CHAPTER 5

CATALYTIC ACTIVITIES OF SYNTHESIZED BIMETALLIC CATION EXCHANGERS BASED ON CERIUM

Heterogeneous catalysis is the most practical method as separation processes are avoided by keeping catalysts and products in different phases. Heterogeneous solid acid catalysts provide an attractive alternative to homogeneous liquid acid catalyst as they possess high catalytic activity and selectivity, lower corrosive effects to the reaction vessels and reactors and finally, repeated use of solid acid catalyst from a reaction mixture is easy. The progress of a heterogeneous catalytic reaction can be described by the sequence of elementary reaction steps, including adsorption, surface diffusion, chemical transformations of adsorbed species and desorption.

Inorganic cation exchangers of the class of tetravalent metal acid salts possess good potential for application as a solid acid catalyst. These materials possess structural hydroxyl groups, the H of the –OH being the exchangeable sites. The presence of acid sites on such materials indicates good potential for application in Bronsted catalysis. These inorganic ion exchanger catalysts offer remarkably simple workup procedure and are reusable without any appreciable loss in its activity. In catalytic reactions, specific surface areas of the catalysts play an important role which is the characteristic feature of the material. Ion exchangers possess very high surface area since they have both internal and external surfaces are available.

5.1. Catalytic activity of TiCeMo and PANI-TiCeMo towards dye degradation

The effluents from textile, leather, food processing, dyeing, paper, cosmetics and dye manufacturing industries are major sources of pollution\(^{179}\). Pollution from effluents has become increasingly alarming with the use of a wide variety of dyes in industries. Many dyes and their breakdown products cause a lot of damage to the environment\(^{180}\). Nowadays, treating the textile effluents has become an environmental concern due to scarcity of water and chronic effects on human beings. High molecular weight and complex molecular structures of synthetic organic dyes cause difficulties in treatment of these dyes from wastewater. Several biological, physical and chemical methods have been used for the treatment of industrial textile wastewater. But many of
these technologies are cost prohibitive, especially when applied for treating large waste streams. In the present endeavour, we have employed cerium based cation exchangers for the degradation of hazardous organic dyes after selective sorption on catalyst surface. In general, the structure of dye molecules contain functional groups such as – OH, -SO$_3$H, -NO$_2$, -N=N etc., when contact with the exchanger, these groups interact with the matrix of the exchanger and get sorbed on the surface of catalysts. The sorption of dye molecules is also facilitated by the exchange of H$^+$ ions in the exchanger. The exchanger can be recovered by using suitable eluents and can be reused for the next cycle.

Cerium based ion exchangers are reported as having enhanced applications like decolourisation of water by adsorption or degradation of organic dyes$^{54,181}$. Cerium based materials have generated great interest due to their redox properties, because of conversion between trivalent and tetravalent states under oxidation and reduction conditions. Cerium containing catalysts are broadly used as effective oxidation systems due to their unique properties such as redox, oxygen release and storage abilities$^{182,183}$. During catalytic degradation of dyes present in effluents of various industries, knowledge of the interaction of certain ions with the cations in the exchanger is very essential since the catalytic reactions are usually carried out in aqueous medium which may contain various cations. Cerium based cation exchangers are most applicable for effluent treatment because almost complete removal of dye molecules is possible by degradation. Ion exchange character, oxidising power of the exchanger and electron exchange property of cerium ions as a whole help in the dye degradation process.

The newly synthesized bimetallic cation exchangers TiCeMo and its poly-o-toluidine composite are found to have the ability to degrade hazardous organic dyes such as methyl red (MR) and crystal violet (CV) from aqueous solutions. In this work, the catalytic potential of TiCeMo and PANI-TiCeMo towards the degradation of these dyes from aqueous solution was carried out. Efforts have also been made to see the effects of operational parameters such as reaction time, pH, temperature, amount of catalyst and interference of various metal ions on the degradation of methyl red.
5.1.1. EXPERIMENTAL

Methyl red and crystal violet were obtained from Loba Chemie (India). Deionized water was used throughout the study. All other reagents and chemicals used were of analytical grade.

Specific surface area of TiCeMo and PANI-TiCeMo exchangers was determined by gas adsorption (BET) method. UV-Vis Diffuse Reflectance Spectrophotometer was used for measuring the absorbance.

The catalytic activity of TiCeMo and PANI-TiCeMo for the degradation of MR and CV was evaluated in laboratory conditions. For this stock solutions (40 ppm) of dyes were prepared in deionized water and were diluted as and when required. The catalytic degradation was observed by the addition of 200 mg of the exchangers to 20 mL dye solutions at room temperature without any irradiation and external catalyst. Decolourisation of the media was measured by taking optical density at their maximum absorbance wavelength ($\lambda_{\text{max}}$ of MR = 521 nm, $\lambda_{\text{max}}$ of CV = 590 nm) in regular time intervals with the help of UV-Vis DRS. The degradation efficiency was calculated using Beer’s law as:

$$\% \text{ Degradation} = \frac{\text{Initial absorbance} - \text{final absorbance}}{\text{Initial absorbance}} \times 100$$

The dye degradation ability of the exchangers was optimized under different conditions and parameters. The effects of catalyst dosage, pH, temperature, reaction time and interference of inorganic cations were studied. The effect of catalyst dosage on catalytic activity was studied at different catalyst doses (100 - 400 mg per 20 mL of 40 ppm dye solutions), keeping temperature 30°C. The effect of pH in the range 2-10 was studied by taking 40 ppm dye solutions, amount of catalyst 200 mg and temperature 30°C. The pH of the solution was adjusted after adding the exchanger by using dilute NH$_3$ and HCl solutions. Initial dye concentration ranging from 10 ppm to 50 ppm was prepared and degradation experiments were conducted using 200 mg of the exchanger. To study the effect of temperature on the removal of dyes, the experiments were carried out at temperatures varying from 30°C to 50°C with 40 ppm initial dye concentration.
5.1.2. RESULTS AND DISCUSSION

Catalytic reactions occurring on the surface of the exchangers mainly depend on the surface area of the material. Dye degradation reaction always follows the adsorption of dye molecules on the surface of the catalysts. Hence large surface areas of the catalysts enhance the rate of adsorption process, thereby increasing the degradation of dye molecules on their surface. The BET surface area analysis diagrams of exchangers TiCeMo and PANI-TiCeMo are shown in Fig. 5.1. Multi point BET plots of the exchangers give the surface area of TiCeMo and PANI-TiCeMo was 8.9056 m$^2$/g and 12.9312 m$^2$/g respectively. That is, the polyaniline composite has large surface area in comparison to its inorganic counterpart TiCeMo.

![Multi point BET plots of TiCeMo and PANI-TiCeMo](image)

**Fig. 5.1: Multi point BET plots of TiCeMo and PANI-TiCeMo**

Preliminary experiments were conducted to check the catalytic activity of the exchangers TiCeMo and PANI-TiCeMo for the degradation of hazardous organic dyes such as methyl red and crystal violet from aqueous solutions. The results of UV-Visible DRS studies (Fig. 5.2) depict a visible outcome suggesting the degradation of MR and CV dye solutions. A drastic change in intensity of original peaks of the dye solutions was observed after treatment with the exchangers at room temperature. The decrease in absorption intensity at each maximum is due to the destruction of aromatic linkages present in the dye molecules.
Fig. 5.2: UV-Vis DR Spectrum of MR and CV degradation by TiCeMo and PANI-TiCeMo

The removed ion exchangers from the dye solution after equilibrium were collected and dried. Absorbance recorded for these samples show close agreement with that of pure samples of the exchangers TiCeMo and PANI-TiCeMo (Fig. 5.3). This shows that no dye molecules are present on the surface of the catalysts. Hence the decolourisation of the dye solutions is surely due to the degradation of dye molecules by the exchangers. These results indicate the strong catalytic activity of the new exchangers towards the degradation of organic dyes.

Fig. 5.3: UV Vis DRS of solid ion exchangers before and after treatment with the dye solutions

The effect of various parameters such as reaction time, temperature, catalyst dosage and concentration of the dye solutions on the rate of degradation were studied to optimize the conditions in which maximum removal takeplace. The pH of the dye solution is an important parameter which affects the catalytic degradation of the dyes; hence the effect of pH on the rate of degradation of MR and CV dyes was investigated in the pH range 2-10. The results are presented in Fig. 5.4. It has been observed that the rate of dye degradation was maximum at pH 4 for MR and pH 6 for CV in presence of
both TiCeMo and PANI-TiCeMo. In high acidic condition, rate of dye degradation remained very slow since the catalyst shows more affinity towards hydronium ions than dye molecules. In alkaline condition, at higher pH, the formation of OH$^-$ ions is favoured. This leads to decrease in the degradation rate because of the repulsion between excess OH$^-$ species on the catalytic surface and the dye surface\textsuperscript{185}.

**Fig. 5.4: Effect of pH on the catalytic degradation of MR and CV**

**Fig. 5.5** shows the effect of contact time for the degradation of MR and CV in presence of the catalysts. It is clear that the rate of degradation increases with increase in time of contact of the dyes with the exchangers and reaches equilibrium at 150 minutes and 120 minutes for MR and CV respectively in presence of TiCeMo. Hence all the factors that affect the dye degradation are investigated systematically by keeping the reaction time 150 minutes for MR and 120 minutes for CV.

**Fig. 5.5: Effect of reaction time for the degradation of MR and CV**
The effect of initial dye concentration on the rate of degradation was investigated by varying the initial concentration from 10 ppm to 50 ppm at constant catalytic dosage of 200 mg at room temperature. The results are shown in Fig. 5.6. It is obvious that the rate of dye degradation decreases with increase in initial concentration of the dyes. In high concentrations of the dye solutions the degradation rate decreased due to multi layer formation of the dye molecules on the material.

Fig. 5.6: Effect of initial dye concentration on the degradation of MR and CV

Fig. 5.7 illustrates the effect of catalyst dosage on the degradation of MR and CV. The increase in decolourisation rate at different catalyst dosages ranging from 100 mg to 400 mg may be due to an increase in the availability of active sites and thus an increase in the number of dye molecules adsorbed on the surface of the catalyst.

Fig. 5.7: Effect of amount of catalyst on dye degradation

Temperature is also a very important factor for all processes associated with catalytic dye degradation. For this degradation experiments were performed at different
temperatures, keeping a constant initial dye concentration, amount of catalyst and pH. It is clear from Fig. 5.8 that the rate of degradation increases with increase in reaction temperature in presence of TiCeMo and PANI-TiCeMo.

**Fig. 5.8:** Effect of temperature on the degradation of MR and CV

The results of degradation studies of organic dyes MR and CV in presence of TiCeMo and PANI-TiCeMo at optimized conditions are summarised in Table 5.1. Tabulated results show that the polyaniline encapsulated TiCeMo nanocomposite is a better catalyst for the degradation of these dyes from their aqueous solutions than the inorganic counterpart TiCeMo. This is due to the better selectivity and oxidation power of PANI-TiCeMo towards these organic dye molecules. BET surface area analysis shows that PANI-TiCeMo has more surface area than TiCeMo. Larger surface area enhances the adsorption of dye molecules on the surface of the catalysts. This again supports the experimental results.
Table 5.1: Degradation of MR and CV dyes in presence of TiCeMo and PANI-TiCeMo

<table>
<thead>
<tr>
<th>Dye solution (40 ppm)</th>
<th>Reaction time (min)</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>% Degradation</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TiCeMo</td>
</tr>
<tr>
<td>MR</td>
<td>150</td>
<td>4</td>
<td>30</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>96</td>
</tr>
<tr>
<td>CV</td>
<td>120</td>
<td>6</td>
<td>30</td>
<td>87</td>
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<td></td>
<td></td>
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<td>40</td>
<td>90</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>95</td>
</tr>
</tbody>
</table>

The catalysts possess such good reproducibility that they can be used for 9 cycles of experiment without any loss in their capacity and after that poisoning by catalysts causes a decrease in degradation rate. The possible mechanism for dye degradation reaction involves three steps. Initially the dye molecules are adsorbed on the surface of the catalysts. Then the oxidation power of the catalysts cause destruction of the dye molecules to smaller products and finally these smaller products adhered on the surface of the catalysts gets desorbed and regenerates the catalyst for the next cycle.

The degradation of dyes present in industrial effluents may often contain various inorganic cations. Hence in dye degradation reactions, the knowledge of interaction of certain metal ions with the exchangers is very essential. Thus our work has been extended to study the effect of inorganic cations such as Pb$^{2+}$, Cu$^{2+}$ and Mn$^{2+}$ on the degradation of MR dye in presence of catalysts (Fig. 5.9).

Fig. 5.9: Effect of inorganic cations on degradation of MR
The interference of cations retards the rate of degradation reaction and they show the following order for degradation yield: $\text{Cu}^{2+} > \text{Mn}^{2+} > \text{Pb}^{2+}$ for both the catalysts which was against the order of distribution coefficient. The inhibitory effect is due to the fact that the cations block the active sites on the surface of the catalyst. The results of the study are summarised in Table 5.2.

| Table 5.2: Effect of inorganic cations on the degradation of MR at 30°C |
|--------------------------|------|
| Reaction time (min)      | 150  |
| % Degradation on TiCeMo  | 81   |
|                         | Cu$^{2+}$ | 74 |
|                         | Mn$^{2+}$ | 69 |
|                         | Pb$^{2+}$ | 60 |
| % Degradation on TiCeMo in presence of |           |
|                         | Cu$^{2+}$ | 77 |
|                         | Mn$^{2+}$ | 71 |
|                         | Pb$^{2+}$ | 65 |
| % Degradation on PANI-TiCeMo |       |
|                         | Cu$^{2+}$ | 77 |
|                         | Mn$^{2+}$ | 71 |
|                         | Pb$^{2+}$ | 65 |

The amazing catalytic property of the exchangers TiCeMo and PANI-TiCeMo towards the degradation of toxic organic dyes like methyl red and crystal violet without any external catalyst show the potentiality of the exchangers in treatment of industrial waste effluents.

5.2. Application of TiCeW and ZrCeW as solid acid catalysts for the esterification of iso-amyl alcohol with acetic acid

Organic esters have been extensively used in the production of latex emulsion polymers, thermoplastic and thermoset plastics and have also been used as solvents, perfumery, flavour chemicals, pharmaceuticals, agrochemicals and other fine chemicals. Hence esterification is a very widely employed reaction in the organic process industry. Generally esterification reactions are carried out in presence of conventional homogeneous acid catalysts such as $\text{H}_2\text{SO}_4$, $\text{HCl}$ etc. Conventional acids are very active in esterification reactions but they are highly corrosive and difficult to separate from the reaction mixture. This also results in sulphur contamination in the final product which is unacceptable. Hence heterogeneously catalysed esterification reactions are gaining more attention. They provide cleaner routes for chemicals due to ease of separation of the products without contamination. Nowadays esterification
reactions have been widely investigated using several heterogeneous solid acid catalysts.

The H⁺ form of inorganic cation exchangers possess Bronsted acidity and can be used as solid acid catalysts. Tetravalent bimetallic acid salts (TMA) containing two different cations and an anion are interesting since they exhibit improved properties in comparison to their single salt counterparts. TMA salts possess good thermal and chemical stability as well as operational simplicity and are thus good candidates for potential utility as solid acid catalysts. Esterification catalysed by cation exchangers is undeniably interesting, not only from a purely physicochemical point of view but also in terms of the advantages of these types of catalyst over the conventional ones. Ion exchangers increase the product yield; they provide high purity of products and regenerate easily for reuse. They can also be used repeatedly over prolonged period of time without any difficulty in handling and storing¹⁸⁷.

In the present endeavor, we report the study of esterification reaction between acetic acid and iso-amyl alcohol catalysed by bimetallic inorganic cation exchangers. The importance of the present investigation is that the product iso-amyl acetate has low toxicity and it has a strong banana flavour and is therefore widely used in food industries and as flavouring agents. The effectiveness of various synthesized inorganic cation exchangers for this reaction was studied and out of them TiCeW and ZrCeW were selected on the basis of better yield of product. The experimental procedures and results obtained are discussed in the following sections.

5.2.1. EXPERIMENTAL

Iso-amyl alcohol and acetic acid used for the esterification reaction were obtained from E-Merck, India. All other reagents and chemicals used were of analytical grade and distilled water was used throughout the study.

Specific surface area of TiCeW and ZrCeW exchangers was determined by nitrogen gas adsorption (BET) method.

Esterification reactions of acetic acid with iso-amyl alcohol were carried out in the presence of TiCeW and ZrCeW as catalysts. The reaction was carried out in a long necked 500 mL round bottom flask fitted with condensor, thermometer and a magnetic stirrer. Heating mantle was used to maintain a constant heating rate. For a typical reaction, acetic acid, iso-amyl alcohol and a known amount of solid acid catalyst were
added in a single lot and the change in concentration of remaining acetic acid was calculated periodically by withdrawing samples from the reaction mixture and titrating against standard sodium hydroxide using phenolphthalein as indicator. During the reaction between acetic acid with iso-amyl alcohol under reflux conditions with continuous stirring, iso-amyl acetate and water were formed. The yield of iso-amyl acetate formed in the reaction was expressed in terms of percentage (%) of converted acetic acid in comparison to the total acid in the reaction mixture using the following equation:

\[
(\% \text{ Conversion}) = \frac{\text{Volume of NaOH (without catalyst)} - \text{Volume of NaOH (with catalyst)}}{\text{Volume of NaOH (without catalyst)}} \times 100
\]

After 4 hours of reaction, the product samples were collected and analysed by Gas chromatography, which was performed on GC-MS using ether as solvent. The product obtained was confirmed by analysing the product samples by FTIR spectroscopic methods. Experiments were carried out at various molar ratios of amyl alcohol and acetic acid between 1.0 to 3.0 at temperatures of 60 to 90°C and at different catalyst loading: 100 mg to 300 mg to optimize reaction conditions to obtain maximum yields of product.

The catalyst was filtered off from the reaction mixture after cooling to room temperature and the catalytic activity was regenerated by keeping it in 1.0M HNO₃ solution and then washed with demineralised water. The regenerated catalyst can be used for the next cycle without any loss in its activity.

5.2.2. RESULTS AND DISCUSSION

Catalytic activity of the material is always related to the surface area. Hence for comparing the catalytic activities of the exchangers (TiCeW and ZrCeW) in esterification reaction, the surface area of the catalysts was calculated using BET method. The multipoint BET plots for the exchangers are given in Fig. 5.10. Figure shows that the exchangers exhibit high surface area and the surface area of TiCeW and ZrCeW was 72.0254 m²/g and 79.7230 m²/g respectively.
Fig. 5.10: Multipoint BET plots of TiCeW and ZrCeW

The efficiency of the newly synthesized bimetallic cation exchangers TiCeW and ZrCeW as solid acid catalysts for the esterification reaction of acetic acid with iso-amyl alcohol was studied and the product obtained in the reaction was identified by GC-MS and confirmed by FTIR analysis. **Fig. 5.11** shows the GC-MS spectrum of the product obtained in the esterification catalysed by TiCeW.

Fig. 5.11: GC-MS spectrum of product

In GC-MS spectrum the peak at time 9.043 minutes indicates the presence of ester product and other significant peaks represent the presence of rest of the reactant molecules in the sample. The mass spectrum of the product (**Fig. 5.12**) is also agreeable with that of pure iso-amyl acetate.
Fig. 5.12: MS spectrum of iso-amyl acetate (9.043 min)

Fig. 5.13 shows the FTIR spectra of the products obtained in the esterification catalysed by TiCeW and ZrCeW. The band in the region of 2955 cm\(^{-1}\) is attributed to the presence of aliphatic –C-H stretching, a sharp peak observed in the region 1718 cm\(^{-1}\) indicates the presence of -C=O stretching vibration of ester molecule. The peak at 1394 cm\(^{-1}\) is due to –CH\(_3\) bending vibrations and strong bands around 1246 cm\(^{-1}\) and 1019 cm\(^{-1}\) represent the -C-O stretching vibration in the molecule. Similar bands in the same region of both spectra imply the formation of same compound; show the catalytic activity of these exchangers in the esterification reaction.

Fig. 5.13: FTIR spectrum of iso-amyl acetate. Reaction catalysed by (a) TiCeW and (b) ZrCeW

The esterification of iso-amyl alcohol with acetic acid is an equilibrium-limited chemical reaction and the position of equilibrium controls the quantity of ester produced. Equilibrium reactions always depend upon several reaction conditions. Hence in our study, the effects of various process parameters like the ratio of iso-amyl alcohol to acetic acid, temperature, reaction time and amount of catalyst were
investigated using the catalysts TiCeW and ZrCeW to optimize the conditions at which maximum yield of product obtained.

The effect of ratio of iso-amyl alcohol to acetic acid was investigated in different alcohol to acid ratio (1:1, 1:2, 2:1, 1:3 and 3:1) respectively at a temperature of 60°C with 100 mg of catalyst loading (TiCeW), keeping the reaction time 3 hours. The results of the study show that the reaction rate increases as the iso-amyl alcohol in the reaction mixture is taken in excess (Fig. 5.14). A change in the ratio of alcohol to acid from 1:1 to 3:1, the percentage conversion of acetic acid to ester increases from 59% to 81%. Similar results were obtained when the reaction is catalysed by ZrCeW under similar conditions. Hence further studies are carried out with iso-amyl alcohol to acetic acid ratio 3:1.

Fig. 5.14: Effect of molar ratio of reactants for the esterification reaction

For a heterogeneously catalysed reaction, study on effect of temperature is extremely imperative since it has a significant effect on the equilibrium of the reaction. The effect of temperature on the esterification was studied in the range of 60-90°C, keeping the molar ratio of alcohol to acid 3:1, and amount of catalyst 100 mg. The % conversion of acid is calculated at regular intervals and is plotted as a function of time (Fig. 5.15). It shows that the higher temperature yields the greater conversion of acetic acid to iso-amyl acetate.
Fig. 5.15: Effect of reaction temperature on esterification

Esterifications are usually carried out at higher temperatures and hence an optimum temperature of 90°C was selected for further studies. It is also observed that after 3 hours, there is no change in the % conversion of acetic acid, which means the reaction attains equilibrium at 3 hours of reaction time. So reaction time was optimized as 3 hours for this study. Higher yield is obtained (91%) at high temperature when the reaction is catalysed by ZrCeW than when it is catalysed by TiCeW.

Fig. 5.16 shows the effect of amount of catalyst on the esterification reaction of acetic acid with iso-amyl alcohol in presence of ion exchangers as solid acid catalysts. It is clear that rate of esterification increases with increase in amount of catalyst loading. On increasing the amount of catalyst, the acidic sites on the surface of the catalyst increases, which enhances the rate of esterification.

Fig. 5.16: Effect of amount of catalyst on esterification

The optimum conditions at which maximum yield of products for the esterification reactions of acetic acid with iso-amyl alcohol in presence of TiCeW and
ZrCeW are given in Table 5.3. Results show that ZrCeW is a better catalyst for the esterification reaction than TiCeW. BET surface area analysis (Fig. 5.10) also supports the increased catalytic activity of ZrCeW with respect to TiCeW.

Table 5.3: Optimum conditions for esterification in presence of TiCeW and ZrCeW

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TiCeW</th>
<th>ZrCeW</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m²/g)</td>
<td>72.0254</td>
<td>79.7230</td>
</tr>
<tr>
<td>Amount of catalyst (g)</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Molar ratio (Iso-amyl alcohol : acetic acid)</td>
<td>3:1</td>
<td>3:1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Reaction time (hours)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>% Conversion</td>
<td>88</td>
<td>91</td>
</tr>
</tbody>
</table>

After completion of the experiment, the catalyst is filtered, washed with 1.0 M HNO₃ and dried for 4 hours to regenerate the catalyst in H⁺ form and they were used for the next cycle of experiments. Fig. 5.17 shows the effect of catalyst reusability on the conversion of acetic acid by performing 4 runs of experiments and it is observed that there was only a marginal decrease in the % conversion. The decrease in catalytic activity for successive experiments is due to blocking of active sites on catalyst surface by bulky molecules. Hence the catalysts are reusable and we can say that the catalysts can be repeatedly used for this esterification reaction without sacrificing catalytic activity.

Fig. 5.17: Effect of catalyst reusability on esterification
SUMMARY

The catalytic activity of cerium based cation exchangers TiCeMo and PANI-TiCeMo towards the degradation of hazardous organic dyes has been investigated. The results of UV-Vis DRS study show that the catalysts possess high degradation efficiency, reusability and stability. The whole study reveals the potential applicability of the materials towards environmental remediation.

Studies on the esterification of iso-amyl alcohol with acetic acid in presence of bimetallic cation exchangers TiCeW and ZrCeW reveal the promising use of the materials as a solid acid catalysts in the synthesis of esters, the advantageous being operational simplicity, mild reaction conditions and eco-friendly nature. The application of inorganic cation exchangers as solid acid catalysts can replace the use of conventional acids for the esterification reactions successfully. The outcome of the entire studies inspired us to continue the research work to explore the potential of bimetallic cation exchange materials in various fields by incorporating their ion exchange properties, catalytic activities and electron exchange properties.