PHOTODESORPTION AND HIGHER-ORDER ASSEMBLIES OF POTASSIUM POLYTITANATE FOR WATER TREATMENT

Submitted by

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Certificate of Authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

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List of Abbreviations

AFM	:	Atomic Force Microscopy
AOPs	:	Advanced Oxidation Processes
BET	:	Brunauer, Emmet and Teller
BJH	:	Barret Joyner Halender
CB	:	Conduction Band
CNTs	:	Carbon Nanotubes
CV	:	Crystal Violet
DO	:	Dissolved Oxygen
DOC	:	Dissolved Organic Carbon
DOM	:	Dissolved Organic Matter
EDS	:	Energy Dispersive X-ray Spectroscopy
EDX	:	Energy Dispersive X-ray
FTIR	:	Fourier Transform Infrared Spectroscopy
HDTMA	:	Hexadecyltrimethylammonium
HMW	:	High Molecular Weight
HOC	:	Hydrophilic Organic Carbon
HP-SEC	:	High Performance Size Exclusion Chromatography
LC-OCD	:	Liquid Chromatography - Organic Carbon Detection
LMW	:	Low Molecular Weight
MB	:	Methylene Blue
PTTF	:	Polytetrafluoro Ethylene
PZC	:	Point of Zero Charge
SEM	:	Scanning Electron Microscope

STM	:	Scanning Tunnelling Microscopy
SWW	:	Synthetic Wastewater
TEM	:	Transmission Electron Microscope
TOC	:	Total Organic Carbon
UV	:	Ultra Violet
VB	:	Valance Band
XRD	:	X-ray diffraction

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Abstract

Nanotechnology has great potential in advancing water and wastewater treatment to improve treatment efficiency. Several nanotechnology approaches to water purification are currently being investigated and some already are in use. Photocatalysis is a new advanced oxidation process based on the irradiation of semiconductor materials, normally TiO_2, with UV light and has been demonstrated to be one of the "green" and more effective strategies for environmental remediation. Recently, photo-induced desorption of dissolved organic compounds in aqueous media during photocatalysis provides an exciting opportunity in wastewater treatment which significantly facilitates the regeneration of the adsorbent with low energy consumption. The scope of this research is to elucidate the photodesorption of organic matter from TiO_2 under UV irradiation. In addition, this research also includes synthesis of titania-based photocatalytic adsorbent nanomaterials produced by self-assembly for water purification. For this purpose, potassium titanate was synthesised using Degussa P25 as a titanium precursor in the presence of hydrogen peroxide as an oxidising agent and potassium hydroxide in alkaline solution via alkaline hydrothermal condition. As a part of nanotechnology, the development of the photocatalytic adsorbent nanofibre is of great importance to establish adsorption and photocatalytic water treatment an attractive and cost-effective process.

Photo-induced desorption of organic compounds from TiO_2 particles in aqueous media during photocatalysis has promising applications in water treatment. Photodesorption is a relatively fast phenomenon that facilitates the regeneration of photocatalysts with low energy consumption while concentrating the waste products in an energy and water efficient process. It has been proposed that this transport phenomenon involves a

significantly reduced affinity between the photocatalyst and pollutants upon UV illumination, and leads to the rapid detachment/decomposition of adsorbed pollutants.

Initially, organic matters were allowed to adsorb on the surface of the photocatalyst (Degussa P25) until adsorption equilibrium was achieved. When adsorption equilibrium had been reached, it was observed that photodesorption was observed shortly with UV-light illumination of TiO_2 before the bulk photocatalytic oxidation takes place. The effects of specific experimental conditions (pH, photocatalyst loading, organic loading, UV light irradiation, flow rate, specific organic compounds) on this phenomenon were also examined. The pH of the solution was found to influence both the adsorption and desorption percentages, thus revealing the role of particle charge on this phenomenon. Additionally, a 1 g/L loading of photocatalyst, 150 ml/min flow rate, 24 W light intensity showed an optimum photodesorption rate using a single strength synthetic wastewater at pH 7.

Photodesorption was observed only for sodium lauryl sulphate (50%), sodium lignin sulphonate (43.47%), beef extract (20.35%) and tannic acid (10.5%) indicating that photodesorption is specific to some organic compounds but not to all. Using liquid chromatography-organic carbon detection, untreated beef extract and sodium lignin sulphonate contained significant amounts of humic substances (~1,000 g/mol), which decreased in concentration after dark phase adsorption. A significant increase in low molecular weight (<350 g/mol) concentrations was observed after photodesorption. UV-treated sodium lauryl sulphate photodesorbed to give both higher molecular weight (HMW) and lower molecular weight (LMW) organics. Thus, the HMW fractions of organic compounds decomposed into smaller compounds after UV irradiation, which subsequently desorbed from the TiO_2 surface. However, untreated tannic acid contained a larger proportion of LMW acids, which showed a high adsorption affinity to TiO_2 during adsorption and poorly desorbed upon irradiation.

Apart from an investigation on photodesorption, this research presents a synthesis of potassium titanate nanostructures by hydrothermal treatment of TiO_2 (P25) in KOH and H_2O_2. As-produced powders were characterised by scanning electron microscopy, energy-dispersive X-ray spectroscopy, transmission electron microscopy, X-ray diffraction, and nitrogen adsorption-desorption methods. Longitudinally-oriented-wire-like structures up to several micrometres in length and diameters ranging from 10 to 30 nm were obtained. BET surface area analysis indicates macroporous sized titanate with had 5-6 times larger specific surface area (235.81-330.10 m^2/g) than the precursor P25. TEM images reflected belt-like structures of an isolated fibre with the presence of lattice fringes, which indicated a crystalline structure aligned with orientation of their basal nanobelts. The XRD spectra of potassium titanate were attributed to the transfer of a portion of anatase into mixed species of potassium titanate ($K_2Ti_8O_{17}$, $K_2Ti_6O_{13}$, K_2TiO_3 and $K_3Ti_8O_{17}$). They were recovered by calcining the specimens suggesting the possible existence of crystallisation sites under hydrothermal treatment in aqueous solution of H_2O_2 and KOH. Larger size fibrous nanowires resulting from the hydrothermal treatment demonstrated high affinity in adsorbing crystal violet (CV), which was mainly due to their high surface area. The photocatalytic bleaching of CV solution revealed that the wires are photoactive under UV light irradiation. Macroporous nanowires are considered to be effective adsorbents of CV, capable of its photocatalytic degradation, and they can be easily separated from the solution by settling.

Solar photocatalytic degradation of organic water pollutants can be used to destroy toxic organic pollutants in water. Hence, potassium titanate nanofibres synthesized by an aqueous peroxide route at high pH were examined as photocatalysts for the photodegradation of methylene blue (MB) using a solar simulator. The results show that potassium polytitanate nanofibres were effective adsorbents of MB and also facilitated its photocatalytic degradation. Sulphate ion evolution during photocatalysis confirms some mineralisation occurred and hence photo-oxidative degradation of MB. The optimum operational conditions for the photocatalytic degradation of MB were found at 0.05 g/L of photocatalyst, 10 mg/L MB and pH 7. The stability of a photocatalyst specimen was also studied for 3 degradation cycles using adsorption/photocatalysis model.

Potassium polytitanate nanofibres prepared via the hydrothermal method were investigated for their possible application in removing toxic metals from aqueous solution. Particular attention was paid to employing the titanate as novel effective adsorbents for the removal of Pb(II). Batch adsorption experiments demonstrated that the adsorption was influenced by various conditions such as solution pH, adsorbent dosage and initial Pb(II) concentration. The results showed that the adsorption rate was faster in the first 5 min and equilibrium was achieved after 180 min. The maximum amount of adsorption was detected at pH 5. Potassium titanate showed much higher adsorption capacity compared to P25. The kinetic studies indicated that the adsorption of Pb(II) onto titanate best fit the pseudo-second-order kinetic model. FTIR spectra revealed that the hydroxyl groups in titanate were responsible for Pb(II) adsorption. It was concluded that ion exchange and oxygen bonding may be the principal mechanisms for the adsorption of Pb(II). The adsorption-desorption results demonstrated that the titanate could be readily regenerated after adsorption. Therefore the titanate exhibited great potential for removing of Pb(II) from wastewater.

List of publications included in the Thesis

Chapter 4

El Saliby, I., **Shahid, M.**, McDonagh, A., Shon, H.K. & Kim, J.-H. 2012, 'Photodesorption of organic matter from titanium dioxide particles in aqueous media', *Journal of Industrial and Engineering Chemistry*, vol. 18, no. 5, pp. 1774-80.

Shahid, M., Saliby, I.E., McDonagh, A., Kim, J.-H. & Shon, H.K. 2014, 'Photodesorption of specific organic compounds from titanium dioxide particles in aqueous media', *Desalination and Water Treatment*, vol. 52, no. 4-6, pp. 867-72.

Chapter 5

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Chapter 6

Shahid, M., El Saliby, I., McDonagh, A., Tijing, L.D., Kim, J.-H. & Shon, H.K. 2014, ' **'**Adsorption and photocatalytic degradation of methylene blue using potassium polytitanate and solar simulator'', **(*Submitted to Journal of Nanoscience and Nanotechnology)*.**

Chapter 7

Shahid, M., El Saliby, I., McDonagh, A., Tijing, L.D., Kim, J.-H. & Shon, H.K. 2014, 'Adsorption behavior of Pb(II) onto Potassium Polytitanate Nanofibre', ***(Abstract submitted to International Conference on Nano Science and Nano Technology 2014).***

Other publications during the PhD candidature*

Kim, J.B., Lee, K.W., Park, S.M., Shon, H.K., **Shahid, M.**, Saliby, I.E., Lee, W.E., Kim, G.-J. & Kim, J.-H. 2013, 'Preparation of Iron-Doped Titania from Flocculated Sludge with Iron-Titanium Composite Coagulant', *Journal of Nanoscience and Nanotechnology*, vol. 13, no. 6, pp. 4106-9.

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*(not related to the Thesis)

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El Saliby, I., **Shahid, M.**, McDonagh, A., Shon, H.K. & Kim, J.-H., 'Photodesorption of organic matter from titanium dioxide particles in aqueous media', Presented at the 4th International Conference on the “Challenges in Environmental Science and Engineering” (CESE-2011), 25-30 September 2011, Tainan City, Taiwan

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