InVO$_4$/TiO$_2$ composite for visible-light photocatalytic degradation of 2-chlorophenol in wastewater

J. Rashid[a], M. A. Barakat[abc], S. L. Pettit[d] & J. N. Kuhn[d]

[a] Department of Environmental Sciences, Faculty of Meteorology and Environment, King Abdulaziz University (KAU), Jeddah, Saudi Arabia

[b] Central Metallurgical R & D Institute, Helwan, Cairo 11421, Egypt

[c] Center of Excellence in Environmental Studies (CEES), King Abdulaziz University, Jeddah, Saudi Arabia

[d] Department of Chemical & Biomedical Engineering, University of South Florida, Tampa, Fl, USA

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J. Rashid[a], M. A. Barakat[a,b,c*], S. L. Pettit[d] and J. N. Kuhn[d]

[a]*Department of Environmental Sciences, Faculty of Meteorology and Environment, King Abdulaziz University (KAU), Jeddah, Saudi Arabia;* [b]*Central Metallurgical R & D Institute, Helwan, Cairo 11421, Egypt;* [c]*Center of Excellence in Environmental Studies (CEES), King Abdulaziz University, Jeddah, Saudi Arabia;* [d]*Department of Chemical & Biomedical Engineering, University of South Florida, Tampa, Fl, USA*

InVO$_4$/TiO$_2$ composite was synthesized via amalgamation of InVO$_4$ with TiO$_2$ (Degussa P-25) powders. Application of the produced composite was evaluated as a catalyst for visible-light photocatalytic degradation of 2-chlorophenol (2-CP) in synthetic wastewater solutions. The catalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy energy dispersive X-ray microanalyses and nitrogen physisorption. The degradation of 2-CP was affected by solution pH, light intensity, photocatalyst dosage and 2-CP initial concentration. InVO$_4$/TiO$_2$ showed higher photocatalytic degradation of 2-CP as compared with Degussa P-25 TiO$_2$. Complete degradation of 2-CP was achieved with the InVO$_4$/TiO$_2$ catalyst under optimized conditions (1 g/L catalyst with a pollutant concentration of 50 mg/L at solution pH 5 and irradiation time of 180 min). Comparatively, 2-CP degradation efficiency of 50.5% was achieved with the TiO$_2$ (Degussa P-25) at the same experimental conditions. The study confirmed that InVO$_4$/TiO$_2$ has high potential for degradation of 2-CP from wastewater under visible-light irradiation.

Keywords: advanced oxidation process; InVO$_4$/TiO$_2$ composite; 2-chlorophenol; visible-light photocatalysis; wastewater

1. Introduction

Phenolic compounds, especially chlorophenols (CPs), are a well-known group of hazardous chemicals that are highly poisonous in nature, weakly biodegradable and retained in the environment for long periods.[1] CPs are commonly utilized in a wide range of domestic, industrial and agricultural applications.[2,3] 2-chlorophenol (2-CP) is used for the production of azo dyes and vulcanization accelerators. 4-CP is used as a refining solvent, disinfectant, denaturant and antifungal agent. Environmental concerns over the release of CPs into surface and groundwater are mainly due to their toxicity to organisms, potential mutagenic and carcinogenic effects and their ability to render odour and taste at concentrations as low as 0.005 mg/L.[4–6] Degradation of pervasive and toxic CPs is critically important. Conventional technologies for wastewater treatment, such as solvent extraction, adsorption using activated carbon and chemical treatment processes like oxidation by ozone (O$_3$), create harmful by-products, generate solid waste and increase disposal and regeneration costs.[7] Furthermore, the phytotoxic effects on the active micro-organisms make biological treatments a less preferable choice for the treatment of CP-containing wastewater.[8]

Advanced oxidation processes involve the complete oxidation of organic compounds into simple products, such as CO$_2$ and H$_2$O, and are a promising emerging technology.[9–12] Crystalline titanium dioxide activated by ultraviolet (UV) radiation is considered a prominent candidate for breaking down a wide range of organic compounds.[13–16] A series of hydroxylation reactions at the catalyst surface in contact with surrounding water result in the formation of hydroxyl radicals, which attack the organic pollutants forming several oxygenated intermediates and eventually resulting in total mineralization into CO$_2$ and H$_2$O.[17–19] Dependence of TiO$_2$ photocatalysis on UV irradiation due to its energy band gap ($\approx 3.0-3.2$ eV) is a limiting factor, as the use of UV radiation is very expensive and prolonged exposure to UV radiation can have chronic health effects, such as premature ageing of the skin, suppression of the immune system, damage to the eyes and skin cancer.[20]

Current research efforts have been focused on developing photocatalytic systems that can efficiently utilize visible light and/or sun light and on shifting the optical response of TiO$_2$ photocatalyst into the visible spectrum.[21–24] Surface modification by doping with metal ions and metal co-deposition can generate intermediate energy impurity states in the band gap of TiO$_2$ and thus increase the transfer of electrons from the valance band of TiO$_2$ and promote formation of electron hole pairs.[25–28] Recently, InVO$_4$ has been reported to be very active in photocatalytic splitting

of water into H_2 and O_2 under visible-light irradiation.[29] The band gap of $InVO_4$ has been experimentally determined in the range of 1.9–2.0 eV.[30,31] Further, it has been shown to have several sub-band gap transitions, including absorption onsets at 2.3 and 2.8 eV in the visible range.[31] The addition of $InVO_4$ to TiO_2 produces a red shift in the absorption edge resulting in a band gap of 2.2–2.3 eV for the composite.[32,33] This indicates that the $InVO_4/TiO_2$ composite photocatalyst may be active in visible-light-induced photocatalysis. To the best of our knowledge, no work has been performed to investigate the efficiency of $InVO_4/TiO_2$ as visible-light photocatalyst for degradation of 2-CP.

2. Experimental design

2.1. Materials

Titanium dioxide (TiO_2) P-25 was procured from Evonik Degussa. Indium (III) oxide (In_2O_3, 99.99%) and vanadium (V) oxide (V_2O_5, 99.2%) were procured from Alfa Aesar. Hydrochloric acid (HCl, 37%), ammonia solution (10−35%) and diethylenetriaminepentaacetic acid (DTPA, 98 + %) were of reagent grade. Standard grade 2-chlorophenol (Merck) was utilized as pollutant in synthetic wastewater for the photodegradation experiments. The visible-light sources were 20–150 W metal halide lamps with UV cut-off filter (Osram Powerball HCl-T). The spectral irradiance for the visible lamp was 390–780 nm, according to the information provided by the manufacturer.

2.2. Synthesis of InVO₄/TiO₂

$InVO_4$ was synthesized using an organic precursor method with freshly precipitated $In(OH)_3$ in a manner similar to the synthesis presented by Zhang.[31] Under continuous stirring, 5.0 g In_2O_3 was dissolved in 30 mL of HCl at 65°C. The ammonia solution was slowly added (in excess). The supernatant was decanted and the $In(OH)_3$ precipitate was washed several times with deionized water. Under continuous stirring, 29.5 g of DTPA was dissolved in 50 mL of deionized water at 85°C. Stoichiometric amounts (In/V = 1/1) of $In(OH)_3$ and V_2O_5 were added to the DTPA solution. The resulting slurry was air dried at room temperature until a brittle, glass-like material formed. The material was ground using mortar and pestle prior to calcination in stagnant air. Calcination was carried out at a 3°C/min ramp rate to 600°C and held for 400 min. The resulting $InVO_4$ powder was mixed at a two percent weight basis with TiO_2, which was determined as the optimal $InVO_4$ to titania ratio in a previous study [34] focused on methyl orange as a model pollutant. In small batches, the mixed powders were ground with an agate mortar and pestle for 15 min.

2.3. Characterization of InVO₄/TiO₂

Scanning electron microscopy (SEM) images and elemental maps were obtained using a Hitachi S-800 scanning electron microscope equipped with an energy dispersive X-ray microanalysis (EDAX) system. Crystallographic information was analysed by powder X-ray diffraction (XRD). XRD patterns were measured with a Philips PANalytical X'pert PRO X-ray diffractometer using CuKα radiation (45 kV accelerating voltage and 20 ma applied current). The surface area was determined by the Brunauer–Emmett–Teller (BET) method using a Quantachrome Autosorb IQ.

2.4. Photocatalytic Experiments

The visible-light photocatalytic activity of $InVO_4/TiO_2$ composite for 2-CP decomposition was evaluated in a 1 L standard immersion well cylindrical pyrex cell reactor. The visible-light source was placed in a vertically arranged quartz immersion tube surrounded by a separate cooling tube immersed inside the reactor. A fixed amount of $InVO_4/TiO_2$ was added to a 1000 mL 2-CP solution of various concentrations under constant stirring and aerobic conditions. As determined in a previous study, a constant supply of O_2 is necessary for consistent measurement of phenol photodegradation rates.[35] Excluding light intensity trials, all other photocatalytic experiments were carried out under 150 W visible-light irradiation produced by Osram Powerball metal halide lamps. The photocatalytic experiments were performed with an irradiation time of 180 min.

2.4.1. Adsorption and photolytic studies.

The adsorption of 50 mg/L 2-CP solution was performed by adding 1 g/L of $InVO_4/TiO_2$ into the photoreactor. The reaction mixture was stirred at 750 rpm under dark conditions at 25°C and pH = 5 for 180 min. For the photolytic study, the 2-CP solution of 50 mg/L was put into the photoreactor under visible light (Osram Powerball 150 W) for 180 min without photocatalyst at pH = 5.

2.4.2. Photocatalytic degradation

The photodegradation experiments were carried out for an initial 30 min under dark conditions to establish equilibrium of 2-CP adsorption over the surface of $InVO_4/TiO_2$ particles followed by irradiation with visible light over a certain period of time. At regular intervals, 5 mL aliquots were collected and filtered through disposable cellulose acetate membrane filters (0.22 µm pore size) to remove solid particles. Samples were analysed for the residual concentrations of 2-CP by UV-visible spectrophotometer (HACH LANGE DR6000) at 270 nm. To assess the impact of solution pH on the photocatalytic efficiency of $InVO_4/TiO_2$, experiments were performed at pH levels ranging from 3 to 7. After determination of the optimal pH, additional parameters, including the concentration of 2-CP, catalyst dose and light intensity, were evaluated.

3. Results and discussion

Morphology and composition were analysed using SEM and EDAX. As displayed in Figure 1, the synthesized $InVO_4$ powder has a grain-like structure, with a typical grain size of 1-2 μm. The $InVO_4/TiO_2$ composite is shown in Figure 2. The centre image displays titanium (Ti with $K\alpha = 4.5$ keV) and the right image displays indium (In with $L\alpha = 3.3$ keV). Elemental mapping confirmed the successful dispersion of indium vanadate throughout the titania sample. The BET surface area of the composite was determined to be 58 m^2/g. The pore volume was 0.073 cc/g with an average pore diameter of 5 nm.

XRD patterns of the individual semiconductors ($InVO_4$ and TiO_2) and the composite powders are shown in Figure 3. The XRD stick pattern (Figure 4) of the as-synthesized $InVO_4$ indicated the presence of orthorhombic crystals and all observed peaks correlated with JCPDS 00-048-0898 ($InVO_4$, orthorhombic, space group Cmcm, no. 63). No other impurities or phases were detected. The $InVO_4/TiO_2$ composite displayed evidence of the orthorhombic $InVO_4$ crystals at 2-theta positions of 18.5° and 33°. The XRD pattern of the as-procured TiO_2 (P-25) is included in Figure 3 for comparison with the composite powders. No significant changes in the relative intensities of the rutile and anatase peaks were observed, thus indicating that grinding
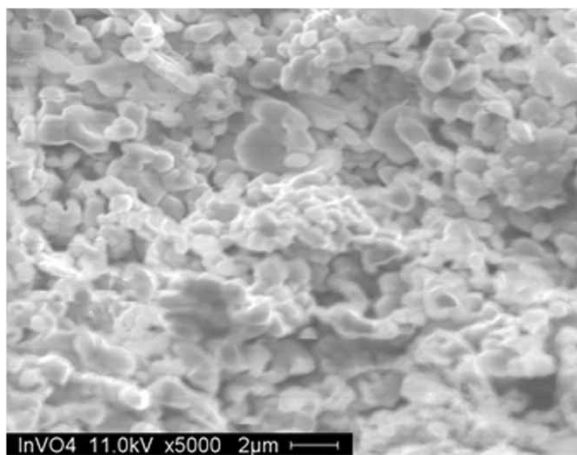

Figure 3. XRD patterns of TiO_2, $InVO_4/TiO_2$ composite and $InVO_4$ powders.

did not induce a phase change in the TiO_2. Previously reported synthesis methods for $InVO_4/TiO_2$ utilize a peroxo titanic acid sol, which crystalizes as anatase TiO_2.[35] The presented method capitalizes on the advantages of mixed-phase Degussa P-25 TiO_2. It has been reported that Degussa P-25 TiO_2 displays better photocatalytic activity than anatase TiO_2 for the degradation of phenolic compounds [36,37] and the detoxification of wastewater.[38] This can be attributed to the fact that in Degussa P-25 the presence of small rutile crystallites creates a structure where rapid electron transfer from rutile to lower energy anatase lattice trapping sites under visible illumination, which leads to a more stable charge separation.

Photolysis of the 2-CP solution was performed with a 150 W visible-light lamp as a control experiment to establish the effect of visible light on overall 2-CP degradation in the absence of the catalyst (Figure 5). It can be illustrated that the concentration of 2-CP decreases with increasing time and only 10% degradation via photolysis was observed in 3 h. The adsorption experiment of $InVO_4/TiO_2$ under dark conditions was performed up to 3 h to establish adsorption equilibrium state,[39] as shown in Figure 4. Within 30 min, the surface adsorption reached equilibrium with the solution concentration and no further adsorption was observed.

The solution pH is a key factor for photocatalytic reaction. It can affect the interaction of pollutants on the

Figure 1. SEM micrograph of as-synthesized $InVO_4$.
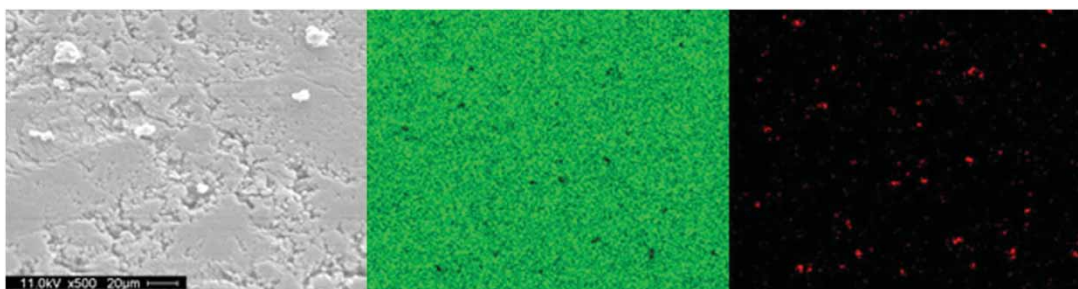

Figure 2. SEM micrograph (left) with elemental mapping (EDS) of $InVO_4/TiO_2$ composite (Ti K map in green (centre), In L map in red (right), scale bar is 20 μm).
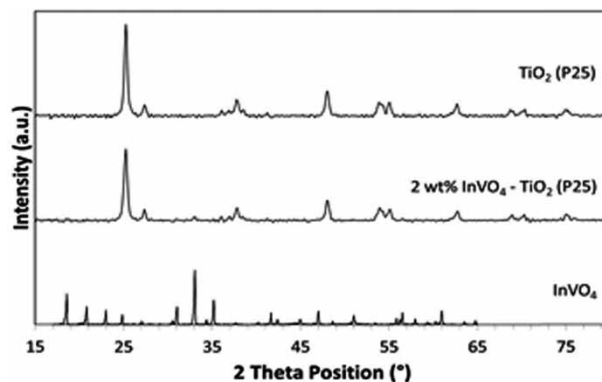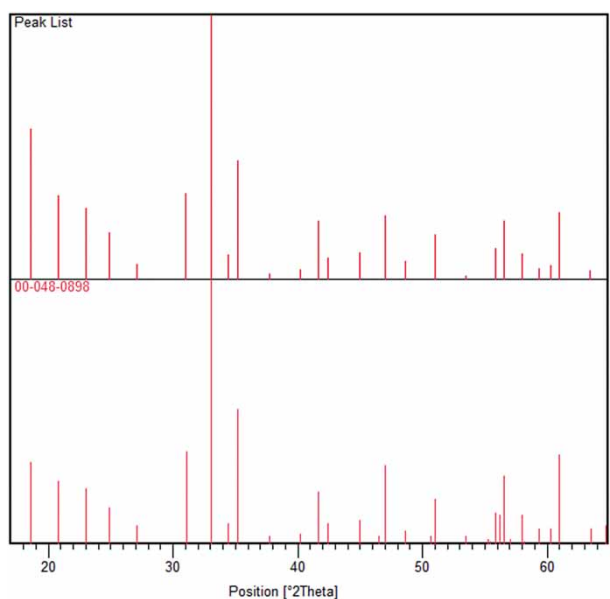
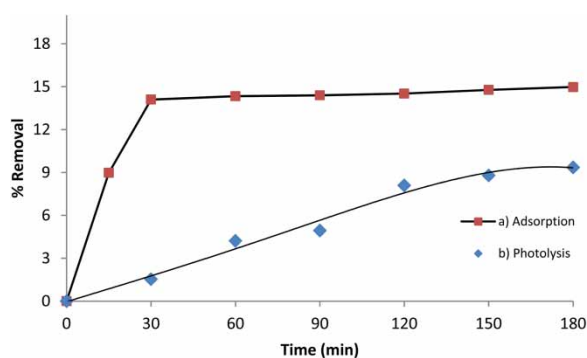Figure 4.　XRD stick pattern comparison of as synthesized and reference orthorhombic InVO₄.

Figure 5.　(a) Adsorption of 2-CP on InVO₄/TiO₂ and (b) photolysis of 2-CP (photolysis: 2-CP initial conc. 50 mg/L, pH = 5, visible-light lamp = 150 W; adsorption: catalyst = 1 g/L, 2-Cp initial conc. 50 mg/L, pH = 5).
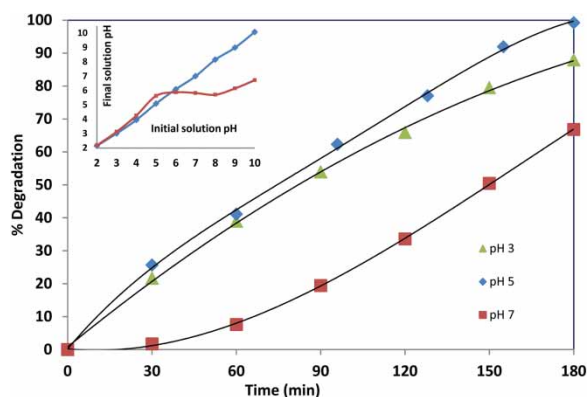

Figure 6.　Effect of pH on photocatalytic degradation of 2-CP and (Inset) point of zero charge (2-CP = 50 mg/L, catalyst = 1 g/L, visible-light lamp = 150 W).

photocatalyst surface as well as control the speciation of hydroxyl radicals generated during photocatalysis. Figure 6 shows the effect of solution pH on the degradation of 2-CP via InVO₄/TiO₂ photocatalysis. Degradation of 2-CP gradually increased with increasing solution pH up to the maximum at pH 5. Further increase in pH, up to 7, showed a significant decrease in degradation efficiency. Such behaviour can be explained on the basis of the point of zero charge (pHzpc) of InVO₄/TiO₂, which was determined to be 5.8 by the salt addition method (0.1 M KCl),[40] as shown in Figure 6 (inset). At a pH below the pHzpc, the InVO₄/TiO₂ surface bears a positive charge, which attracts anions. The lower degradation efficiency of 2-CP at a pH of 3 may be attributed to the competition between the dissociated Cl⁻ ions (from HCl used for balancing pH) and 2-CP molecules on the TiO₂ surface.[41,42] On the contrary, at higher pH (pH > pHzpc) the InVO₄/TiO₂ surface bears a

negative charge that could repel the phenolate ion species and result in low degradation efficiency. Moreover, high pH also favours the formation of carbonate ions, which are effective scavengers of hydroxyl radicals and can reduce the degradation rate.[43] At pH 5, the electrostatic binding of 2-CP with the positively charged surface of TiO₂ resulted in maximum photocatalytic degradation of 2-CP. These results are supported by the values of the apparent rate constant (k_{app}) provided in Table 1.

The effect of catalyst dose on degradation of 2-CP was studied over a range of 0.1–2.0 g/L InVO₄/TiO₂. As shown in Figure 6, 50% degradation of 2-CP was achieved with 0.1 g/L InVO₄/TiO₂ in 3 h. As the InVO₄/TiO₂ dose was increased, 2-CP degradation showed a significant increase, reaching the maximum of 100% at a dose of 1 g/L. This may be attributed to the increase in number of catalyst active sites with an increase in catalyst dose. Further increase in the catalyst dosage, above 1 g/L, showed a decrease in photocatalytic efficiency due to catalyst agglomeration and reduction in light penetration.[44] On comparison at 1 g/L catalyst dose, the InVO₄/TiO₂ composite displayed a 50% improvement in degradation over TiO₂ Degussa P-25, demonstrating the significance of InVO₄ doping in visible-light-initiated photocatalysis.

Intensity of incident light plays a major role in photocatalyst activation. Therefore, lamps of different power ranging from 20 to 150 W were used in the photoreactor to optimize the intensity of incident light. As illustrated in Figure 7, it was observed that photocatalytic degradation efficiency increased with increase in light intensity 3- and 5-fold with 70 and 150 W lamps, respectively. Under the optimal conditions, complete degradation of 2-CP was achieved with 150 W visible-light lamp within 3 h. The role of the light intensity can be explained as follows; since the photocatalytic process fundamentally relies on incident light, therefore increased light intensity theoretically means increased number of photons and higher electronic excitation probability should favour the rate of reaction.[45] The nonlinear increase in the photocatalytic efficiency is due to

Table 1.   Effects of catalyst dose, solution pH and initial 2-CP concentration on the photocatalytic activity of InVO$_4$/TiO$_2$.

Catalyst dose (g L^{-1})[a]	k (min^{-1})	R^2	Solution pH[b]	k (min^{-1})	R^2	Initial 2-CP concentration (mg/L)[c]	k (min^{-1})	R^2
0.5	0.0083	0.9796	3	0.013	0.9796	25	0.066	0.9171
1	0.0218	0.9666	5	0.0218	0.9666	50	0.0218	0.9666
2	0.0151	0.9795	7	0.0071	0.9254	100	0.0066	0.9906

[a]2-Cp = 50 mg L^{-1}, pH = 5.1, time = 180 min, visible-light lamp = 150 W.
[b]2-Cp = 50 mg L^{-1}, catalyst dose = 1 g L^{-1}, time = 180 min, visible-light lamp = 150 W.
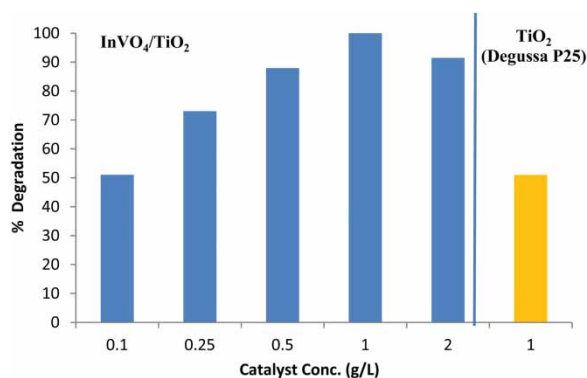[c]Catalyst dose = 1 g L^{-1}, time = 180 min, pH = 5.1, visible-light lamp = 150 W.

Figure 7.   Catalyst dose effect (2-CP initial conc. = 50 mg/L, pH = 5, visible-light lamp = 150 W, irradiation time = 180 min).

Figure 8.   Effect of light intensity (2-CP initial conc. = 50 mg/L, catalyst amount = 1 g/L, pH = 5).

that at lower intensity range (20–70 W) e − /h+ generation is dominant process over recombination, whereas at higher light intensity (70–150) e − /h+ recombination becomes significant.[46,47] Finally, the effect of initial 2-CP concentration was evaluated over the range of 25–100 mg/L with a fixed dose of InVO$_4$/TiO$_2$, as shown in Figure 8. Since the number of active species on the catalyst surface and the irradiation time remained the same, the probability of 2-CP molecules reacting with the active species decreased with increase in initial 2-CP concentration. Furthermore, a decrease in photon path length associated with increased concentration of 2-CP in solution may also be responsible for the decrease in 2-CP degradation efficiency.[44] The apparent rate constant values calculated from the Langmuir–Hinshelwood (LH) equation also decrease with the increase in 2-CP concentration, as given in Table 1.

LH kinetics is the most appropriate first-order reaction kinetic model for photocatalytic degradation of organic pollutants in solution.[48] The model was fitted with the experimental data to evaluate the kinetic parameters involved in 2-CP degradation. The simplified LH relationship is shown in Equation (1).

$$\ln\left(\frac{C_0}{C}\right) = k_{app}\, t, \tag{1}$$

where C represents the concentration in solution of the molecule being degraded (mg/L), k_{app} is the apparent first-order reaction rate constant (min^{-1}) and t is time (min).
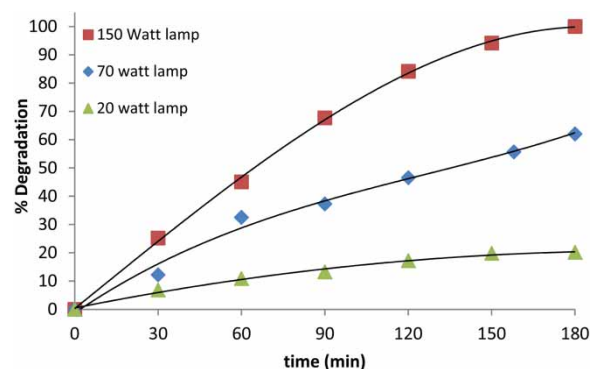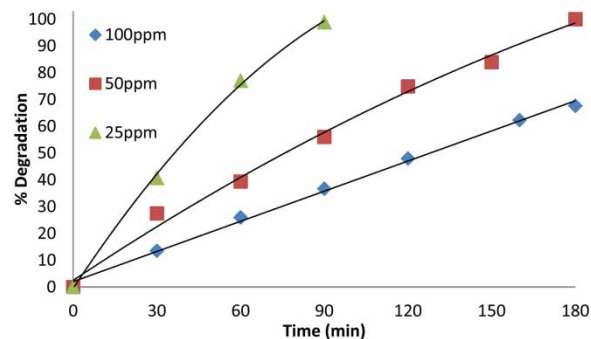

Figure 9.   Substrate concentration effect (pH = 5, catalyst amount = 1 g/L, visible-light lamp = 150 W).

It was observed that the value of k_{app} decreased from 0.066 to 0.0063 min^{-1} with the increase in 2-CP concentration. The values of the apparent rate constants for the parameters of 2-CP initial concentration, pH and catalyst dose were obtained from the slope of their regression plots and are provided in Table 1. The maximum rate constant value of 0.0218 corresponded to the 1 g/L catalyst dose (Figure 9).

4.   Conclusions

InVO$_4$ was synthesized using an organic precursor method and was amalgamated with TiO$_2$ (P-25) powder via mechanical grinding. The photocatalytic activity of the synthesized composites was evaluated by visible-light photocatalytic degradation of 2-CP in synthetic wastewater

solution. $InVO_4/TiO_2$ showed higher photocatalytic degradation of 2-CP pollutant in solution (as compared with the TiO_2 Degussa P-25). The optimal conditions for photodegradation were found to be 1 g/L catalyst with a pollutant concentration of 50 mg/L and solution pH value of 5. Under these conditions, complete degradation for 2-CP was achieved within 180 min of irradiation time.

Acknowledgements

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