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Behavior of the new composites obtained from fly ash and titanium dioxide in removing of the pollutants from wastewater

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ABSTRACT

The goal of this paper was to develop a low-temperature TiO_2-fly ash (TiO_2-FA) composite based on interaction in alkaline solution using hydrothermal methods, to obtain crystalline nanocomposite at low temperature. These composites are interesting to be applied in visible photocatalysis/adsorption simultaneous advanced wastewater processes. Combining fly ash with titanium dioxide has the following advantages: (1) the titanium oxide crystallites grow on the support (active fly ash); (2) pollutant molecules migrate to the surface of TiO_2 can be degraded by photocatalysis; and (3) activated fly ash substrates are regenerated in situ.

The composites were characterized by the scanning electron microscopy (SEM) and atomic force microscopy (AFM) for morphological characterization of the surface, X-ray diffraction (XRD) for phase and crystallinity analysis, UV–vis spectroscopy to calculate the energy band gap, surface analysis by determining the contact angle, porosity analysis (BET).

The photocatalytic property of the composites was evaluated by dye (methylene blue), surfactant (dodecylbenzenesulfonate–SDBS) degradation under UV and Visible irradiation. The adsorption tests were made on heavy metal (Cu^{2+}) cation. Properties of composites were correlated with the adsorption/photocatalytic activity of the samples.

1. Introduction

Wastewater, highly loaded with heavy metals, dyes, surfactants, polyglucides along with micro-organisms are generated from chemical industry, textile industry and food industry [1].

The textile industry use water over 90% for production and wastewater resulted has become a growing environmental concern in line with rapid industrialization. More attention has been given to remove the pollutants from wastewater because degradation of water resources is a social concern. The dyes, heavy metals, surfactants from wastewater are absorbed from living organisms then pas up in the food chain to humans causing various illnesses. Over one million kilograms per year of dyes are discharges into waste streams by the textile industry [2]. The effluents loaded with dyes are unacceptable and their color interfere with light penetration that disturbs biological processes of the aquatic environment.

Anionic and cationic surfactants are widely employed in the domestic and industrial sectors. They case serious ecological problems, since the surfactants do not undergo natural degradation.

Many treatment technologies for dyes and surfactants have investigated such as: chemical coagulation, flocculation, filtration, membrane filtration, photo-degradation [3], oxidation, adsorption [4] or simultaneous adsorption and photo-degradation [5,6].

The adsorption process provides an attractive method for remove these pollutants especially if the adsorbents are inexpensive: modified fly ash, bentonite [7] composite (Fly ash withTiO_2 or WO_3).

In the recent years, photocatalytic oxidation process using different semiconductor oxides: TiO_2 WO_3 or theirs combinations with fly ash [8] were widely used for wastewater treatment. Under UV or VIS light irradiation are generated the hydroxyl radicals with strong oxidative ability to degrade the refractory organic pollutants [9].

As advanced oxidation processes (AOP), especially heterogeneous photocatalysis emerged as promising alternatives to the current wastewater treatment to remove recalcitrant pollutants, the use of fly ash was considered mainly as substrate for the photocatalyst deposition. Recent reports are on the synthesis of the photocatalyst from a precursor system directly on nano-sheets [10] and on the fly-ash grains/cenospheres [11,12]. These materials are using FA as an inert substrate and the organics degradation is expected only due to the photocatalytic effect. Lately, the active adsorption effect of natural clay was reported combined with photocatalysis, and previous work outlined that the fly ash–TiO_2 mix can effectively activate in adsorption–photocatalysis [13].

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For dyes removal from wastewaters, most of the papers report the results obtained from mono-pollutant solutions; but, industrial wastewaters contain more than one pollutant that can interact in the aqueous environment and can develop concurrent processes on the active sites, therefore this type of data is required for an accurate process design.

As advanced oxidation processes, especially photodegradation of surfactants using semiconductor particles as catalyst represent an efficient kind of AOP methods.

The goal of this paper was to develop a low-temperature TiO_2-fly ash (TiO_2-FA) composite based on interaction in alkaline solution using hydrothermal method. These composites are interested to be applied in UV and Visible photocatalysis/adsorption simultaneous in removing the organic pollutants (methylene blue), anionic surfactant (dodecylbenzenesulfonate–SDBS) and heavy metal Cu^{2+}.

2. Experimental

2.1. Substrate preparation

For increasing the efficiency of the VIS-activated photocatalysis and for developing processes to simultaneously remove organic (dyes, surfactants, etc.) and inorganic pollutants (heavy metal cations) one feasible path is to develop composite materials. According to the role of the components in photocatalysis, the composites can be described as having: active matrix (by associating two semiconductors in a tandem) or with non-active matrix, by associating an adsorbent (e.g. activated carbon, ion exchanger or fly ash (FA)) with a photocatalysis. In addition, the use of secondary raw materials (fly ash) can significantly decrease costs of such material, increasing sustainable and character.

Fly ash (FA) was collected from the electro-filters of the CHP plant in Brasov, Romania which uses a mixture of bituminous and pit coal. The main oxides in the fly ash composition (as given by the CHP plant) are: SiO_2, Al_2O_3 and Fe_2O_3 and small amounts of the other metals (Ba, Cu, Sn, Pb, Cr, Ni, V, Zn) were identified by atomic absorption spectrometry with graphite furnace. According to the ASTM standards (C618-05) [14], the fly ash is of F type (pozzolanic) because the sum of the major oxides SiO_2, Al_2O_3 and Fe_2O_3 is over 70%, thus during long contact with water there is no aggregation. The SiO_2, Al_2O_3 ratio (2.41) is quite large and shows that FA represents a possible zeolite precursor.

At these stage composites TiO_2/FA obtained by hydrothermal synthesis (denoted by FLY1, FLY2 and FLY3) were the starting point for the production of composites with inactive matrix.

The ash was washed with double distilled water in the ratio: 1:10 (100 g ashes: 1000 mL double distilled water) by stirring for 48 h; wet ash was filtered, dried in an oven at 115 °C for 24 h. Sieved and dry ash for the experiments was chosen fraction of 20–40 μm, this fraction was treated with 2 N NaOH solution (ratio of 1:10) for 24 h and then dried in an oven at 115 °C for 24 h. This substrate is denoted FACETNaOH2N.

Materials of the type FA: TiO_2 (Fly1, Fly2 and Fly3) were synthesized by a hydrothermal method; were mixed 50 g FACETNaOH2N with TiO_2 Degussa P25 (ca. 80% anatase, 20% rutile) with 500 mL NaOH solution 2 N (1:10). The mass ratio of mixing of FACETNaOH2N with Degussa P25 was 3:1 (FLY1), 1:1 (FLY2) 1:2 (FLY3). Hydrothermal synthesis parameters were: $t = 150$ °C, $p = 5$ atm during 24 h. In one of them (FLY2) was added Pt nanoparticles in ultrasonic mode for increase the photocatalytic activity of material. This material was noted FLY2NP. This material was denoted FLY2NP. After synthesis, the material was washed for several times with double distilled water until the washings had a constant pH (around 7). The suspension was filtered and the resulting material was dried at 110–115 °C temperature for 24 h and then analyzed.

2.2. Characterization of the new substrate

The crystalline structure was evaluated by XRD (Bruker D8 Discover Diffractometer), over the 2θ range 10–70°. Morphology studies (roughness and macro-pore size distribution) were done using AFM (Ntegra Spectra, NT-MDT model BL222RNTE); images were taken in semi-contact mode with Golden silicon cantilever (NCSG10), with constant force 0.15 N/m, having the tip radius of 10 nm. Scanning was conducted on three or more different places with a certain area of 5 μm × 5 μm for each position, chosen randomly at a scanning grate of 1 Hz. Further surface investigations were done using scanning electron microscopy (SEM, S-3400N-Hitachi) at an accelerating voltage of 20 KV. Surface compositions were measured using energy dispersive X-ray spectroscopy (EDS Thermo Scientific Ultra Dry). Surface characterization was completed by porosity analysis and BET surface (Autosorb-IQ-MP, Quantachrome Instruments).

2.3. Adsorption and photocatalytic experiments

The pollutant systems were synthetically prepared using bidistilled water and, $CuCl_2{\cdot}2H_2O$ (Scharlau Chemie S.A., $c < 98\%$), methlene blue ($C_{16}H_{18}N_3S$; Fluka AG, reagent grade) and sodium dodecylbenzenesulfonate, SDBS ($CH_3(CH_2)_{11}C_6H_4SO_3Na$) technical grade (98% purity, Sigma–Aldrich).

Experiments were done using heavy metal solutions in the concentration range of $c_{Cu} = 0, \ldots, 350$ mg/L, respectively, methlene blue $c_{MB} = 0.3125$ mMol, using MB Fluka AG, reagent grade) and surfactant initial concentration was: and $c_{SDBS} = 25$ mg/L, being lower than the critical micelle concentrations ($CMC_{SDBS} = 418$ mg/L), evaluated based on conductivity measurements. The solutions were used at their natural pH; the initial pH of the solutions containing surfactants and heavy metals in contact with FA-TiO_2 was 6.53, which is higher than the TiO_2 point of zero charge (PZC = 6.25), allowing thus a slightly negative charge on the photocatalyst.

These composites were tested in adsorption and photo-catalysis processes. Photodegradation studies were done on suspensions, under UV and VIS irradiation, using quartz beakers. The homemade reactor is equipped with three F18W/T8blacklight tubes (Philips), emitting UV light, typically 340–400 nm, with λ_{max} (emission) = 365 nm and with VIS iradiation (400–700 nm, with $\lambda_{max} = 565$ nm, 15% UV and 85% VIS) – the solar spectrum (excluding the IR part). Preliminary experiments proved that heavy metals, dye and surfactants losses due to adsorption to the container walls are negligible.

The kinetic adsorption/photodegradation parameters of cooper cations from pollutant system were evaluated from batch experiments according to the experimental study: in each experiment, 0.1 g of substrate was stirred (200 rpm) at room temperature (20–23 °C), with 50 mL solution, at initial concentrations. In the kinetic studies, aliquots were taken each at 15, 30, 60, 90, 120 180, 240, 300, 360 min, when stirring was briefly interrupted and the substrate was removed by centrifugation (GL-20G, Shanghai, China).

The supernatant was further analyzed by AAS (Analytic Jena, ZEEnit 700), at: $\lambda_{Cu} = 324.75$ nm and UV–vis absorbance measurements (Perkin Elmer UV–VIS spectrophotometer, Lambada-950) were done at the maximum absorption wavelength 223 nm for SDBS and 664 nm for MB.

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