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FULL LENGTH ARTICLE

Copper nanoparticles supported onto montmorillonite clays as efficient catalyst for methylene blue dye degradation

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Abstract The paper describes the production of copper nanoparticles through the reduction of copper chloride ($CuCl_2{\cdot}2H_2O$) by hydrazine in the aqueous cetyle trimethyl ammonium bromide (CTAB) solution. The copper nanoparticles were then supported on chemically activated Montmorillonite clay (MMT). The native and modified clays as well as synthesized Cu-nanoparticle-clay were structurally and texturally characterized by XRD, FTIR, BET, SEM and TEM in addition to the estimation of exchange capacity parameters. BET surface characterization revealed a decrease in surface area of the clay support after the incorporation of Cu nanoparticles. Cu/clay was then utilized as a catalyst for the degradation of aqueous solutions containing methylene blue (MB) over a wide pH range. Diverse kinetics models were employed to examine the degradation process revealing a better fit with pseudo-first-order model. The present study offers a novel modified clay based catalysts for the degradation of methylene blue dye contaminant from wastewater.

1. Introduction

Metal nanoparticles have attracted a great attention of researchers for sound applications recently especially in the field of waste water recycling. Nano metals are defined as clusters containing tens to thousands of metal atoms, and their sizes vary between one to tens of nanometers [1]. They have been considered as very attractive catalysts due to the acquired large surface area acquiring in turn higher catalytic efficiency, optical, electrical and antifungal/antibacterial applications [2–6].

The stabilizers for synthesizing nanoparticles play an important role in controlling nano size, shape as well as morphology. Various supports/stabilizers like mesoporous solid, organic ligand, polymer, carbon materials, etc. are reported [7–15]. Montmorillonite clay is one of the suitable supports where metal nanoparticles can be stabilized within the interlayer spacing or into the pores on the surface [16–19].

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The surface properties of MMT clay were even improved further with regard to the surface area, and porosity after having activated through acid and organic treatments making the clay appropriate for stabilizing metal nanoparticles [20,21]. Synthesis and applications of clay supported nanoparticles in catalysis is an emerging topic, when compared to the conventional homogeneous catalysts [22–24].

Supported nanoparticles play a crucial role in the degradation of dyes, which are becoming a serious environmental problem due to their inflected toxicity on humans, high chemical oxygen demand content, and biological degradation [25,26]. Among various dyes, methylene blue (MB) is difficult to degrade and is often utilized as a model dye contaminant [27].

The present study aimed to synthesize and investigate well dispersed Cu onto activated MMT clay and to examine the effectiveness of materials in immobilization and catalytic degradation of MB dye from aqueous solutions.

2. Experimental and methodology

2.1. Materials

(a) Clay mineral

Montmorillonite clay from Sadat city, Egypt was firstly washed by 0.5 M HNO_3 for 48 h at 60 °C prior use. The MMT clay's main characterization features were measured and found as below:

- Cation exchange capacity (CEC) = 50 meq/100 g.
- Surface area = 39.186 m^2/g.
- Chemical compositions: 50.29% SiO_2, 18.21% Al_2O_3, 8.38% Fe_2O_3, 1.72% Cao, 2.09% MgO, 3.81% Na_2O, 0.89% K_2O, 1.21% TiO_2, 0.19% P_2O_5, 0.35% SO_3.

(b) Chemicals

HCl, HNO_3, H_2SO_4, NaOH, NH4OH, cetyle trimethyl ammonium bromide (CTAB), copper chloride ($CuCl_2{\cdot}2H_2O$), ρ-amino benzoic acid (ρ-ABA), Hydrazine hydrate ($N_2H_4{\cdot}xH_2O$), methylene blue (MB), and Hydrogen peroxide (H_2O_2) were of pure analytical grades.

2.2. Preparation and synthesis

2.2.1. Acid treated clay (AT-MMT)

The pretreated clay (100 g) was soaked in 750 ml of 2 M H_2SO_4 for 48 h at 70 °C. The clay was then filtered and washed with distilled water several times till neutral and finally dried at 80 °C for 24 h.

2.2.2. Organo-treated clay (PA-MMT)

The ρ-amino benzoic acid was firstly prepared by dissolving 1 g in 250 ml distilled water with the addition of a few drops of HCl. Afterward, 15 g of pretreated clay was soaked in a mixture of 200 ml distilled water and 80 ml of ρ-amino benzoic acid solution for 3 days. The pH was adjusted at ~1–2 using concentrated hydrochloric acid. The resulting modified clay was then filtered and well washed with boiled distilled water several times to withdraw all adsorbed impurities and finally dried at 50 °C for 24 h.

2.2.3. Cu nanoparticles immobilized onto modified clay

In a typical synthesis process, the starting solution was prepared in two conical flasks, in the first flask 0.0268 g copper chloride (Cu $Cl_2{\cdot}2H_2O$) was dissolved in a small amount of DI water and then 0.0286 g of CTAB was dissolved in another 10 ml DI water. After mixing both solutions, ammonia solution was gently dropped until the solution pH = 10, where the color of solution changed from light blue to dark blue without formation of any precipitate (solution-I).

In the second flask 0.05 ml hydrazine hydrate was added to 0.0286 g of CTAB already dissolved in 25 ml DI water (solution-II). Then the addition of solution-I into solution-II was performed with continuous stirring and heating till the temperature reached 80 °C. As the reaction proceeded, the solution color changed from colorless to light yellow to orange to brown and finally to red color, which confirmed the formation of metallic colloidal suspension. The reduction reaction can be expressed as:

$$2[Cu(NH_3)_2]^{2+} + N_2H_4 + 4OH^- \leftarrow 2Cu + N_2 + 4NH_4OH$$

Finally, 1 g of each modified clay samples was mixed with the metallic solution at 80 °C, the resulting paste of metal/clay nanocomposite was finally dried at 70 °C for 18 h designated as Cu/MMT.

2.3. Characterization techniques

2.3.1. Structural characteristics of raw, modified montmorillonite samples and Cu supported modified clay nanocomposites

2.3.1.1. XRD analysis. Crystallinity patterns of native (Raw-MMT), acid treated (AT-MMT) and ρ-amino benzoic treated montmorillonite (PA-MMT) as well as Cu nanoparticles immobilized onto modified clay samples (Cu-AT-MMT and Cu-PA-MMT) were studied using XRD (PANalytical Xpert Pro) using Cu Kα radiation (λ = 1.5418 Å) in the range of 2θ = 5–70°.

2.3.1.2. FT-IR spectroscopic analysis. The chemical structural features of the native, modified and cu nanoparticle supported modified clays were assessed through FT-IR spectroscopy (FT-IR 4000 type A from Jasco Company, USA).

2.3.2. Morphological studies

(a) Texture properties of raw, modified montmorillonite samples, and Cu supported modified clay nanocomposites.

The surface areas were estimated using surface area characters [28,29] (based on N_2 adsorption-desorption isotherms at −196 °C).

(b) Cation exchange capacity of various modified montmorillonite samples

The cation exchange capacity (CEC) of the native and tow modified clay samples were measured, in meq/100 g, using the