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Abstract: Present study focuses on the potential use of polyaniline encapsulated titanium cerium molybdate nanocomposite exchanger (TCM-PANI) for the removal of methyl red (MR) dye from aqueous solution. It was synthesized by ex-situ polymerisation method and was characterized by various techniques. The environmental applicability of TCM-PANI was explored by studying its degradation potential towards MR dye and the results were compared with its inorganic counterpart for the same. Optimization of process parameters for the degradation of dye has also been assessed with the help of UV DRS. The studies reveal that the material can be an attractive option for dye removal from industrial effluents.

Keywords: Nanocomposite exchanger; degradation; methyl red

1. INTRODUCTION

The effluents from textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries are important sources of dye pollution. Many dyes and their breakdown products may be toxic for living organisms. Pollution from the effluents has become increasingly alarming with the usage of a wide variety of dyes in industries. Nowadays, treating the textile effluents are becoming an environmental concern due to scarcity of water and chronic effects on human beings. However, it is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems. Several biological, physical and chemical methods have been used for the treatment of industrial textile wastewater including microbial biodegradation, membrane filtration, oxidation ozonation etc. However, many of these technologies are cost prohibitive, especially when applied for treating large waste streams.
Ion exchangers are now extensively used in heterogeneous catalysis. During the catalytic reaction, especially when catalytic degradation of dyes present in effluents of various industries is carried out, 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 materials got great interest due to their redox properties, because of conversion between Ce$^{3+}$ to Ce$^{4+}$ valence 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$^4, 5$. Cerium based ion exchangers are reported having enhanced applications like decolourisation of water by adsorption or degradation of organic dyes$^6, 7$.

Nowadays the studies of organic–inorganic composite materials got great attention in the field of ion exchanger due to their unusual properties by the combination of both organic and inorganic characteristics within a single molecular scale. Composite exchangers have more advantages over organic and inorganic ion-exchangers as they overcome two major drawbacks from which the latter suffers like thermal and chemical stability as well as reproducibility$^8$. Due to these advantageous composite ion exchange materials have been extensively used in environmental remediation, analytical and electroanalytical processes such as waste water treatment, separation of metal ions, catalysis, polymer electrolyte membrane fuel cells and gas perm-selectivity$^9$–$11$. Recently, polyaniline (PANI) as an organic binder has been used to prepare new composites. Titanium cerium molybdate is a new candidate in the family of bimetallic inorganic cation exchanger. By modifying its mechanical and ion exchange properties, the new organic-inorganic composite, titanium cerium molybdate-polyaniline (TCM-PANI) was synthesized and introduced in this paper.

In the present work the catalytic potential of new inorganic-organic composite exchanger, TCM-PANI was evaluated for the degradation of MR without any irradiation and external catalyst and the results were compared with its inorganic counterpart for the same. Efforts have also been made to see the effects of operational parameters such as: reaction time, pH, and temperature, the amount of catalyst and interference of various metal ions on the degradation of methyl red.
2. EXPERIMENTAL

2.1. Reagents

Titanium chloride (Loba Chemie, India) Ammonium ceric(IV) nitrate (E.Merck) and sodium molybdate (E.Merck) were used for the synthesis of the exchanger. All other reagents and chemicals used were of analytical grade.

2.2. Instrumentation:

ELICO LI613 pH meter was used for pH measurements and an electric thermostat oven was used for heating the sample at various temperatures. UV-Visible spectrophotometer model JASCO V660 was used for spectrophotometric measurements. FTIR spectrometer model Thermo Nicolet Avtar370 for IR studies, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies, Perkin Elmer Diamond TG/DTA Analysis System for thermal analysis and an electric shaking machine for shaking were also used. JEOL Model JSM - 6390LV for Scanning Electron Microscopic analysis and chemical composition was determined using EDS.

2.3. Synthesis of the exchanger

2.3.1. Synthesis of titanium cerium molybdate (TCM)

It was prepared by first preparing 0.05M solutions of the reagents titanium chloride, ceric ammonium nitrate and sodium molybdate. Then sodium molybdate solution was added with constant stirring to a mixture of titanium chloride and ceric ammonium nitrate with constant stirring in different volume ratios. Yellow precipitates were obtained when the pH of the mixture was adjusted to 1.012.

2.3.2. Synthesis of Polyaniline

Polyaniline gels were prepared by mixing of the acidic solutions of 10% aniline and 0.1M ammonium persulphate in different volume ratios with continuous stirring by a magnetic stirrer, keeping the temperature below 10°C for half an hour. Green colored polyaniline gels were obtained and kept overnight in a refrigerator.

2.3.3. Synthesis of titanium cerium molybdate-polyaniline nanocomposite exchanger (TCM-PANI)

The gels of polyaniline were added to the yellow inorganic precipitates of titanium cerium molybdate and mixed thoroughly with constant stirring. The resultant green colored gels were kept for 24 hrs at room temperature (25 ± 2 °C) for digestion. The supernatant liquid was decanted and gels were filtered under suction. The excess acid was removed by washing with
deminerlized water (DMW) and the material was dried in an air oven at 50\(^{0}\)C. The dried products were immersed in DMW to obtain small granules. They were converted to H\(^{+}\) form by treating with 1.0 M HNO\(_{3}\) for 24 hrs with occasional shaking, intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and the material was dried at 50\(^{0}\)C\(^{13}\). The particles of the size range (~125 \(\mu\)m) of the material was obtained by sieving and kept in desiccators for further studies. Hence, a number of samples of ‘TCM-PANI’ composite cation exchanger were prepared and on the basis of Na\(^{+}\) ion-exchange capacity, yield and physical appearance of beads one sample was selected for detailed studies.

2.4. CHARACTERISATION OF THE EXCHANGER

2.4.1. Ion exchange capacity (IEC): Ion exchange capacity of the material was determined by column method\(^{14}\). One gram of the exchanger in H\(^{+}\) form was taken in the column. The H\(^{+}\) ions were eluted by percolating 100 ml of 1M sodium chloride solution at the rate of 5-6 drops per minute. The eluent was collected and titrated against standard sodium hydroxide solution. IEC in milli- equivalents of H\(^{+}\) ions per gram was calculated from the titre values by using the equation

\[
IEC = \frac{av}{w}
\]

Where ‘a’ is the molarity, ‘v’ is the volume of alkali used during titration and ‘w’ is the weight of the exchanger taken.

2.4.2. pH titration: Topp and Pepper method\(^{15}\) was used for pH titration using NaOH/NaCl, KOH/KCl systems. 500 mg of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. pH of each solution was measured after attainment of equilibrium and plotted against milliequivalents of OH\(^{-}\) ions.

2.4.3. Chemical stability: The chemical stability of the exchanger was assessed in mineral acids like HCl, HNO\(_{3}\) and H\(_{2}\)SO\(_{4}\), bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this 500 mg of the exchanger was kept separately in 50 ml of different solvents at room temperature for 24 hours. The change in colour and weight were noted.

2.4.4. Effect of temperature on IEC: The effect of temperature on IEC was studied by heating several 100 mg sample of the exchanger at different temperatures for three hours in an air oven and Na\(^{+}\) ion exchange capacity in meqg\(^{-1}\) was determined by column method after cooling them to room temperature.
2.4.5. Distribution studies (Kd): Distribution studies were carried out for various metal ions in demineralised water by batch method\textsuperscript{16}. The distribution before and after equilibrium were determined volumetrically using EDTA as the titrant. The Kd values as depicted in figure 7, were obtained from the formula:

\[ K_d = \frac{I-F}{F} \times \frac{V}{w} \]

Where ‘I’ is the initial volume of EDTA used, ‘F’ is the final volume of EDTA used, ‘v’ is the volume of the metal ion solution and ‘w’ is the weight of the exchanger.

2.5. Application of TCM-PANI as catalyst for the degradation of Methyl red:

The catalytic activity of TCM-PANI on the degradation of methyl red dye was evaluated in laboratory conditions. For this a stock solution (40 ppm) of MR dye was prepared in deionised water and was diluted as and when required. The catalytic degradation was observed by the addition of 200 mg of TCM-PANI to the dye solution at room temperature without any irradiation and external catalyst. Decolourisation of media was measured by taking optical density at different time intervals using UV-Vis DRS and the results were compared with MR degradation ability of TCM, the inorganic counterpart. The degradation efficiency was calculated\textsuperscript{17} using Beer’s law as:

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

2.5.1. Optimization of process parameters: The catalytic activity of the exchanger towards MR degradation was optimized under different conditions and parameters. The effects of catalyst dosage, pH, temperature, reaction time and interference of inorganic cations were studied.

2.5.2. Recycling power of the catalyst: The catalyst’s life time is an important parameter of the catalytic process, due to the fact that its use for a longer period of time leads to a significant cost reduction of the treatment. For this reason, the catalyst was recycled three times. After the optimized conditions for the degradation of the dye solution were determined, the catalyst was recovered by acid wash using dilute HCl and hot water and again used to study its recyclability.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of the exchanger

Titanium cerium molybdate samples of different composition were synthesized and its ion exchange capacity was determined (Table-1). It is evident from table that the ion exchange capacity of the material greatly depends upon the concentration of reactants, mixing volume ratio.
and pH of mother liquor. Among the samples, TCM 4, having maximum IEC (1.24 meq g⁻¹) was selected and was tried to incorporate in to the polymeric matrix of polyaniline. Analysis of IEC of composite material reveals that it shows higher IEC (2.0 meq g⁻¹) than its inorganic counterpart, may be due to more number of freely movable H⁺ ions and H₂O molecules situated in the cavities of the polymeric matrix.

Table 1: conditions of synthesis and properties of different samples
Of titanium cerium molybdate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar conc. (M)</th>
<th>Mixing Volume Ratio</th>
<th>pH</th>
<th>Appearance</th>
<th>IEC for Na⁺ (meq g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCM1</td>
<td>0.05 0.05 0.05</td>
<td>1:1:1</td>
<td>1</td>
<td>Yellow</td>
<td>1.06</td>
</tr>
<tr>
<td>TCM2</td>
<td>0.05 0.05 0.05</td>
<td>1:2:1</td>
<td>1</td>
<td>glassy</td>
<td>0.89</td>
</tr>
<tr>
<td>TCM3</td>
<td>0.05 0.05 0.05</td>
<td>1:2:3</td>
<td>1</td>
<td>solids</td>
<td>0.82</td>
</tr>
<tr>
<td>TCM4</td>
<td>0.05 0.05 0.05</td>
<td>1:2:4</td>
<td>1</td>
<td></td>
<td>1.24</td>
</tr>
<tr>
<td>TCM5</td>
<td>0.05 0.05 0.05</td>
<td>2:1:4</td>
<td>1</td>
<td></td>
<td>0.79</td>
</tr>
<tr>
<td>TCM-PANI</td>
<td>0.05 0.05 0.05</td>
<td>1:2:4</td>
<td>1</td>
<td>Dark green solid</td>
<td>2.00</td>
</tr>
</tbody>
</table>

The EDS analysis (Figure1) of the materials TCM and TCM-PANI gives strong evidence for the formation of composite exchanger by the encapsulation of polymeric matrix to its inorganic counterpart.

Figure 1: EDS of (a) TCM and (b) TCM-PANI
The material was found to be quite stable in different concentrations of mineral acids such as 10.0M HNO₃, 5.0M H₂SO₄ and 12.0M HCl, 0.05M solutions of bases and organic solvents like ethanol, acetone, CCl₄, DMSO, DMF etc.

pH titration curves of TCM and TCM-PANI were shown in Figure 2(a) and 2(b), reveals that the functionality of the material changed from monofunctional to bifunctional when polyaniline composite is formed by the encapsulation of organic part to the matrix of inorganic precipitate which contains only one ionogenic group. The ion exchange capacities obtained from the curves are in agreement with that obtained from the column method.

Figure 2: pH titration curves of (a) TCM and (b) TCM-PANI

FTIR spectra of TCM and TCM-PANI are represented in (Figure 3). FTIR spectrum of TCM (Figure 3(a)), shows a broad band in the region of about 3385 cm⁻¹ and a sharp peak in the region 1612 cm⁻¹. These bands justify the presence of – OH stretching and bending mode. A small peak at 2364 cm⁻¹ is attributed to Ti-O bond. The band observed in the 650-967 cm⁻¹ region is due to the symmetric and asymmetric stretching of M-O-H bond. Bands in the region 1308 cm⁻¹ to 1460 cm⁻¹ was due to deformation vibrations of metal hydroxyl groups and interstitial water. In the IR spectrum of TCM-PANI (Figure 3(b)), an assembly of bands in the region 1380–1570 cm⁻¹ may be ascribed to the stretching vibration frequency of C–N bonds and a band around 3500 cm⁻¹ may be related to the stretching of NH bonds of benzenic and quinonic rings present in the material. The bands in the region 510 cm⁻¹ to 940 cm⁻¹ were due to the presence of metal- oxygen bending vibrations. Other characteristic bands associated with inorganic precipitate are reflected with slight shift in the composite material. It gives an evidence for the encapsulation TCM in the polymeric matrix of polyaniline and forms TCM-PANI composite material.
The XRD patterns provide significant informations in relation to the nature and size of the sample. The X-Ray diffraction patterns of inorganic precipitate and its polyaniline composite were shown in Figure 4(a) and 4(b). XRD pattern of TCM sample shows an amorphous nature whereas the XRD pattern of TCM-PANI shows an intense peak at around 27.5° and a number of small peaks, signifying the crystalline nature of the composite material. The crystalline size of the material is estimated from the peak width (FWHM) using Scherrer’s formula:

\[ D = \frac{K\lambda}{\beta_{2\theta}\cos\theta} \]

Where, \( \lambda \) is the X-Ray wave length, \( K \) is the Scherrer’s constant of the order of unity for usual crystals (here \( K = 0.9 \)), \( \beta_{2\theta} \) is full width at half maximum (FWHM) of a diffraction peak and \( \theta \) is the diffraction angle. The crystalline size of the sample was found to be 1.145 nm. Hence XRD studies expose that formation of composite from inorganic precipitate leads to change in crystallinity from amorphous to nanocrystalline.
Surface study has found to be in great use for understanding the surface feature of the materials. The scanning electron micrographs of both the materials (Figure 5) clearly show the porous morphology with granular structure. The granular nature makes them suitable for column operations and increased surface area increases rate of ion exchange and catalytic activity.

![SEM of TCM and TCM-PANI](image)

**Figure 5:** SEM of (a) TCM and (b) TCM-PANI

Thermograms of the synthesized materials were shown in Figure 6(a) and 6(b). Thermogram of TCM (Figure 6(a)) shows 12% weight loss till 140°C was due to the evaporation of external water molecules and a 2% weight loss from 296°C to 335°C was due to condensation of structural hydroxyl groups. Above this temperature, the material is almost stable up to 950°C as the sample retained 80% of its initial weight at this temperature. Figure 6(b) illustrates that weight loss of about 16% up to 200°C, due to the evaporation of external water molecules. The decrease in weight observed from 448°C to 688°C may be due to the elimination of interstitial water molecules. After 688°C the thermogram shows a sharp decrease in weight, which is due to the decomposition of organic moieties from the exchanger at high temperatures.

![TGA of TCM and TCM-PANI](image)

**Figure 6:** TGA of (a) TCM and (b) TCM-PANI
Distribution studies of different metal ions on the exchangers were performed in DMW. It is apparent from the figure that both the exchangers are highly selective for Pb\(^{2+}\) has been painstaking as the key pollutant in water. The order of selectivity of the studied metal ions was depicted in figure 7.

**Figure 7:** Distribution studies of various metal ions in DMW on TCM and TCM-PANI

3.2. TCM-PANI as catalyst for dye degradation

The analytical application of the material was studied by controlling the hazardous organic pollutants in waste water by degradation of methyl red on the ion exchange surfaces. UV-Visible absorption spectrum of methyl red before and after equilibration with the exchanger is shown in Figure 8. The drastic change in the intensity of each peak at absorption maxima reveals the effectiveness of the exchanger for removing MR from aqueous solution and the results were compared with the degradation of MR by TCM itself. TCM-PANI composite exchanger removes greater percentage of MR dye (93.35%) than the MR removal by TCM (85.85%) within 24 hours under stationary conditions.

**Figure 8:** UV-Visible Spectra of degradation of MR on TCM and TCM-PANI
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 exchangers (Figure 9). This shows that no dye molecules is present on the surface of the catalysts. Hence the decolourisation of the dye solution is surely due to the degradation of the dye molecules by the exchangers. These results indicate the strong catalytic activity of the new exchangers towards MR dye degradation.

Figure 9: (a) solid samples of TCM before and after treatment with MR and (b) solid samples of TCM-PANI before and after treatment with MR

3.2.1. Optimization of process parameters

Effect of various parameters such as reaction time, temperature, catalyst dosage and concentration of the solution on the rate of degradation were studied (Figure 10) and it was found that the rate of degradation increased with increase in reaction time, temperature and catalyst dosage. The degradation efficiency of the dyes at different concentrations and temperatures were studied by determining their residual concentrations spectrophotometrically. Residual percentage content of dyes was plotted against time.

\[
\text{Residual content of dye} = \frac{C_t}{C_0} \times 100,
\]

where \(C_t\) is dye concentration at time \(t\) and \(C_0\) is initial concentration of dye. In high concentrations of the dye solutions the degradation rate decreased due to multi layer formation of the dye molecules on the material. The increase in decolorization rate at different catalyst dosages ranging from 0.10 to 0.40 g 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.
The pH of the dye solution is likely to affect the catalytic degradation of the dye; hence the effect of pH on the rate of degradation of MR dye was investigated in the pH range 2-10. The results are presented in figure 10(d). It has been observed that the rate of dye degradation was maximum at pH 6. 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 favored. This leads to decrease in the degradation rate because of the repulsion between excess OH\(^-\) species on the catalytic surface and the dye surface\(^23\).

3.2.2. Effect of inorganic cations on the degradation efficiency:

Dye effluents discharged from different industries often contains various inorganic cations. The cations may influence the rate of dye degradation. For that the effect of Pb\(^{2+}\), Cu\(^{2+}\) and Mn\(^{2+}\) (0.005M, 5ml) was investigated (Figure 11(a)) on MR (40ppm,10ml) degradation catalyzed by TCM-PANI (0.20g) at pH 6. The cations show the following order for degradation yield: Cu\(^{2+}\)>Mn\(^{2+}\)> Pb\(^{2+}\) (Figure 11(a) and 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.

Figure 11: (a) Effect of inorganic cations on the degradation of MR and (b) Recycling power of the catalyst

3.2.3. Recycling power of the catalyst

Catalysts can be recycled effectively, which makes the process cost effective. For this reason, the catalyst was recycled four times as shown in figure 11(b). After the optimized conditions for the degradation of MR dye were determined, the catalyst was recovered by giving acid wash and again used to study its recyclability. The results of the study showed that the efficiency of the catalysts decreases, which may be due to the fouling of the catalyst and loss due to repeated acid wash.

4. CONCLUSION

Polyaniline encapsulated titanium cerium molybdate nanocomposite cation exchanger was synthesized and characterized. The ion exchange properties and dye degradation efficiency of the novel exchanger was studied and compared with its inorganic counterpart. The results of UV-Visible DRS studies showed that the composite possessed high degradation efficiency and reusability than its inorganic counterpart. The rate of degradation can be controlled reaction time, pH, amount of catalyst and temperature. The entire studies revealed that TCM-PANI was an effective catalyst for the removal of methyl red, which showed the potential applicability of the material towards environmental remediation.
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REFERENCE


