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# INNOVATIVE APPROACHES FOR THE PHOTOCATALYTIC DEGRADATION OF PESTICIDES

## Abstract

Mono- and tri-vanadium-substituted Keggin-type heteropolyoxoanions  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  and  $[\text{PW}_{12}\text{O}_{40}]^{4-}$  were evaluated as photocatalysts for the photodegradation of three hazardous food pesticides: Atrazine, Chlorpyrifos and Dieldrin. Kinetic experiments were performed under UV irradiation at 254nm. The degradation of each pesticide was assessed by investigating its disappearance with time using High Performance Liquid Chromatography connected to an Ultra-Violet spectrophotometer detector (HPLC-UV). The photocatalytic degradation of the three pesticides exhibited first order kinetics. It was found that the introduction of vanadium addenda atoms into the Keggin-type polyoxometalates decrease the degradation rate for the photocatalytic transformation of each pesticide as well as the degradation percentage. This effect was significantly related to the number of vanadium metal ions substituting the tungsten addenda atoms. As a general trend, the photocatalytic efficiency of  $\{\text{XVW}_{11}\}$  was better than that of  $\{\text{XV}_3\text{W}_9\}$ . A marked drop was noticed in the photocatalytic degradation of Atrazine. 90% of Atrazine was decomposed in the presence of  $[\text{a-SiW}_{12}\text{O}_{40}]^{4-}$  at a rate of 1 ppm/min whereas the degradation percentage decreased to 55% in the presence of  $[\text{a-SiV}_{11}\text{O}_{40}]^{5-}$  at a decreased rate of 0.7 ppm/min.

## Keywords

Photocatalysts, Degradation, Atrazine, Chlorpyrifos, Dieldrin, Polyoxometalates

# INNOVATIVE APPROACHES FOR THE PHOTOCATALYTIC DEGRADATION OF PESTICIDES

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**ABSTRACT:** *Mono- and tri-vanadium-substituted Keggin-type heteropolyoxoanions  $[SiW_{12}O_{40}]^{4-}$  and  $[PW_{12}O_{40}]^{4-}$  were evaluated as photocatalysts for the photodegradation of three hazardous food pesticides: Atrazine, Chlorpyrifos and Dieldrin. Kinetic experiments were performed under UV irradiation at 254nm. The degradation of each pesticide was assessed by investigating its disappearance with time using High Performance Liquid Chromatography connected to an Ultra-Violet spectrophotometer detector (HPLC-UV). The photocatalytic degradation of the three pesticides exhibited first order kinetics. It was found that the introduction of vanadium addenda atoms into the Keggin-type polyoxometalates decrease the degradation rate for the photocatalytic transformation of each pesticide as well as the degradation percentage. This effect was significantly related to the number of vanadium metal ions substituting the tungsten addenda atoms. As a general trend, the photocatalytic efficiency of  $\{XVW_{11}\}$  was better than that of  $\{XV_3W_9\}$ . A marked drop was noticed in the photocatalytic degradation of Atrazine. 90% of Atrazine was decomposed in the presence of  $[a-SiW_{12}O_{40}]^{4-}$  at a rate of 1 ppm/min whereas the degradation percentage decreased to 55% in the presence of  $[a-SiVW_{11}O_{40}]^{5-}$  at a decreased rate of 0.7 ppm/min.*

**KEYWORDS:** *Photocatalysts, Degradation, Atrazine, Chlorpyrifos, Dieldrin, Polyoxometalates*

## 1. INTRODUCTION

Photocatalysis based on Polyoxometalates (POMs) is a very promising Advanced Oxidation Process (AOP) for organic contamination in different matrices (Arántegui, 1995) (Arnold, 1995) (Balmer, 1999), 1999). This method is among different processes that are based on the irradiation of UV light to the photocatalyst leading to the production of hydroxyl radicals (as shown as Fig. 1) (Chen, 2006). POMs generally contain more than one type of metal and have been increasingly recognized as unique class of metal oxide clusters that can be efficient candidates for wide catalytic applications (Keyes, 2003) (Troupis, 2003) (Zhang, 2006). These complexes are highly stable at most of the redox states and are able to participate in multiple and reversible electron reductions without affecting their structure (Song, 2013). Upon light irradiation in the region of  $\lambda = 200-500$  nm, the light absorption is attributed to Ligand Metal Charge Transfer (LMCT) bands, thus an electron on a doubly occupied bonding orbital (HOMO) is promoted is excited to an empty antibonding orbital (LUMO). As a consequence, these as photoexcited species are highly reactive and can play the role of good reducing agent as well as oxidizing agent (Botar, 2009).

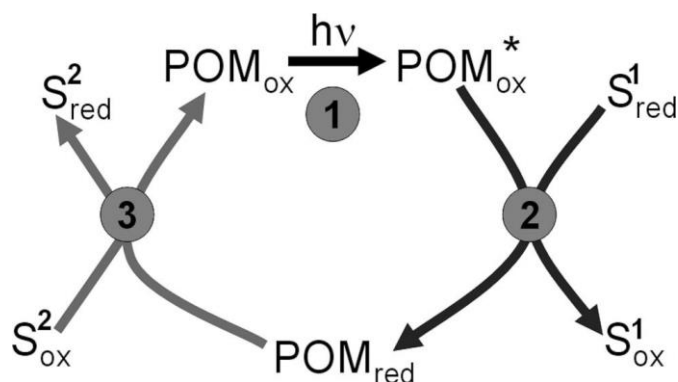


Fig. 1 A General scheme of the POM Photoredox Cycle  
Reference: (Botar, 2009)

The most dominant class of POMs is the heteropolyoxometalates of the Keggin-structure  $[XM_{12}O_{40}]^n$  with  $X = Si, P,$  and  $S; M = Mo$  or  $W$ . However, most of the electrochemical catalytic studies have focused on the tungstate chemistry over years (Wang, 2015) (Li, 2002) (López, 2001). Moreover, less attention was drawn to the electrocatalytic activity of the vanadium-substituted tungstates. The replacement of  $W^{VI}$  with  $V^V$  changes the electrochemical properties of the polyoxometalates as well as it introduces new redox properties (Li, 2009). The HOMO–LUMO gap is 2.2 eV in tri-vanadium-substituted tungstates that is only 0.6 eV smaller than the parent  $[SiW_{12}O_{40}]^{4-}$  anion (López, 2012). In addition, the incorporation of vanadium into 1:12

Keggin compounds shifts the absorption to higher wavelengths and its stability to higher pH values (Argitis, 1986) (Liu, 2016).

Herein, we report the photocatalytic activity of mono-, di- and tri-vanadium-substituted Keggin-type heteropolyoxoanions  $[SiW_{12}O_{40}]^{4-}$  and  $[PW_{12}O_{40}]^{4-}$  (as shown as Fig. 2) on the mineralization of three hazardous pesticides: Atrazine, Chlorpyrifos and Dieldrin, under UV irradiation at 254 nm for different time intervals. These chemicals are among the various organic substances, which are known as persistent pollutants in the environment (Reddy, 2015). The studied pesticides belong to three different chemical classes: Triazine Herbicides, Organophosphorus and Organochlorine Insecticides respectively. Both Atrazine and Chlorpyrifos were banned since 2008 by the European Union however the American Environmental Protection Agency (US-EPA) set strict regulations on their uses in agriculture (EEA, 2015) (EPA, 2015). On the other hand, Dieldrin is now banned in most countries all over the world due to its extremely persistence and high ability to enter our food chain.

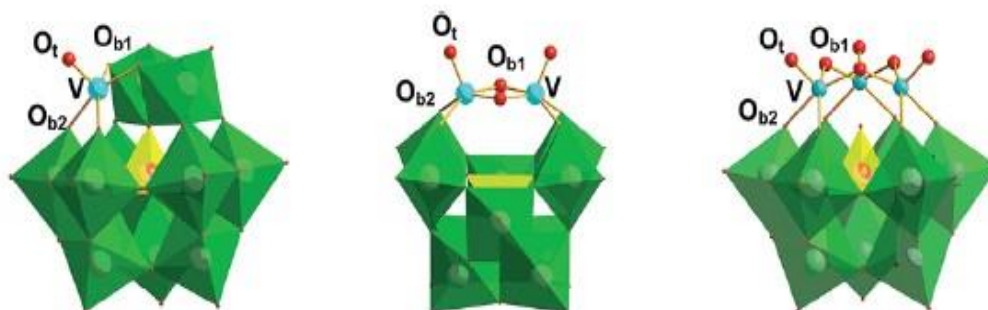


Fig. 2 The Structures of Vanadium Substituted Keggin POMs  
Reference: (Li, 2009)

## 2. MATERIALS and METHODS

All chemicals were purchased from Sigma Aldrich. The examined Polyoxometalates were synthesized according to published procedures in the literature (Canny, 1986). Standard solution of each pesticide was prepared in acetonitrile solvent (HPLC-grade) at 200 ppm and stored in dark vial at 0°C maximum for 15 days. Calibration curve for each tested analyte was obtained using freshly prepared pesticide's solutions. Aqueous solutions of the mixture (Pesticide + POM) were prepared freshly by mixing the same mass of the tested POM in its powder form in 100 ppm pesticide's solution.

All mixtures were irradiated using AC glass photoreactor for 90 minutes in case of Atrazine and 120 minutes for both Chlorpyrifos and Dieldrin. Oriel 100W Mercury lamp was used equipped with a cool water circulating system. Atrazine mixtures were irradiated for 90 minutes whereas those of Chlorpyrifos and Dieldrin were irradiated for 120 minutes. All experiments were repeated twice and the percent relative standard deviation was found below 0.97 %.

The concentration of each pesticide was determined by High Performance Liquid Chromatography (HPLC) coupled to UV detector every 10 minutes. A reversed phase HS C18 analytical column by Supelco (25cm x 4.6mm, 5µm) was used. The injection volume was 20 µL.

For Atrazine, the gradient elution was as the following: acetonitrile/water (30:70, v/v) for 5 minutes, then acetonitrile/water (70:30, v/v) for 10 minutes and finally return to the initial condition for 2 minutes at a flow rate of 1 mL/min. The detector wavelength was set at 222 nm.

For Chlorpyrifos, the isocratic elution was as the following: 40% methanol + 60% water. The flow rate was set at 1.2 mL/min. The detector wavelength was set at 228 nm.

For Dieldrin, the gradient elution was as the following: acetonitrile/water (80:20, v/v) for 15 minutes, then acetonitrile 100% for 10 minutes at a flow rate of 1 mL/min. The detector wavelength was set at 218 nm.

## 3. RESULTS and Discussion

The degradation percentage of each pesticide in the presence of the examined polyoxometalates is reported as shown as Fig. 3. As shown, the UV irradiation is an important factor to enhance the catalytic mineralization of all the analytes. The photocatalytic degradation of Atrazine is prominent over the other pesticides in the presence of all photocatalysts under both conditions. 90% of Atrazine was degraded in the presence of {SiW<sub>12</sub>} whereas just 57% was decomposed in the presence of {PW<sub>12</sub>}. Moreover, the nature of the heteroatom affects the photocatalytic activity of polyoxometalates. The Si-based POMs gave better results than P-based ones. The long Si-O comparing to that of P-O increases the electron density on the tungsten atoms in the Keggin structured {SiW<sub>12</sub>} thus affecting the redox properties of these metal oxide clusters (Allmen, 2015).

On the other hand, the replacement of tungsten by vanadium in both {SiW<sub>12</sub>} and {PW<sub>12</sub>} had a negative effect on the degradation percentage of all the tested pesticides. This effect was dominant in tri-vanadium – substituted tungstates. In Si-based POMs, the degradation percentage drops from 90% to 38%, 83% to 32% and 60% to 23% for Atrazine, Chlorpyrifos and Dieldrin respectively. Similar effect was observed in P-based POMs. This can be contributed that the incorporation of vanadium into Keggin metal oxides shifts the absorption to higher wavelengths, thus allowing photochemistry to be performed well into the area of high-intensity solar light (Galloni, 2015). Shorter wavelengths lead to more production of photons thus higher photocatalytic effect (Devi). The addition of a more electronegative ion as V<sup>5+</sup> changes the charge basicity as well as the HOMO-LUMO band gap thus different redox behavior in our experimental conditions (Keita, 2002). As well as, the replacement of tungsten by vanadium decreases the photosensitivity of the clusters despite the more positive reduction potential, with the greater negative charge on polyoxometalates which disfavors the reaction with the organic compounds (Papaconstantinou, 1989). Moreover, the metal doping of V<sup>5+</sup> on the surface of the most common photocatalysts TiO<sub>2</sub> and ZnO<sub>2</sub> for pesticides' degradation decreases the photocatalytic efficiency (Wang, 2012) (Khaki, 2017).

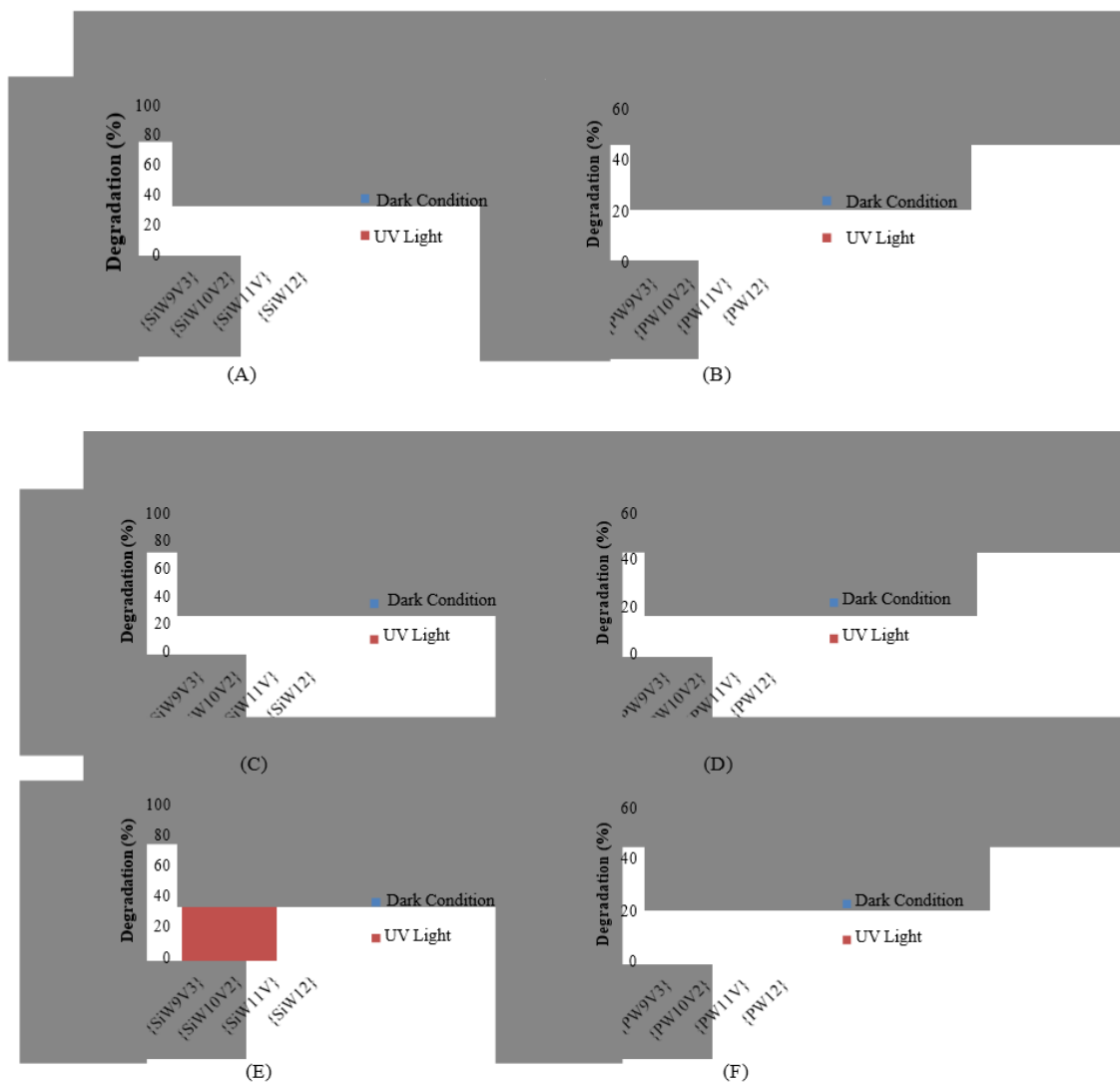


Fig. 3 The Degradation Percentage of Atrazine (A & B), Chlorpyrifos (C & D), and Dieldrin (E & F) in the presence of examined POMs under Dark Condition and UV Light

The kinetic behavior of all the catalytic reactions of the tested analytes in the presence of the two Keggin structured catalysts is illustrated as shown as Fig. 4 and Fig. 5. It is obvious that the photocatalytic degradation of the three pesticides exhibited first order kinetics despite the nature of the present catalyst. The first order of Atrazine and Chlorpyrifos photodegradation under the UV irradiation at 254 nm was also observed in several works (Moreira, 2017) (Wang, 2006).

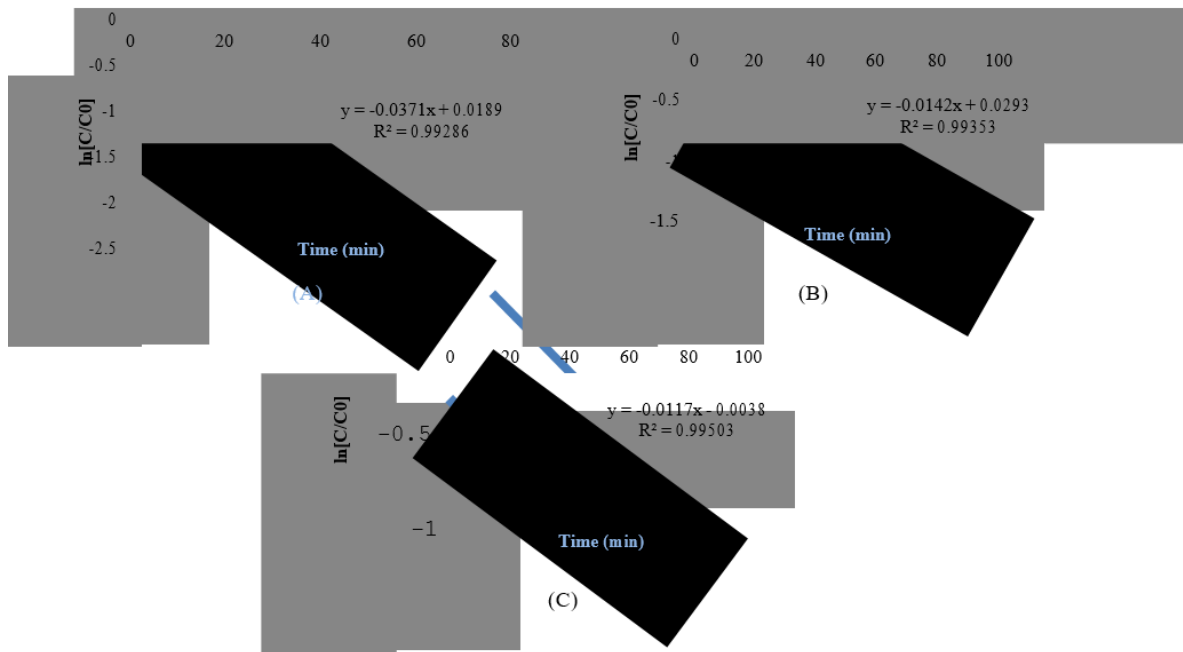


Fig. 4 The First Kinetic Order of Photodegradation of Atrazine (A), Chlorpyrifos (B), and Dieldrin (C) in the presence of  $\{SiW_{12}\}$  under 254 nm UV Irradiation.

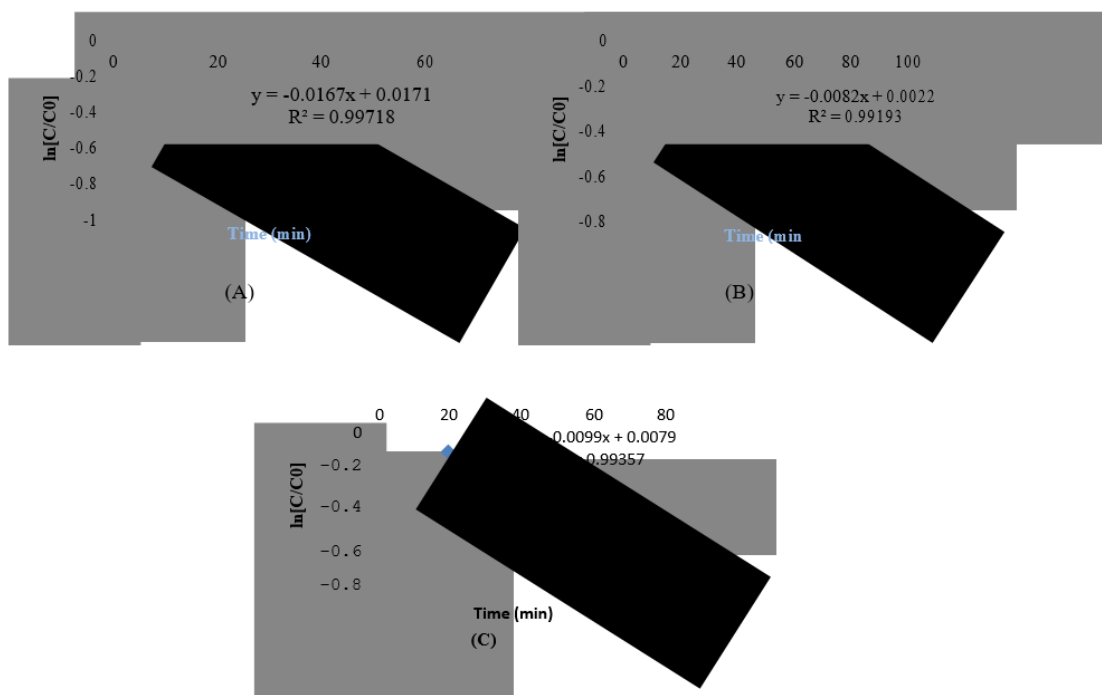


Fig. 5 The First Kinetic Order of Photodegradation of Atrazine (A), Chlorpyrifos (B), and Dieldrin (C) in the presence of  $\{PW_{12}\}$  under 254 nm UV Irradiation

Fig. 6 and Fig. 7 illustrate the variation of the rate constant of each reaction as the number of substituted vanadium ions in the tungstate clusters increases. It is clear that the rate constant decreases as the number of  $V^{5+}$  increases in both Keggin polyoxometalates. Moreover, the highest rate was achieved in the photocatalytic

degradation of Atrazine in the presence of  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  as a photocatalyst. Dieldrin showed the lowest degradation rate in the presence of Si-based POMs. This can be attributed that this pesticide is the most persistent among the studied ones. However, an important observation was noticed in the presence of P-based POMs. The photodegradation of Dieldrin is slightly faster than that of Chlorpyrifos upon irradiation in the presence of  $\{\text{PW}_{12}\}$  although more Chlorpyrifos was degraded. The rate constant for Dieldrin was found to be  $0.99 \times 10^{-2} \text{ min}^{-1}$  and that for Chlorpyrifos  $0.82 \times 10^{-2} \text{ min}^{-1}$ .

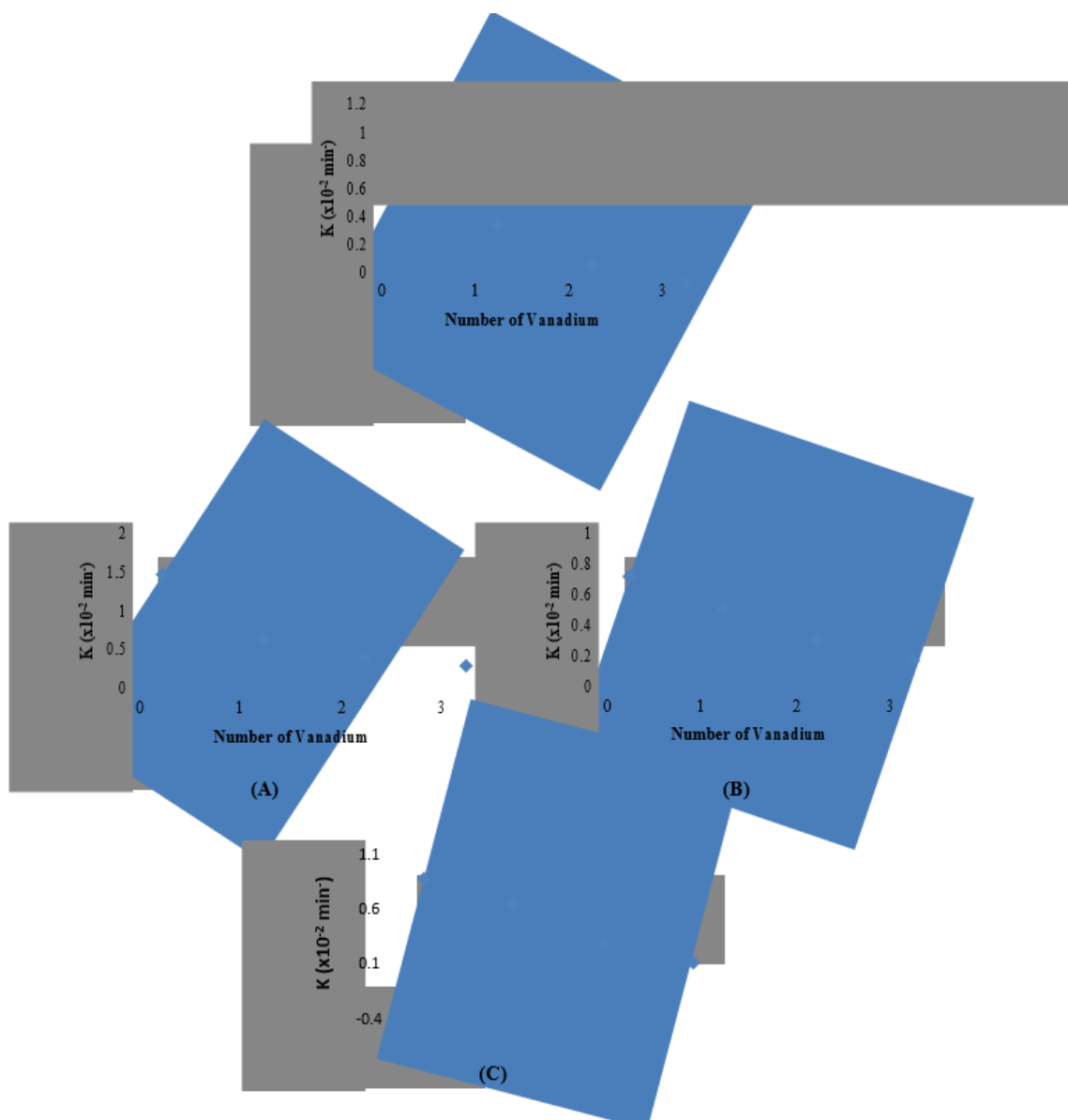


Fig. 6 and 7

- 6: The Rate Constant as a function of number of Vanadium in Si-based POMs for the Photocatalytic Degradation of Atrazine (A), Chlorpyrifos (B), and Dieldrin (C)
- 7: The Rate Constant as a function of number of Vanadium in P-based POMs for the Photocatalytic Degradation of Atrazine (A), Chlorpyrifos (B), and Dieldrin (C)



#### 4. CONCLUSION

This study is an innovative approach for the effect of incorporation of vanadium ion  $V^{5+}$  into dodecatungstosilicate and dodecatungstophosphate photocatalysts on the photodegradation of pesticides. The replacement of tungsten by vanadium had a negative effect on the photocatalytic degradation processes. This effect was enhanced as the number of vanadium substituted increased. The Keggin structured metal oxide cluster  $[a-SiW_{12}O_{40}]^{4-}$  showed the better catalytic activity for the mineralization of all the three tested pesticides upon UV irradiation at 254 nm. 90% of Atrazine was degraded whereas 83% of Chlorpyrifos and 60% of Dieldrin were decomposed under the studied conditions. All the reactions were found to obey first order kinetic rule. The rate constant was inversely proportional to the number of vanadium ions. This work is a prominent study for the photocatalytic degradation of pesticides that can contaminate our food chain and environment as well as an important illustration for the usage of polyoxometalates as photocatalysts.

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