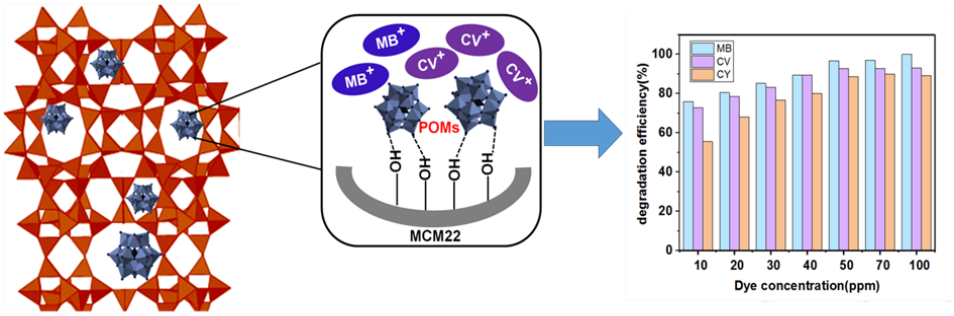
ANNEXURE

New Application: Catalytic degradation of some organic dyes over anchored Silicotungstic acid



Dye degradation over SiW_{12}/MCM-22 catalyst

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RESEARCH ARTICLE

New catalyst comprising Silicotungstic acid and MCM-22 for degradation of some organic dyes

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Abstract

A heterogeneous catalyst comprising Keggin type polyoxometalate, silicotungstic acid (SiW_{12}), and MCM-22 was synthesized using wet impregnation method and characterized by acidity measurement, BET, FT-IR, XRD, and SEM. Their catalytic activity was evaluated for the degradation of cationic organic dyes like methylene blue (MB), crystal violet (CV), and an azo dye Chryosidine Y (CY) in an aqueous solution. The experimental parameters such as catalyst amount, initial dye concentration, and contact time were studied for the degradation of dyes, and it was found that the cationic dyes like methylene blue and crystal violet show better activity as compared to azo dye Chryosidine Y. This may be attributed to better electrostatic interaction of these cationic dyes with the residual negative surface charge of the catalyst, due to presence of SiW_{12} ion as it is rich in surface oxygens and surface hydroxyl groups. The control experimental results showed that the presence of SiW_{12} at the surface of MCM-22 promoted the degradation reactions, and presence of multiple W–O bonds in polyoxometalate also played a key role in this reaction. The catalyst exhibits recycling ability without any significant loss in activity up to four cycles.

Synthetic chemical dyes are primarily used in textile industries, paints, printing inks, paper, and plastics [1,2]. The natural dyes were replaced by these dyes because of their strong binding with the fabric and can retain colour for longer time. The chemical dyes are generally water soluble and organic in nature. They are classified into four types (i) reactive, (ii) direct, (iii) basic and (iv) acidic dyes [3]. As they exhibit high solubility in water, it is difficult to remove them by conventional methods. Exposure to such dye bearing waste water exhibits severe harmful effects causing an environmental pollution and it is also associated with health hazards as the degradation products of dyes are carcinogenic in nature [4,5]. In this regard, legislation on the limits of colour discharge by industrial activities has become stringent by the authorities and the treatment of dye water is essential before submerging it with natural water bodies [6].

Methods such as physical, chemical and biological [7] can be applied to remove dyes from polluted water bodies. In this direction, many techniques like reverse osmosis[8], electrochemical coagulation [9], nano filtration [10], adsorption [11], oxidation [12], electrocatalysis [13] and degradation by enzymes and microorganisms [14] have been explored. Removal of dyes by chemical method can be carried out by their conversion into smaller molecules i.e., degradation via oxidation and/or catalytic processes.

In an era of two decades, the use of zeolite-based composites, particularly in the form of zeolite/inorganic composite has gained tremendous attention for the adsorption of toxic matters such as dyes from water bodies [15–20]. zeolite-based composites possess, better physicochemical stability, easy reusability and, higher adsorption capacity as compared to raw zeolite which has led to much attention of researchers to the zeolite-based composites for the adsorption process. In this regard, we thought to explore the versatile behavior of our one such zeolite MCM-22 based catalyst, SiW_{12}/MCM-22 for the degradation of some cationic dyes. The purpose of choosing this catalyst is to exploit the

adsorption property of MCM-22 along with excellent acidic character of SiW_{12} which can damage the dye chromophore and break it into smaller fragments or molecules that are less hazardous or non-polluting [21].

It is noteworthy that for this study we have chosen SiW_{12}/MCM-22 based catalyst over our best-found catalyst, SiW_{12}/nMCM-48 because it is observed that the dye degradation studies are more likely to happen when zeolitic catalyst are used as compared to siliceous mesoporous catalysts [19].

In the present work, the cationic dyes like Methylene Blue (MB), Crystal Violet (CV) and an azo dye Chrysoidine Y (CY) were chosen as representative dyes to evaluate the degradation capability of the catalyst by investigating various reaction parameters like dye concentration, catalyst amount, and reaction time were investigated for obtaining maximum degradation efficiency.

EXPERIMENTAL

Materials

All chemicals used were of A.R. grade. Silicotungstic acid, was used as received from Merck. MCM-22 was acquired commercially from BEE CHEMS (Kanpur, UP). All the three dyes methylene blue, crystal violet and an azo dye Chrysoidine Y were received from Nice Chemicals Pvt. Ltd (Bangalore).

Synthesis of catalyst

The synthesis of silicotungstic acid (SiW_{12}) anchored to MCM-22, SiW_{12}/MCM-22 was carried out by the same method reported in Part B Chapter 1.

Characterization

Characterization of SiW_{12}/MCM-22 was carried out by the same physicochemical techniques as mentioned in General Introduction [41-46].

Catalytic activity

The performance of SiW_{12}/MCM-22 was investigated for the degradation of multiple dyes like MB, CV and CY at 28 ℃. At regular time intervals, 2 mL of the mixture was taken out from the reaction mixture and filtrated by using a 0.22 µm syringe filter in order to completely remove the catalyst particles. The dye concentration in the solution was measured by UV-Visible spectrophotometer (ShimadzuUV-1800) at the maximum adsorption wavelength of dye. For recyclability experiments, the catalyst was centrifuged, washed with water and dried at 60°C. The following equation was used to calculate dye degradation efficiency.

$$\text{Degradation efficiency (\%)} = (C_0 - C)/C_0 \times 100\%$$

Where C_0 was the initial dye concentration and C was the dye at certain concentration time t during the reaction.

RESULTS AND DISCUSSIONS

Characterization

Detailed discussion of characterization of catalyst is mentioned in Part B Chapter 1.

Catalytic activity

Control experiments

The control experiments were first conducted to check the activity of original constituents of the catalysts, that is only SiW_{12} and MCM-22. It is evident from Figure 1 that the SiW_{12} as such shows the degradation efficiency nearly 16, 12 and 10 % for MB, CV and CY dyes. Whereas MCM-22 shows much higher degradation efficiency 48, 46 and 40 % for MB, CV and CY dyes respectively. The higher degradation efficiency of MCM-22 can be attributed to its high surface area as compared to bare SiW_{12}. The SiW_{12} exhibits surface area as low as <10 $m^2 g^{-1}$ with very good solubility in aqueous solvents [22] that makes it difficult to

separate from reaction mixture. Whereas the catalyst SiW_{12}/MCM-22 exhibits much better degradation efficiency. The large surface area of catalyst enhances the accessibility of catalytic active sites that eventually explains the better dye degradation efficiency of the catalyst. The large surface area and pore diameter of the catalyst enables the greater adsorption of the dye molecules on to the catalyst and accessibility to active cites and eventually desorption of degradation products. This explains the better performance of SiW_{12}/MCM-22 as compared to bare SiW_{12} and MCM-22 in dye degradation.

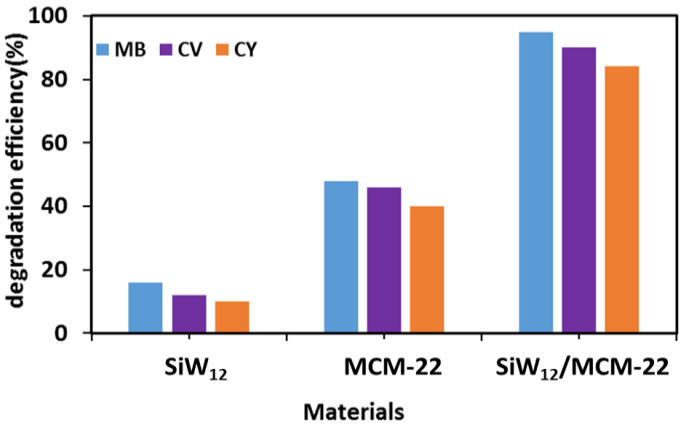

Figure 1 Control experiments, degradation efficiency of MCM-22, SiW_{12} and catalyst SiW_{12}/MCM-22. Reaction conditions: dye concentration,100ppm; amount of materials taken MCM-22 = 20 mg/mL, SiW_{12},1 mg/ml; reaction time, 60 minutes.

Effect of dye concentration

The concentration of all the dyes MB, CV and CY, were varied from 10 ppm to 100 ppm as depicted in Figure 2A. Degradation efficiency increases for all the dyes with increase in concentration and then reaches saturation level which may be due to maximum surface coverage of the catalyst by these dyes. Hence all the experiments were carried out in 100 ppm dye concentration. The amount of catalyst was varied from 0.5 mg/ml to 2.5 mg/ml (Figure 2B). As the amount of catalyst increases the degradation efficiency increases as expected. The maximum degradation efficiency as achieved at 2.5 mg/ml catalyst for multiple dyes.

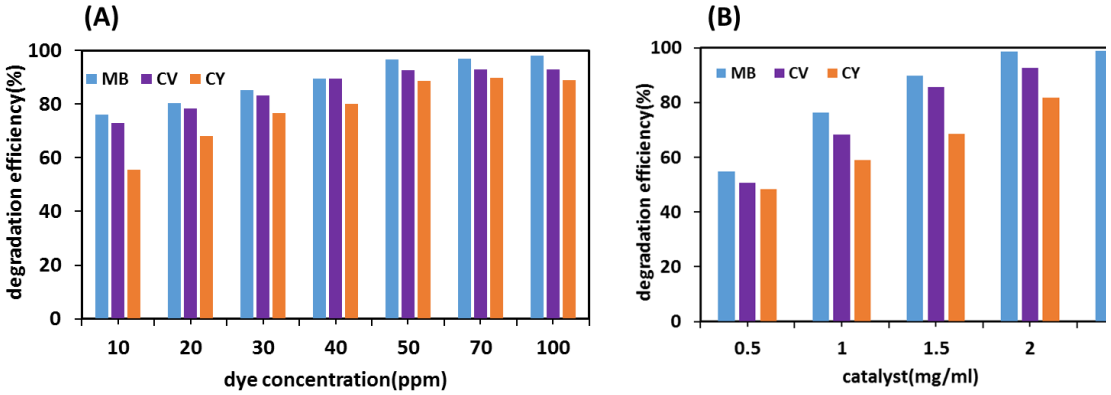

Figure 2 (A) Effect of dye concentration(ppm); the concentration of MB, CV and CY was varied from 10 to 100ppm. (B) Effect of catalyst amount; the amount of catalyst SiW_{12}/MCM-22 was varied from 0.5mg/mL to 2.5mg/mL; dye concentration,100ppm; reaction time, 60 minutes

Effect of time

The degradation efficacy of the catalyst was monitored at different time points from 15 min to 90 min and the maximum efficacy was achieved in 60 min itself (Figure 3A). The trend was similar for all the dyes. Hence the optimised conditions for multiple dye degradation are: dye concentration, 100 ppm; amount of catalyst, 2 mg/ml; reaction time 60 min.

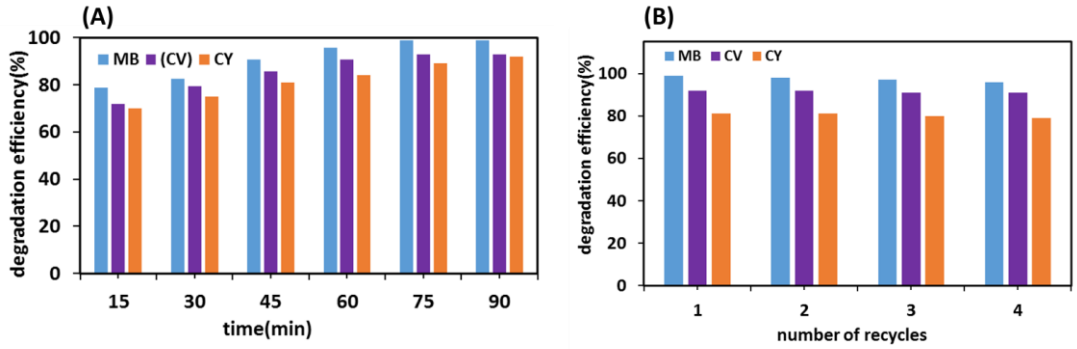

Figure 3 (A) Effect of reaction time (min) (B) Recyclability of the catalysts

The catalyst was recycled for all the dye samples and there was no significant decrease in degradation efficiency up to four cycles (Figure 3B). The recycling results depicts that there is no significant loss in dye removal efficiency up to

four cycles with different dyes MB, CV and CY. These results also indicate the stability and activity of the catalyst was not perturbed with subsequent recycles. For cationic dyes MB and CV catalyst shows better activity throughout all the experiments but for an azo dye CY the efficacy observed was slightly lower, as CY has residual negative charge at pH 7, and at this pH in water medium all the experiments were carried out. This is further explained in the mechanism of the dye degradation in the following section.

Mechanism of dye degradation

The proposed oxidative degradation mechanism for multiple dyes MB, CV and CY with MCM-22 supported POM; SiW_{12} is schematically depicted in Figure 4. Due to very high negative charge on $[SiW_{12}O_{40}]^{4-}$ anions, the adsorption mechanism of dye molecules might be predominantly attributed to an electrostatic interaction between the cationic MB and CV dyes with the negatively charged surface of SiW_{12}/MCM-22. Additionally, MCM-22 possesses quite large number of hydroxyl groups on the surface which also facilitates the adsorption of more dye molecules through hydrogen bonding. Once the dye molecules are adsorbed on the surface of the catalyst follows the catalytic degradation of dye molecules into smaller fragments due oxidation where in W in SiW_{12} has role to play. The CY being slightly negative charged dye molecule might experience slow adsorption on catalyst surface. Specifically, the degradation of MB is well documented in literature. The oxidation of MB is initiated by demethylation resulting in degradation products of mono-demethylation, di-demethylation, tri-demethylation and complete demethylation of nitrogen followed by ring opening. The similar results were also reported previously [23,24].

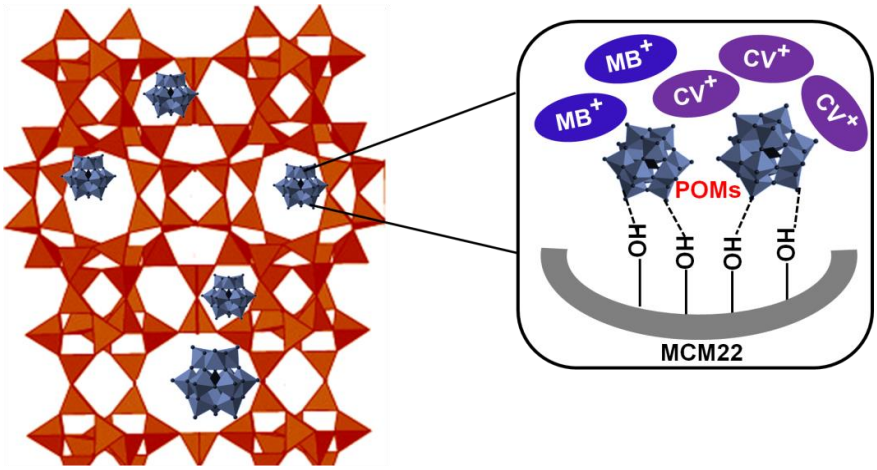

Figure 4 Proposed mechanism of dye degradation over SiW_{12}/MCM-22 catalyst, Electrostatic interaction with negatively charged surface of catalyst with cationic dyes followed by catalytic degradation of dyes by SiW_{12}

CONCLUSION

- The comparison between the degradation efficiency of two dyes studies revealed that the catalytic oxidation in the aqueous solutions of cationic dyes like methylene blue (MB) and crystal violet (CV) could be carried out under the same operating conditions.
- The maximum degradation efficiency was found to be 95% and 90% for MB and CV respectively in 60 min. Whereas the azo dye Chrysoidine Y (CY) exhibits lower degradation efficiency (84%) in similar conditions, that can be improved at higher time scale.
- The catalyst was recycled for four cycles and no significant decrease in activity was observed.
- Thus, the present material can be a promising catalyst for the management of toxic organic dyes and other pollutants in the coloured wastewater effluents.

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