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Heat treatment effect of MoO_3 on the MB removal and its reuse

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ABSTRACT

Microstructural change and MB removal tests were studied of MoO_3 as a function of heat treatment. Synthesized materials were mill and stabilize it structure for MB removal by milling and heating process. It was found that the optimized material can be reused cyclically, obtaining always 100% of the MB removal. Around 90% of MB removal was reached in ~30 min. The removal process has not influence by UV-Vis illumination, it works by adsorption. Morphology and microstructure were studied by electron microscopy techniques and XRD techniques. By infrared spectroscopy was characterize the material for recycling process on MB removal. XRD patterns were refine by Rietveld method to determine lattice parameters, percentage of phases, crystal sizes and anionic vacancies concentration. The thermal stability of materials was study by thermogravimetric analysis and differential scanning calorimetry. Optimized material could be reused to MB removal.

1. Introduction

Dyes and pigments (released from several industries, especially by textile dyeing) are the main organic pollutant compounds in wastewaters [1]. The presence of dyes in water sources, even at low concentrations is very harmful to human beings and microorganisms [2]. Due to this type of contamination, there is a great need for dealing with dyes before discharge to receiving waters [3]. Several technologies developed for removing contaminants (dyes) from wastewater include coagulation/flocculation, advanced oxidation processes, ozonisation, membrane filtration, electrochemical processes, biological treatment and adsorption techniques [4–9]. Due to the high efficiency, profitability and simple operation, adsorption of contaminant dyes from wastewater has received significant attention [10]. Some adsorbents, such as activated carbon, clays, zeolites and other porous materials, are widely investigated [11and12]. Nevertheless, the difficulties for the regeneration of those materials, as well as their further processing increases the application costs [13]. Recently have been found that molybdenum trioxide adsorbs methylene blue in a short period of time [14].

Hexagonal and orthorhombic phases of MoO_3 were analyzed by in situ X-ray diffraction thermal study to observe their microstructural behavior and phase transformation. The behavior of the crystal structure was analyzed by Rietveld refinement for both phases. The main objective of this research was to study their ability of molybdenum trioxide nanoparticles capacity as the cationic dye adsorbed using methylene blue (MB) from aqueous solutions and its reuse capability.

2. Experimentation

2.1. Chemicals

Ammonium heptamolybdate tetrahydrate ($(NH_4)\ 6Mo_7O_{24}4H_2O$), nitric acid (HNO_3, 70 wt. %), methylene blue ($C_{16}H_{18}N_3SCl$) from Sigma-Aldrich brand and tri-distilled water was used for all synthesis process.

2.1.1. Orthorhombic and hexagonal MoO_3 synthesis

For MoO_3 orthorhombic phase synthesis by using a standard method [16], first a precursor of salt ammonium heptamolybdate was made in dissolution at 0.3 M and the acidity was tuned to pH 5 using nitric acid at 2.2 N. The dissolution was aged for 48 h in a tight closed flask on an ongoing stirring basis at 70 °C. Then the mixing of 5 ml of tridistilled water, plus 5 ml of nitric acid and 5 ml of the aged dissolution was transferred to a quartz vial for the microwave radiation treatment at 200 °C for 90 min; the resulting material was then filtered, and washed with tri-distilled water. Afterwards, it was dried for 5 h at 90 °C. This material was called OW. For synthesis of MoO_3 with hexagonal phase,

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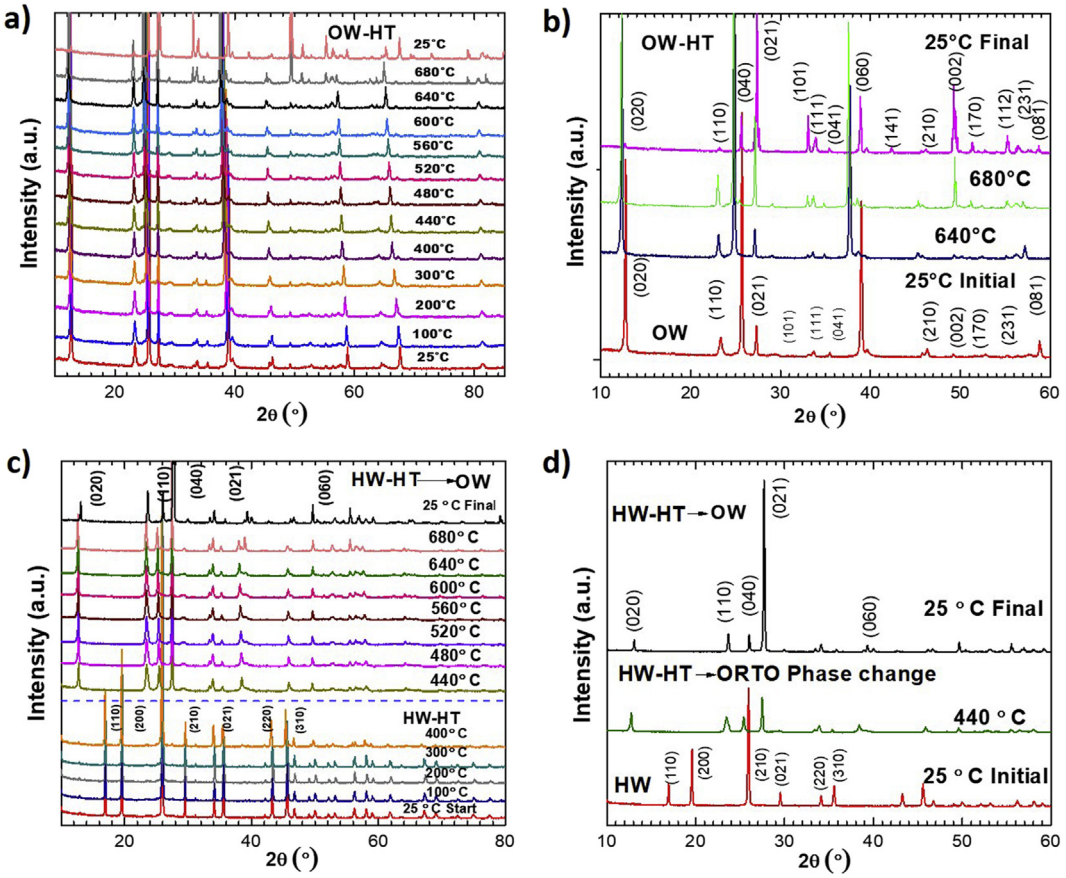

Fig. 1. XRD patterns of the microwave synthesis (OW, HW), submitted to heat treatment a) OW and c) HW, New orientation after heat treatment 680 °C for samples b) OW and d) HW.

the same procedure exposure above was used (same quantities), but the dissolution was fresh at room temperature (not aged) and it was transferred to a quartz vial for the microwave radiation treatment at 200 °C for 10 min. This material was called HW. The other way to obtain MoO_3 orthorhombic phase in short time was using the previous hexagonal phase synthesized (HW material) heating for 45 min at 450 °C inside the furnace, this material was called HWC.

Heat treatments (HT) (for samples OW and HW) were started with a temperature of 25 °C for in situ XRD, with a heating rate of 10 °C/min up to 680 °C (by increasing the temperature at intervals of 100 °C up to 400 °C, from this temperature the increases were at intervals of 40 °C and so on).

In order to obtain nanometric particles sizes, the HWC material was ground through a high energy mechanical milling (MM) at room temperature during 30 min in a stainless-steel vial, using three spheres of zirconium dioxide (each one with a diameter of 1 cm, and total weight of 10 g). The spheres-ground material weight ratio was 5:1. The equipment used was a SPEX 8000 mill. The material after the MM was referred as HWCM.

2.1.2. Process removal of MB

The photocatalytic test were carried out in batch type reactor with 1000 ml capacity. it was magnetically stirred and irradiated with UV lamp (UV Trojan, Model V-1416, 25 W, λ = 254 nm). The photo-reactor and the lamp is placed inside a container with reflecting walls, in all experiments were used aqueous solution having 20, 60, 90, 120, 180 and 400 ppm concentration of MB dye, with MoO_3 NPs dispersion of 160 mg/L as catalysts [17], the absorption spectra were taken every 5 min.

2.2. Characterization

The X-ray diffraction patterns were recorded on a Philips X'Pert MPD diffractometer, with Cu $K\alpha_1$ radiation (λ = 1.54056 Å) working at 40 kV and 30 mA current. The microstructural parameters were determined through Rietveld refinement methodology of the x-ray diffraction patterns using Fullprof free software.

Scanning electron microscopy (SEM) images were acquired by cold field emission JEOL JSM-7401 F microscope working at 5 and 17 kV to get images and elemental analysis, respectively. This SEM has energy dispersive X-ray spectrometer (EDS) facility (Oxford Inca model).

Transmission electron microscope (TEM) and scanning transmission electron microscope (STEM) images were acquired by field emission JEOL JEM-2200FS microscope working at 200 kV, this equipment has EDS facility (Oxford-Inca), the images were acquired by bright field (BF) and high angle dark field (HAADF) detectors. The samples for TEM study were dispersed in methanol by sonication and a drop of it was deposited onto a lacy carbon film on a copper grid.

The Brunauer-Emmett-Teller (BET) methodology was used to measure the specific surface area, using nitrogen adsorption in a Quadrasorb SI, Quantachrome equipment. The samples were degassed previously at 250 °C for 12 h before start the measurement.

The thermo gravimetric techniques (TGA-DSC) analysis was carried out in a TA Q600 Instruments with a heat ramp of 10 °C/min from room temperature to 800 °C.

The progress of the MB removal was monitored by UV-VIS spectroscopy using Agilent model Cary 60 Instrument. The signal value was following the intensity of the maximum absorption of methylene blue at 665 nm.

IR spectra was acquired by Spectrum Gx FT-IR system (Perkin-