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Dual-function hydrotalcite-derived adsorbents with sulfur storage properties: Dyes and hydrotalcite fate in adsorption-regeneration cycles

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ABSTRACT

Thermal treatment of hydrotalcite at increasing temperatures resulted in formation of mixed oxides that exhibited different adsorption behavior toward anionic and cationic industrial dyes. The material annealed at 450 °C was characterized by the highest maximum adsorption capacity for both types of dyes. The adsorption was strongly pH dependent and for the anionic dye abatement low pH was favored whilst higher pH was more preferable for removal of the cationic dye. According to the equilibrium experiments, the maximum adsorption capacity increased from 179 ± 5 to 291 ± 8 mg g^{-1} in case of the anionic dye at pH 3.5 and from 6 ± 2 to 48 ± 2 mg g^{-1} in case of the cationic dye at pH 8.0, on starting and thermally treated material at 450 °C, respectively. Detailed characteristics of spent adsorbent and its reconstructed form revealed that after each cycle of adsorption and thermal regeneration the maximum adsorption capacity of the material decreased due to changes in the structure and accumulation of sulfur compounds. Evolution of specific surface area and porosity was correlated with annealing temperatures and behavior of dye's residues.

1. Introduction

Colored wastewater is created as a result of the production of the dye and as well as a direct consequence of its use in the textile and related industries. Consumption of colored textiles, which is one of the basic technologies in human civilization, is steadily increasing worldwide, following the growth of world population [1]. The textile dyeing and finishing industry, being one of the most chemically intensive industries on earth has created major environmental problems and is the second greatest polluter of clean water, right after agriculture. Many of chemicals present in wastewaters are cause of significant environmental degradation and human diseases [2]. Dyes can exhibit acute toxicity, sensitization, chronic effects after repeated application, mutagenic and carcinogenic effects on human. Dyestuffs, being intensely colored, are usually the first contaminant to be recognized in wastewaters and present special problems because even a small amount is highly visible. They can exhibit ecotoxicity and affect transparency and gas solubility of water bodies. By absorbing the sunlight entering water they alter growth of the aquatic species and hinder photosynthesis upsetting natural ecosystems. Synthetic dyes are in general not readily biodegradable and chemically stable thus traditional wastewater treatment techniques are ineffective. It is also important to handle the residues and byproducts obtained after decolorization process because many of them have negative influence on environment [3] The development of efficient, economic and environmentally friendly technologies to remove color and detoxify the wastewaters to acceptable levels and decrease their environmental impact at affordable cost is the first and major concern of the utmost importance [4,5]. Among many other techniques adsorption is considered as one of the best wastewater treatment methods due to its universal nature, ease of operation, ability to remove soluble and insoluble organic pollutants, high removal capacity and possibility to recycle and reuse many of adsorbents [6,7]. Activated carbon is the most widely used adsorbent

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however, its preparation is generally energy-consuming and commercially available product are relatively expensive, which may hamper its application [4,8]. This has triggered a growing interest in production of low-cost adsorbents.

Hydrotalcite-like (HTL) materials, layered double hydroxides (LDH) or anionic clays are the common names given to a wide family of layered materials with both divalent and trivalent metallic cations in the main, positively charged layers and an interlayer anionic species balancing the layers charge. The interlayer anion can be almost freely exchanged for a wide possible selection of anionic compounds present in liquid phase. The principal areas of interest, among others, include their application as adsorbents. A unique property of such materials is that after thermal treatment under mild conditions, they are able to reconstruct the layered structure which opens a possibility for regeneration of a spent adsorbent [9,10].

Hydrotalcite-like materials (HT) have been already tested as adsorbents of various pollutants. Regarding removal of dyes by MgAl-hydrotalcite and derived mixed oxides Li et al. [11] investigated adsorption of Congo Red onto raw and HT calcined at 700 °C. Heraldy et al. [12] focused of removal of Eosin Yellow, Methyl Orange and Methylene Blue by commercial and synthesized hydrotalcite. Shan et al. [13]; Zhang et al. [14]; Mustapha Bouhent et al. [15] tested adsorption properties of HT towards removal of Reactive Red, Congo Red, Acid Red 1, and Brilliant Red, and Orange II, respectively. Santos et al. [16] removed Acid Green 68:1 with uncalcined and HT annealed at 550 °C, Extremera et al. [17] used temperature of 500 °C to calcine HT in order to remove Acid Orange 10. The influence of pH and temperature on the on adsorption of Ramazol Yellow GR110 and Ramazol Gonden Yellow RNL onto calcined at 500 °C hydrotalcite was investigated by Teixeira et al. [18]. Flores et al. [19] prepared their adsorbent at 450 °C to adsorb Astrazon Remazol, Briliant Blue and Direct Red. Temperature of 600 °C was used by El Gaini et al. [20] to obtain material to remove Indigo Carmine, 500 °C was applied by Drici Setti et al. [21]; Auxilio et al. [22]; Bascialla and Regazzoni [23]; and Zhu et al. [24] to remove Benzopurpurine 4B, Acid Blue 9, Acid Blue 113, and Brilliant Blue R, respectively. Hydrotalcite, its calcined at 500 °C version, and calcined and intercalated with sodium dodecylsulfate material were applied for removal of Green Beznatyl-F2B by Bouraada et al. [25]. Orthman et al. [26] studied removal of colored substances (dyes and melanodin) form various aqueous solutions by hydrotalcite with varying Mg:Al ratio.

With respect to adsorption of other pollutants by LDH, Das et al. [27] investigated adsorption of selenite on raw and calcined at 500 °C $MgFeCO_3$ layered double hydroxide. Barriga et al. [28] evaluated effects of layer charge, interlayer anion and nature of the trivalent cation in LDH on sorption of 2,4,6-trinitrophenol in raw and calcined at 500 °C adsorbents. Terephthalate anions were adsorbed onto uncalcined and calcined at 500 °C $MgAlCO_3$ hydrotalcite by Crepaldi et al. [29]. The same type of adsorbent was tested by Lazaridis [30] paying special attention to phosphates, thiocyanates, cadmium, lead and nickel ions.

However, only a few authors raise the issue of recycling and reuse of prepared adsorbents in adsorption-desorption cycles, which is essential in order to reduce deleterious after-effects on the environment during cleanup processes, known as the "footprint" of remediation [31]. Das et al. [27] used a solution of NaOH to regenerate the developed material, Crepaldi et al. [29] turned to thermal regeneration at 500 °C as well as Teixeira et al. [32] and Drici Setti et al. [21]. Recycling by application of ion exchange using chloride, carbonate, and hydroxide anions was found ineffective by Teixeira et al. [18]. Extremera et al. [17] touched the problem of regeneration of spent adsorbent and recovery of adsorbed dye for further use. The dye was successfully desorbed in aqueous solution containing carbonates. However, an attempt to regenerate such treated adsorbent by calcination did not produce good results and the adsorption capacity was not regained. Thermal regeneration was also used by Orthman et al. [26] to successfully remove adsorbed organic compounds form their adsorbent. Furthermore, characterization of spend adsorbents is neglected and very rarely found in the literature. Understanding what changes the adsorbent is subjected to upon each cycle of adsorption and regeneration is crucial to the design of water treatment processes in order to avoid production of waste sludge which disposal is still a problem and generates additional costs [33,34].

The aim of this study was to present a broad insight on changes in the functionality as adsorbents of hydrotalcite derived mixed oxides depending on calcination temperature used in their treatment and pH of the wastewater, and to provide an ample study on fate of the spent adsorbent on each step of its recycling in several adsorption/desorption cycles.

2. Experimental

2.1. Materials

2.1.1. Adsorbent preparation and characterization

Hydrotalcite (HT) with formula $[Mg_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165}\cdot 2H_2O$, was prepared by co-precipitation method. A solution of 0.667 M $MgCl_2$ and 0.333 M $Al(NO_3)_2\cdot 9H_2O$ was added drop-wise from one dropping funnel and a solution of 2 M NaOH was added from another dropping funnel to a 0.160 M solution Na_2CO_3 while keeping it at pH 10, temperature 60 °C under constant stirring. Prepared HT was washed four times in hot water (70 °C), filtered, left to dry for 24 h at 100 °C and ground with a mortar.

Hydrotalcite-derived mixed oxides (HTox) were prepared by calcinating of HT in a muffle furnace at different temperatures 300, 450, 600 and 750 °C (originating HToxC300, HToxC450, HToxC600 and HToxC750 respectively) according to the following procedure: heating rate of 2 °C min^{-1} followed by 6 h of calcination at given temperature.

The structure of the materials was studied with X-ray powder diffractometer (Bruker, D2 PHASER) equipped with CuKα radiation source. Infrared spectra of the samples were recorded using attenuated total reflectance technique (Nicolet 6700 FT-IR, Thermo Scientific). UV–Vis-diffuse reflectance spectra were recorded using an Evolution 600 (Thermo) spectrophotometer. Samples were diluted before measurements with Al_2O_3 to lower the absorbance in order to obtain the measurable range (30 mg of the sample ground with 270 mg of Al_2O_3 in a mortar). The textural parameters of the samples were determined by adsorption of N_2 at −196 °C using a 3Flex (Micromeritics) surface characterization analyzer on outgassed samples. The elemental organic analysis was performed using Vario Micro Cube elemental analyzer with electronic microbalance.

2.1.2. Adsorbate

Two dyestuffs, kindly supplied by DyStar, were used in the pH optimization, kinetics, equilibrium and adsorbent regeneration experiments: a cationic dye, Astrazon Red FBL 200% (AR), CI 85496-37-3 and an anionic dye, Levafix Amber CA gran (AMB), which formula was not revealed by the manufacturer however, it is known to have a fluorotriazinedivinylsulphone structure.

Additionally, in order to better understand interactions of the dyes with adsorbent AMB and three other dyes, Reactive Red 184 (R), Congo Red (CR) and Methyl Orange (MO), were used to saturate adsorbent calcined at 450 °C with excess of concentrated solutions (5 g L^{-1}). Suspensions were stirred for 24 h, centrifuged (5 min at