

Fig. 2. FTIR spectra of $PW_{12}@V$ -MCF.

The XRD patterns of the $PW_{12}@V$ -MCF samples are illustrated in Fig. 4. It can be observed that the PW_{12} impregnated products are crystalline. But some peaks of PW_{12} overlapped with that of V-MCF. This may be due to the interaction of PW_{12} with that of the support.

3.1.3. BET

The maintenance of the well-defined MCF frameworks after introduction of vanadium or HPA is further supported by the nitrogen sorption data. Fig. 5 shows the N_2 adsorption-desorption isotherms and pore size distributions of MCF silica, $V@MCF$ and $PW_{12}@MCF$. All the samples exhibited typical IV type isotherms and H1 type hysteresis loops at high relative pressures. This indicated that MCF silica samples with large pore size distribution were successfully prepared. The pore size distribution of the samples shown in the inset of Fig. 5 unambiguously reveals that the 3D mesocellular structure of the support has been preserved.

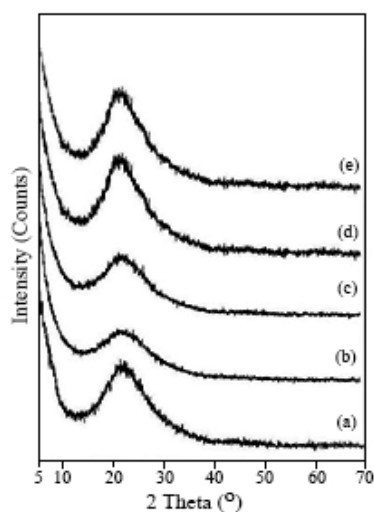


Fig. 3. XRD patterns of (a) MCF; (b) 1.4V-MCF; (c) 2.8V-MCF; (d) 4.2V-MCF; (e) 5.6V-MCF.

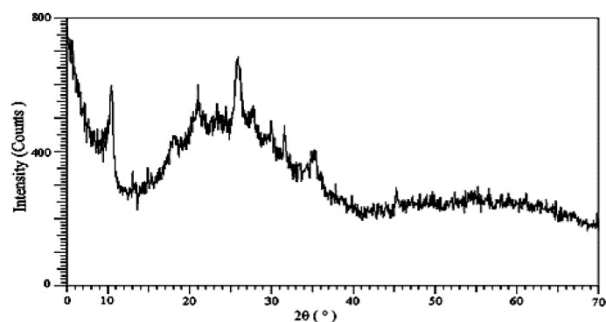


Fig. 4. XRD patterns of $PW_{12}@V$ -MCF.

As expected, the BET surface areas, total pore volumes and mesopore sizes of MCF material are decreased after the functionalization with V or PW_{12} (Table 1). These changes reflect that part of the mesopore volume in the MCF matrix is filled with V or PW_{12} , resulting in pore diameters that are less to that of MCF silica channels.

3.2. Photocatalytic activity

3.2.1. Effect of photocatalyst dosage

The effect of different photocatalytic dosage on the degradation rate of OY has been investigated. The results are shown in Fig. 6. It shows the dependence of the OY photodecolorization rate on the catalyst amount. As it indicates, the photodecolorization rate of OY increases with increasing the catalyst and the photodecolorization rate begin to decrease. The photodecomposition rate of the organic pollutant is influenced by the number of the active sites as well as the light absorption ability of the photocatalyst. For a suitable high concentration of the catalyst, the degradation occurs rapidly because more $h\nu_{B+}$ and e_{CB-} are generated. Excessively high concentration (3 gL^{-1}) of photocatalyst results in decreased photodecolorization rate, which could be attributed to the aggregation of solid particles and shorter light penetration rate brought about by the high absorption coefficient of photocatalyst [43].

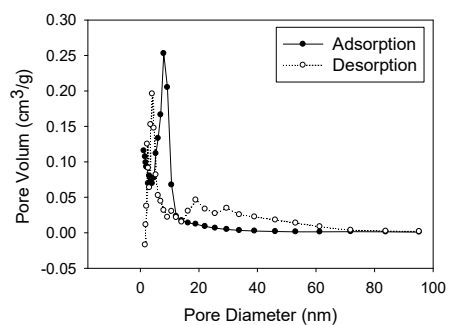
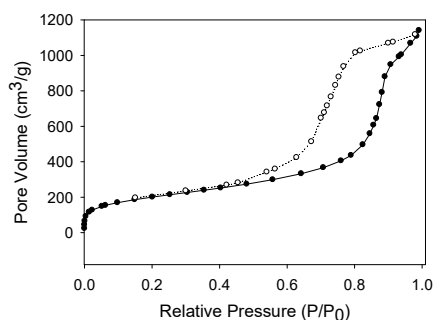
In order to calculate photodecolorization rate constant, k values $\ln(C_0/C)$ is plotted as a function of the irradiation time. The rate constant values, k (min^{-1}) are calculated from the slopes of the straight-line portion of the first-order plots as a function of the catalyst mass (Fig. 6 (right)) which are listed in Table 2.

As the results show maximum degradation of OY was observed after 120 min with the maximum rate constant $6.3 \times 10^3 \text{ min}^{-1}$ in the presence of 2.5 gL^{-1} of the catalyst for OY.

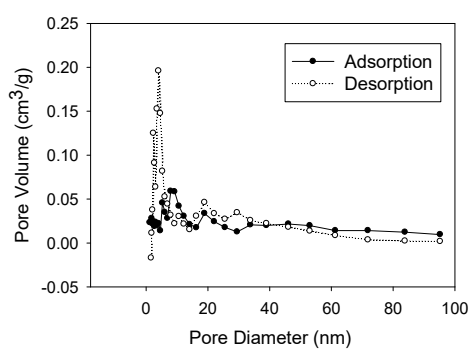
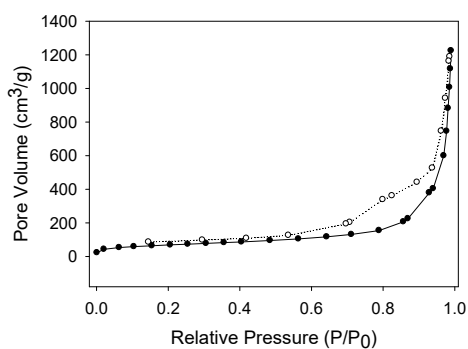
3.2.2. Effect of initial concentration of the pollutants

The Effect of initial concentration of the OY on the degradation rate was also investigated by varying concentration from 10 mgL^{-1} to 50 mgL^{-1} .

(a)



(b)



(c)

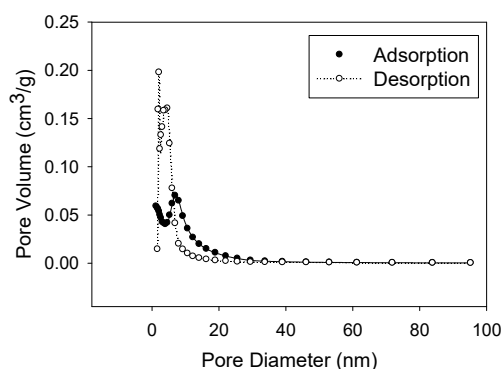
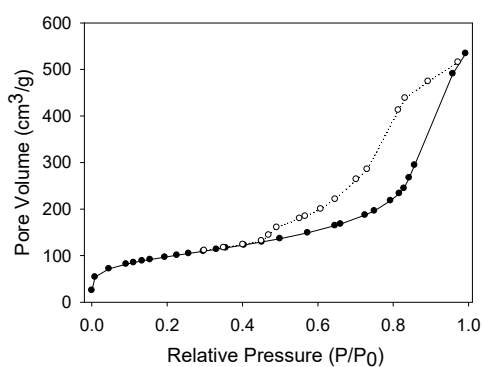


Fig. 5. (Right): N_2 -adsorption-desorption isotherms and, (Left): isotherm patterns of pore size distributions of (a) MCF; (b) V-MCF. (c) $PW_{12}@V$ -MCF.

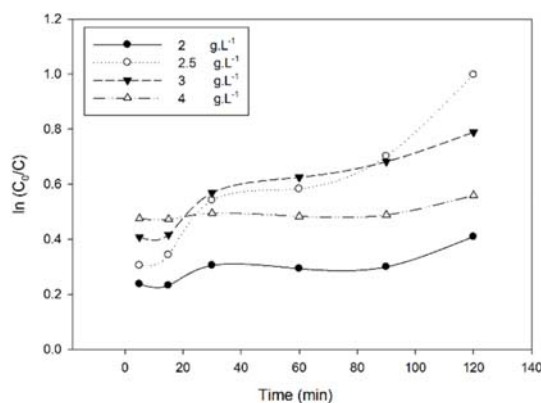
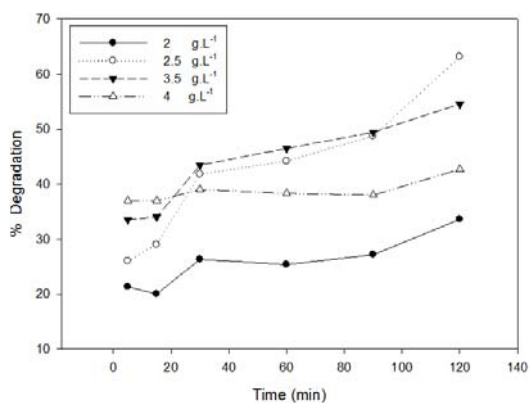


Fig. 6. Effect of dosage of $PW_{12}@V$ -MCF on degradation rate of OY, (initial concentration of OY=25 mg/l and in pH=6.7).

Table 2. Kinetic analysis of the photodecolorization of OY.

Parameter	Value ^a	$k \times 10^3$ (min ⁻¹)
Catalyst mass (g L ⁻¹)	0	0
	2	3.1
	2.5	4
	3	3.2
	4	0.6
C _{OY} (mgL ⁻¹)	10	1.3
	20	4.5
	30	1.8
	40	1.7
	50	1
pH	3	10.3
	5	14.1
	6.8	9.4
	9	4.1
	11	7.1

^a10 mgL⁻¹ OY under dark conditions.

It can be seen from Fig. 7 that the degradation efficiency is decreased with increasing the concentration of OY. The k value are listed in Table 2.

It is obvious that when the concentration is larger than 20 mgL⁻¹ the degradation of pollutants will not be effective. This phenomenon can be explained by the following reasons. The first reason is that at higher dye concentration, higher transmission of the solution is reduced to some extent due to UV-screening effect of the dye itself, which in turn causes fewer incident photons to reach the catalyst surface, and it results in a decrease of degradation rate [44].

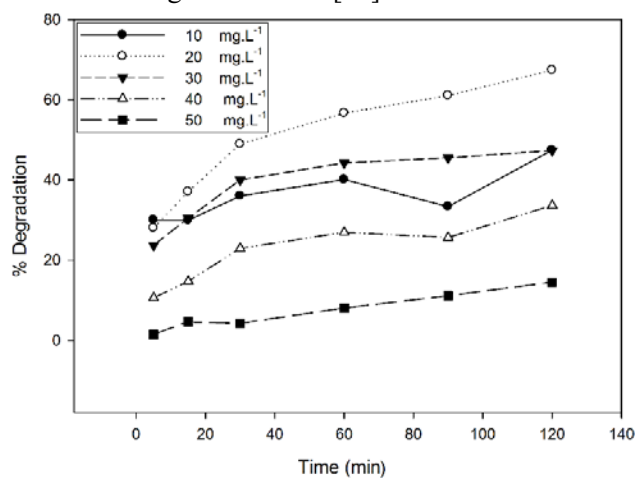


Fig. 7. Effect of initial concentration of the OY on rate of the photodecolorization using 2.5 g L⁻¹ of PW₁₂@V-MCF in pH=6.7.

Another reason is that, when the intensity of light source and illumination time are fixed the amount of radicals produced is also a constant [45]. Consequently excess dyes cannot be oxidized and low degradation is obtained at higher OY concentration.

3.2.3. Effect of initial solution pH

One of the important factors in photodecolorization is pH, because the photocatalysis take place on the surface of photocatalyst depends on pH. In order to investigate the effect of pH, the degradation rate and the ph change were measured at different initial pH (Fig. 8).

It is found that the lower pH values of the reaction system and the higher photocatalytic activity of the PW₁₂@V-MCF at pH=1. PW₁₂@V-MCF exhibited the highest photodecolorization efficiency towards OY. Additionally, when pH value is in the range of 2-5, the degradation rate of OY changes a little. However, in the range of pH 6-11, the degradation rate of OY is obviously reduced. Eosin Y is an anionic/acidic dye contains two relatively acidic protons (pKa 2.0, 3.8 in water).

The mentioned results suggest that in acidic conditions the surface of the catalyst is positively charged due to the high concentration of H⁺, so that is favourable to the degradation of OY molecules.

The obviously increased degradation of OY with the decrease of pH value could be interpreted as follows. On the one hand, in acidic condition more H⁺ are adsorbed into the photocatalyst and regenerate the catalyst surface sites through timely removal of the intermediate species from the surface [46] thereby improve the degradation of OY. Additionally, it is well known that the absorption of the dye on the catalyst surface directly affects the occurrence of electron transfer between the excited dye and catalyst and it influences the degradation rate.

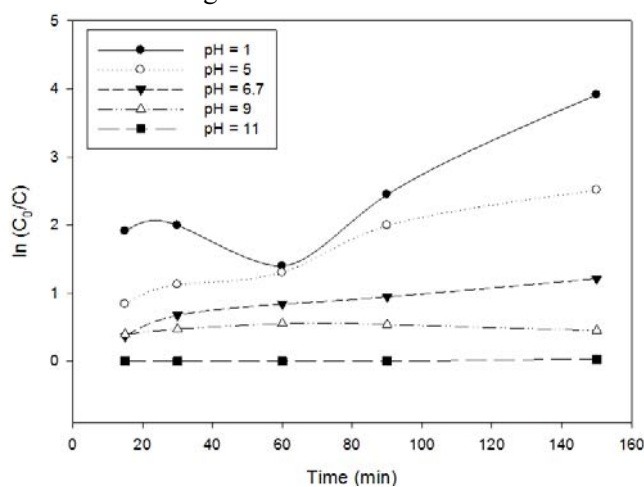


Fig. 8. Effect of solution pH on decolorization efficiency of OY, (initial concentration of the pollutant=20 mg/l and 1 g L⁻¹ PW₁₂@V-MCF).

From above discussion, optimum condition for photocatalytic degradation of OY solution (15 ml, $C^0 = 20 \text{ mgL}^{-1}$) are 2.5 gL^{-1} dose of catalyst and $\text{pH}=1$. Fig. 9 shows the photocatalytic behaviour of $\text{PW}_{12}@V\text{-MCF}$ under optimum conditions. The $\text{PW}_{12}@V\text{-MCF}$ catalyst can be easily separated and recovered and the deactivation of the catalysts was observed after four catalytic activity (Table 2).

As shown in Fig. 9, monitored UV-vis spectra of OY using $\text{PW}_{12}@V\text{-MCF}$ as the photocatalyst indicate that UV-vis intensities of OY decrease obviously upon irradiation that confirm the photocatalytic activity property of $\text{PW}_{12}@V\text{-MCF}$.

In order to determine the degradation of substrates, photolysed solution (300 mg.L^{-1}) of the OY were analysed by HPLC. The HPLC chromatograms show the degradation of pollutant into smaller fragments, which are subsequently mineralized completely. A sharp peak of the dye was detected at 0 h irradiation; whereas, only 11.8% was observed at the end of 2h. The dye peak showed a significant decrease at the end of 2h and some new peaks were observed at different retention times during irradiation which confirmed the formation of degradation products.

3.2.4. Reusability

Apart from presenting a good catalytic activity, long-term stability and the absence of leaching are of primary importance for solid catalysts. In order to determine if the photocatalyst suffered from permanent deactivation, $\text{PW}_{12}@V\text{-MCF}$ was reused several times. The standard procedure, described in the experimental section, was followed to perform the 1st-3rd runs. The wet catalyst was recycled and no appreciable change in activity was noticed after three cycles (Table 3).

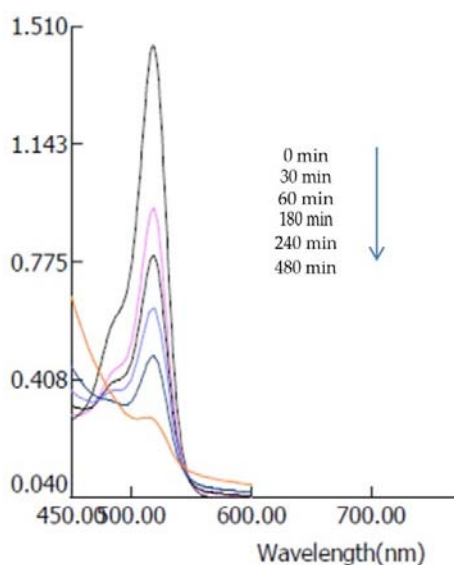


Fig. 9. Changes in the UV-vis absorption spectra of OY in optimized conditions.

After the third run, the PW_{12} were leached from the supports (shown by NAA), and this led to the deactivation of the heterogeneous catalyst. It is well known that due to solubility of PW_{12} in polar solvents, PW_{12} leaching will be significant from $\text{PW}_{12}@$ support system.

4. Conclusions

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ impregnated on V-MCF is very active as a photocatalyst towards photodecolorization of OY. Undoubtedly the MCF matrix provides a better dispersion of active sites and free accesses of the dyes molecules to these isolated sites, thereby facilitating in photocatalytic activity. The present study however, my serve as a preliminary step towards designing further studies on the photochemical aspect being in our laboratory at present.

High specifies surface area of $\text{PW}_{12}@V\text{-MCF}$ would result in high catalytic activity because the active sites (W-O-W bonds) were better spread on the surface and in the micropores of silica matrix.

Acknowledgements

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Table 3. Investigation of the feasibility of reusing of $\text{PW}_{12}@V\text{-MCF}$ in the photodegradation of OY.

Run	Degradation (%)	Amount of W leached (%) ^a
1	98	-
2	96	-
3	93	-
4	43	0.07

^aDetermined by NAA.

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