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Solid phase extraction and removal of brilliant green dye on zinc oxide nanoparticles loaded on activated carbon: New kinetic model and thermodynamic evaluation

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ABSTRACT

The brilliant green (BG) solid phase extraction of carried out following accumulation on including zinc oxide nanoparticles loaded on activated carbon (ZNO-NP-AC) non-toxic and green as material. The influence of variables such as pH, initial BG concentration, contact time, amount of adsorbent, eluent and temperature on BG removal and recoveries were studied and optimized. The high correlation coefficient and possibility of accurate prediction and explanation of experimental data by novel kinetic model show its applicability and superiority for representation of experimental data. The results of present model compared with traditional kinetic models (pseudo-first and second order and intraparticle diffusion model). Additionally, fitting the experimental equilibrium data to numerous conventional isotherm models show that the Langmuir model with high correlation coefficient and low error analysis is more usable to explain the experimental data. The calculated change in entropy and enthalpy of BG adsorption on proposed adsorbent was 136.59 J mol^{-1} K^{-1} for 15.0 mg L^{-1} and 65.2 J mol^{-1} K^{-1} 35.2 kJ/mol and 16.1 kJ/mol for 15 mg L^{-1}. The quantitative elution of retained BG by 2.0 mL of EtOH make permit accurate and repeatable monitoring off BG over wide linear range (0.2–500 ng mL^{-1}) with limits of detection (LODs) of 0.08 ng mL^{-1}. The preconcentration factors were 75 and loading half time ($t_{1/2}$) values were less than 5 min.

1. Introduction

The major part of dyes entrance to food products and industry through waste water of textiles, beverage industries and printing processes [1]. Most applied dyes used in the paper printing and textile industries generate serious problems for the most organisms and human. Brilliant green (BG) dye (odorless yellow-green to green powder) used for various purposes, e.g. biological stain, dermatological agent, veterinary medicine and also as additive to inhibit propagation of mold, intestinal parasites and fungus [2]. BG exposure and inhalation lead to generation of hazards such as gastrointestinal tract; nausea, vomiting and diarrhea, while its ingestion and inhalation cause damaging target-organ [3]. BG decomposition leads to generation of carbon dioxide, sulfur and nitrogen oxides. Using inexpensive dye for treating fungal and gram-positive bacteria possible infections in fishes. Therefore, routine monitor and evaluation of BG content by the FDA and many other international institutes is a required and emergency task [4]. Extensive use of dyes generate huge amount of color wastewater that most of them are not degraded and/or removed by conventional treatment processes. Among general and traditional previously reported dyes treatment procedures adsorption benefit from advantages such as high efficiency, capacity and ability for large scale dye removal [5–9]. The wide applicability of this method depends to re-generality, softy and non-toxic nature of adsorbent [10–33]. Nano-particles as novel sorbents attain great interest for preconcentration of trace elements and toxic dyes owing to their effectiveness and high number of reactive atoms [15–18]. Solid phase extraction (SPE) is sensitive, fast and economic method for the enrichment of trace amounts of inorganic and organic species. These procedures have many advantages such as high preconcentration factors, simple phase separation and efficient automation [20]. To the best of our knowledge, limited effort has been devoted to the application of nano-particles for SPE of dyes in aqueous solution. Zinc oxide (ZnO) nanoparticles have

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wide technological applications in catalytic, photocatalytic, electrical and optoelectronic processes and systems [28]. Accurate and repeatable monitoring and evaluation of the BG ultra trace level require primary SPE procedure.

Generally the rate of adsorption give useful information about its behavior under different operating conditions is essential for best selection of the optimal variables in adsorbent design. It is interesting to recognize the adsorption kinetic and determine respective coefficients and constant that characterizes the transport of sorbate within adsorbents [29–33]. Appropriate identification of an adsorption process required preliminary knowledge about equilibrium and kinetics data. Thermodynamic data only provide information about final state of process. The kinetics investigation deals with the changes in chemical properties with. Several traditional kinetics models are not so validated over all key variables such as pH, initial dye concentration and adsorbent dose. Dependency of adsorption data on several conditions enhance devoting, the attempt to make any theoretical kinetics mode valid over all key operating variables.

The objective of this study was to investigate kinetics, isotherms and thermodynamics of BG removal on zinc oxide nanoparticle loaded on activated carbon (ZnO-NP-AC).

2. Experimental

2.1. Instruments and reagents

Brilliant green (BG) (Fig. 1) has formula of $C_{27}H_{34}N_2O_4S$, CI = 42 040; FW = 482.64 g mol^{-1}, know as basic green 4 with λ_{max} of 623 nm. SPE was studied in batch experiments using 100 mL capacity glass beaker. After stirring for 20 min, the mixture was centrifuged and the solid adsorbent was eluted and quantified according to calibration curve obtained at the similar conditions. The stock BG solution (100 mg L^{-1}) was prepared by dissolving 100 mg of BG in 1000 mL double distilled water. The test solutions were prepared by diluting the stock solution to the desired concentrations, daily. The pH was adjusted by addition of dilute HCl and/or KOH using pH/Ion meter model-686 (Switzerland, Metrohm, and Swiss). The absorption was measured using Jusco UV-Visible spectrophotometer model V-570. Chemicals such as HCl and KCl with the highest purity available are purchased from Merck, Darmstadt, Germany. X-ray diffraction (XRD) pattern was recorded by an automated Philips X'Pert X-ray diffractometer with Cu Kα radiation (40 kV and 30 mA) for 2θ values over 10–80°. The shape and surface morphology of the ZnO nanoparticles were investigated by field emission scanning electron microscope (FE-SEM, Hitachi S4160) under an acceleration voltage of 15 kV. For FE-SEM, it is necessary to coat the ZnS nanoparticles by gold, which was carried out by an Auto Fine Coater (JFC-1300, JEOL).

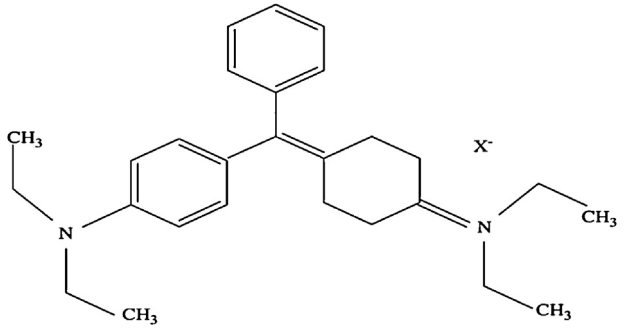

Fig. 1. Chemical structure of BG.

2.2. Measurements of dye uptake

BG concentrations were estimated using the linear regression equations obtained by plotting absorbance versus concentration. The adsorption of adsorbent was determined at the time intervals in the range of 1–15 min for 15 mg mL^{-1} and 1–30 min for 20 mg mL^{-1} at room temperature. It was found that equilibrium was established after 12 and 27 min for 15 and 20 mg mL^{-1} of BG solution. The effect of initial pH in the range of 2–8 on BG adsorption on to ZnO-NR-AC was studied at 15 mg L^{-1}, while isotherm studies was recorded in the range of 10–35 mg L^{-1}. The amount of adsorbed BG by adsorbent (q_e (mg g^{-1})) was calculated by the following mass balance relationship:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

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

2.3. Preconcentration procedure

30 mg of ZnO-NP-AC poured into the column and following preconditioning, 100 mL of BG aqueous sample (5 mg mL^{-1} of BG at pH 5) was passed through the column gravitationally. BG retained on the solid phase was eluted with 2 mL of methanol and its content was determined by UV–vis spectrophotometer at 623 nm.

3. Results and discussion

3.1. Characterization of the ZnO-NP-AC

It is known that ZnO-NP synthesis depend to various conditions such as pH, reaction time and temperature, concentration and order of addition of all reagents. Conducting various experiments at different conditions show that maximum amount of ZnO nanoparticle with smallest size was achieved at pH 6 after '12 h' at low concentration of reagent (homogenous reaction) [34,35].

Absorption spectra measurements over 12 h (Fig. 2) in glycol solution posses show distinguished absorption maximum with blue shift that strongly support (as the decrease in size of ZnO). The glycol in the solution inhibit from crystal growth. At higher time or in the in the absence of glycol solution, the size of ZnO particles changed significantly. Based on the ZnO nanorods absorption

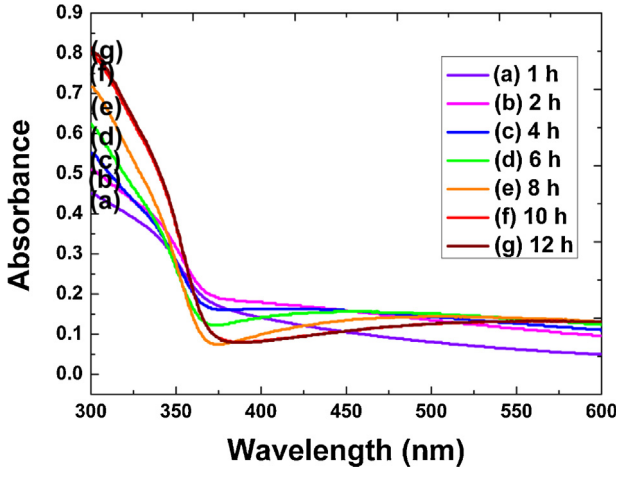

Fig. 2. Evolution of absorption spectra of the ZnO nanorods taken at 2 h intervals following the initiation of the reaction for the first 12 h.