Effective Degradation of Methylene Blue in Aqueous Solution Using Pd-Supported Cu-doped Ti-Pillared Montmorillonite Catalyst

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ABSTRACT

The effluents from the textile, paper and food industries contain organic dyes that are strongly colored and reveal harmful effect on living systems. In order to reduce water pollution, the degradation of dye into non toxic form is desirable. Methylene blue is one such organic dye, discharged from textile industries. In this work, the catalytic degradation of methylene blue was investigated using a montmorillonite supported trimetallic catalyst, prepared by supporting Pd on a Cu-doped Ti pillared montmorillonite. The catalyst exhibited excellent performance to reduce methylene blue, in the presence of $NaBH_4$. The decolorization was appreciable and the results indicated that methylene blue could be

successfully decolorized and degraded using the catalyst under room conditions. Almost complete degradation was achieved within 20 minutes. The results obtained were better than those reported for other catalysts.

Keywords: Pd-montmorillonite supported catalyst; Doped pillared clay minerals; Titania pillared clay minerals; Reductive Degradation of Dyes

1. Introduction

Natural dyes have been used by human since the start of human civilization; later synthetic dyestuffs mostly supplanted natural dyes. Dyes are designed to be chemically and photochemically stable. Organic dyes contaminated water cause ecotoxic hazard which leads to potential danger of bioaccumulation and indirectly affect humans by transport through food chain. Most of organic dyes are recognized as potential carcinogens that may cause health risk problems and meanwhile a huge amount of 700,000-1,000,000 tons dyes are reported to be produced worldwide annually with at least 15% of them finally discharged from printing, textile, paper, paints, plastic, leather, food and other industries (Dojcinovic et al., 2011). These synthetic organic dyes cause substantial environment pollution as they cannot be degraded by conventional water treatment process due to their complex aromatic structures, hydrophilic nature and high stability against light, temperature, water, chemicals, etc. even very low concentration of these dyes could cause heavy color to strongly absorb sunlight and thus impede sunlight penetration into water to promote the photosynthesis of aquatic life, and finally interfere with the ecological imbalance in the aquatic ecosystem (Ji et al., 2015; Okesola and Smith, 2016).

Methylene blue, [7-(Dimethyl-amino)phenothiazin-3-ylidene]-dimethylazanium chloride, is used to dye paper and office supplies, but also to tone up silk colors. Besides, it has largely been used in human and veterinary medicine for several therapeutic and

diagnostic procedures, and it is used clinically in a wide range of indications, including the emergency treatment of methaemoglobinemia, ifosfamid-induced encephalopathy or poisoning by cyanide, nitrate or carbon monoxide, for intraoperative tissue staining, and for some psychiatric disorders. Its historical use as antimalarial drug has been recently revived (IARC, 2016). Up to our knowledge, no exposure limits for MB have been established.

A number of catalysts were reported for methylene blue (MB) degradation in the past decade. Bentonite was modified with the natural surfactant rarasaponin for MB degradation (Kurniawan et al., 2011), and also ZnO supported montmorillonite was found to be active for the degradation of MB, although having the limitation of the preparation of ZnO and much longer time for the complete degradation (Fatimah et al., 2011). Fe_3O_4 activated montmorillonite nanocomposite (Chang et al., 2015), magnetic Fe_3O_4 supported graphene composite (Yao et al., 2012), SiO_2 supported bimetallic heterogeneous photo-Fenton catalyst (Ahmed et al., 2016), copper nanoparticles supported on montmorillonite (Mekewi et al., 2016), activated carbon-TiO_2 (Ramli et al., 2014), individual and iron modified Ni and Co-oxide systems (Stoyanova et al., 2011), acid treated rectorite (Gaoke et al., 2011), and cross-linked chitosan/bentonite composite (Bulut et al., 2014) have been reported for MB degradation. Chabazite was recently reported as an effective adsorbent for this dye (Aysan et al., 2016).

Clay minerals are important materials that are readily available in nature. These are used as very good adsorbents, discoloration agents, ion exchangers, molecular sieves or catalysts (Bergaya and Lagaly, 2013). Clay minerals showed diversified applications such as catalyst, pollutants removal/remediation, due to their high surface area, selective adsorption behavior towards cationic sensitizers and high adsorption capacity. Inorganically modified clays were recently reported as good adsorbents of arsenic in contaminated water and soil (Mukhopadhyay et al., 2017). The clay minerals most used as nano-adsorbents belong to

montmorillonite and kaolinite groups. Catalysts developed using clay minerals are found to be cost effective and environmentally benign. Although the degradation of dyes is usually undertaken by means of oxidation reactions, in the present case a reductive approach has been employed, using $NaBH_4$ as reducing agent. A similar approach has been recently employed by Sahoo et al. (2016) using reduced graphene oxide/Co dendritic nanocomposites, by Edison et al. (2016) using Ag nanoparticles, and Saikia et al. (2017) using Au/CeO_2-TiO_2 nano-hybrid, and a very similar one by Zainal Abidin et al. (2017) using Ag-doped zeolite X, although in this case the reducing agent was KBH_4. In this context, as a continuation of our effort to find various applications of clay minerals and their modified forms, we report in the present study on MB degradation by Pd-supported Cu-doped Ti pillared montmorillonite catalyst.

2. Experimental

2.1. Preparation of MTiCuPd500 catalyst

The clay mineral used in this work was a raw montmorillonite from Cheto, Arizona, USA (The Clay Minerals Repository, where this sample is denoted as SAz–1). The purified montmorillonite was pillared by a Ti^{4+}-pillaring solution doped with Cu^{2+}, the resulting solid being later impregnated with a Pd^{2+} precursor, giving rise to the final trimetallic MTiCuPd500 catalyst. The catalysts were obtained in powder form, after grinding them in an agate mortar. The properties of the parent montmorillonite and the preparation of the pillared solid and the final supported catalyst have been reported elsewhere (González–Rodríguez et al., 2015; Vellayan et al., 2018).

2.2. Catalytic procedure

The methylene blue dye and the reducing agent $NaBH_4$ were obtained from Sigma Aldrich. Distilled water was used throughout the study and the percentage of dye removal from the aqueous solution was estimated by UV-visible spectroscopy, measuring the

adsorption at the wavelength of the maximum absorbance (λ_{max}=665 nm), using UV-Vis spectrometer (Systronics double beam spectrophotometer 2202). The absorbance at this wavelength was previously calibrated, showing a linear response, according to the Beer-Lambert law, in the concentration range employed, from 2.0 10^{-6} mol/L to 1.2 10^{-5} mol/L. Generally, 2 mL MB (2 g/L) and 2 mL $NaBH_4$ (0.1 mol/L) aqueous solutions were mixed with 7 mL distilled water, followed by the addition of the catalyst, and the mixture was magnetically stirred at room temperature at the constant speed of 200 rpm. The dark blue color of MB disappeared and its time dependent absorbance was monitored at 665 nm as previously indicated. The slurries were previously filtered using a syringe filter (Millipore 0.45µm) to remove particles completely.

Reaction conditions such as catalyst dose, and time were considered. The Ti-pillared montmorillonite (MTi500), not containing Cu neither Pd, was used as reference catalyst, to study the effect of the incorporation of these metals. Its catalytic efficiency was determined in the same conditions above described.

3. Results and discussion

3.1. Characterization of MTiCuPd500

The properties of the parent montmorillonite, the catalyst and the reference solid here used have been reported elsewhere (González–Rodríguez et al., 2015; Vellayan et al. 2018). Briefly, purified (by dispersion–decantation) montmorillonite had a BET specific surface area of 49 m^2/g, basal spacing of 13.60 Å and cation exchange capacity of 0.67 meq/g. The pillaring with Cu-doped Ti-polycations was effective, giving rise to a pillared solid with the following composition (in water-free basis): SiO_2: 55.53%; Al_2O_3: 15.97%; Fe_2O_3: 1.44%; MnO: 0.01%; MgO: 5.34%; CaO: 0.10%; Na_2O: 0.03%; K_2O: 0.04%; TiO_2: 21.12%; CuO: 0.41%. This solid showed, after calcination at 500ºC, a basal spacing of 16.49 Å and a BET specific surface area of 329 m^2/g. The amount of Pd incorporated was 5%, incorporation was

carried out by impregnation (without filtration), and so all the targeted amount was incorporated. The impregnation blocked most of the internal porosity of the pillared solid, but without collapsing the structure, and thus the supported MtTiPd500 catalysts showed, also after calcination at 500ºC, basal spacing of 16.49 Å and BET specific surface area of 89 m^2/g.

3.2. Catalytic performance

First of all, the effect of catalyst loading on reduction of MB by MTiCuPd500 was investigated by varying the catalyst doses from 2 mg to 6 mg, keeping the time constant for 30 minutes. The degradation profile of the MB solution over the several doses of catalyst in this range (Fig. S1) indicated that the degradation efficiency increased as the catalyst dosage increases from 2 mg to 5 mg, being practically complete for 5 mg, and remaining constant for 6 mg (Fig. 1). Thus, the dose of 5 mg was selected for further experiments.

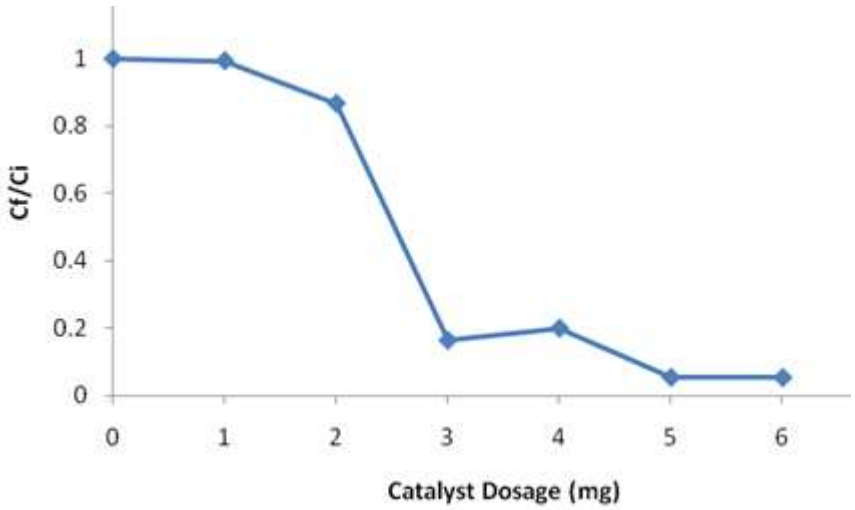

Fig 1. Evolution of the intensity of the maximum absorption band of MB with MTiCuPd500 catalyst dose for 30 minutes of treatment.

The addition of MTiCuPd500 to MB solution in the presence of $NaBH_4$ caused a rapid decrease in the absorbance at λ_{665} nm to zero in twenty minutes, with fading and ultimate bleaching of blue color with time (Figs. S2 and 2 (blue line), in which the standard deviation is 0.37). That is, the absorption peak intensity at 665 nm decreased with time, and became almost zero after 20 minutes, demonstrating the completion of the reaction.

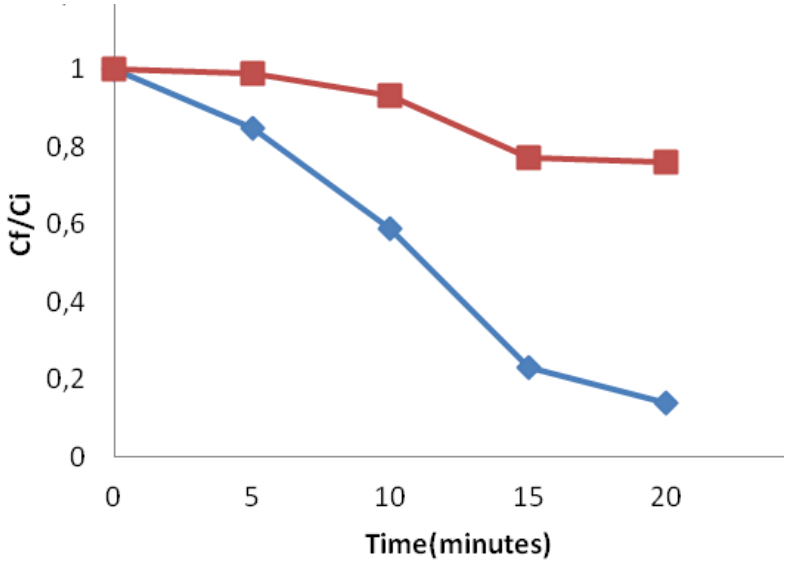

Fig 2. Evolution with time of the relative concentration of MB in solutions treated with 5 mg of MTiCuPd500 catalyst in the presence of light (blue line) and in the absence of light (red line).

To verify the catalytic effect of MTiCuPd500 solid, the reaction was conducted without adding the catalyst. The intensity of UV-VIS spectra (Fig. S3) slightly decreased in the initial 10 minutes, and then remained unchanged. This strongly suggested that $NaBH_4$ was able to degrade, in absence of catalyst, a limited amount of the dye (about 10%), and this degradation could not continue without the presence of the catalyst.

Similarly, the reaction was carried out in the presence of the catalyst but in the absence of $NaBH_4$ (Fig. S4). The intensity of the absorption progressively decreased to reach about 20% after 25 minutes of contact. Such decrease may be due to the adsorption of the dye on the surface of the catalyst; such adsorption may remove a certain amount of dye from the solution decreasing the absorption in the spectra, but in any case such absorption may be low. Eventually a small amount of the dye may be degraded by photooxidation in the presence of the catalyst and of light, but such process is expected to be negligible in the case of MB. In any case, the efficiency of the degradation is much lower than in the presence of both the catalyst and the reducing agent (Fig. S2).

To gain information on these processes, the catalytic performance was investigated in the darkness, that is, in the presence of 5 mg of MTiCuPd500 catalyst, but in the absence of light. The degradation (Fig. S5) was clearly lower than in the presence of light, as compared in Fig. 2, reaching values close to 20% for the largest times considered (15-20 minutes). In oxidation processes, the contribution of the photooxidation to the degradation should be expected, but this is not reasonable under the strong reducing conditions given by $NaNH_4$. More probably, the highest activity found in presence of light should be due to a synergic reduction effect of light and Pd-Cu-Ti species, although not enough evidences are available.

To verify the influence of the different components of the catalyst in its catalytic performance, the catalytic efficiency of MTi500 solid was also investigated. This solid was Ti-pillared montmorillonite, that is, a solid similar to MTiCuPd500, but without doping with Cu during the pillaring and without further impregnation with Pd. Thus, this solid did not contain these transition metals, but it had better textural properties than MTiCuPd500 (González–Rodríguez et al., 2015; Vellayan et al. 2018). MTi500 was relatively efficient for degradation of MB, reaching about 40% degradation after 30 minutes of reaction (Fig. S6), but in any case its activity was also much lower than that of MTiCuPd500. It may be

considered that MTi500 had textural properties much better than MTiCuPd500, particularly specific surface area and micropore volume, which were strongly blocked during the impregnation with the Pd phase, and besides this solid was strongly acidic (González–Rodríguez et al., 2015; Vellayan et al. 2018). The comparison of the catalytic efficiency of both solids showed the importance of the presence of Cu and Pd for enhancing the catalytic ability of the trimetallic catalyst, also proving that the presence of these elements was much more decisive that the textural properties and the acidity of the solids.

The evolution of the pH with the advance of the reaction was followed when using MTiCuPd500 as catalyst (Fig. 3). As observed, the pH decreased as the reaction progressed. This may influence the surface charge of the catalyst and the acid-base equilibrium of the pollutant, affecting the kinetics of the reaction. The evolution of the pH agreed with the advance of the reaction. BH_4^- anions generated from the reducing agent acted as electron injection species, slightly charging negatively the surface of the catalyst; subsequently these electrons were transferred to MB causing its reduction. Considering the positive charge on MB at reaction conditions, the effect of pH on the catalytic degradation can be explained on the basis of the electrostatic model, where MB^+ cations should be accommodated at the negative sites. The decrease in pH during the reaction indicated that it was favorable in alkaline medium as compared to acidic medium.

The reuse of the catalyst was studied by filtering and washing it, and then submitting it to new catalytic runs. No leaching of the active metals was found and a moderate decrease in the activity of the catalyst was observed after four runs (Fig. 4), so the reuse of the catalyst can be considered acceptable.

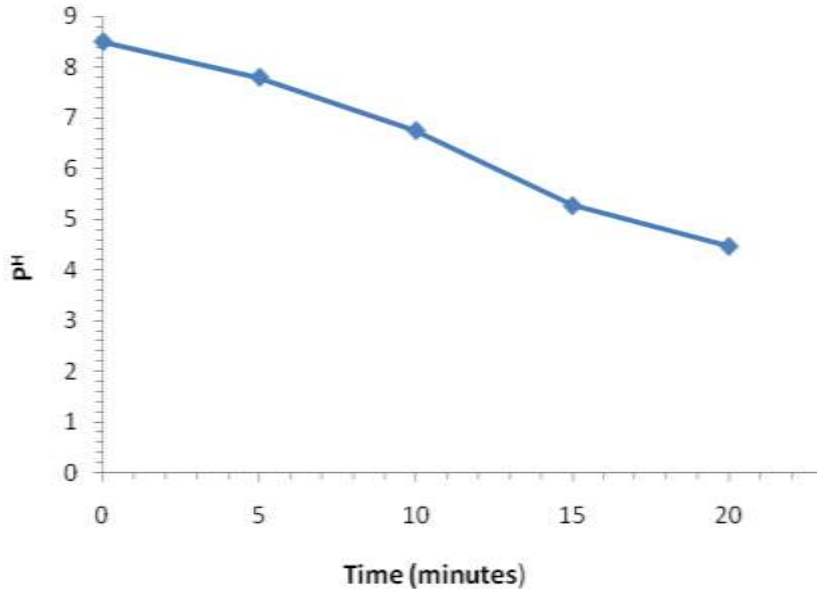

Fig 3. Evolution of pH on degradation of MB over modified MTiCuPd500.

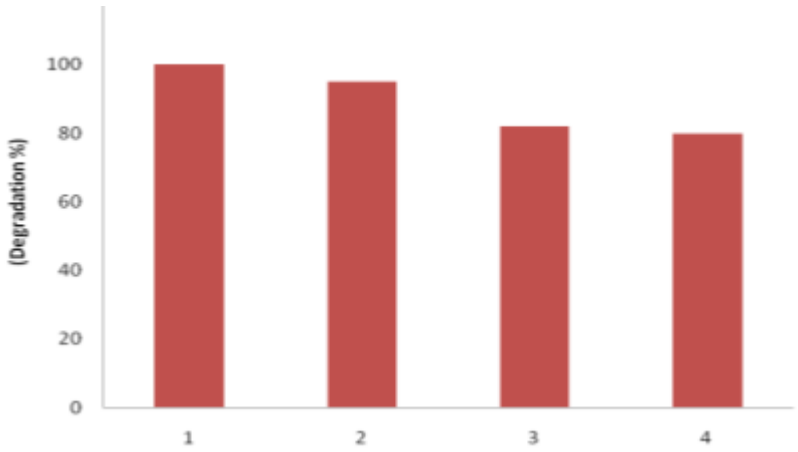

Fig 4. Evolution of MB degradation using MTiCuPd500 catalysts under four consecutive catalytic runs.

With all these data, it can be suggested that the degradation of MB may begin with the electron transfer from BH_4^- to MB through the catalyst surface. The adsorption of the dye on the surface of the catalyst should strongly favor this process. The acceptation of the electron

by methylene blue may lead to its reduced form, leucomethylene blue (LMB), which in spite of its name is colorless. The reduction may involve the two terminal $–N(CH_3)_2$ groups and even the sulfur atom, thus involving up to three electrons. At least one of these groups may be protonated considering the cationic character of the dye, but also the other groups may be protonated depending on the pH, causing a decrease in the pH of the reaction media from the initial value close to 8.5 to a final value of ~ 4.5.

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Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clay.2018.10.009.

4. Conclusions

The montmorillonite based catalyst MTiCuPd500, containing Pd supported on Cu-doped Ti-pillared montmorillonite, acted as an effective reducing agent for the removal of Methylene Blue dye from aqueous solutions under ambient conditions, in the presence of $NaBH_4$. In general, the dye removal was rapid at room temperature, being complete after about 20 minutes. The Ti-pillared montmorillonite, MTi500 solid, was less efficient in the degradation of the dye, in spite of having larger specific surface area and acidity than MTiCuPd500, showing the importance of the incorporation of Cu and Pd as active phases.

The enhanced removal efficiency makes MTiCuPd500 as a promising catalyst and opens new ways to investigate the reductive degradation of environmental pollutants.

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