Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 118 (2014) 55–65

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Optimization of the combined ultrasonic assisted/adsorption method for the removal of malachite green by gold nanoparticles loaded on activated carbon: Experimental design

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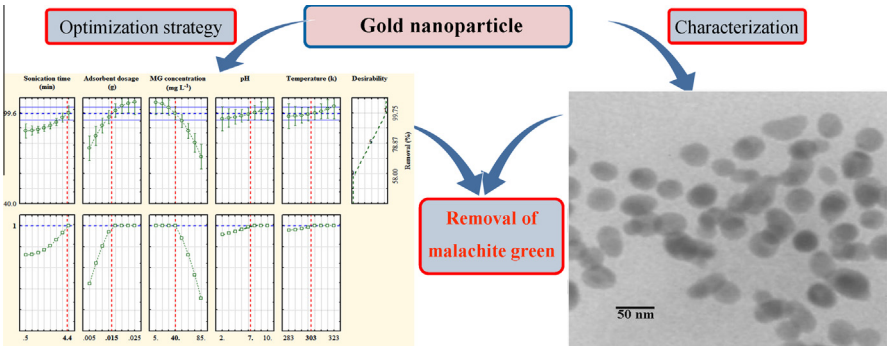
HIGHLIGHTS

- Combined ultrasound-assisted/ nanoparticle adsorption as a new dye removal method.
- Ultrasound assists the whole adsorption time leading to omit undesirable effects.
- We demonstrate a metrology for fast removal of dye from aqueous solution.
- Ultrasound shows considerable advantages on the removal yield of dyes.
- An experimental design was used for optimize the parameters.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 May 2013
Received in revised form 11 August 2013
Accepted 15 August 2013
Available online 28 August 2013

Keywords:
Activated carbon
Adsorption
Experimental design
Gold nanoparticles
Malachite green
Removal of dyes

ABSTRACT

The present study was aimed to experimental design optimization applied to removal of malachite green (MG) from aqueous solution by ultrasound-assisted removal onto the gold nanoparticles loaded on activated carbon (Au-NP-AC). This nanomaterial was characterized using different techniques such as FESEM, TEM, BET, and UV–vis measurements. The effects of variables such as pH, initial dye concentration, adsorbent dosage (g), temperature and sonication time on MG removal were studied using central composite design (CCD) and the optimum experimental conditions were found with desirability function (DF) combined response surface methodology (RSM). Fitting the experimental equilibrium data to various isotherm models such as Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich models show the suitability and applicability of the Langmuir model. Kinetic models such as pseudo -first order, pseudo-second order, Elovich and intraparticle diffusion models applicability was tested for experimental data and the second-order equation and intraparticle diffusion models control the kinetic of the adsorption process. The small amount of proposed adsorbent (0.015 g) is applicable for successful removal of MG (RE > 99%) in short time (4.4 min) with high adsorption capacity (140–172 mg g^{-1}).

Introduction

The dyes in industries effluents such as textile, leather, paper and plastics are of serious concern because of their adverse effects to human beings and environment [1,2]. The dyes significant, importance and associated environmental problem come from their high visibility, undesirability and recalcitrance. Therefore, their removal from such industrial effluents is challenging requirement to produce a safe and clean environment [3].

Malachite green (MG) is classified as a basic dye consume in many industries (silk, wool, cotton, leather and paper) for coloring

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1386-1425/$ - see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.saa.2013.08.082

purposes, the structure is shown in Fig. 1. Furthermore, it is also employed as therapeutic agent to treat parasites, fungal and bacterial infections [4,5]. Despite its extensive use, MG dye consists of toxic properties which are known to cause injuries to humans and animals by direct contact of inhalation and ingestion [6]. Therefore, the removal of MG from wastewater before discharging to the environment is necessary.

Many technologies have been developed for dye removal from industrial effluent including flocculation, coagulation, precipitation, biosorption, membrane filtration, electrochemical techniques and adsorption [7–10]. Among them, adsorption application follows a simple design, guarantees high efficiency and capacity, ease of operation, large scale ability with generable adsorbents [11–13]. Various materials such as Activated carbon (AC), natural materials, polysaccharide materials, starch, bioadsorbents and agricultural wastes have been used for the removal of dyes from solution [14–17]. AC as non-toxic, low cost and easy available adsorbent has relatively high surface area, porous structure, total pore volume and large adsorption capacities. It is considered as a universal adsorbent for the removal of pollutants such as dyes from the wastewater with fast adsorption kinetics [18]. AC contain various reactive sites such OH, COOH, C=O and amide groups that in coincide to nanoparticle properties synergically improve the efficiency of adsorption based treatment procedure. In this technique application of nano scale materials with high surface area enhance the removal percentage and adsorption capacity of AC based adsorbent. Nanoparticles oppose distinguished properties such as high number of reactive atoms, high mechanical and thermal strength, high ordered structure and large number of vacant reactive surface sites in addition to metallic or semi-metallic behavior applied for removal of various toxic materials [19,20].

Ultrasound irradiation is well known to accelerate chemical process due to the phenomenon of acoustic cavitation, that is, the formation, growth and collapse of micrometrical bubbles, formed by the propagation of a pressure wave through a liquid. Ultrasound, and its secondary effect, cavitation (nucleation, growth and transient collapse of tiny gas bubbles) improve the mass transfer through convection pathway that is emerged from physical phenomena such as micro-streaming, micro-turbulence, acoustic (or shock) waves and microjets without significant change in equilibrium characteristics of the adsorption/desorption system [21–23]. Shock waves have the potential of creating microscopic turbulence within interfacial films surrounding nearby solid particles. Acoustic streaming induced by the sonic wave is the movement of the liquid, which can be considered to be the conversion of sound to the kinetic energy [24]. Ultrasound has been proven to be a very useful tool in intensifying the mass transfer process and breaking the affinity between adsorbate and adsorbent [25,26].

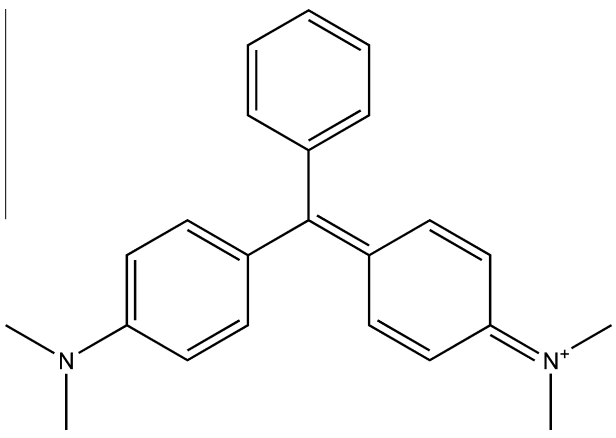

Fig. 1. Chemical structure of MG.

There are several experimental variables affecting the ultrasound-assisted removal of MG. A statistical design of experiment can be preferred to decrease the number of experiments and considered the interaction between variables [27,28]. Designing and optimization of experiments and evaluation of the variables influence need to apply methods to be able for simultaneous optimization while consider the interaction of variables.

In the present work, ultrasound assisted as a simple, sensitive, inexpensive and rapid/assisted adsorption method followed by UV detection has been developed for removal of MG. Influence of important variables (sonication time, pH, initial MG concentration, temperature and amount of adsorbent) were investigated and optimized by central composite design (CCD) combined with response surface methodology (RSM) using the desirability function (DF) as maximize criterion of the response. The results obtained from the presented models were compared with the experimental values.

The gold nanoparticles loaded AC (Au-NP-AC) was synthesis and subsequently characterized via different techniques such as field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Brunauer, Emmett and Teller (BET), and UV–Vis measurements. Then the adsorption kinetics and isotherms of MG removal on this adsorbent was investigated. The adsorption rates were evaluated by fitting the experimental data to conventional kinetic models such as pseudo first and second-order and intraparticle diffusion models. The proposed sorbent is useful for quantitative adsorption of the MG with high sorption capacities in short time.

Experimental

Instruments and reagents

An ultrasonic bath with heating system (Tecno-GAZ SPA Ultra Sonic System, Italy) at 60 Hz of frequency and 130 W of power was used for the ultrasound-assisted adsorption procedure. The pH measurements were carried out using pH/Ion meter model-686 (Metrohm, Switzerland, Swiss) and the MG concentration was determined using Jusco UV–Vis spectrophotometer model V-530 (Jasco, Japan) at a wavelength of 619 nm.

The morphology of the Au-NP-AC was observed by scanning electron microscopy (SEM; Hitachi S-4160, Japan) under an acceleration voltage of 15 kV. A BET surface analyzer (Quantachrome NOVA 2000) was used to measure nitrogen adsorption–desorption isotherm at 77 K while before the measurement, the samples were degassed using helium at 553 K for 3 h. The BET surface area, total pore volume, and micropore area were obtained from the adsorption isotherms. TEM samples were prepared by dropping diluted solutions of Au nanoparticles onto 400-mesh carbon-coated copper grids with the excessive solvent immediately evaporated. The morphology and electron diffraction pattern of the Au nanoparticles were determined by a Hitachi H-800 TEM (Hitachi, Japan) at an operating voltage of 200 kV. Absorption measurements were carried out on a Perkin Elmer Lambda 25 spectrophotometer using a quartz cell with an optical path of 1 cm. The stock solution (200 mg L^{-1}) of MG was prepared by dissolving 100 mg of solid dye in 500 mL double distilled water and the working concentrations daily were prepared by its suitable dilution. All chemicals including malachite green, $HAuCl_4.3H_2O$, soluble starch, activated carbon, NaOH, and HCl with the highest purity available were purchased from Merck Co. (Darmstadt, Germany).

Ultrasound assisted adsorption method

The removal of dye solutions were examined using ultrasound power combined with Au-NP-AC. The sonochemical adsorption