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Optimization of the ultrasonic assisted removal of methylene blue by gold nanoparticles loaded on activated carbon using experimental design methodology

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ABSTRACT

The present study was focused on the removal of methylene blue (MB) from aqueous solution by ultrasound-assisted adsorption onto the gold nanoparticles loaded on activated carbon (Au-NP-AC). This nanomaterial was characterized using different techniques such as SEM, XRD, and BET. The effects of variables such as pH, initial dye concentration, adsorbent dosage (g), temperature and sonication time (min) on MB removal were studied and 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. Analysis of experimental adsorption data to various kinetic models such as pseudo-first and second order, Elovich and intraparticle diffusion models show the applicability of the second-order equation model. The small amount of proposed adsorbent (0.01 g) is applicable for successful removal of MB (RE > 95%) in short time (1.6 min) with high adsorption capacity (104–185 mg g^{-1}).

1. Introduction

The dyes in industries effluents such as textile, leather, paper, and plastics are serious concern because of their adverse effects on human and environmental ecosystems [1,2]. The dyes associated environmental problem come from their high visibility, undesirability and recalcitrance. Therefore, their removal from industrial effluents as most urgent task make possible to either a safe and clean environment [3,4]. Methylene blue (MB) (Fig. 1) (3,7-bis(Dimethylamino)-phenothiazin-5-iumchloride) as a thiazine cationic dye is commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools and so on and can cause eye burns which may be responsible for permanent injury to the eyes of human and animals [5,6]. Many technologies have been developed for dye removal from aquatic environments, including flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation and biosorption [7]. Among them, the wide application of adsorption is emerged from advantages including high efficiency, capacity and large scale ability of generable adsorbents [8–13]. The design of novel procedure based on nontoxic, low cost and easy available adsorbents are the best choice for wastewater treatment. Nanoparticles possess distinguished properties such as high number of reactive atoms and large number of vacant reactive surface sites in addition to metallic or semi-metallic behavior applicable for interaction of various functional and reactive groups (atoms) of target compound for their quantitative removal [5]. Activated carbon (AC) as the nontoxic, low cost and easy available adsorbent is considered as a universal adsorbent for the removal of pollutants such as dyes and heavy metals from the wastewater due to its high surface areas, porous structure, large adsorption capacities, fast adsorption kinetics and general material as support for loading nanomaterial [14,15]. AC contain various reactive sites such OH, COOH, C=O and amide groups that in conjunction with nanoparticle properties synergically improve the efficiency of adsorption procedure.

Ultrasound irradiation is well known to accelerate chemical process due to the phenomenon of acoustic cavitation. In this procedure, the formation, growth and collapse of micrometrical bubbles formed by the propagation of a pressure wave through a liquid is useful tool in intensifying the mass transfer process and breaking the affinity between adsorbate and adsorbent [16,17]. Shock waves have the potential of creating microscopic turbulence within interfacial films surrounding nearby solid particles [18,19]. Acoustic streaming induced by the sonic wave is the movement of the liquid, which can be considered to be the conversion of sound

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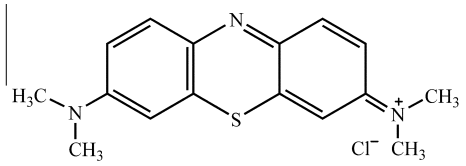

Fig. 1. Chemical structure of MB.

to the kinetic energy [20]. These phenomena increase the rate of mass transfer near the surface.

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 [21–25].

There are several experimental variables affecting the ultrasound-assisted removal of MB. A statistical design of experiment can be preferred to decrease the number of experiments, while consider the interaction between variables [26,27].

In the present work, USA-DLSMA as a novel, simple, sensitive, inexpensive and rapid/assisted adsorption method followed by UV–vis detection has been developed for efficient short time removal of MB. Influence of important USA-DLSMA variables (sonication time, pH, initial MB concentration 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 synthesized and subsequently characterized via different techniques such as scanning electron microscopy (SEM), X-ray diflraction (XRD) and Brunauer, Emmett and Teller (BET) analysis. Then the adsorption kinetics and isotherms of MB removal on this adsorbent was investigated and its applicability for treatment of waste water and this dye removal was investigated. The adsorption rates were evaluated by fitting the experimental data to traditional kinetic models such as pseudo first and second-order and intraparticle diffusion models. The proposed sorbent is useful for quantitative adsorption of the MB with high sorption capacities in short time.

2. Experimental

2.1. Instruments and reagents

The stock solution (200 mg L^{-1}) of MB 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. An ultrasonic bath with heating system (Tecno-GAZ SPA Ultra Sonic System) at 40 kHz of frequency and 130 W of power was used for the ultrasound-assisted micro adsorption. The pH measurements were carried out using pH/Ion meter model-686 (Metrohm, Switzerland, Swiss) and the MB concentration was determined using Jusco UV–vis spectrophotometer model V-530 (Jasco, Japan) at a wavelength of 664 nm.

The morphology of the Au-NP-AC was observed by scanning electron microscopy (SEM; Hitachi S-4160) 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. To do that, degassing is done by helium gas as blank run due to the fact that helium does not adsorb onto the sample. 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 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. All chemicals including NaOH and HCl with the highest purity available were purchased from Merck (Darmstadt, Germany).

2.2. Ultrasound assisted adsorption method

The MB removal was examined using ultrasound power combined Au-NP-AC. The sonochemical adsorption experiment was carried out in a batch mode as follows: specified amounts of dye solution at known concentration (18 mg L^{-1}) and initial pH of 7 with a known amount of adsorbent (0.01 g) were poured into the flask and maintained the desired sonication time (1.6 min) at the desired temperature (303.15 k). At the end of the adsorption experiments, the sample was immediately centrifuged and analyzed.

2.3. Measurements of dye uptake

The dye concentrations were determined according to calibration curve obtained at maximum wavelength over working concentration range. The efficiency of MB removal was determined at different experimental conditions optimized according to the CCD method. The experiments were also performed in the initial MB concentration range of 5–40 mg L^{-1} to obtain adsorption isotherms. The MB removal percentage was calculated using the following equation:

$$\%\ \text{MB removal} = ((C_0 - C_t)/C_0) \times 100 \quad (1)$$

where C_0 (mg L^{-1}) and C_t (mg L^{-1}) is the concentration of target at initial and after time t respectively. The adsorbed MB amount (q_e (mg g^{-1})) was calculated by the following mass balance relationship:

$$Q_e = (C_0 - C_e)V/W \quad (2)$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium dye concentrations in aqueous solution, respectively, V (L) is the volume of the solution and W (g) is the mass of the adsorbent.

2.4. Preparation of Au-NP-AC

The Au nanoparticles were synthesized according to our previous report [28,29] as follow: 200 μL aliquot of 0.05 mol L^{-1} $HAuCl_4.3H_2O$ aqueous solution was added into 50 mL of an aqueous solution containing 0.2% (w/w) of the soluble starch and vigorously stirred for 1 h in the 0.05 mol L^{-1} NaOH solution. The starch caped Au nanoparticles are stabile for several months that show the actual role of starch as both reducing and stabilizing agent. Subsequently, the light pink color of solution indicates the initial formation of the Au nanoparticles. The mixture was maintained at 70 °C for 6 h and the color of the reaction solution became winy red. Starch is a naturally occurring polysaccharide (polymer) with biocompatibility and biodegradation, which have been used to stabilize gold nanoparticles. Previously in the synthesis of Au nanoparticles in aqueous solutions it was reported that the role of soluble starch as capping agents [30]. This method benefits from the advantage that lack of consumption organic solvents and was a green biologically compatible procedure. It was suggested that