Journal of Hazardous Materials 341 (2018) 404–423

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Review

TiO_2/porous adsorbents: Recent advances and novel applications

Shayan MiarAlipour[1], Donia Friedmann[*,1], Jason Scott, Rose Amal[*]

Particles and Catalysis Research Group, School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

HIGHLIGHTS

- Coupling TiO2 with an adsorbent to promote photocatalytic performance was examined.
- The composites capacity to behave as a readily regenerative adsorbent was appraised.
- Future outlook, application and knowledge gaps in the field were identified.

ARTICLE INFO

Article history:
Received 3 May 2017
Received in revised form 19 July 2017
Accepted 31 July 2017
Available online 5 August 2017

Keywords:
TiO_2
Adsorption
Organic pollutants
Photocatalysis
Regeneration

ABSTRACT

This article reviews two interrelated areas of research: the first is the use of TiO_2-supported adsorbent materials as enhanced heterogeneous photocatalysts and their application to various reactions for organic pollutant removal from air and water; the second is the combination of adsorbent materials with TiO_2 photocatalysts which aims to efficiently regenerate adsorbent materials using illumination. By reviewing both areas of research, the following topics are covered; (i) photocatalytic activation of TiO_2; (ii) related properties of photocatalytic TiO_2; (iii) shortcomings of photocatalytic processes; (iv) preparation methods of composite TiO_2/adsorbent materials and their photocatalytic performance; (v) properties of common adsorbents and their applications for pollutant removal from air and water; (vi) adsorbent regeneration methods and their economic and operational issues; (vii) conclusions and future outlooks. This topic has not been previously reviewed to such an extent, and considerable knowledge can be gained from assembling the large number of studies on adsorption-photocatalysis combinations. As such, this review provides guidance for researchers working in the fields of environmental and chemical engineering focussing on organic pollutant removal and the engineering of new high performance photocatalytic TiO_2-supported porous adsorbent materials.

Contents

1. Introduction ... 405
2. TiO_2 as a photocatalyst ... 406
3. Methods for loading TiO_2 onto various supports and related issues ... 407
   3.1. TiO_2 loading methods ... 407
      3.1.1. Chemical vapor deposition (CVD) ... 407
      3.1.2. Impregnation ... 408
      3.1.3. Precipitation ... 408
      3.1.4. Sol-gel ... 408
   3.2. Issues related to TiO_2 loading onto various supports ... 408
4. Physical and chemical parameters affecting adsorption ... 408
   4.1. Pore size ... 409
   4.2. Surface chemistry ... 409

* Corresponding authors.
E-mail addresses: s.miaralipour@unsw.edu.au (S. MiarAlipour), donia.friedmann@unsw.edu.au (D. Friedmann), jason.scott@unsw.edu.au (J. Scott), r.amal@unsw.edu.au (R. Amal).
[1] Both S. Miar Alipour and D. Friedmann contributed equally as first author.

http://dx.doi.org/10.1016/j.jhazmat.2017.07.070

5. Effect of different adsorbents as TiO_2 supports for photocatalytic applications 409
5.1. TiO_2/carbon based material photocatalysts 409
5.2. TiO_2/alumina photocatalyst 411
5.3. TiO_2/Zeolite photocatalysts 412
5.3.1. Natural zeolites 412
5.3.2. Synthetic zeolites 413
5.4. TiO_2/silica photocatalysts 413
5.4.1. Silica gel 413
5.4.2. MCM-41 413
5.4.3. MCM-48 and KIT-6 414
5.4.4. SBA-15 414
6. Regeneration by illumination 415
7. Conclusion and future perspectives 418
Acknowledgements 419
References 419

1. Introduction

Industrialization has led to a substantial aggravation of the natural environment. The pollution crisis has increased to a great extent affecting water and air, two of the most essential substances for all life on Earth. Reliable access to clean water is considered as a major global challenge. Problematic pollutants in water which have recently received a lot of attention are natural organic matter (NOM). It has been realized that some NOM components are involved in the production of harmful by-products during water disinfection using the chlorination process, referred to as disinfection by-products (DBPs) [1–3].

Air is mainly polluted by chemicals found in automobile exhaust and factory emissions (outdoor air) and solvents and synthetic materials (indoor air). Problematic atmospheric pollutants are volatile organic compounds (VOCs) such as formaldehyde, acetaldehyde, acetone, 2-propanol, and toluene released mainly from paints and adhesives used in building and construction materials [4,5].

There are a number of methods available to treat water and air pollutants. In this review we focus on heterogeneous photocatalysis, which is considered to be a promising advanced oxidation technology for removing trace contaminants and microbial pathogens. It is a useful treatment method for hazardous and non-biodegradable contaminants to enhance their biodegradability. Photocatalysis can also be used as a polishing step to treat recalcitrant organic compounds [6–11]. Photocatalytic reactions are attractive since they do not require a high operating temperature and they can potentially be solar driven [12].

Titanium dioxide (TiO_2) as a semiconductor photocatalyst has drawn a lot of attention over the past four decades as it is non-toxic, stable, readily available, cheap and shows good ability for air and water purification [6,7,12–20]. Upon adsorbing a UV photon, electrons in the valence band of TiO_2 migrate to the conduction band and generate positive holes in the former. These holes react with H_2O or hydroxyl ions (OH^-) to form hydroxyl radicals ($OH^\bullet$) while exited electrons in the conduction band react with oxygen molecules to form superoxide radicals ($O_2^{\bullet-}$). The radicals subsequently participate in oxidation-reduction reactions with pollutant molecules and can typically achieve complete mineralization to form CO_2 and H_2O [6,21–23].

Practical applications of TiO_2 as a photocatalyst suspended in aqueous solutions remain limited due to catalyst recovery issues associated with the fine photocatalyst particles. This problem can be overcome by fixing the TiO_2 onto suitable supports which eliminates the need for complex and costly TiO_2 recovery techniques. However, since photocatalysis predominately takes place at the catalyst surface, fixing the photocatalysts onto supports or applying them as thin films typically reduces the reaction efficiency due to the reduced available surface area, particularly in systems where the reactant concentration is low (for example in air) [24–27]. One strategy is the application of a porous adsorbent support, whereby pollutant molecules can potentially adsorb in close proximity to photocatalytic sites, enhancing the degradation process [28–36]. Additionally, the adsorbent support may retain reaction intermediates that are formed during the photocatalytic oxidation process so that, depending on the system, potentially toxic intermediates are more likely to be completely mineralized. Finally, the application of certain types of adsorbents can result in better electron-hole separation thereby also improving the overall photocatalytic activity [37–41]. The addition of an adsorbent to achieve better contact between the semiconductor and the organic pollutants while decreasing the pollutant level in the water to be treated is one approach to overcome hurdles to applying photocatalysis commercially as a water treatment technology [42].

Adsorption is an important physicochemical process used for pollution control and its economical application depends on regenerating and reusing the spent adsorbents. The development of low-cost adsorbents used on a once through basis, eliminates the need for regeneration [43,44]. One issue with the latter approach is the leaching of the pollutants back into the environment once they are disposed of. Various strategies are available to regenerate spent adsorbents and these methods have been reviewed specifically when organic pollutants are adsorbed from aqueous solutions [45]. While the commercially accepted method for regeneration is thermal regeneration, there is a number of emerging alternative regeneration technologies. Regeneration by photocatalysis is one such method. This involves combining an adsorbent material with TiO_2 with the resulting composite being responsive to UV irradiation which induces the degradation of the adsorbed organic contaminants. Hence, from a materials perspective, such composite TiO_2/adsorbent materials are similar to the ones described for enhanced photocatalysis through greater adsorption [28–36]. From an operational point of view there are differences between the two applications. Given the relevance, photocatalysis as a regeneration method will also be included in this review.

Numerous adsorbent materials have been used as supports for TiO_2, for example, activated carbon (AC), alumina, zeolites and various kinds of silica. Such systems are considered here and their contributing parameters to the overall photocatalytic performance are assessed. Upon scanning the scientific literature on this topic it is clear that in general, the application of adsorbent materials as supports for TiO_2 photocatalysts can enhance the efficiency of organic pollutant removal. However, each material has its own advantages and its application is typically suitable for a specific range of reactions. It is noted that, by varying the reaction parameters, the performance of the supported photocatalysts can be optimized.