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Removal of Alizarin Red S by gold nanoparticles loaded on activated carbon combined with ultrasound device: Optimization by experimental design methodology

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ABSTRACT

The present study is developed to investigate Alizarin Red S removal process from aqueous solution which was carried out through the application of ultrasound onto gold nanoparticles loaded on activated carbon (Au-NP-AC). The fully detailed characterization of this nanomaterial using TEM, SEM, XRD, and BET shows its high surface area alongside its porous structure which makes this adsorbent a candidate for the removal of a large amount of pollutants. Central composite design and response surface methodology were applied to evaluate the main effect and interaction among the variables. The experimental equilibrium data efficiency fitted the Langmuir model with a high adsorption capacity, while second-order equation was suitable to explain the kinetics of the adsorption. A small amount of adsorbent (0.015 g) was applied for a successful removal of ARS (RE >95%) in a short time (5 min) and with a high adsorption capacity (123.4 mg g^{-1}).

1. Introduction

The production and the subsequent entrance of dyes, as wastewater pollutants, from industries such as textile, leather, paper, and plastics into aqua and various other media cause severe problems, directly or indirectly, for humans and other organisms [1,2]. Alizarin Red S (ARS, $C_{14}H_7NaO_7S \cdot H_2O$, see Fig. 1), water-soluble, is widely used in textile industry as a staining agent. This dye belongs to the category of the most recalcitrant and durable pollutants, forcing the researchers to focus on designing and developing a simple, easy and efficient protocol for their safe and economic removal [3,4]. Among all well-known and traditional applicable protocols such as photocatalytic degradation [5], oxidation [6], biosorption [7] and adsorption [8,9] more attention is paid to adsorption process that is more frequently used for its high efficiency, non-toxicity, and easily available adsorbents [10,11]. These adsorbents, especially on a nano scale, possess high capacities, useful for sustaining and keeping the quality of water undisturbed [12–14]. Nanotechnology and nanometer materials, due to their special physical and chemical properties (from their high surface areas and volume ratios to the presence of various surface reactive atoms) attract a lot of attention in many areas, especially in wastewater treatment and its efficient remediation [15–17]. Activated carbon (AC) that shows unique and distinguished features such as high surface areas, porous structure, large adsorption capacities, non-toxicity, low cost, and fast adsorption kinetics, as a general material or as a resultant of loading a nano scale material on its surface is considered as a universal adsorbent for the removal of pollutants such as dyes and heavy metals [18,19]. This combination and modification through enhancing the pathways and mechanism of mass transfer result in the enhancement of the removal percentage and adsorption capacity of AC-based adsorbents.

Ultrasound through its secondary effects such as nucleation, growth and collapse of tiny gas bubbles improves the mass transfer through micro-streaming, micro-turbulence, acoustic (or shock) waves and microjets without any significant change in the equilibrium characteristics of the adsorption/desorption system [20–22]. Ultrasound irradiation is a well-known device and helps accelerate the chemical process due to the phenomenon of acoustic cavitation. The formation and change in the size and the property of bubbles occurred following the propagation of a pressure wave across each liquid fluid. Therefore, through different mechanisms it is a useful tool to accelerate the migration of dye molecules that are transferred to the adsorbent surface following the breaking of the affinity between adsorbate and adsorbent [23].

Experimental variables affecting the ultrasound-assisted removal of ARS can be explained using statistical designs and programs that enable the researchers by at least a number of experiments to estimate the interaction between the variables [24,25].

In the present work combination of the ultrasound-assisted adsorption onto Au-NP-AC has been developed for the removal of ARS in simple and rapid method followed by UV–Vis detection. The influence of important variables (sonication time, pH, initial ARS concentration

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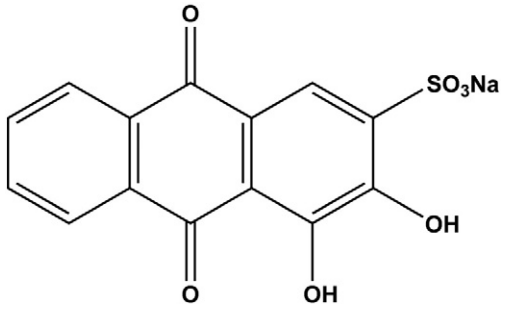

Fig. 1. Chemical structure of ARS.

and the amount of adsorbent) was investigated and optimized by central composite design (CCD) combined with response surface methodology (RSM) using the desirability function (DF) as the maximized criterion of the response.

The gold nanoparticles loaded on activated carbon (Au-NP-AC) were synthesized simply in our laboratory and were subsequently characterized via different techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD) transmission electron microscopy (TEM), and Brunauer, Emmett and Teller (BET) analysis. Further loading of Au nanoparticles on AC allowed for the achievement of a high removal percentage due to the increase in the surface area and the attained porous structure. Due to their high ability to eliminate the bacteria present in the water and also their diagnostic ability, gold nanoparticles prevent health problems and allow for a safe and clean environment [26,27]. These distinguished properties compensate the high cost of gold nanoparticles. Therefore, it seems that the removal process based on gold nanoparticles simultaneously removes dye compounds and other organisms such as bacteria and yeast. The adsorption kinetics and isotherms of ARS removal on this adsorbent and their applicability for the treatment of waste water and the dye removal were 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 a quick quantitative adsorption of the ARS with high sorption capacities.

2. Experimental

2.1. Instruments and reagents

The stock solution (200 mg L^{-1}) of ARS was prepared by dissolving 100 mg of solid dye in 500 mL double distilled water and the working concentrations were daily prepared in its suitable dilution. An ultrasonic bath with heating system (Tecno-GAZ SPA Ultra Sonic System, Bologna, Italy) 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 ARS concentration was determined using Jusco UV–Vis spectrophotometer model V-530 (Jasco, Japan) at a wavelength of 520 nm.

The morphology of the Au-NP-AC was observed by scanning electron microscopy (SEM; Hitachi S-4160, Tokyo, Japan) under an acceleration voltage of 15 kV. A BET surface analyzer (Quantachrome NOVA 2000, Quantachrome Instruments, USA) 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 the size distribution 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 (Massachusetts, USA) using a quartz cell with an optical path of 1 cm. All chemicals including NaOH, and HCl were purchased from Merck (Darmstadt, Germany) with the highest purity available.

2.2. Ultrasound-assisted adsorption method

The ARS removal was examined using ultrasound power combined with Au-NP-AC. The sonochemical adsorption experiment was carried out in a batch mode as follows: specified amounts of dye solution at a known concentration (35 mg L^{-1}) and initial pH of 4.2 with a known amount of adsorbent (0.015 g) were poured into the flask and maintained the desired sonication time (5.0 min) at room temperature (298 K). At the end of the adsorption experiments, the sample was immediately centrifuged and analyzed.

2.3. Measurements of dye uptake

Dye concentrations were determined according to the calibration curve obtained at maximum wavelength over the working concentration range. The efficiency of ARS removal was determined in different experimental conditions optimized according to the CCD method. The experiments were also performed in the initial ARS concentration range of 2–70 mg L^{-1} to obtain adsorption isotherms. The ARS removal percentage was calculated using the following equation:

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

where C_0 (mg L^{-1}) and C_t (mg L^{-1}) are the concentrations of the target at initial and after time t respectively. The adsorbed ARS 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), the volume of the solution and W (g), the mass of the adsorbent.

2.4. Synthesis of gold nanoparticle

The Au nanoparticles (Au NP) were synthesized according to our previous report [28,29] as follows: 200 μL aliquot of 0.05 mol L^{-1} $HAuCl_4 \cdot 3H_2O$ aqueous solution was added to 50 mL of an aqueous solution containing 0.2% (w/w) of the soluble starch and was vigorously stirred for 1 h in the 0.05 mol L^{-1} NaOH solution and the subsequent heating of the mixture at 70 °C for 6 h allowed for a winy red precipitate namely gold nanoparticles.

Then, mixing 500 mL of Au NP (0.5 g L^{-1}) with activated carbon (10 g) in a 1000 mL flask under magnetic stirring for up to 12 h made possible the deposition of the Au nanoparticles on the activated carbon. The non-loaded Au nanoparticle was evaluated using UV–Vis spectrophotometry.

2.5. Central composite design

The CCD was used to investigate the significance of the effects of parameters including sonication time, pH, initial dye concentration and the amount of adsorbent that was designed using STATISTICA 7. A five-level CCD was performed to evaluate the influence of the quantities of removal yield (Table 1) leading to 30 runs for the optimization process. Table 2 shows the experimental design points consisting of 2^n factorial points with 2n axial points and Nc central points and the test results for the response variables. The center points are used to determine the experimental error and the reproducibility of the data. The independent variables are coded based on $(-1, +1)$ interval where the low and high levels are coded as -1 and $+1$, respectively. The