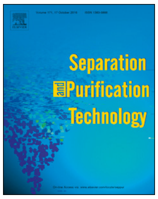
Separation and Purification Technology 206 (2018) 226–238

Contents lists available at ScienceDirect

Separation and Purification Technology

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



Silver vanadium oxide materials: Controlled synthesis by hydrothermal method and efficient photocatalytic degradation of atrazine and CV dye

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ARTICLE INFO

Keywords:
Photocatalysis
Silver vanadate
Visible light
Atrazine
Crystal violet
Water treatment

ABSTRACT

Silver vanadium oxides have received remarkable attention in recent years because of their stability, suitable band gaps, and relatively superior photocatalytic abilities. This study reports the synthesis of silver vanadates by the hydrothermal method and the investigation of their photocatalytic abilities for removing crystal violet (CV) and atrazine pollutants under visible-light irradiation. The as-prepared silver vanadates are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and UV–vis diffuse reflectance spectra (DRS). Crystal violet and atrazine could be successfully degraded in the presence of the silver vanadate catalyst under visible-light irradiation. The obtained results show complete degradation of crystal violet after 24 h of treatment and over 97% degradation of atrazine after 72 h. The as-prepared silver vanadate materials show extremely high catalytic stability and maintain stable activity after three catalytic cycles. The scavenger studies indicate that $^{\cdot}O_2^{-}$ radicals are the main active species in the degradations of CV and atrazine, while $^{\cdot}OH$ and h^{+} play an assistant role in these processes. Liquid chromatography coupled with electrospray ionization mass spectrometry is used to analyze the samples obtained from the photocatalytic degradation of CV and atrazine. The degradation pathways of atrazine are evaluated suggesting two different routes including dechlorination–hydroxylation and alkylic-oxidation–de-alkylation. On the other hand, the degradation of the CV takes place via *N*-de-methylation in a stepwise manner generating the various *N*-de-methylated intermediate CV species. The excellent activity and photostability reveal that silver vanadates (including $Ag_4V_2O_7$) are promising visible-light-responsive photocatalysts for water and wastewater treatment.

1. Introduction

Semiconductor photocatalysts have attracted strong attention due to their efficiency in environmental purifications and splitting of water into hydrogen and oxygen gases [1–4] in addition to the importance of catalysis in various domains of research. Silver-based oxides, with the unique hybridized valence bands (O 2p and Ag 4d orbitals), exhibit a narrow band gap (≤ 3 eV) and highly dispersed valence bands (VB), resulting in useful photoabsorption ability and high mobility of photoholes, respectively. Therefore, these materials are prospective candidates as visible-light-sensitive photocatalysts in interesting applications [5–7]. Among the different silver-based semiconductors, the efficiency of silver vanadium oxide materials (silver vanadates, SVO) in photocatalytic applications using visible irradiation has been documented, owing to their narrow band gap and good crystallization [8–11]. SVO materials are among the most complex metal oxides, with a number of phases present even in the case of a single atomic composition [12,13]. Moreover, SVO semiconductors exhibit a band gap transition that allows strong absorption in the visible light region [14]. They also have potential uses in rechargeable high-energy density lithium batteries, solar energy conversions, and sensors [15–18].

Significant effort has been devoted in the past years to synthesize different types of silver vanadates as well as different morphologies [19–21]. Nevertheless, there are few studies that describe the impact of the preparation factors on these vanadates such as the ratio of the silver and vanadium sources, which has not yet been probed, and the effect of the pH on the preparation [22]. Specifically, there exist four main types of silver vanadates: $AgVO_3$, $Ag_2V_4O_{11}$, Ag_3VO_4, and $Ag_4V_2O_7$. Among

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https://doi.org/10.1016/j.seppur.2018.06.011
Received 3 February 2018; Received in revised form 18 May 2018; Accepted 3 June 2018

Table 1
Catalyst codes and crystalline phases of the silver vanadate samples prepared under different reaction conditions.

Catalyst code	Molar ratio	pH	Crystalline phase
Ag1V1-5	1:1	5	$AgVO_3$
Ag1V1-7	1:1	7	$AgVO_3$
Ag1V1-9	1:1	9	$AgVO_3$
Ag2V1-5	2:1	5	$Ag_4V_2O_7$
Ag2V1-7	2:1	7	$Ag_4V_2O_7$
Ag2V1-9	2:1	9	$Ag_4V_2O_7$
Ag3V1-5	3:1	5	$Ag_4V_2O_7$
Ag3V1-7	3:1	7	$Ag_4V_2O_7$ + Ag_3VO_4
Ag3V1-9	3:1	9	$Ag_4V_2O_7$ + Ag_3VO_4

them, Ag_3VO_4 shows the highest photocatalytic activity. Research has generally overlooked the activity of $Ag_4V_2O_7$, which often coexists with Ag_3VO_4, and investigations that focus on the photocatalytic efficiency of $Ag_4V_2O_7$ are *hitherto* limited [11,14,23]. Wang et al. have shown that pure $Ag_4V_2O_7$ materials prepared by the hydrothermal method exhibit high photocurrent response, strong absorption in the region of visible light, and high catalytic efficiency in RhB photodegradation using visible irradiation [22]. Hence, $Ag_4V_2O_7$ has potential applications as visible-light-sensitive photocatalysts in the removal and decomposition of organic pollutants. In the continuity of our research related to photocatalysis and degradation of contaminants [24–28], we have been interested in the preparation of $Ag_4V_2O_7$ and its applications in the photocatalytic decomposition of toxic molecules under visible-light irradiation.

Considering organic contaminants, atrazine herbicides are widely used to control grassy weeds in cotton, corn, soybean, rice, and wheat crop fields. Currently, around forty types of common herbicides contain atrazine as one of the basic ingredients, and more than sixty countries utilize this organic compound [29]. Atrazine and its byproducts are known to be mutagens, possible carcinogens, and endocrine disruptors that persist in the environment, making their way into both surface and ground water [30,31]. These compounds have been frequently detected in water supplies causing serious pollution problems, especially due to their long half-lives. According to USEPA, long exposure to atrazine has led to mammary gland tumors and endocrine perturbations in studies carried out on animals. Moreover, even low quantities of atrazine can adversely influence the sexual development of amphibians [32]. Hence, the negative impact of atrazine and similar pollutants on ecosystems and human health urges further investigations in order to develop efficient and environmentally friendly technologies for water treatment.

On the other hand, dyes constitute a widely used class of chemicals for industrial and medicinal uses [33–38]. A great variety of dyes are classified as environmental pollutants, which have different effects ranging from skin irritations and moderate toxicity to more serious carcinogenic and mutagenic effects on the aquatic system. The process of detection of dyes is complex due to the diversity of functional groups in different dyes. Crystal violet [Tris((dimethylamino)phenyl) methylium chloride] dye is very stable and non-biodegradable due to the electron-donating group in its unique structure. It is a known carcinogen, which raises concern as most of the commonly used primary and secondary aromatic amines [39,40]. Thus, various semiconductors are being studied in the removal of dyes [41–43].

The traditional techniques of water treatment involve biological treatments, chemical oxidations, and activated carbon adsorptions, among others. These methods suffer from limitations. For instance, biological treatments need the disposal of activated sludge and are still long processes due to the slow rates of these reactions. The adsorption

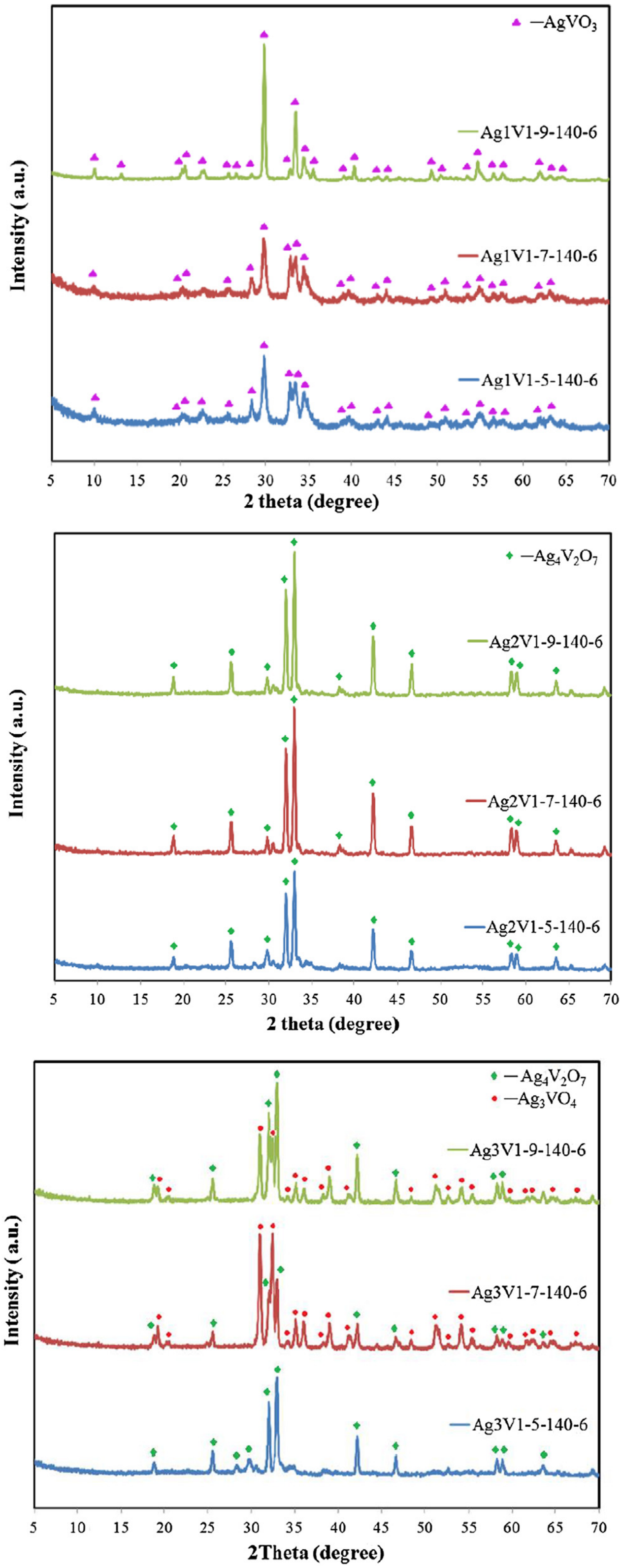

Fig. 1. XRD patterns of the as-prepared silver vanadate samples under different pH values and Ag/V molar ratio, at reaction temperature 140 °C and reaction time 6 h.