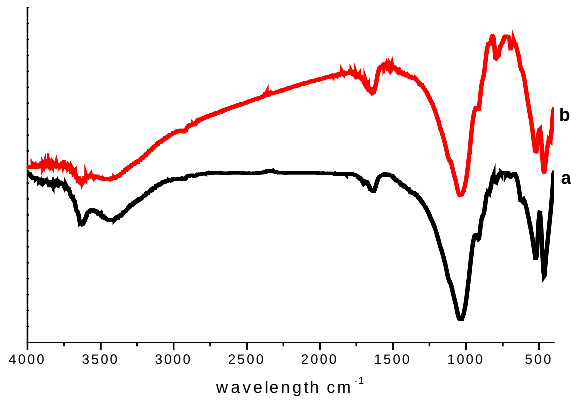


Figure 11. FTIR spectra of (a) PTA-Ben after 1st cycle, (c) PTA-Ben after 6th cycle

Characterization of coumarine derivatives

Structural assignments of the various coumarin derivatives are based on their ^{1}H NMR and IR analysis. The analysis of complete spectral and compositional data revealed the formation of coumarin derivatives.

6-Hydroxy-4-methylcoumarin. IR (υ in cm^{-1}) 3258 (OH strech), 1516, 1473 (aromatic ring), 1689 (C=O), 1209, 1096 (C-O); ^{1}H NMR δ 9.4 (s, 1H, OH), 7.5 (d, 1H, $H_{8\ Aromatic}$), 6.8 (d, 1H, $H_{7\ Aromatic}$), 6.2 (s, 1H, $H_{5\ Aromatic}$), 3.0 (s, 1H, $H_{3\ Aromatic}$), 2.2 (s, 3H, CH_3).

7-Hydroxy-4-methylcoumarin. IR (υ in cm^{-1}) 3502 (OH strech), 1504, 1455 (aromatic ring), 1671 (C=O), 1277, 1074 (C-O); ^{1}H NMR δ 10.5 (s, 1H, OH), 7.5 (s, 1H, $H_{8\ Aromatic}$), 6.8 (d, 1H, $H_{6\ Aromatic}$), 6.6 (d, 1H, $H_{5\ Aromatic}$), 3.4 (s, 1H, $H_{3\ Aromatic}$), 2.3 (s, 3H, CH_3).

6-Amino-4-methylcoumarin. IR (υ in cm^{-1}) 3376, 3234 (NH strech), 1610, 1512, 1493 (aromatic ring), 1636 (C=O), 1286, 1170 (C-O); ^{1}H NMR δ 10.1 (s, 2H, NH), 8.3 (d, 1H, $H_{8\ Aromatic}$), 8.1 (d, 1H, $H_{7\ Aromatic}$), 7.2 (s, 1H, $H_{5\ Aromatic}$), 3.4 (s, 1H, $H_{3\ Aromatic}$), 2.3 (s, 3H, CH_3).

8-Amino-4-methylcoumarin. IR (υ in cm^{-1}) 3467, 3248 (NH strech), 1519, 1578, 1457 (aromatic ring), 1644 (C=O), 1248, 1155 (C-O); ^{1}H NMR δ 10.1 (s, 2H, NH), 7.5 (s, 1H, $H_{8\ Aromatic}$), 6.8 (d, 1H, $H_{6\ Aromatic}$), 6.6 (d, 1H, $H_{5\ Aromatic}$), 3.4 (s, 1H, $H_{3\ Aromatic}$), 2.3 (s, 3H, CH_3).

6-Formyl-4-methyl coumarin. IR (υ in cm^{-1}) 1598, 1574, 1411 (aromatic ring), 1773,1607 (C=O), 1281, 1263 (C-O); ^{1}H NMR δ 10.1 (s, 1H, CHO), 8.3 (d, 1H, $H_{8\ Aromatic}$), 6.9 (d, 1H, $H_{7\ Aromatic}$), 6.7 (s, 1H, $H_{5\ Aromatic}$), 4.5 (s, 1H, $H_{3\ Aromatic}$), 1.9 (s, 3H, CH_3).

8-Formyl-4-methylcoumarin. IR (υ in cm^{-1}) 1606, 1558, 1474 (aromatic ring), 1716, 1610 (C=O), 1211, 1091 (C-O); ^{1}H NMR δ 10.0 (s, 1H, CHO), 7.8 (d, 1H, $H_{7\ Aromatic}$), 6.9 (d of d, 1H, $H_{6\ Aromatic}$), 6.7 (d, 1H, $H_{5\ Aromatic}$), 6.1 (s, 1H, $H_{3\ Aromatic}$), 2.8 (s, 3H, CH_3).

6-Nitro-4-methylcoumarin. IR (υ in cm^{-1}) 1500 1496 (aromatic ring), 1613 (C=O), 1592,1335 (NO_2), 1294,1199 (C-O); ^{1}H NMR δ 8.1 (d, 1H, $H_{7\ Aromatic}$), 7.2 (s, 1H, $H_{5\ Aromatic}$), 6.9 (d, 1H, $H_{8\ Aromatic}$), 6.4 (s, 1H, $H_{3\ Aromatic}$), 1.9 (s, 3H, CH_3).

8-Nitro-4-methylcoumarin. IR (υ in cm^{-1}) 1510, 1450 (aromatic ring), 1600 (C=O), 1591,1335 (NO_2), 1295, 1195 (C-O); ^{1}H NMR δ 7.8 (d, 1H, $H_{7\ Aromatic}$), 7.1 (d of d, 1H, $H_{6\ Aromatic}$), 6.9 (d, 1H, $H_{5\ Aromatic}$), 3.3 (s, 1H, $H_{3\ Aromatic}$), 2.5 (s, 3H, CH_3).

7,8-Benzo-4-methylcoumarin. IR (υ in cm^{-1}) 1593, 1576, 1474 (aromatic ring), 1632 (C=O), 1278, 1084 (C-O); ^{1}H NMR δ 8.5 (d, 1H, $H_{Aromatic}$), 7.8 (d, 1H, $H_{Aromatic}$), 7.5-7.6 (m, 2H, $H_{Aromatic}$), 7.4 (d, 1H, $H_{aromatic}$), 6.9 (d, 1H, $H_{aromatic}$), 6.4 (s, 1H, $H_{3\ Aromatic}$), 2.5 (s, 3H, CH_3).

6,7-Benzo-4-methylcoumarin. IR (υ in cm^{-1}) 1601,1512, 1466 (aromatic ring), 1631 (C=O), 1277, 1216 (C-O); ^{1}H NMR δ 7.7 (s, 2H, $H_{Aromatic}$), 7.6 (d, 1H, $H_{Aromatic}$), 7.2-7.4 (m, 2H, $H_{Aromatic}$), 7.1 (d, 1H, $H_{aromatic}$), 5.2 (s, 1H, $H_{3aromatic}$), 1.7 (s, 3H, CH_3).

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Received: 17. 09. 2013.
Accepted: 19. 11. 2013.