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Dye removal from aqueous solution by cobalt-nano particles decorated aluminum silicate: Kinetic, thermodynamic and mechanism studies

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ABSTRACT

This article describes the preparation of a nanoadsorbent containing Co-nanoparticles decorated functionalized SiO_2–Al_2O_3 mixed-oxides as a scavenger toward removal of methyl orange. SiO_2–Al_2O_3 mixed-oxides were functionalized with pyridine-2-carbaldehyde and thereafter, in the next step, Co-nanoparticle was prepared over the modified mixed-oxides. The as-prepared nanoadsorbent was characterized by Fourier transform infrared (FTIR), UV–visible diffuse reflectance spectra (UV–vis DRS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), Brunauer–Emmett–Teller (BET), transmission electron microscopy (TEM), electron paramagnetic resonance (EPR), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Results showed that Co-nanoparticle with average size of about 5–25 nm was immobilized successfully on the surface of modified mixed-oxides and was widely dispersed. EPR and CV of Si/Al-PAEA = PyCA@CoNP confirmed that most of the covalently bond active sites of the nano-adsorbent are in the form of Co(II) ions. The supported cobalt is a suitable and efficient adsorbent for the removal of methyl orange from aqueous solution. The heterogeneous Co-NPs were found to be effective adsorbent for the removal of methyl orange ions from solution. The adsorption process was spontaneous and endothermic in nature and followed pseudo-second-order kinetic model. The CV and EIS of the Co-NPs-MO indicates an easily oxidizable environment, this being in agreement with the FTIR data, where the electron density at Co-NPs is higher due to the presence of a donor-electron ligand (methyl orange), that is, reduction of Co-NPs from +3 to +2 oxidation state is more favored.

1. Introduction

Our environment is continually exposed to pollution by organic compounds such as dyes and pesticides. Essentially all industrial processes generate by-products that become waste materials. These organic waste materials have the potential of contaminating the environment. Dye, solvents organic compounds, and petroleum products account for most of the contaminants, where, dyes usually have a synthetic origin and complex chemical structure that make them persistence to light and oxidation and very troublesome toward biodegradable process [1–4]. Many dyes are toxic to some organisms and may cause direct annihilation of aquatic communities. In addition to their unwanted colors, some of these dyes may break down to yield carcinogens and toxic compounds. Nowadays, more than one hundred thousand kinds of commercial dyes are utilized with the production of over nine million tons annually. Therefore, improving a sustainable method of wastewater management for the coloring industry has long been a challenge for monitoring dyes in the environment. In particular, many efforts have been made to develop adsorbents to remove dyes from drinking water.

Adsorption processes have been reported to be the low-cost promising alternatives for the treatment of dyes present in wastewater. The use of activated carbons, modified clays, polymeric resins, waste materials, and zeolites as adsorbents has also been described. For most of natural adsorbents such as clays, zeolites, agricultural waste, and chitosan their particles show negatively charged surfaces and consequently, excellent adsorption properties for cationic organic compounds can be obtained [5–8]. However, these systems generally have some disadvantages to

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dye removal, such as the difficulty in separating those powdery natural adsorbent, except high speed centrifugation, from treated effluent, nonresistance against acid solution, do not have considerable adsorption capacities or need relatively long adsorption contact times, e.g., from several hours to a couple of days, their poor mechanical strengths and less adaptable to a wide range of dye wastewater limit their practical applications. Thus, it is needed to design effective adsorbent with short contact times for the removal of dye ions from aqueous solutions. Activated carbon is the most prevailing adsorbent for this process because of its high surface area, high adsorption capacity, and high degree of surface reactivity; however, it is expensive and must be regenerated on a regular basis. Inorganic supports present several advantages with respect to activated carbon, including stability, high surface area, possible reuse, relative rapidity in reaching equilibrium, better high mechanical resistance, easy modifications and a higher concentration of chelating groups on the surface, and they are often much cheaper than their organic counterparts.

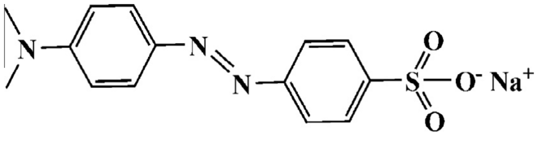
Nanoparticles of a variety of shapes, sizes and compositions are changing nowadays the wastewater treatments [9,10]. Preparation and investigation of novel nanomaterials are important in material science. There are various nano-materials including carbon nanotubes, nano-wires and nano-particles those are important for scientific works. The nanostructures with large specific surface area and ease with which they could be immobilized onto solid support and the ability to functionalize with different functional active sites to increase their affinity toward target compounds, could provide an important and feasible platform for catalysis, separation, sensing, and fuel cells [11]. Derivatization of inorganic solids with organic functional groups was widely studied and successfully applied in many divergent areas of research. This synthetic route is still the subject of considerable interest due to the numerous possibilities of designing new materials, especially by exploiting the versatility of sol–gel chemistry. It is essential to look for a new method with high sensitivity, simplicity and efficiency for the removal of contaminations from aqueous media.

This paper releases the results of the application of SiO_2–Al_2O_3 mixed oxides supported cobalt nanoparticles (Si/Al-PAEA = PyCA@-CoNP) for the removal of methyl orange from aqueous solution. Methyl orange (M.O.) with IUPAC name of Sodium 4-[(4-dimethylamino) phenyldiazenyl] benzene sulfonate (Scheme 1) is a typical water-soluble anionic dye and has harmful effects on living organisms in a short period of exposure. The structure of the obtained organometallic-modified Si–Al mixed oxides was confirmed by elemental analysis, BET (N_2 adsorption–desorption technique), FT-IR spectroscopy, TEM, ICP-AES, CV, EIS and EPR. Meanwhile, the essential analysis and characterization of the nano-adsorbent have been conducted by electrochemical techniques, for the first time, to reveal the possible mechanism of MO adsorption from aqueous solution.

2. Experimental

2.1. Materials and characterization techniques

All reagents (A.R.) were purchased from Merck or Fluka and were used without further purification, except that solvents were treated according to the standard methods. Graphite powder (particle diameter = 0.1 mm) and carbon nanotubes [(>90% MWCNT basis, $d \times l = (110\text{–}70\ \text{nm}) \times (5\text{–}9\ \mu\text{m})$ (Fluka))] were used as the substrates for the preparation of the carbon paste electrode as a working electrode (WE).



Scheme 1. Chemical structure of MO.

Diffuse reflectance spectra were recorded on a JASCOV-550 UV–Vis spectrophotometer. Fourier transform IR spectra were measured using a JASCO FT/IR (680 plus) spectrometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm^{-1}). Approximately 40–50 mg of material, which had been previously calcined in air at 25 °C for 4 h, with 10–15 times KBr was pressed (for 3 min at 15 metric tons/cm^2 pressure under approximately 10–2 Torr vacuum) into a self-supporting wafer of 0.9 mm diameter. The FTIR spectra of synthesized materials were recorded at 4 cm^{-1} resolution and scan number of 16. Elemental analysis was performed by a CHNO-Rapid Heraeus elemental analyzer (Wellesley MA). Chemical analyses are carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Shimadzu ARL 34000 instrument (spectro-flamed; typically, 30 mg sample was dissolved in 500 µl 40% HF solution, 4 mL 1:4 HCl:H_2SO_4 solution and 45 mL H_2O). Nitrogen (99.999%) adsorption experiments have been performed at −196 °C using a volumetric apparatus (Quantachrome NOVA automated gas sorption analyzer). Before the adsorption experiments, the sample was out gassed at 120 °C for 16 h. The specific surface areas are calculated from the BET method. The image of transmission electron microscopy (TEM) was taken using a Philips 501 micro-scope and a Tecnai F30TEM operating at 300 kV. Electron paramagnetic resonance (EPR) spectra were recorded with a Bruker EMX spectrometer operating at X-band (m = 9.42 GHz) frequency and a 100 kHz field-modulation. The spectra were recorded at 80 K using a Bruker BVTB 3500 variable temperature controller. The magnetic field was calibrated with a Bruker ER 035 M NMR gaussmeter and the microwave-frequency was calibrated with a frequency counter fitted in a Bruker ER 041 XG-D microwave bridge unit. Electrochemical measurements were taken with Micro-Autolab, potentiostat/galvanostat instrument (µ3AUT70751), connected to a three-electrode cell. Conventional three electrode cells were used for the all experiments. The modified multi-walled carbon nanotubes paste electrode used as a working electrode, platinum wire as an auxiliary electrode, and an Ag/AgCl/KCl electrode as a reference electrode were used.

Electrochemical impedance measurements were taken in a conventional three-electrode cell, powered by an electrochemical system comprising the Autolab (AUT83593) at a frequency range of 0.1–10,000 Hz. The AC voltage amplitude was 5 mV.

2.2. Preparation of the organo-cobalt functionalized SiO_2–Al_2O_3 mixed-oxide

SiO_2–Al_2O_3 support was prepared by sol–gel method as follows; Aluminum tri-sec-butylate (97%) and tetraethyl orthosilicate (98%) were used as the precursors, and 2,4-pentandione (H-acac) as the complexing agent. Appropriate amounts of aluminum tri-*sec*-butylate and tetraethyl orthosilicate were dissolved in *n*-butanol and the solution was heated to 60 °C. The components were thoroughly mixed, then it was cooled down to room temperature, and then H-acac was added. The produced clear solution was hydrolyzed with deionized water (11.0 mol H_2O/mol alkoxide). The solution was left overnight to hydrolyze the alkoxides, yielding transparent gel. The transparent gel was dried at 110 °C to remove water and any solvent, and then it was calcined at 500 °C for 5 h to remove the organic materials. The SiO_2–Al_2O_3-supported 2-aminoethyl-3-aminopropyl-trimethoxy silane (2-AE-3-APTMS) was prepared by refluxing 5.2 g of SiO_2–Al_2O_3 that was activated at 550 °C for 6 h under air with 3.5 mL (0.0195 mol) of 2-AE-3-APTMS in dry dichloromethane (100 mL) for 24 h. The solid was filtered and washed off