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Investigation of photocatalytic performance of keggin type heteropolyacid in degradation of methylene blue

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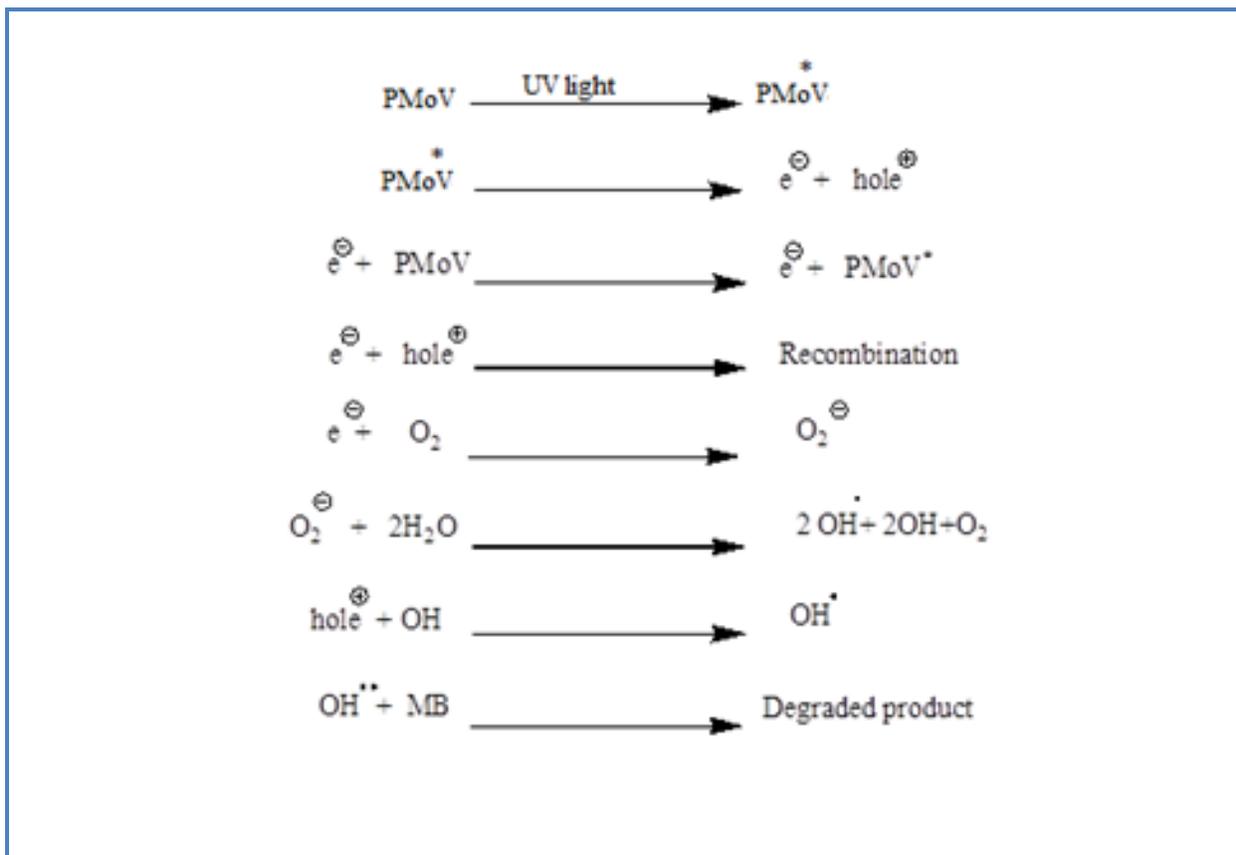b Department of Chemistry, Birjand University, 97179-414, Birjand, Iran

ABSTRACT

In this project, keggin-type polyoxometalate, cationic exchange $Q_5PMoV_2O_{40}$ (denoted as TBA-PMoV) was synthesized to produce a recovarable catalyst. This catalyst was characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), Field Emission scanning electron microscopy (FESEM) and UV-vis diffuse reflectance spectroscopy (UV-DRS). The synthesized catalyst showed high photocatalytic activity in the degradation of methylene blue as a pollutant under UV light irradiation. The effect of various factors such as catalyst amount, contact time and pH on degradation of methylene blue (denoted as MB) were investigated. Formal batch adsorption studies was applied for investigation of effects of various parameters, such as initial solution pH, initial dye concentration, catalyst amount, temperature, etc. Optimization results for 20 mg/L methylene blue showed that maximum degradation efficiency 96.8 % at the optimum conditions was found to be: catalyst amount 25 mg, pH= 7.6 and time 60 min at ambient pressure and temperature.

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Graphical Abstract

$$PMoV \xrightarrow{UV\ light} PMoV^{*}$$

$$PMoV^{*} \longrightarrow e^{\ominus} + hole^{\oplus}$$

$$e^{\ominus} + PMoV \longrightarrow e^{\ominus} + PMoV^{*}$$

$$e^{\ominus} + hole^{\oplus} \longrightarrow Recombination$$

$$e^{\ominus} + O_2 \longrightarrow O_2{}^{\ominus}$$

$$O_2{}^{\ominus} + 2H_2O \longrightarrow 2\,\dot{O}H + 2OH + O_2$$

$$hole^{\oplus} + OH \longrightarrow \dot{O}H$$

$$\ddot{O}H + MB \longrightarrow Degraded\ product$$

Introduction

The versatility and accessibility of polyoxometalates have led to various applications in the field of electrochemistry, medicine, chemistry and photochemistry [1-3]. As of not long ago, different catalytic frameworks, especially oxygenated molybdenum and tungsten compounds, have been accounted for photocatalytic reactions. Among them, the interest for the use of hetropolyacids (HPAs) has been expanded significantly, due to their high activities in mild conditions for catalytic and photocatalytic applications [4-6]. In addition, among different structures of polyoxometalates as participate in photocatalysts, keggin type hetropolyacid is of particular importance because of its high chemical and mechanical resistance under reaction conditions. In addition, the lowest vacant d molecular orbital in octahedra (MO_6) of this structure is a nonbonding metal-centered causing its reversible reduction to form multivalance species [7]. Disregarding every one of these capacities, HPAs have low surface area and high solubility in aqueous media, limiting their applications in catalytic reactions. The main obstacle to industrial applications of homogeneous polyoxometalate is that they are difficult to recover from the reaction medium. To meet such a challenge, we have unsoluble polyoxometalate in water with cationic exchange by quaternary ammonium salts.

Recently the application of polyoxometalate in degradation of dyes were reported [8-11]. Among these approaches, entrapment of POMs into the inorganic matrix was considered as an attractive methodology for sensor fabrication due to stability and simplicity. Many efforts, including immobilization of POMs on inorganic support have been devoted. Polyoxometalate has empty d orbitals and can be used as good electron acceptors. POM, which are available from accessible materials via the simple method of synthesis and which are easily seperatable by centrifuging in hemogeneous system, have attracted much attention in the past few decades due to their vast applications including drug delivery, biosensors, supported immobilization, environmental remediation and so on. Recently, their applications as catalyst has become a hot subject due to such unique properties as high stability, good dispersion, high catalytic and photocatalytic activity as well as low toxicity. The most attractive feature of polyoxometalate as catalysts is that they can be recycled by simple separation. Furthermore, improved activity is usually achieved in the nanometre-sized supported catalyst due to its high catalytic and photocatalytic activity and good dispersion properties. In the past few years, several transition-metal catalysts, organocatalysts and enzyme catalysts have been applied with good performances in degradation of dyes. Organic, inorganic as well as microbial pollutants have been reported to thrive in such waste waters. Among these, some organic and inorganic pollutants are not biodegradable, and persist in the environment for a long time. Such pollutants are toxic, pose a serious threat to the environment and are harmful to animal life and human. Toxic organic pollutants include dyes, polynuclear aromatic hydrocarbons, pesticides, polychlorinated biphenyls, plasticizers, phenols and drug residues. In addition toxic inorganic or metal ions include mercury, cadmium, antimony and lead. Now-a-days, water pollution is a serious subject due to its affects our lives and is expected to get worse over the coming decades and thus has boosted the importance of water technology. In recent years many supports such as carbon nanotube (CNT), titanium dioxide (TiO_2), mesoporous carbon material, $CNT-TiO_2$ nanocomposite, ZnO/CuO and ZnO/CdO nanocomposites have been used for degradation of dyes [12-17]. In addition several researchers investigated the dyes adsorption ability on a large variety of low cost non-conventional adsorbents such as industrial waste, agricultural waste etc [18-21]. Formal batch adsorption studies depend on different process parameters, such as initial solution pH, initial dye concentration, catalyst amount, temperature, etc. Thereupon, the main aim of the present study is to consider a novel system for photocatalytic properties for degradation of methylene blue (MB) as pollutant by using cationic exchange keggin type polyoxometalate. In addition, we describe the photocatalytic activity of the catalyst and photodegradation by UV irradiation of methylene blue as pollutants using a synthesized photocatalyst with keggin type

polyoxometalate as owing to have vacant d orbitals for exciting the electron for electron transfer reactions.

Experimental section

Materials and methods

$Na_2MoO_4.2H_2O$, $Na_2HPO_4.12H_2O$, V_2O_5, Na_2CO_3, H_2SO_4, methylene blue ($C_{16}H_{18}N_3SCl$), tetrabutylammonium bromide, were purchased from Sigma-Aldrich. All of the solvents were purchased from Fluka.

Preparation of keggin type polyoxometalate (denoted as PMoV)

Keggin type polyoxometalate (denoted as PMoV) was synthesized by before hand reported technique, to describe it briefly: 18.0 g of $Na_2HPO_4.12H_2O$ was dissolved in 250 mL distilled water and 11.5 g of V_2O_5 was dissolved in 100 mL of 2 mol /L Na_2CO_3 solution. Then, they were mixed and heated until boiling. After thirty minutes, a 400 mL solution containing 121.0 g of $Na_2MoO_4.2H_2O$ was icluded in the above solution, keeping the temperature at 90 ºC for 30 min. Then, 1:1 H_2SO_4 was added (dropwise and with stirring) to the solution until pH=2. The mixture was cooled to room temperature under stirring, and 50 mL ether was added [22].

Preparation of $(TBA)_5PV_2Mo_{10}O_{40}$

The polyoxometalate by cationic exchange (abbreviated to $Q_5PV_2Mo_{10}O_{40}$, Q = tetrabutylammonium bromide (TBA) was synthesized as follows: A solution made of quaternary ammonium (5 mmol Tetrabutyl ammonium bromide) in 20 ml ethanol was added in a dropwise manner into the 40 ml aqueous solution of $H_5PV_2Mo_{10}O_{40}$ (1 mmol); this was done under stirring at room temperature. A brown precipitate was immediately formed through a cationic exchange. Following the continuously stirring for 2 h, the resulting mixture was filtered and dried at 60 ºC in vacuum for 24h, producing the cationic exchange polyoxometalate (Q=TBA).

Characterization

The samples were ground into a fine powder for characterization. FT-IR spectra were obtained as potassium bromide pellets in the range of 400-4000 cm^{-1} with a Nicollet-Impact 400D instrument. ^{1}H NMR spectra were recorded on a Bruker 250 MHz. Scanning electron micrographs (SEM) of the catalysts and supports were taken on SEM Philips XL 30 instrument. UV–vis spectra were recorded on a 160 Shimadzu spectrophotometer. X-ray diffraction (XRD) patterns were recorded with a Philips X-ray diffractometer (Model PW1840).

Photocatalytic activity

Since heterogeneous catalysts are recoverable, heterogenization of homogeneous catalysts is of incredible interest. Therefore, we decided to synthesized cationic exchange PMoV, and investigate its photocatalytic activity in the degradation of methylene blue as pollutants. For consider photocatalytic degradation of dye methylene blue (MB) was selected as model dye. The degradation of Methylene Blue (MB) was probed in the aqueous solution, using UV light irradiation. Due to the imporance of the preadsorption of dyes before irradiation for photocatalysis experiments, the preadsorption degree of MB, using the synthesized catalyst, was measured at ca. 663 nm.

Characterization of $Q_5PV_2Mo_{10}O_{40}$

It is well known that all R_4N^+ counter ions exhibit a very low polarizing power. They are not hydrogen-bond donors, thereby giving water-free compounds with polyanions. So, according to the zero-order approximation, all the R_4N^+ with the same polyanions could be expected to give the same spectra (apart from the bands characteristic of the cations) [23]. Figure 1 shows the FT-IR spectrum of freshly prepared keggin polyoxometalate before and after treating by tetrabutylammonium bromide (denoted as TBA-POM). In the FT-IR spectrum of TBA-POM, the peaks that were observed at 2852 and 2924 cm $^{-1}$ were assigned to the symmetric and asymmetric stretching vibrations of $-CH_2$ group of tetrabutylammonium; on the other hand, 1476 was attributed to C-H scissoring vibrations of CH_3-N^+ moiety. Absorption bands were observed at 1064, 945, 867, 868 and 789 cm^{-1}. These peaks could be attributed to (P=Oa), (Mo=Ot), (Mo-O_b-Mo) and (Mo-O_c-Mo). (Ot= terminal oxygen, O_b = bridged oxygen of two octahedrals sharing a corner, and O_c = bridged oxygen sharing an edge). UV-vis spectrum of this polyoxometalate had absorption peaks around 223nm and 325 nm. These peaks could be assigned to the metal–oxygen charge transfer absorption (Figure 2).
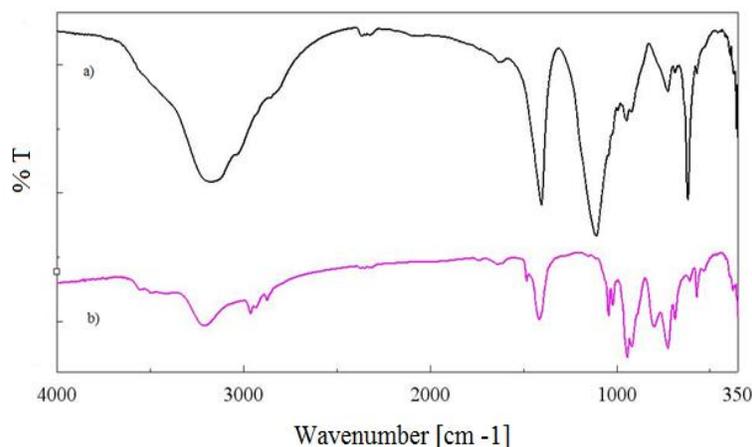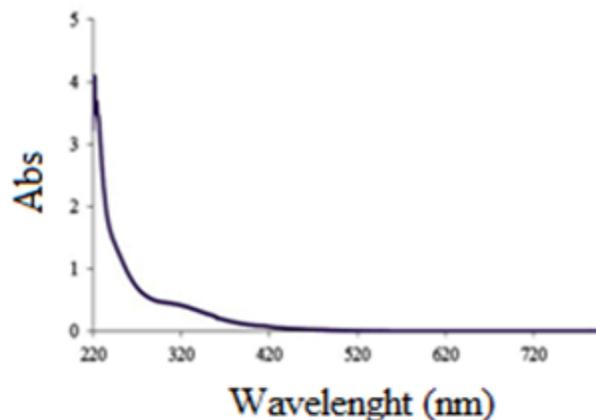
Figure 1. FT-IR spectrum of a) fresh PMoV and b) TBA-PMoV.

Figure 2. UV-vis spectrum of $(TBA)_5PMo_{10}V_2$ in acetonitrile (223, 325 nm).

The morphology of freshly prepared the prepared $(TBA)_5PV_2Mo_{10}O_{40}$ were studied by SEM and the size of nanoparticles for $(TBA)_5PV_2Mo_{10}O_{40}$, it was in the range of 20-25 nm (Figure 3). The large particle size for $(TBA)_5PV_2Mo_{10}O_{40}$ campare to keggin polyoxometalate (PMoV) could be due to the larger size of the cations(tetrabutylammonium) instead of hydrogen cations in the prepared cationic exchange polyoxometalate.
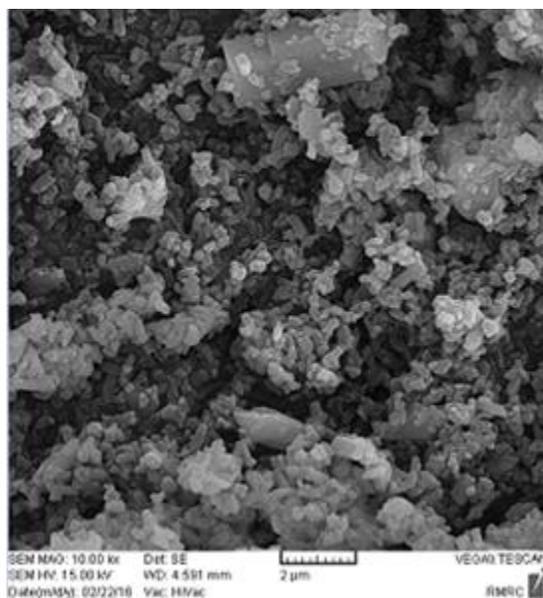
Figure 3. SEM image of TBA-PMoV

^{1}HNMR study of TBA-PMoV showed peaks at 1-4 ppm for CH_2 and CH_3 groups in this structure (Figure 4).These peaks belonged to hydrogen's tetrabutylammonium bromide in TBA-PMoV. Figure 5 shows the XRD patterns of TBA-PMoV. This pattern confirmed that characteristic peaks in PMoV

were present in TBA-PMoV and the structure of keggin polyoxometalate remaind in the cationic exchange polyoxometalate.
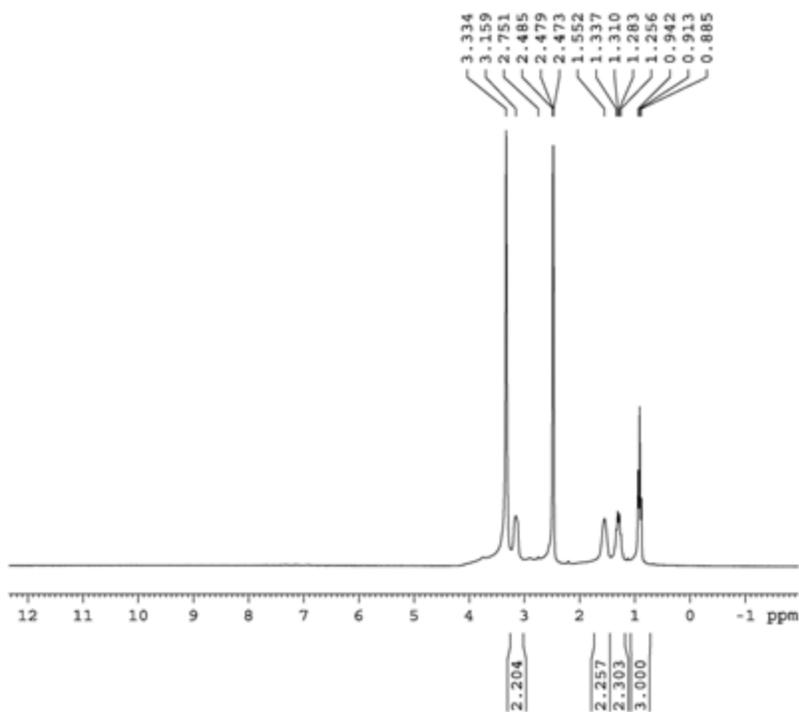
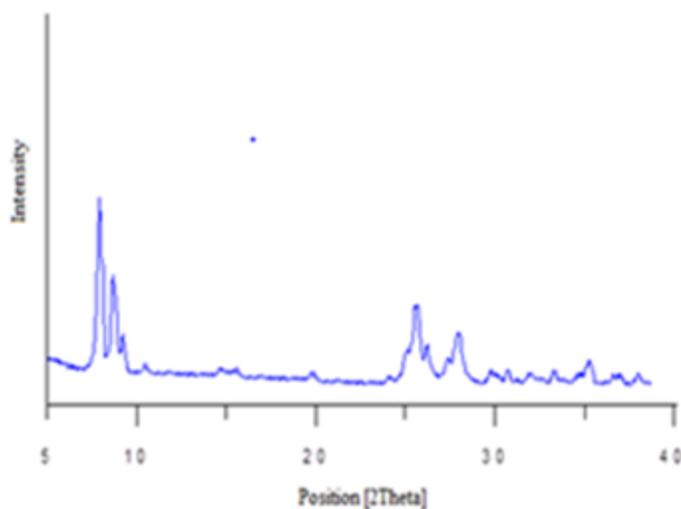

Figure 4. 1HNMR spectrum of TBA-PMoV

Figure 5. XRD patterns of TBA- PMoV.

Degradation of methylene blue (MB)

Methylene blue was selected as a model dye for consideration of photocatalytic degradation of dyes as pollutants. Methylene blue is a heterocyclic aromatic chemical compound with the molecular

formula $C_{16}H_{18}N_3SCl$. At room temperature it appears as an odourless dark green powder, which yields a blue solution when dissolved in water and gives a characteristic spectrophotometric absorbance at 663 nm. It has many applications in the various fields. Methylene Blue (MB) is a cationic dye, extensively used in a variety of industrial application with main applications in coir and textile industries. It is most commonly used dye for coloring cotton, wood, paper stocks, and silk. It is also utilized in the field of medicine [24]. Scheme 1 shows the structure and spectrum of MB.
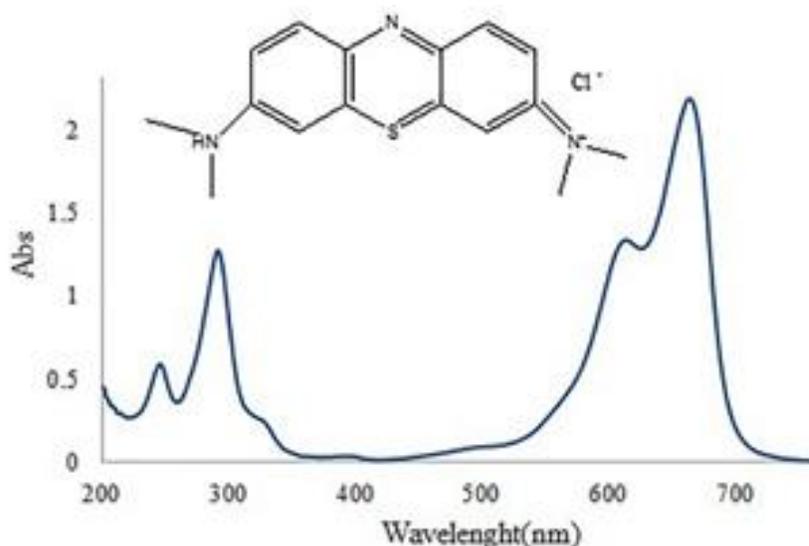
Scheme 1. Structure and UV-vis spectrum of methylene blue.

The photocatalytic reactions were performed for 20 mg/L initial concentration of MB under different experimental conditions, using different amounts of catalyst, time and various pH for degradation of methylene blue; this was done without irradiation, and the pH conditions were changed from acidic to basic.

Effect of various factors on the photocatalytic degradation of methylene blue

The influence of various factors on the photocatalytic degradation of methylene blue was investigated and we examined effects of pH, the amount of catalyst and time on the photocatalytic degradation of MB as pollutants. For consideration of the effect of time on the photocatalytic procedure studies involve a 30 mL of 20 mg/L aqueous solution of methylene blue with a certain catalyst amount, which was optimized by the above experiment. Before irradiation the system was magnetically stirred for 15 minutes under dark to establish the adsorption-desorption equilibrium between the catalytic surface and the dye. After placing under UV irradiation, around 3 mL of the suspension was pipette out from the solution at an interval of 15 minutes. The pipetted sample was

centrifuged and measured the absorbance at 663 nm. In addition the influence of time on the degradation of dyes was examined for 30 min up to 150 min and the results showed that with increasing the time the degradation was increased, but after 60 min the degradation was nearly constant, so the optimized time was 60 min (Figure 6).
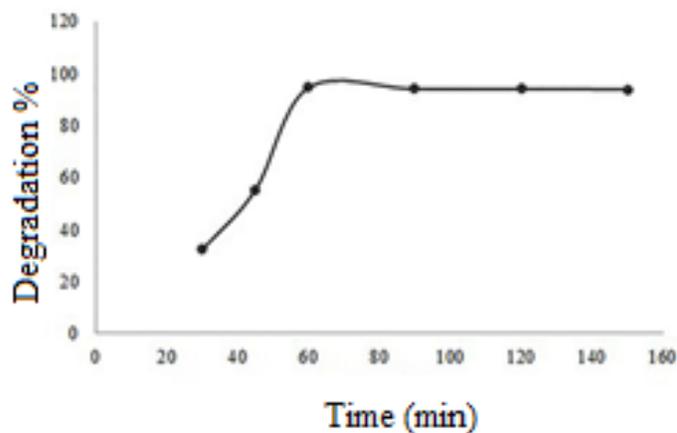

Figure 6. Effect of time on photocatalytic degradation of methylene blue.

Accordingly, dye degradation was studied at various pHs as one of the important factors. It was revealed that optimized pH was 7.6. The wastewater from textile industries usually has a wide range of pH values, so the interpretation of pH effects on the efficiency of dye photodegradation process is a very difficult task because of its multiple roles. First, is related to the ionization state of the surface according to the following reactions, as well as to that of reactant dyes and products such as acids and amines. pH changes can be thus influence the adsorption of dye molecules onto the modified polyoxometalate surfaces, an important step for the photocatalytic oxidation to take place. Generally, pH has a vital role in the characteristics of textile wastes and in the generation of hydroxyl radicals. Hence, attempts have been made to study the influence of pH in the degradation of dyes. In this study the pH was changed at 5 to 9 and optimized pH was obtained at 7.6 (Figure 7).
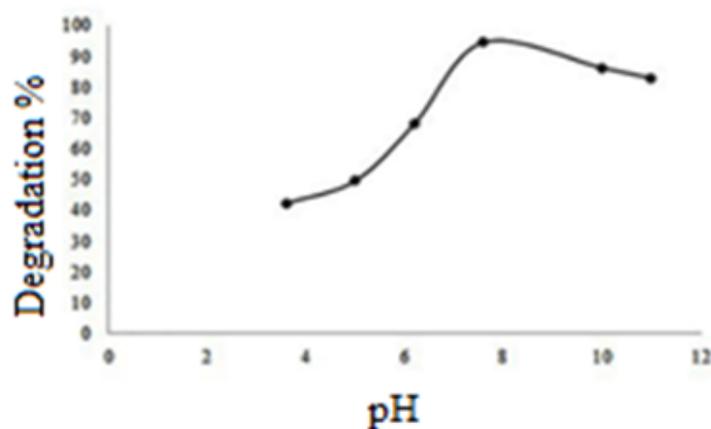
Figure 7. Effect of pH on photocatalytic degradation of methylene blue.

For investigation of effect of catalyst amount on the photocatalytic activity in degradation of methylene blue it was found that the optimum amount of the catalyst for the photocatalytic degradation of methylene blue was around 25 mg of the synthesized catalyst which was made for 30 mL of the methylene blue dye solution, as displayed in Fig. 8. The rate of dye degradation was increased by enhancing the amount of catalyst. This could be due to the increase in the exposed surface area of the catalyst. However, it must be noted that after a certain limit (25 mg), if the amount of catalyst had been increased further, there would have been a saturation point. Both the number of active sites on photocatalyst and the penetration of light through the suspension are influence by the amount of photocatalyst. The increase in the loading of photocatalyst can increase the rate of the deactivation of activated molecules by collision with the ground state photocatalyst.
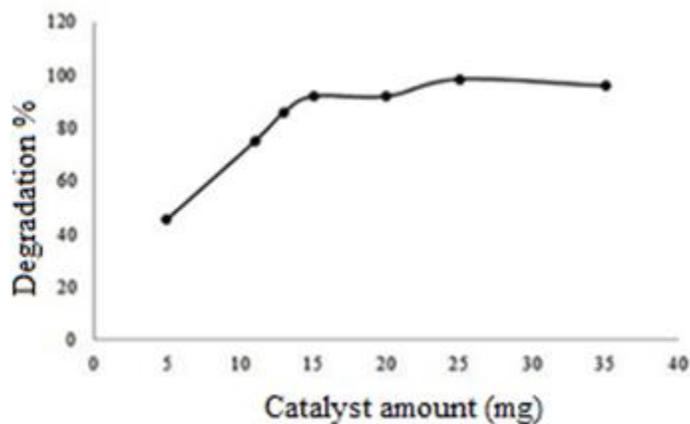

Figure 8. Effect of catalyst amount on photocatalytic degradation of methylene blue

For considering the effect of methylene blue concentration on the photocatalytic activity, the experiments were performed at 6 different dye concentrations (20, 30, 50, 60, 80, 100). Fig. 9 shows that percentage degradation by catalyst is decreased by increasing the initial dye concentration from 20 to 60 mg/L and pH=7.6. The reduction of degradation by raising the dye concentration can be explained by the decrease in active sites on the adsorbent surface due to aggregation of particles. In addition, after 60 mg/L the degradation was nearly constant. The effect of initial dye concentration on degradation showed in Figure 9.
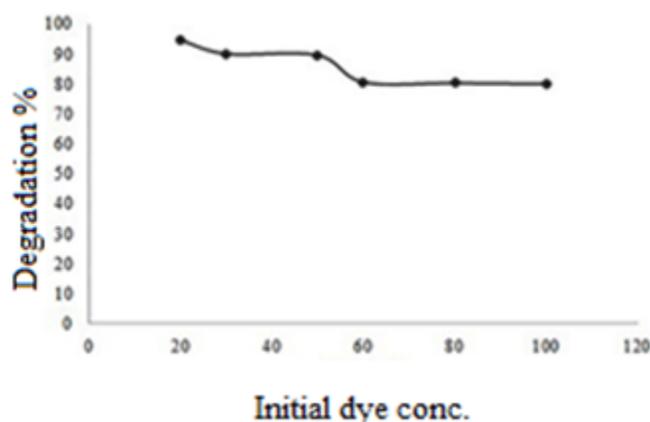

Figure 9. Effect of initial concentration of dye on the photocatalytic degradation of methylene blue, $C_o=x$ mg/L, pH=7.6, Time=60 min.

Catalytic behavior, separation and recyclability

We monitored the stability of the supported catalyst by using multiple sequential degradation of dyes with synthesized catalyst under UV light. For each of the repeated reactions, the catalyst was recovered, washed thoroughly with water and dried before being used with fresh methylene blue solution. Figure 10 shows that the catalyst was consecutively reused five times without the loss of activity.
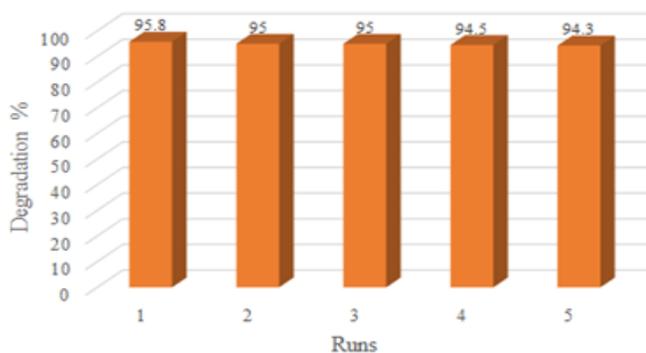

Figure 10. Reusability of catalyst in degradation of MB with synthesized catalyst.

For investigation of the catalyst was intact after photocatalytic reaction, the FT-IR spectrum of catalyst after reused was taken and the result showed the peaks corresponding to the supported catalyst was shown at 775 cm^{-1}, 840 cm^{-1}, 950 cm^{-1}, 1050 cm^{-1}, 1081 cm^{-1}, 594 cm^{-1} and 463 corresponding to catalyst structure with a shift due to the adsorption procedure (Figure 11).
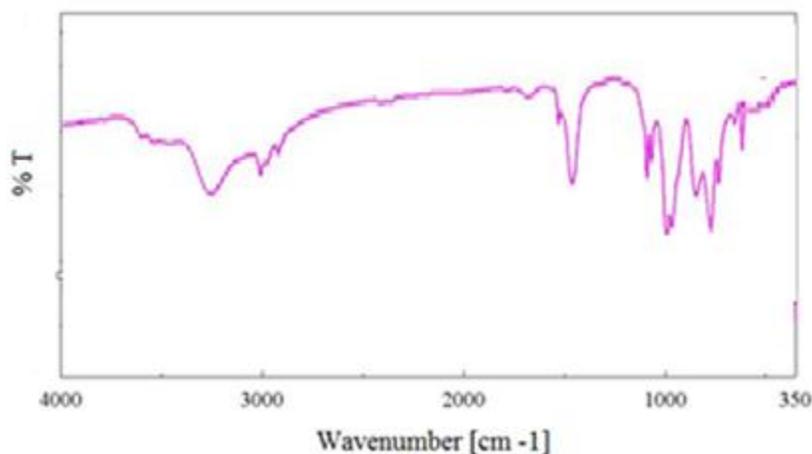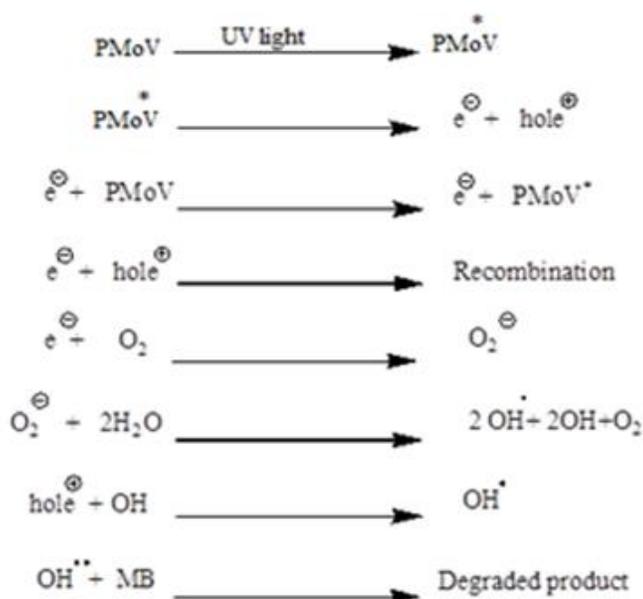

Figure 11. FT-IR spectrum of reused catalyst after degradation of MB.

Proposed mechanism for degradation of dyes under UV light irradiation

Many investigators have suggested various mechanisms for the degradation of dyes as pollutants. To exposure to UV light irradiation, the metal ions excited by light to give exited electron. This excited state will provide an electron in the conduction band leaving a hole in the valance band. This electron is then trapped by molecular O_2 forming O_2^- ions. The valance band hole generates hydroxyl radical from hydroxyl ions which can easily attack the adsorbed dye, thus leading finally to their complete mineralization. Scheme 2 suggests the photocatalytic degradation of MB pathways.

$$PMoV \xrightarrow{\text{UV light}} PMoV^{*}$$

$$PMoV^{*} \longrightarrow e^{\ominus} + hole^{\oplus}$$

$$e^{\ominus} + PMoV \longrightarrow e^{\ominus} + PMoV^{*}$$

$$e^{\ominus} + hole^{\oplus} \longrightarrow \text{Recombination}$$

$$e^{\ominus} + O_2 \longrightarrow O_2^{\ominus}$$

$$O_2^{\ominus} + 2H_2O \longrightarrow 2\overset{\cdot}{O}H + 2OH + O_2$$

$$hole^{\oplus} + OH \longrightarrow OH^{\cdot}$$

$$OH^{\cdot\cdot} + MB \longrightarrow \text{Degraded product}$$

Scheme 2. Proposed mechanism for degradation of MB by catalyst.

Conclusions

Cationic exchange PMoV was prepared by simple preparation method. This catalyst showed excellent photocatalytic activity and high performances in degradation of methylene blue and could, therefore, be reused at least five times, with only a slight decrease in photocatalytic activity.

Acknowledgement

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