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Enhanced heterogeneous photodegradation of VOC and dye using microwave synthesized TiO_2/Clay nanocomposites: A comparison study of different type of clays

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A B S T R A C T

Supply of pure drinking water and air is a perquisite for sustaining of civilization and in this respect the clays are found to have significant importance as a semiconductor support material due to their layered morphology, chemical as well as mechanical stability, cation exchange capacity, non-toxic nature, low cost and availability. In spite of availability of technique very few studies have been done on the effect of clay structure on photocatalytic efficiency of semiconductor/clay nanocomposites. The TiO_2/clay nanocomposites were synthesized from different clays having textural differences (1:1 and 2:1); by a simple and time as well as cost effective method under microwave conditions. Formation of anatase TiO_2 nanoparticles on surface of different clays was achieved at 180 °C within 10 min of time. Phase composition, particle morphology, specific surface area, chemical bonding, etc. of those samples were characterized by using XRD, TEM, FESEM, FTIR and nitrogen gas adsorption-desorption (BET) methods. Formation of TiO_2 nanoparticles on clay surface were confirmed by monitoring peaks of anatase TiO_2 with crystallite size 10–20 nm in X-Ray diffraction pattern of TiO_2/Clay nanocomposites. The TiO_2/clay nanocomposites exhibited high surface area and uniform pore distribution compared to pure clays and TiO_2 (Degussa P25, Germany). The photocatalytic activities of the nanocomposites were found to be depended on clay texture as well as optical characteristics apart from their surface area. The 2:1 clay (bentonite, kunipia-F) was observed to act as better support for TiO_2 in comparison with 1:1 clay (kaolin); regarding its photo-catalytic degradation of methylene blue (MB) and volatile organic compound (VOC) such as chlorobenzene (CB) due to their different texture and optical properties. TiO_2/bentonite nanocomposite has high optical absorbance under UV spectrum. It also showed surface area of 112 m^2/g with high photocatalytic activity with a rate constant 0.02886 and 0.0460 min^{-1} for MB and CB degradations respectively. It had also been found that, the photocatalytic activity of the TiO_2/bentonite nanocomposites were 8 and 5 times higher for MB and CB degradation respectively in compare with Degussa P25.

1. Introduction

Industrial malpractices such as improper disposal of hazardous chemicals and emission of toxic gasses have degraded the quality of water, air and soil and the whole industrial community nowadays employ advanced physiochemical processes to detoxify these hazardous wastes [1]. Heterogeneous photocatalysis on the surface of semiconductor is one of the extensively rising areas for basic and applied researches, primarily for cases such as detoxification of pollutants in water or air [2]. The above statement deals with two reactions which occur simultaneously, the first being oxidation from photo generated holes and second being reduction from photo generated electrons. Both these phenomena should be balanced precisely to get an effective photocatalytic activity [3]. These two phenomena proceed via absorption of ultraviolet light corresponding to band gap. The photo generated holes in valence band and electrons in conduction band diffuse to the semiconductor surface and interact with adsorbed water molecules to form OH• (hydroxyl) radicals. The OH• radical oxidize organic molecules presence of TiO_2 (surface exposed) and electrons in the conduction band react with molecular oxygen to form $O_2{}^{\bullet 2-}$ (superoxide)

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radical and in turn promote reduction process [4]. The availability of TiO_2 is one of the most important aspects in the field of photocatalysis, as it is inexpensive and very close to an ideal photoactive material in many other respects such as chemically inert, less toxic, etc [5]. However, it suffers from some technical barriers which tend to impede its industrial applications such as low adsorption capacity of hydrophobic pollutants, low surface area and formation of uniform suspension in water which makes its recovery difficult. For making photocatalytic activity of TiO_2 more effective, some efforts were made by imbedding nano size TiO_2 on supports materials including mesoporous silica [5], activated carbon, zeolites, clays, etc [6]. Among these materials clays found to have significant importance as a TiO_2 support material due to their layered morphology, chemical as well as mechanical stability, cation exchange capacity, non-toxic nature, low cost and availability. Also the nanocomposites obtained by incorporating TiO_2 on clay tend to have high surface area, enhanced porosity which means availability of enhanced surface active sites. Hence, TiO_2/clay nanocomposites found to have several applications for water and air purification. Due to its popularity TiO_2/clay nanocomposites have been synthesized by several researchers using different methods [7–10]. On the basis of textural difference clays are of primarily of two types which are 2:1 clay or Montmorillonite (MMT) clays and 1:1 clay such as kaolin. MMT clays comprise of two tetrahedral layers of silica and one octahedral layer of alumina sandwiched in between and thus forms a category of 2:1 clays. Lattice imperfection and isomorphological substitution generates net negative charge which helps in adsorption of alkaline and alkaline earth metal ions in interlayer space [11–13]. Bentonite, laponite and kunipia-F come under the category of MMT clays. Daniel et al. synthesized TiO_2/laponite nanocomposites with high surface area and porosity and also investigated effect of Ti content on surface area and photocatalytic activity of the resulting composite [14]. In our previous work, we had synthesized TiO_2/bentonite nanocomposites by microwave assisted synthesis method and the composites were found to possess high pore volume and superior photocatalytic activity [15]. Jagtap et al. [16] synthesized TiO_2/kunipia-F composites both by conventional and ultrasonic methods and studied the influence of concentration of oxidant, photocatalyst and nature of solvent on photo-oxidation of aniline. Kaolin consists of tetrahedral silica sheet alternating with octahedral alumina sheet forming a 1:1 clay mineral structure. It is non-expanding and due to its molecular stability; isomorphous substitution in these material is very limited or negligible [17–19]. Nanocomposites of TiO_2 with kaolin have been synthesized and are found to possess high stability and posses good photocatalytic and antibacterial activity [20]. Yang et al. [7] incorporated TiO_2 nanosol into clays by partially modifying the octahedral sites with divalent metal cations such as Mg^{2+} and Fe^{2+}. Tubular halloysite clays were used as supports by to synthesize visible light active polyanaline-crystalline TiO_2-halloysite composite photocatalyst to carry out photocatalytic degradation of rhodamine-B [8]. Similarly, photocatalytic degradation of methylene blue under visible light using CdS/TiO_2-MMT nanocomposites was reported by Wang et al. [9]. Surfactant modified Na^+ beidellite clay was used by Rhouta et al. [10] using surfactants with different carbon chain lengths as support for TiO_2 nanoparticles. Similarly, surfactant modified TiO_2/MMT nanocomposites were synthesized using cationic surfactants and showed to have excellent photocatalytic activity with only one third of TiO_2 content in the sample [11,12]. Though TiO_2/clay nanocomposites have been synthesized from different clays yet very few efforts have been made to investigate the effect of different aspects of clays such as texture (1:1 or 2:1) and optical behavior (absorption and scattering) on the photocatalytic activity of the resulting TiO_2/clay nanocomposites. In this regard only Kibanova et al. [21] compared the nanocomposites of TiO_2 with hectorite (2:1 clay) and kaolin (1:1 clay) and found that the synthesis efficiency depends upon clay structure. Significant incorporation of TiO_2 on hectorite as compared to kaolin leading to morphological changes; however the photocatalytic activity of nanocomposites was comparable to commercial TiO_2 [21]. Recently, Yang et al. [7] investigated the effect of optical transparency on photocatalytic activity of Na-Mica clays modified with divalent cations such as Mg^{2+} and Fe^{2+}.

Since; MMT and kaolin are the principle clay minerals of the northern hemisphere for soils and sediments; therefore, we have selected these clay materials for our study. In this work we have synthesized a series of different TiO_2/clay nanocomposites by microwave assisted method which is simple, reproducible, time and cost effective. In our study we have taken MMT (bentonite and kunipia-F) and kaolin clay and made TiO_2/clay nanocomposites to investigate different aspects of photocatalytic activity using MB and CB as model water/air pollutants.

2. Experimental section

2.1. Materials

Kunipia-F [$(Na_{0.3}Ca_{0.03}K_{0.04})(Al_{1.6}Mg_{0.3}Fe_{0.3})Si_4O_{10}(OH)_2$] was supplied by Kunimine Industries Co. Ltd. Japan. Bentonite [$Na_{0.4}Ca_{0.03}K_{0.01})(Al_{1.6}Mg_{0.3}Fe_{0.1})Si_4O_{10}(OH)_2$], Titanium (IV) butoxide and MB were purchased from Sigma Aldrich, USA and kaolin [$Al_2Si_2O_5(OH)_4$] from Himedia, India. All reagents were used without further purification. Dye solutions were prepared with deionized water (18.2 MΩ cm). The photocatalytic performance of the samples were compared with that of pure TiO_2 nano-powder (Degussa P25) from Degussa (Germany).

2.2. Preparation of TiO_2/clay nanocomposites

TiO_2/clay nanocomposites were synthesized by a modified process as reported by Miao et al. [22]. The clay suspensions were made by dissolving 0.5 g of oven dried clay in 10 ml of ethanol and slurry was treated at 180 °C for 5 min under microwave (Anton Par, Monowave-300). After that 0.5 ml of titanium butoxide (density 1 g ml^{-1}) was added drop wise; followed by addition of 10 ml of water with continuous stirring. The suspension was again transferred to the microwave and kept at 180 °C for 5 min. The final slurry was obtained, washed 5 times with ethanol/water, dried at 60 °C and calcined at 550 °C for 4 h.

2.3. Characterization of TiO_2/clay nanocomposites

X-ray diffraction analysis (XRD) of the TiO_2/clay nanocomposites were performed by PAN ANALYTICAL X-ray diffractometer using Cu Kα radiation (λ = 1.54 Å), operating at 45 kV with scan speed of 2° per minute and scan range of 2-60°. Morphological analysis of nanocomposites were done by SU8180, Hitachi FESEM operating at 15 kV. Detailed structural analysis of TiO_2 loaded clay samples were done using FEI TECHNAI-G2 high resolution transmission electron microscope (HRTEM) operating at 200 kV. IR spectroscopy of TiO_2-clay nanocomposites were carried out using Carry-660, Agilent Technologies FTIR spectrophotometer. UV–Vis diffuse reflectance spectroscopy of the as synthesized nanocomposites were carried out in “Diffuse Absorbance” mode through Hitachi-3900H spectrophotometer. Nitrogen sorption analysis (BET) were carried out using BEL mini-II, Micro Trac Corp. Pvt. Ltd., surface area and pore size analyzer after pretreatment of 0.1 g of sample at 150 °C for 3 h.