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Molybdenum Disulphide/Polypyrrole Hybrid Composite for Photocatalytic Degradation of 2-Chlorophenol from Aqueous Solution

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This investigation highlighted on the photocatalytic degradation of 2-chlorophenol in aqueous solution by using molybdenum disulphide (MoS_2)/polypyrrole (PPy) composite. The composite was prepared via *in-situ* oxidation polymerization method using $FeCl_3$ as oxidation agent. The synthesized MoS_2/PPy composites were comprehensively characterized using X-ray diffraction (XRD) and Fourier transforms infrared spectroscopy (FTIR). The photodegradation of 2-chlorophenol was performed under direct sunlight for 180 minutes and using different parameter such as contact time with initial concentration and also different pH. The results indicated that MoS_2/PPy composite have efficient photocatalytic activity compared to PPy and MoS_2. The best pH reveals at pH 5 while the best initial concentration was 50 mg/L with 79.59% degradation efficiency

Keywords: Molybdenum disulphide (MoS_2); polypyrrole; photocatalytic degradation; 2-chlorophenol

I. INTRODUCTION

Growing amounts of non-conventional chemicals discharge in wastewater, surface water as well as drinking water have elevated great distress. These pollutants, which are mostly connected to the usage of substances such as pharmaceuticals, personal care, agriculture, are regularly found in traces amount. Nevertheless, their adverse effects on health and environment have been largely recognized (Pomati *et al.*, 2006). Phenolic groups have a high toxicity to human being even at low concentration exposure (Huong *et al.*, 2016). The presence of these compounds in the environment is also related to the production and degradation of pesticides such as chlorobenzene and others. The existence of these contaminants in aquatic environment caused harmful effects such as biological, physical or chemical threats. 2-chlorophenol is widely used as an ingredient in fertilizer for agricultural applications. The US Environment Protection Agency (USEPA) impose very strict regulation for 2-chlorophenol amount in wastewater, the maximum concentration must be below than 1 mg/L (Michałowicz and Duda, 2007). The exposure of 2-chlorophenol to human and the environment may cause cancer, gene mutation and unstable ecosystem (Texier *et al.*,2018). Moreover, 2-chlorophenol can cause skin irritation, gastrointestinal problems, and in some case poses a serious ecological threat as environmental contamination (Mondal *et al.*, 2011). Therefore, the development of efficient and versatile technique in removal of this toxic element is necessary.

Breakthrough in the removal of 2-chlorophenol from wastewaters has taken interest among scientists. Photocatalysis has seemed as one of the most favourable techniques amongst the wide variety of methods to degrade

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health- threatening waste materials, specifically organic compounds, to less poisonous or less unsafe materials (Julinová and Slavík, 2012). Despite the successful TiO_2 material to degrade various kind of pollutants the degradation only can be done under UV light due to the large band gap of TiO_2 material (3.2 eV). Novel photocatalysts for example ZnO, ZnS, ZrO2, semiconductor-graphene, perovskites, MoS_2, WO_3, CdS and Fe_2O_3 were actively studied this past few years (Shaham-Waldmann and Paz, 2016; Vinoth *et al.*, 2016; Wang *et al.*, 2017). Recently, utilizing renewable energy sources (solar) for photodegradation has attracted more attention due to its pollution-free and low cost. To utilize the visible light, 43% of the solar spectrum, the band gap must be in the range of 1.7–2.2 eV. This value may be in the range of many other semiconductor materials, including oxides, oxynitrides, and oxysulphide (Pasternak and Paz, 2013). However, their practical uses have been limited by their low photocatalytic activity under solar light. Among these, MoS_2 semiconductor is believed to be the best photocatalyst that works under visible light due to the separation of the charge carrier. MoS_2 have a powerful absorption within the visible and has been exploited as a completely unique visible sensitive semiconductor for photocatalyst.

Integration of MoS_2 with conducting polymer such as polypyrrole to form composite displayed significantly enhanced conductivity and electrocatalytic activity (Sabarinathan *et al.*, 2017). Conducting polymer has excellent processability, environmental stability, and photoelectric property. Polythiophene, polyacetylene, polypyrrole, polyphenylene, and polyaniline are examples of conducting polymers that have been widely studied (Shahabuddin *et al.*, 2016) Integration of polyaniline-anastase TiO_2 have established in the degradation of synthetic dye, methylene blue (George *et al.*, 2016). According to Ullah *et al.*, (2017), the used of polypyrrole in photodegradation of environmental pollutants and solar water splitting are one of the best methods in water treatment. In recent study, polypyrrole-TiO_2 composite have narrow band gap and useful in absorption of visible light. Hence, the combination of conducting polymer with the noble metal nanoparticle is the best way to produce sustainable and advance materials which can be used in photodegradation. In the present investigation, integration MoS_2 with polypyrrole can be applied as a photocatalyst to degrade 2-chlorophenol in aqueous solution under solar irradiation.

II. MATERIALS AND METHOD

A. Reagents and Chemicals

Ferric chloride ($FeCl_3$), 0.1% of sodium hydroxide (NaOH), 0.1% of nitric acid (HNO_3), 2-chlorophenol, ethanol, pyrrole and molybdenum disulphide nanoparticle (MoS_2) (90 nm) were purchased from Merck (Darmstadt, Germany).

B. Preparation of Polypyrrole

4g of $FeCl_3$ was added into beaker that contains 25 mL of deionized water. The mixture was stirred for 5 minutes while 1 mL of pyrrole monomer was added dropwise. The mixture then was sonicated for 1 hour at temperature below 10°C. The product was filtered and washed using deionized water followed by ethanol. Finally, the sample product was dried in vacuum oven at 60°C overnight (Appavu and Thiripuranthagan, 2016).

C. Preparation of MoS_2/PPy composite

0.1 g of MoS_2 was added into the beaker that contained 25 mL of deionized water. Then, the mixture was sonicated for 30 minutes. 1 mL of pyrrole monomer was added into the mixture and was sonicated for 30 minutes. Next, 4 g of $FeCl_3$ was added into the mixture and sonicated for 4 hours. Lastly, the sample was filtered and washed with deionized water and ethanol prior dried for 15 hours at 60°C (Appavu and Thiripuranthagan, 2016).

D. Characterisations of MoS_2/PPy composite

PPy, MoS_2, and MoS_2/PPy composite were analysed using ATR-FTIR Perkin Elmer Fourier Transform Infrared (FTIR) Model 100 recorded between 4000 and 400 cm^{-1} (Perkin Elmer, Massachusetts, USA. Phase structure of the samples were determined using X-ray Diffractometer (XRD) Panalytical model Empyrean at 40 kV and 35 mA using Cu, Kα radiation is λ= 1.54059 Å.

E. Photocatalytic Studies

The photocatalytic properties of MoS_2/PPy composite were evaluated by employing 2-chlorophenol as a target degradation product 10 mg of MoS_2, PPy and MoS_2/PPy each were added into 5 mL of 50 mg/L of 2-chlorophenol solution and were exposed to the sunlight for 180 minutes in

the pH range of 3- 9 and concentration between of 50, 150 and 250 mg/L. The mixtures were centrifuged, and supernatant solutions were measured its absorbance at 290 nm by using UV-Vis spectrophotometer.

The percentage degradation was calculated by using this following equation:

$$\text{Percentage degradation (\%)} = \frac{A_o - A}{A_o} \times 100$$

where A_o is an initial absorption of 2-chlorophenol and A is an absorption of 2-chlorophenol at sampling time after the photocatalytic activity (Ibrahim, 2015).

III. RESULT AND DISCUSSION

A. Characterisation of MoS_2/PPy composite

Figure 1 shows various pertinent peaks in the IR spectra of MoS_2, PPy and MoS_2/PPy. 3397.26 cm-1 corresponding to stretching vibration of N–H bonds polypyrrole. Two absorption peaks of C=C stretching of PPy ring at 1535.08 cm^{-1} and 1456. 82 cm^{-1} had been observed at 1536.43 cm^{-1} and 1468.72 cm^{-1} in composite (Xu et *al.*, 2010). Meanwhile, C-N stretching of PPy was found at 1295.7 cm^{-1} while 1286.65 cm^{-1} in MoS_2/PPy. This slightly shifted changes due to the interaction between molybdenum disulphide with polypyrrole which causes to the partial π-electron transferring from polypyrrole to the molybdenum disulphide NPs (Xu *et al.*, 2010). The peaks at 892.22 cm^{-1} indicate Mo-S bond in composite spectrum. Meanwhile, the S-S bond of molybdenum disulphide was observed at 914.21 cm^{-1} in MoS_2 and 961.65 cm^{-1} in composites (Ding *et al.*, 2016). Thus, this reveals that PPy was successfully integrated with MoS_2 forming MoS_2/PPy.

Figure 2 shows the phase arrangements and the crystal structure of MoS_2, PPy and MoS_2/PPy composite. Broad peak of MoS_2/PPy indicated the presence of amorphous PPy phase in the lattice. The distinctive peaks of MoS_2/PPy composite occurred at $2\theta = 14.68^o$, 33.52^o, 40.00^o, 50.00^o, 58.97^o and 60.00^o which can be indexed to the (002), (100), (103), (105), (106) and (110) (Ding *et al.*, 2016). Hence, diffractogram (c) clearly revealed MoS_2 and PPy structure phase was present in the MoS_2/PPy composite.

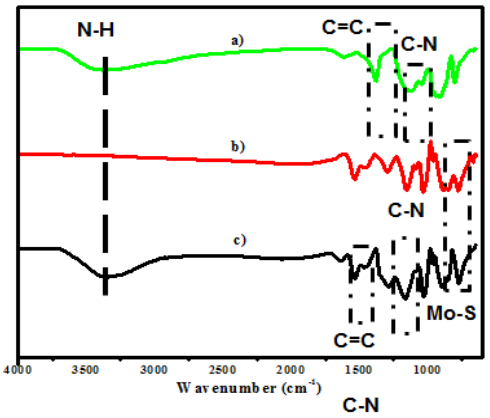

Figure 1. FTIR spectrum of a) PPy, b) MoS_2 and c) MoS2/PPy composite

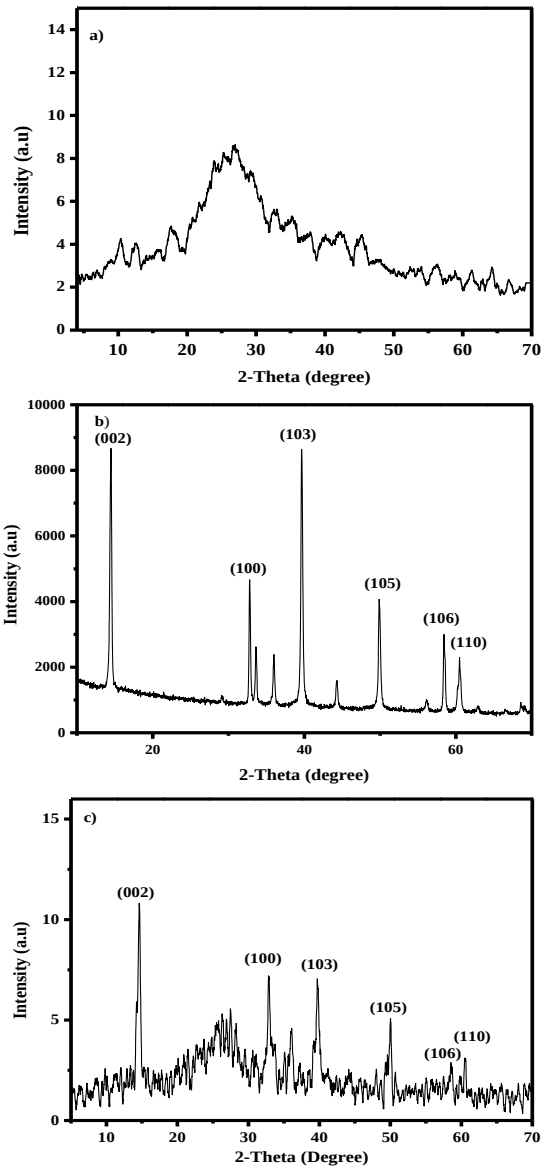

Figure 2. Diffractogram a) PPy b) pure MoS_2 and c) MoS_2/PPy composite

B. Photocatalytic Activity of MoS_2, PPy and MoS_2/PPy Composite

Figure 3 reveals the efficiency of three different photocatalysts PPy, MoS_2 and MoS_2/PPy towards photodegradation of 2-chlorophenol in aqueous solution under solar radiation. From the results, it is clearly observed MoS_2/PPy have highest degradation efficiency compared with PPy and MoS_2. MoS_2/PPy achieved stronger visible light absorption compared to PPy and MoS_2 due to the integration of MoS_2 and PPy producing narrow band gap and photogenerated electrons were transfer from excited state into the conduction band of MoS_2 particles efficiently (Quinn *et al*., 2013).

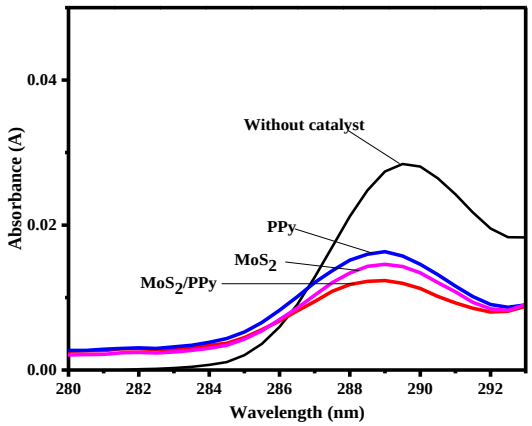

Figure 3. Photocatalyst activity for degradation of 2-chlorophenol (condition: 10 mg composite, 5 mL of 50 mg/L of 2-clorophenol at pH 5 and exposed to the sunlight for 180 minutes)

C. Effect of Contact Time with Different Initial Concentration

As illustrates in Figure 4, percentage of degradation were decreased with increasing of 2-chlorophenol concentration from 50 mg /L to 250 mg/L. Highest percentage of degradation was observed at 50 mg/L with the percentage of 76.86%, while the lowest degradation occurred at concentration of 250 mg/L. This may be due to the surface sites of catalyst was saturated with the 2-chlorophenol molecule, thus lower the catalytic activity. Moreover, as the concentration of 2-chlorophenol increased, more compound gets absorbed on the photocatalyst surface which more production of OH needed in order to increase the degradation efficiency (Ahmed *et al.*, 2010). The graph revealed the increasing percentage of degradation with increasing time with rapid degradation for the first 15 minutes and slowly degraded until 180 minutes. This situation occurred since at the first 15 minutes, there is more available site for efficient catalytic activity. Meanwhile, when reached 180 minutes, the active sites become saturated and eventually lower the degradation efficiency.

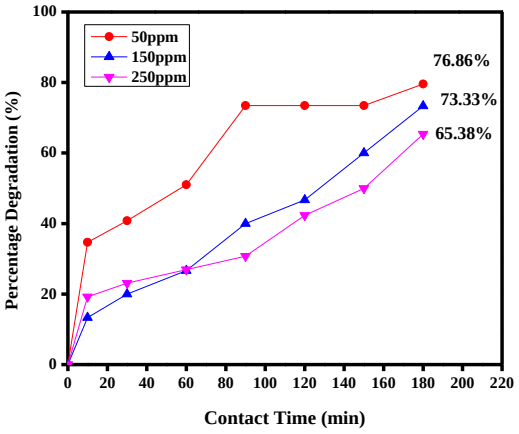

Figure 4. Percentage degradation of different contact time with different initial concentration of 2-chlorophenol (condition: 10 mg composite, 5 mL of 50- 250 mg/L 2-clorophenol at pH 5 and exposed to the sunlight for 0-180 minutes)

D. Photodegradation Efficiency of 2-chlorophenol at Different pH

Figure 5 shows percentage of degradation of 2-chlorophenol. From the graph, pH 5 (79.59%) demonstrates highest percentage degradation compares to pH 3 (63.33%), pH 7 (78.57%) and pH 9 (50%). In photocatalytic degradation, adsorbed water is oxidized by positives hole generated from the excitation of electron of MoS_2/PPy from valence band to conductive band to produces OH radicals. The OH radicals eventually, degrade the pollutants to intermediate and further degrade to CO_2 and H_2O. At low pH the presence of water is limited, to react with the positive holes to form hydroxyl radicals (•OH) (Ahmed *et al.*, 2011). Thus, it will decrease the photodegradation efficiency of 2-chlorophenol. Meanwhile, in the alkaline regime, the percentage degradation decreased may be due to the surface of the MoS_2/PPy becomes negatively charge and thus repelled the 2-chlorophenol. Nevertheless, the degradation will still occur but in less efficient.

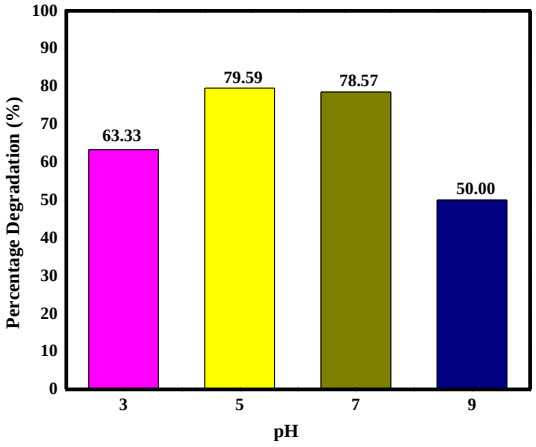

Figure 5. Percentage degradation of different pH (condition: 10 mg composite, 5 mg/L 2-chlorophenol and exposed to the sunlight for 180 minutes)

E. Comparison Photocatalyst Efficiencies in Different Photocatalyst

A comparative study of the photocatalytic efficiencies of the photocatalysts reported in the literature with the present catalyst is substantial and is demonstrated in Table 1. Ahmed *et al.*, (2010), reported 92% degradation efficiency of phenol in the UV light condition at pH 5 using TiO_2 (Ahmed *et al.*, 2011). 2-chlorophenol was successfully degraded by Co-TiO_2 which is done under UV light by Ahmed *et al.*, (2010) .On the other hand, MoS_2 and MoS_2/Gr/Ag_3PO_4 degraded phenol in visible light condition with degradation percentage of 55% and 75% at pH 5 and 3 respectively (Zhang *et al.*, 2017; Peng *et al.*, 2014). Thus, in this context, it is very well recognized that our MoS_2/PPy offers higher degradation percentage.

IV. CONCLUSION

Based on overall result and discussion, it can be concluded that the MoS_2 was successfully coated with PPy. The synthesized MoS_2/PPy were characterized by using FTIR and XRD. FTIR and XRD results revealed the successful integration of PPy and MoS_2. In the photocatalytic activity test towards 2-chlorophenol, MoS_2/PPy (53.33%) show the highest percentage of degradation compared to MoS_2 (50%). In addition to this, the concentration of 50 mg/L has the highest percentage degradation which is (76.86%) at the contact time of 180 minutes compared to other concentration. Furthermore, the best condition of pH towards 2-chlorophenol in these studies are clearly observed to be at pH 5 (79.59%). The proposed method may be utilized for the synthesis of numerous composites materials, with other conducting polymers to overcome the present-day issue of environmental pollution affected by various organic pollutants. Furthermore, the enhanced photocatalytic activity in visible light region is more economical compared to UV irradiation and may further apply for industrial purposes.

IV. ACKNOWLEDGEMENTS

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Table 1 Comparative study of photocatalytic efficiencies of the different photocatalyst.

Photocatalyst	Pollutant	Light Source	Concentration (mg/L)	pH	Contact Time (min)	Degradation (%)	Ref.
TiO_2	Phenol	UV	50	5	360	92	[22]
Co-TiO_2	2-chlorophenol	UV	25	9	150	93	[22]
CMK/PANI	Phenol	UV	250	3	240	81	[23]
MoS_2	Phenol	Visible	10	5	120	55	[24]
MoS_2/Gr/Ag_3PO_4	Phenol	Visible	10	3	60	75	[25]
MoS_2/PPy	2-chlorophenol	Visible	50	5	180	79.59	This work

V. REFERENCES

Ahmed, S, Rasul, MG, Brown, R & Hashib, MA 2011, 'Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review', *Journal of Environmental Management*, vol. 92, no. 3, pp. 311–330.

Ahmed, S, Rasul, MG, Brown, R, & Hashib, MA 2011, 'Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review', *Journal of Environmental Management*, vol. 92, no. 3, pp. 311–330.

Ahmed, S, Rasul, MG, Martens, WN, Brown, R & Hashib, MA 2010, 'Heterogeneous photocatalytic degradation of phenols in wastewater: a review on current status and developments', *Desalination*, vol. 261, no. 1–2, pp. 3–18.

Anbia, M & Ghaffari, A 2009, 'Adsorption of phenolic compounds from aqueous solutions using carbon nanoporous adsorbent coated with polymer', *Applied Surface Science*, vol. 255, no. 23, pp. 9487-9492.

Appavu, B, Kannan, K, & Thiripuranthagan, S 2016, 'Enhanced visible light photocatalytic activities of template free mesoporous nitrogen doped reduced graphene oxide/titania composite catalysts', *Journal of Industrial and Engineering Chemistry*, vol. 36, pp. 184-193.

Ding, G, Cheng, L, Zhang, S, Wang, Y, & Jiao, Z 2016, 'Ternary P25–graphene–Fe_3O_4 nanocomposite as a magnetically recyclable hybrid for photodegradation of dyes', *Materials Research Bulletin*, vol. 73, pp. 77-83.

George, R, Bahadur, N, Singh, N, Singh, R, Verma, A, & Shukla, AK, 2016, 'Environmentally benign TiO_2 nanomaterials for removal of heavy metal ions with interfering ions present in tap water', *Materials Today: Proceedings*, vol. 3, no. 2, pp. 162-166.

Huong, P, Lee, BK; Kim, J 2016, 'Improved removal of 2-chlorophenol by a synthesized Cu-nano zeolite', *Process Safety and Environmental Protection*, vol. 100, pp. 272–280.

Ibrahim, HMM, 2015, 'Photocatalytic degradation of methylene blue and inactivation of pathogenic bacteria using silver nanoparticles modified titanium dioxide thin films', *World Journal of Microbiology and Biotechnology*, vol. 31, no. 7, pp. 1049–1060.

Julinová, M, & Slavík, R 2012, 'Removal of phthalates from aqueous solution by different adsorbents: a short review', *Journal of Environmental Management*, vol. 94, no. 1, pp. 13–24.

Martínez-Jardines, M, Martínez-Hernández, S, Texier, AC & Cuervo-López, F 2018, '2-chlorophenol consumption by cometabolism in nitrifying SBR reactors', *Chemosphere*, vol. 212, pp.41-49.

Michałowicz, J, & Duda, W 2007, 'Phenols-sources and toxicity', *Journal of Environmental Studies*, vol. 16, no. 3, pp. 347-362.

Mondal PK & Sabir, S 2011, 'Bioremediation of 2-chlorophenol containing wastewater by aerobic granules-kinetics and toxicity', *Journal of Hazardous Materials*, vol. 190, no. 1–3, pp. 222–228.

Pasternak, S, & Paz, Y 2013, 'On the similarity and dissimilarity between photocatalytic water splitting and photocatalytic degradation of pollutants', *Chem Phys Chem*, vol. 14, no. 10, pp. 2059-2070.

Peng, WC, Wang, X & Li, XY 2014, 'The synergetic effect of MoS 2 and graphene on Ag_3PO_4 for its ultra-enhanced photocatalytic activity in phenol degradation under visible light', *Nanoscale*, vol. 6, no. 14, pp. 8311-8317.

Pomati, F, Castiglioni, S, Zuccato, E, Fanelli, R, Vigetti, D, Rossetti, C & Calamari, D 2006, 'Effects of a complex mixture of therapeutic drugs at environmental levels on human embryonic cells', *Environmental Science & Technology*, vol. 40, no. 7, pp. 2442-2447.

Quinn, MD, Ho, NH & Notley, SM 2013, 'Aqueous dispersions of exfoliated molybdenum disulfide for use in visible-light photocatalysis', *ACS Applied Materials and Interfaces*, vol. 5, no. 23, pp. 12751-12756.

Sabarinathan, M, Harish, S, Archana, J, Navaneethan, M, Ikeda, H, & Hayakawa, Y 2017, 'Highly efficient visible-light photocatalytic activity of MoS_2–TiO_2 mixtures hybrid photocatalyst and functional properties', RSC *Advances*, vol. 7, no. 40, pp. 24754-24763.

Shahabuddin, S, Muhamad Sarih, N, Mohamad, S, & Joon Ching, J 2016, '$SrTiO_3$ nanocube-doped polyaniline nanocomposites with enhanced photocatalytic degradation of Methylene Blue under visible light', *Polymers*, vol. 8, no. 2, pp. 27.

Shaham-Waldmann, N, & Paz, Y 2016, 'Away from TiO_2: a critical minireview on the developing of new photocatalysts for degradation of contaminants in water', *Materials Science in Semiconductor Processing*, vol. 42, pp. 72-80.

Ullah, H, Tahir, AA, & Mallick, TK 2017, 'Polypyrrole/TiO_2 composites for the application of photocatalysis', *Sensors*

and Actuators B: Chemical, vol. 241, pp. 1161-1169.

Vinoth Kumar, J, Saravanakumar, K, Senthil Kumar, P, & Muthuraj, V 2016, 'Visible light photocatalytic activity of rhombus like Fe_2O_3 for degradation of organic contaminants', *Energy and Environment Focus*, vol. 5, no. 3, pp. 222-228.

Wang, L, Wang, P, Huang, B, Ma, X, Wang, G, Dai, Y, Qin, X 2017, 'Synthesis of Mn-doped ZnS microspheres with enhanced visible light photocatalytic activity', *Applied Surface Science*, vol. 391, pp. 557-564.

Xu, YF, Hu, KH, Hu, XG, Xu, & Sun, JD 2010, 'Synthesis of nano-MoS_2/TiO_2 composite and its catalytic degradation effect on methyl orange', *Journal of Materials Science*, vol. 45, no. 10, pp. 2640-2648.

Zhang, S, Wang, L, Liu, C, Luo, J, Crittenden, J, Liu, X, & Liu, Y 2017, 'Photocatalytic wastewater purification with simultaneous hydrogen production using MoS_2 QD-decorated hierarchical assembly of $ZnIn_2S_4$ on reduced graphene oxide photocatalyst', *Water Research*, vol. 121, pp. 11-19.