Ɛ-Caprolactone and Tetrahydrofuran Copolymerization with a Green Acid Activated Montmorillonite Catalyst: Reaction Optimization with the Taguchi Method

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ABSTRACT: *In this study, poly (ε-Caprolactone-co-Tetrahydrofuran) copolymer was synthesized using a green solid acid catalyst prepared with Montmorillonite clay (MMT). The prepared nanocatalyst was characterized by X-Ray Diffraction (XRD) analysis. The synthesized copolymer was investigated with Fourier Transform InfraRed (FT-IR), Hydrogen Nuclear Magnetic Resonance (HNMR), Gel permeation Chromatography (GPC), and Differential Scanning Calorimetry (DSC) analysis. T_g of the synthesized copolymer was found to be 28.91 °C. The highest average molecular weight (M_n) was calculated at about 2366 at 65 °C and 24 h of reaction time. The PDI data extracted showed a narrow PolyDispersity Index (PDI) of the synthesized copolymers. The reaction conditions were optimized with the Taguchi method and Design of Experiments (DOE). 10%wt of nanocatalyst amount, 65 °C of reaction temperature, 24 h of reaction time, and Toluene as solvent were found to be optimum levels for the reaction. Up to 64% of the yield was obtained for copolymerization. Different factor interactions were studied with ANOVA interaction plots. Taguchi analysis results were in agreement with GPC results. The prepared nanocatalyst was recovered and its reusability for three cycles was approved.*

KEYWORDS: *Copolymer, Montmorillonite, Nanocatalyst, Cationic Ring Opening Polymerization, Taguchi.*

INTRODUCTION

Biodegradable and biocompatible polymers are highly considerable materials due to their wide application in different fields such as the drug industry. The non-toxicity and convenient permeability against drugs are some of the desired properties in this manner [1]. Polycaprolactone (PCL) is one of the biocompatible polymers that is greatly used for biomedical purposes due to its unique properties [2].

However, some drawbacks such as inappropriate mechanical or thermal properties of PCL have led researchers to investigate the copolymerization of Caprolactone with various monomers like tetrahydrofuran (THF) [3], lactide [4], glycolide [5], and polyethylene glycol (PEG) [6] to enhance its specification for further applications. One of the methods extensively used for Caprolactone polymerization is using

of cationic initiators, however, one of the most important disadvantages of such initiators limiting its application is their high cost. Furthermore, such initiators' toxicity and the possibility of poisoning the product restricting its usage in medical applications, and releasing heavy metals in the environment causing health problems to the users are the other known problems of these initiators. Moreover, workup and removing the catalyst from the reaction environment and the required low or very high temperatures or increased pressures are among the hindering factors of these catalysts [7].

Green synthesis trying not to use high-cost catalysts [8] and heterogeneous catalysis are still highly used in different reactions because of provide mild reaction conditions, environmentally friendly usage, and easy workup [9]. Different materials such as Zeolites [10], metal oxides [11-14], Metal-Organic Frameworks (MOFs) [15], graphene oxide [16], and clay [17] are used as heterogeneous catalysts in various reactions. Nanoclays are extensively used in some of the reactions because of their unique properties. Montmorillonite (MMT) as a natural clay is one of the most used clays for catalysis [18]. The acid-activated MMT is a great alternative to be used as a non-corrosive and environmentally friendly catalyst with an easy recovery possibility from the reaction after its completion. In this respect, a simple filtration of the catalyst would be enough to separate it from the product and retrieve it for further usage. In addition, requires mild reaction conditions using MMT, as the catalyst is the other advantage of this catalyst. The acid-activated MMT can impose the required acidic environment for cationic polymerization.

Ring-Opening Polymerization (ROP) is one of the methods used for the polymerization of cyclic monomers by different radical [19], anionic [20], and cationic [21] polymerization mechanisms. Cationic Ring Opening Polymerization (CROP) is one of these methods that a cationic catalyst is needed for reaction completion. In this respect, acid-activated MMT, or in other words, proton-exchanged MMT is an appropriate option to be used as a solid acid nanocatalyst for CROP.

In this study, a sulfuric acid-activated MMT was prepared and used as a solid acid catalyst for the copolymerization of ε-Caprolactone and THF through ring-opening polymerization. The prepared nanocatalyst was investigated by XRD. The copolymer was successfully synthesized and its triumphant preparation was affirmed by FT-IR, HNMR, DSC, and GPC techniques.

The reaction conditions such as temperature, reaction time, and catalyst amount were studied by conversion efficiency calculation by the Taguchi Design of Experiments (DOE) method. The prepared catalyst recoverability was examined and its multiple usage ability was confirmed. Taguchi is a statistical method developed by Genichi Taguchi as one of the most effective methods for experiment design and data analysis. This method can be used for product quality enhancement [22].

EXPERIMENTAL SECTION
Materials
ε-Caprolactone (99%) was purchased from Sigma Aldrich and used with no further purification. Tetrahydrofuran and Toluene were obtained from Merck and both were dried using Sodium pieces under distillation. Montmorillonite clay needed for catalyst preparation was bought from Sigma Aldrich.

Characterization
The characteristic functional groups of the monomers and the prepared copolymer were studied with Fourier Transform InfraRed (FT-IR) analysis (AVATAR, Thermo). The prepared solid acid Montmorillonite clay nanocatalyst was characterized using X-ray diffraction (XRD), (Philips, PW1730). The confirmation of copolymer synthesis was accomplished via HNMR analysis. The thermal properties and the glass transition temperature (T_g) of the copolymer as one of the important specifications f or a polymer was investigated by the Differential Scanning Calorimetry (DSC) technique (DSC Q100 V9.0 Build 275). The molecular weight of the copolymer samples synthesized in various conditions was achieved through Gel Permeation Chromatography (GPC) (WATERS). The reaction efficiency was determined gravimetrically by weighting the monomers used and the final product as follows:

$$\%R = \frac{P}{M} \times 100 \tag{1}$$

Where R is the efficiency, P is the final product weight and M is the total weight of the initial monomers.

Nanocatalyst preparation
Acid-activated Montmorillonite (AA-MMT) clay used as a solid acid catalyst in this study was prepared as follows: A required amount of clay was crushed using a grinder for 30 min. Then the crushed clay was poured

Table 1: Copolymerization conditions

Entry	Catalyst amount (%wt)	Time (h)	Temp. (°C)	Solvent type
1	1	6	25	Toluene
2	1	12	45	Toluene
3	1	18	65	Chloroform
4	1	24	85	Chloroform
5	5	6	25	Chloroform
6	5	12	45	Chloroform
7	5	18	65	Toluene
8	5	24	85	Toluene
9	7	6	25	Toluene
10	7	12	45	Toluene
11	7	18	65	Chloroform
12	7	24	85	Chloroform
13	10	6	25	Chloroform
14	10	12	45	Chloroform
15	10	18	65	Toluene
16	10	24	85	Toluene

into a distilled water-filled beaker and kept under stirring for a while and then a 0.3 M sulfuric acid was added to the mixture. The stirring was continued for 48 h to obtain a saturated clay with acid. The activated clay was filtered and rinsed with distilled water several times and dried at 90 °C for 24 h. The prepared catalyst was kept in a dry place and dried in an oven before every use.

Design of Experiments (DOE) with the Taguchi method

The Design of Experiments (DOE) method using Taguchi was used to determine the reaction conditions and optimization of the reaction. For this purpose, a mixed 2-4 level design via L16 array was used to complete the design. Four factors (Nanocatalyst amount, Temperature, Reaction time, and type of solvent) were chosen for this study. The levels defined for each factor and the complete DOE are tabulated in Table 1. For all factors except the solvent type, four different factors are given. For the solvent type, 2 types of solvent (Toluene and Chloroform) are defined. The yield for reaction optimization was obtained by bigger is better S/N ratio amounts and the diagrams were depicted according to this fact by Minitab 11 software.

Copolymer synthesis

CROP method was used for the preparation of the desired poly (ε-Caprolactone-co-Tetrahydrofuran) copolymer.

In this respect, equal amounts of 0.1M Caprolactone and THF solutions were mixed and stirred. Different amounts of the AA-MMT were added to the stirring solution to study the catalyst amount effect on the reaction according to Taguchi's Design of Experiment (DOE). In addition, the temperature, the reaction time, and the solvent type as well, were adjusted according to the DOE. The mixture was kept under reaction conditions to be completed. After completion of the reaction, the AA-MMT was removed from the reaction by a simple filtration process. The final product was obtained by removing the solvent and not reacting monomers by evaporating. The filtered catalyst was collected for recovering process and further use. Reaction efficiency was determined by Eq. (1).

Catalyst regeneration

The prepared catalyst was regenerated to study its recoverability and multiple usage possibilities. For this purpose, the used catalyst in the reaction was filtered out after its completion. The filtered catalyst was washed several times with Toluene followed by filtration. Then, the catalyst was washed and rinsed with distilled water several times and was kept in an oven at 90 °C to make it dry. The dried MMT was processed again according to the nanocatalyst preparation mentioned in this study to obtain a recovered catalyst. The regenerated nanocatalyst was tested for 3 cycles to investigate its reusability.

RESULTS AND DISCUSSION
Copolymer FT-IR analysis

The functional groups of the synthesized copolymer were investigated with FT-IR and the spectrum is shown in Fig. 1. The sharp peak that appeared at 1731 cm^{-1} is associated with the ester carbonyl group of Polycaprolactone while 1169 cm^{-1} is related to the C-O bond of the ester function. The peak at 1094 cm^{-1} appeared due to the ether C-O bond of the polytetrahydrofuran confirming the successful synthesis of the copolymer. The methylene groups C-H bonds asymmetrical and symmetrical are observed at 2940 and 2867 cm^{-1} respectively.

Nanocatalyst characterization with XRD

The prepared solid acid montmorillonite nanocatalyst was characterized via the XRD technique. The pristine MMT and sulfuric acid-activated MMT both were analyzed and the resulting patterns are shown in Fig. 2.
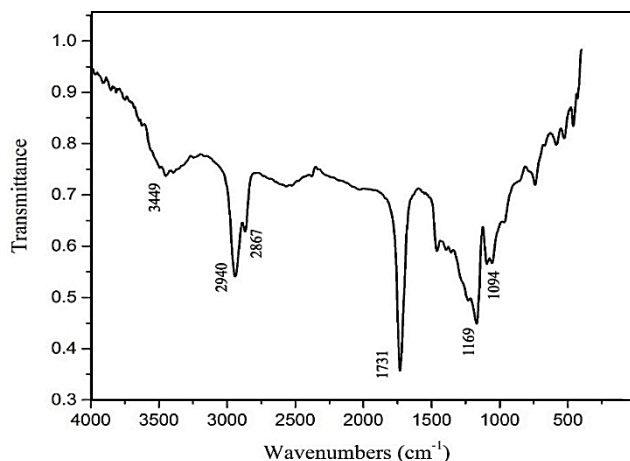
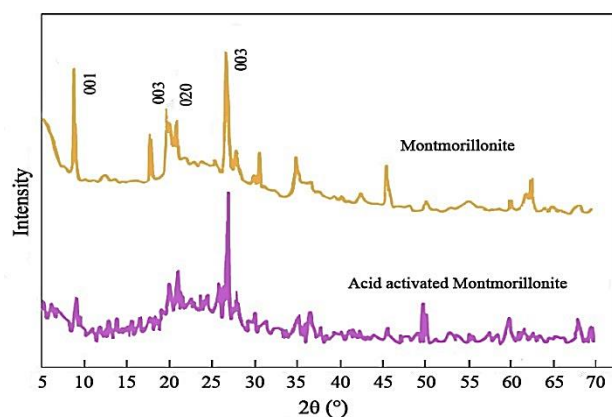*Fig. 1: FT-IR spectrum of the synthesized (ε-Caprolactone-co-Tetrahydrofuran) copolymer*

Fig. 3: HNMR spectrum of the synthesized (ε-Caprolactone-co-Tetrahydrofuran) copolymer

Fig. 2: XRD patterns of MMT and acid-activated MMT

Fig. 4: DSC thermogram of the synthesized (ε-Caprolactone-co-Tetrahydrofuran) copolymer

As can be interpreted, the peaks that appeared at 001, 003, and 020 belong to MMT [23]. There is no considerable change in XRD patterns of the MMT and AA-MMT, however, a decrease in 001 peak intensity exhibits an alteration in the structure of the MMT due to the acid activation. Generally, a drop in AA-MMT peak intensity is due to a decrease in MMT crystallinity because of acid molecules substitution into MMT layers. A little shift of the peaks to higher degrees can be observed, while the existence of characteristic peaks confirms the 2D lattice of the material. This approves the activation of MMT with no effect on its basic structure maintaining its unique properties. Furthermore, measurements using Bragg's law showed an increase in the d-spacing of the layers after activation by acid at 2θ=8° as an expected effect. The calculations show that the d-spacing between layers is about 1.10 nm, while this amount is increased by 0.16 nm after activation by acid. The finding exhibits that the crystallinity
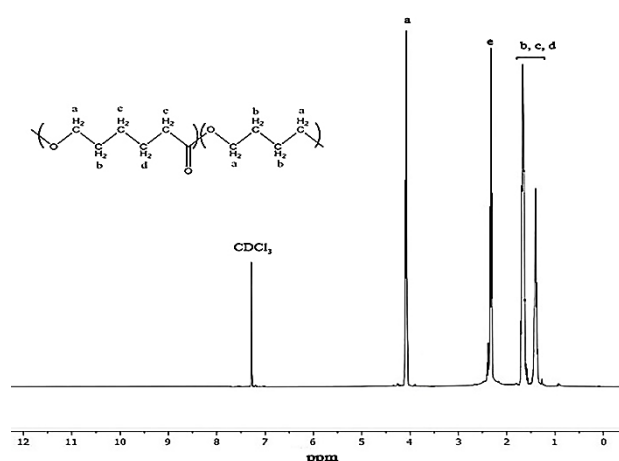
of the activated MMT is decreased which may be in as much as the replacement of acid molecules within the layers.

HNMR analysis of the prepared copolymer

The HNMR spectrum of the synthesized copolymer was obtained and the result is shown in Fig. 3. Three signals correlated to Caprolactone methylene groups (positions 3, 4, and 5) and tetrahydrofuran methylene groups (positions 3 and 4) appeared between 1.74 and 1.76 ppm. A peak at 2.61 ppm is related to the proton of Caprolactone (position 2). The peak at 4.21 ppm is associated with the protons of Caprolactone (position 6) and tetrahydrofuran (positions 2 and 5). The aforementioned positions are shown in Fig. 3.

DSC analysis of the copolymer

The DSC thermograms (Fig. 4) of the synthesized copolymer were obtained in the range of -70 to 50 °C
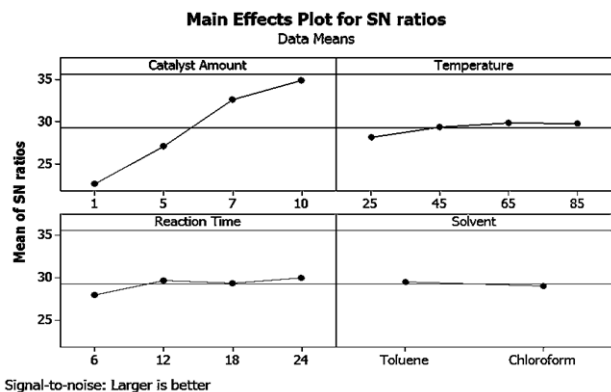
Fig. 5: Taguchi S/N analysis results for the investigated factors

Fig. 6: Interaction plots of the studied factors

(10 K/min heat rate) to find out the glass transition temperature (T_g) and a second thermogram was obtained to check out the degradation temperature of the copolymers. According to the achieved results, the (ε-Caprolactone-co-Tetrahydrofuran) copolymer showed a T_g of 28.91 °C. By increasing the heat to upper temperatures from 50 to 300 °C, a melting point of (T_m) can be observed at 55.14 °C. As the temperature increases, an exothermic peak at 280 °C appears that is related to copolymer degradation showing its thermal stability up to this temperature.

Taguchi's analysis of the factors that affect copolymerization efficiency

One of the most important factors in reaction efficiency is the amount of nanocatalyst used. In this respect, the amount of the prepared solid acid catalyst was studied through the Taguchi method and the results are illustrated in Fig. 5. 1, 5, 7 and 10 %wt of nanocatalyst amount were the levels investigated for this factor. According to the obtained results, reaction efficiency is directly correlated to the amount of used catalyst. In other words, better monomer conversion to the copolymer is achieved by higher amounts of nanocatalyst. This can be because of the increase in active sites of the catalyst in the reaction as its amount is enhanced. These active sites act as polymerization initiation spots to open the rings and initiate the reaction. The active role of the prepared AA-MMT as a catalyst is observable. As can be seen, the slope of the nanocatalyst plot is greater than all other three factors confirming the fact that the catalyst is the most effective factor. 10 %wt of catalyst is the optimum level for the reaction.

On the other side, temperature as the other effective factor was studied and the Taguchi analysis shows that
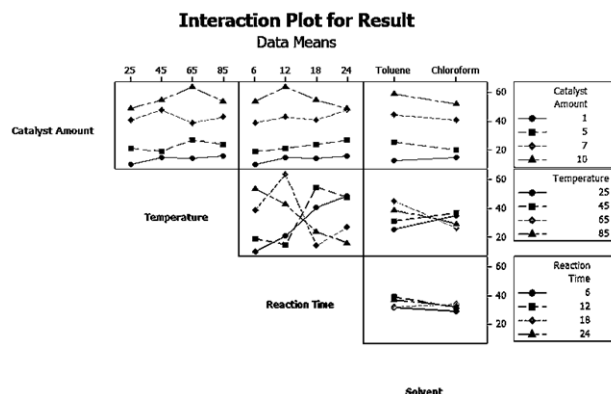
the efficiency is enhanced by an increase in temperature up to 65 °C. By reaching the temperature of 85 °C, a slight decrease in efficiency is observed that can be due to a possible polymer chain degradation. Therefore, 65 °C is the optimum temperature for the studied reaction.

Reaction time as another factor was investigated by Taguchi. As can be seen, letting the reaction be completed more times makes its efficiency higher than expected. The reaction reached its highest S/N ratio after 24 h. Hence, 24 h was the optimal level for this factor.

The solvent type was also studied to find out its effect on the reaction yield. The results showed that Toluene could act as a better solvent in comparison to Chloroform. This can be due to the better dissolution of monomer in Toluene and enhancing the copolymerization yield. The highest yield was achieved in entry 15 under the following conditions: 10 %wt of nanocatalyst, 65 °C of reaction temperature, 12 h of reaction time, and Toluene as the catalyst.

ANOVA interaction plot analysis

Interaction plots (Fig. 6) of the studied factors according to Taguchi's design of experiments were investigated to find out the interaction between factors and their levels. According to the obtained plots and the interactions of nanocatalyst amount with other factors, it can be interpreted that 10 %wt of nanocatalyst amount has given the highest yield at 65 °C. Nearly all amounts of nanocatalyst have the highest yield at 65 °C exhibiting that this temperature has a high impact on efficiency. In the interaction plot of nanocatalyst amount with reaction time, it can be interpreted that 10 %wt of nanocatalyst has the highest yield in 12 h of reaction time which shows the superior effect of nanocatalyst amount in comparison to other factors. Moreover, lower amounts of nanocatalyst
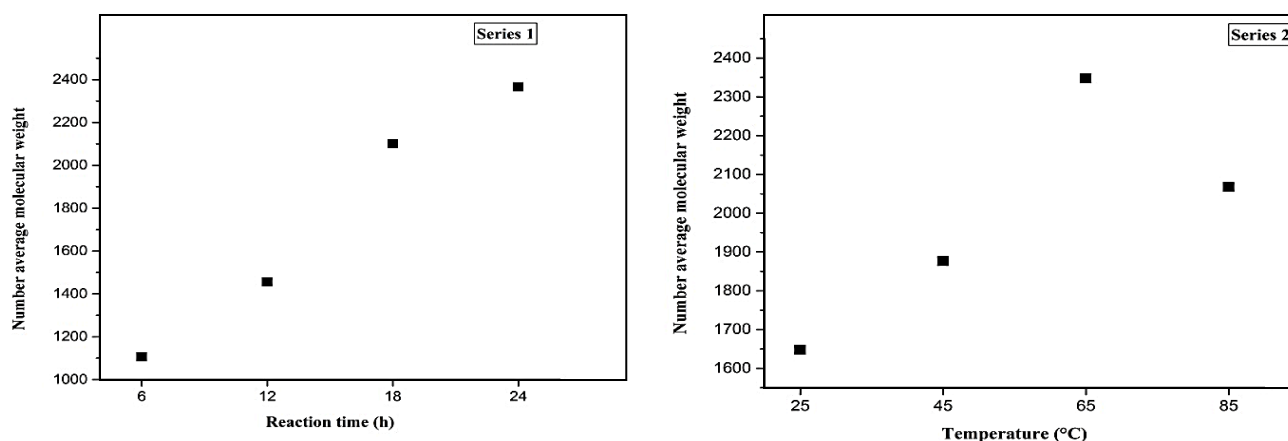
Fig. 7: Effect of reaction time (Series 1) and temperature (Series 2) on the molecular weight of the copolymer

have the highest yields in 24 h of reaction time which exhibits that more reaction time is needed to reach the zest by low catalyst amounts. Furthermore, as can be observed from the interaction plot of nanocatalyst amount versus solvent type, it is seen that Toluene has a better effect on efficiency in comparison to Chloroform confirming the obtained results of Taguchi analysis. The plot of temperature versus reaction time shows high interactions; however, 65 °C exhibits the highest yield. It can be concluded that temperature and reaction time are highly effective on each other, and the results can be various. In the interaction plot of the temperature and type of solvent, at 65 and 85 °C Toluene shows better efficiency while at 25 and 45 °C Toluene is more effective. Despite achieving different results, the slope of the plot associated with Toluene is greater. This indicates that Toluene is more effective than Chloroform. In the obtained interaction plots of the reaction time and solvent type, all interactions show that Toluene led to higher yields.

GPC analysis

To study the effect of imposed different conditions on the reactions, GPC analysis was accomplished for some of the samples and the results of the number average molecular weight (M_n) were shown in Fig. 7. Toluene was used as solvent according to the results confirming its superiority to Chloroform and 10 %wt of Nanocatalyst was used for the reaction as it was proved in Taguchi analysis as the best amount for the catalyst. Hence, only the effects of temperature and reaction time were investigated. Reactions were completed in two separate series. In this respect, the first and second series of reactions were completed as follows: 1. Reaction times were changed while the

temperature was constant at 65 °C. 2. Temperatures were changed while the time was kept constant at 24 h. As can be seen, increasing the reaction time has led to higher molecular weights reaching 2366 at 24 h enough time for completing the reaction can be the reason for this phenomenon. Lower M_n (1107) is achieved at 6 h of reaction time. In series 2 reactions, that reaction time is constant and temperature is changed, M_n is increased by temperature up to 65 °C (2347), while molecular weight is decreased to 2067 by rising temperature up to 85 °C indicating a possible growing polymer chains degradation. The findings support the results of yield calculations and Taguchi analysis.

The PDI results are shown in Table 2. As can be interpreted, the obtained PDI amounts are lower than 2 near 1.5 showing a nearly narrow dispersity. In addition, the PDI starts to increase by M_n enhancement; however, in series 1 even after reaching the highest molecular weight in the experiment, the PDI is decreased to 1.6 showing fine molecular weight distribution. In conclusion, all PDI for both series is close to 1.5 proving the narrow distribution for all molecular weights and the appropriate efficiency of the cationic ring-opening polymerization method in this study.

Nanocatalyst regeneration

The regenerated nanocatalyst was used for copolymerization completion for three cycles and the results are shown in Fig. 8. The results confirm the reusability of the nanocatalyst after its regeneration without any significant loss of catalytic activity. It can be observed that the reaction efficiency in the optimum conditions (entry 15 of DOE) is not decreased considerably even after three cycles of catalyst recovery.

Table 2: PDI of the series 1 and 2 copolymers

Series 1		Series 2	
M_n	PDI	M_n	PDI
1107	1.5	1647	1.7
1457	1.6	1876	1.8
2101	1.7	2347	1.6
2366	1.6	2067	1.5
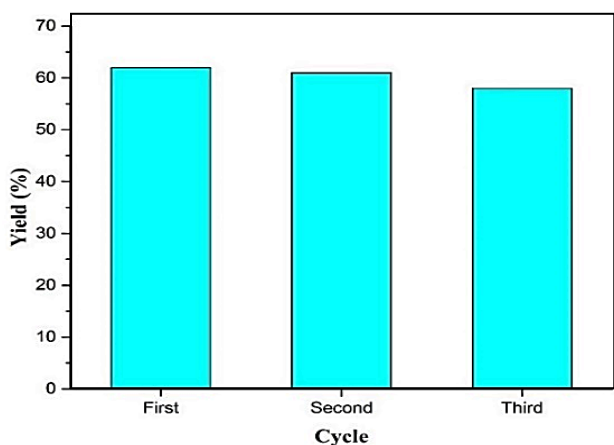
Fig. 8: AA-MMT regeneration and reusability study after three cycles

CONCLUSIONS

The CROP was used to synthesize the poly (ε-Caprolactone-co-Tetrahydrofuran) copolymer using a green solid acid catalyst prepared from Montmorillonite clay. The nanocatalyst was analyzed with XRD spectroscopy. The copolymer was synthesized successfully with the prepared nanocatalyst with acceptable efficiency. The copolymer was investigated with FT-IR, HNMR, DSC, and GPC analysis. The successful synthesis of the copolymer was confirmed by FT-IR and HNMR. T_g of the synthesized copolymer and its degradation were found as 28.91 and 280.60 °C respectively. Reaction conditions were optimized with the assistance of the Taguchi method and the related DOE was accomplished in this respect. Four different factors and a mixed 2-4 levels were used in this respect. 10 %wt of nanocatalyst amount, 65 °C of reaction temperature, 12 h of reaction time, and Toluene solvent were the conditions in which the highest yield for reaction (64%) was achieved. The interaction of the studied factors was studied with ANOVA interaction plots. The highest M_n of the prepared copolymer (2366) was obtained at 65 °C and 24 h of reaction time. It was found that the molecular weight of the copolymer increases with reaction time.

However, the molecular weight was decreased in temperatures higher than 65 °C. The prepared nanocatalyst was recovered and its reusability was tested. It was proved that the catalyst could be used even after 3 cycles with no significant loss of its activity.

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