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Review

Photocatalytic TiO_2/adsorbent nanocomposites prepared via wet chemical impregnation for wastewater treatment: A review

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ABSTRACT

Recent progress on preparation of TiO_2/adsorbent nanocomposites (TNC) via wet chemical impregnation has been reviewed. The potential applications of TNC are growing continuously and the material is very likely to find its place in future applications of wastewater treatment. In a TNC preparation via wet chemical impregnation, electronic properties (i.e. amount of charger carrier and its lifetime) and morphological properties (i.e. particle size, surface area and crystal phase) of TiO_2 in as-prepared resultants are sensitively dependent on the experimental conditions during the synthesis. Currently, one major limitation in this promising area is that visible-light capacity has yet to be introduced into TNC systems. It is envisaged that this could be realized via a single wet chemical procedure without significant increase of the process complexity.

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1. Introduction

Long-term water shortages driven by population growth and climate change are forcing people to learn to live with less water. Manufacturing industries consume a large quantity of clean water, but until now very limited reuse has taken place. In many cases, such as meat or food processing factories, industrial wastewater streams are only slightly contaminated and contain low levels of dissolved organic compounds (DOC), e.g. polysaccharides, proteins, amino sugars, nucleic acids, humic and organic acids and cells. These dissolved organics pose a problem to the direct reuse of the lightly contaminated water without treatment, due to issues of bacterial growth, odour generation and biofouling on the utility surface. Of the current applicable treatments, adsorption process, through functionalizing the adsorbents to trap DOCs, has shown promise due to the reasonable efficacy and comparatively low costs. Highlighting its commercial viability is the fact that activated carbon (AC) adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies [1]. However, the main disadvantage of such methodology is its non-destructive nature, i.e. DOCs will be adsorbed but not decomposed; as a result, the spent or saturated

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adsorbents must be regenerated before reuse, or otherwise must simply be disposed of as hazardous waste. Therefore, decomposition of the adsorbed DOCs and regeneration of the adsorbents is a very critical step to the cost-effective use of porous adsorbents and continuous large-scale operation in wastewater treatment. Several methods, based on either desorption or decomposition, have been used to regenerate the spent adsorbents, such as activated carbon [2]. For example, the most commonly used thermal or microwave treatments promote the drying and loss of highly volatile compounds below 200 °C, vaporization and decomposition of unstable compounds at temperatures between 200 and 500 °C, and the pyrolysis of non-volatile adsorbates at temperatures over 500–700 °C. In these methods, special high temperature facilities such as multiple hearth furnaces or rotary kilns are needed to desorb effectively, and usually at the expense of decreased adsorption capacity of adsorbents due to carbon loss and surface alteration after repeated regeneration cycles.

An alternative for the degradation of DOCs and regeneration of spent porous adsorbents, heterogeneous photocatalysis can effectively oxidize a wide range of organic compounds, more to its advantage, at room or moderate ambient conditions. Scientific research in heterogeneous photocatalysis began as early as the 1970s. In recent years, applications to environmental cleanup, especially water treatment, have been one of the most active areas in the heterogeneous photocatalysis [3,4]. Some other advantages of heterogeneous photocatalysis over other adsorbent regeneration methods include: (1) No dedicated post-treatment is needed since the organic pollutants can be mineralized into non-toxic by-products such as H_2O, CO_2, and mineral acids; (2) The possibility of being activated by solar radiation could result in low energy cost; (3) Possible on-site regeneration of spent adsorbents and destruction of adsorbed organic materials; (4) Reduced loss of adsorbents due to attrition and burn-off which occurs in thermal regeneration. In the literature, materials with photocatatlytic abilities could be found abundantly. These mainly belong to the metal oxide semiconductors. As the nature of wastewater purification for human consumption and more stringent water quality standards demand the minimal level of toxicity, many metal oxides with photocatalyitc ability are excluded. Among those available, TiO_2 nanoparticles has proven to be the most promising [5], with reported advantages of low cost, non-toxicity, greatly enhanced surface area, tunable properties which can be modified by size reduction, doping, or sensitizer, no substantial loss of photocatalytic activity after repeated process cycles, enhanced photo-induced charge transport [6] and no depletion layer formation on the surface [7]. Besides, due to the intensive research on the photocatalytic activity of TiO_2, the mechanism of its purification on DOC is well understood. It usually involves the following [8]:

1. Absorption of efficient photons ($h\nu \geq$ EG = 3.2e) by TiO_2

$$(TiO_2) + h\nu \rightarrow e^-_{CB} + h^+_{VB} \quad (1)$$

2. Oxygen ionsorption (first step of oxygen reduction; oxygen's oxidation degree passes from 0 to −1/2)

$$(O_2)_{ads} + e^-_{CB} \rightarrow O_2^{\bullet -} \quad (2)$$

3. Neutralization of OH^- groups by photoholes which produces $OH^\bullet$ radicals

$$(H_2O \Leftrightarrow H^+ + OH^-)_{ads} + h^+_{VB} \rightarrow H^+ + OH^\bullet \quad (3)$$

4. Oxidation of the organic reactant via successive attacks by OH radicals

$$R + OH^\bullet \rightarrow R'^\bullet + H_2O \quad (4)$$

5. Direct oxidation by reaction with holes

$$R + h^+ \rightarrow R^{\bullet +} \rightarrow \text{degradationproducts} \quad (5)$$

Although the research in this direction began with the interest to utilize photocatalysis as a separate procedure for post-adsorption regeneration of the spent adsorbent, it soon became evident that incorporating the photocatalytic regeneration during the adsorption process by coating TiO_2 photocatalyst on the surface of adsorbents would combine the advantages of both techniques: on one hand, large surface area adsorbents work as the support of nano-sized TiO_2 photocatalyst and concentrate the pollutants and intermediates around the TiO_2, of which the photodecomposition rate is intrinsically low due to the limited surface area; on the other hand, nano-sized TiO_2 photocatalysts can decompose the pollutants thus regenerating the adsorbents in situ. A variety of coating methods for the synthesis of TiO_2/adsorbent nano-structured composites (TNC) have been reported. Some are chemical methods, such as carbonization of coal and TiO_2 mixture [9], ionized cluster beam deposition [10], chemical vapor deposition [11] and wet chemical methods [12,13]. Others are physical methods, such as impregnation–desiccation [14], boiling and dip-coating deposition [15]. At the current stage, wet chemical impregnations are of great interest, i.e. hydrolysis and impregnation of TiO_2 precursors to adsorbents, due to their facile nature, continuous process ability, low temperature and energy costs, uniform coating with good reproducibility and adhesion, and the simplicity in controlling crystal structure/morphology and particle size by simple variations in experimental conditions, such as hydrolysis rate, solution pH and solvents.

In summary, progress on developing TNC has been made in lab-scale synthesis particularly via wet chemical impregnation. A systematic study of different experimental conditions during these published TNC preparation is yet to be conducted. This gap has seriously hindered its optimization and commercial viability at present. In such context, the recent progress on various TNCs synthesized via wet chemical route, along with a special focus on its potential and current limitations are reviewed here. Relevant experimental conditions and properties of as-synthesized products in each study are highlighted where possible and compared in order to identify and optimize the key preparation parameters.

2. Parameters influencing wet chemical synthesis of TNC

In the literature, wet chemical assembly of TNC could be simplified as a three-module procedure, which is illustrated in Fig. 1: (1) contacting the adsorbents with the TiO_2 impregnating solution for a certain period of time, (2) drying the support to remove the absorbed liquid, and (3) activating the catalyst by calcinations [16].

Relevant studies of TNC synthesis via wet chemical impregnation in literature are summarized in Table 1, where key variables of the preparing conditions and corresponding as-synthesized TNC properties are listed for comparison. Each variable and its influences on the TNC prepared via wet chemical hydrolysis are further discussed in the following sections.

2.1. Influence of porous adsorbents

The overall performance of TNC on the DOC removal basically consists of two parts: adsorption by porous substrate and photocatalytic decomposition by nano-sized TiO_2. Even with the latest progress in this field, the adsorption by porous substrates still works as the major mechanism in DOC removal, because the adsorption rate is far better than that of photodecomposition. As a result, choosing a proper adsorbent is critical to the efficient TNC synthesis for practical wastewater purification. However, to facilitate the effective photocatalysis by loaded TiO_2, a balance between adsorption capacity and affinity of the TNC needs to be taken into consideration, that is, the adsorbing capacity should be