Application of artificial neural network and response surface methodology for the removal of crystal violet by zinc oxide nanorods loaded on activate carbon: kinetics and equilibrium study

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Ebrahim Alipanahpour Dil [a], Mehrorang Ghaedi [a,*], Abdolmohammad Ghaedi [b], Arash Asfaram [a], Mahdi Jamshidi [a], Mihir Kumar Purkait [c]

[a] Chemistry Department, Yasouj University, Yasouj, 75918-74831 Iran
[b] Chemistry Department, Islamic Azad University, Gachsaran Branch, Gachsaran, Iran
[c] Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, 781039 Assam, India

A B S T R A C T

The present work discusses the removal of crystal violet dye from aqueous solution by ultrasound assisted adsorption using zinc oxide nanorods loaded on activate carbon as an adsorbent. The said adsorbent was prepared and characterized using field emission scanning electron microscopy, X-ray diffraction and Fourier transform infrared analysis. The important process parameters, such as initial crystal violet concentration (8–24 mg/L), solution pH (3.0–7.0), adsorbent doses (0.005–0.025 g), and sonication time (2–6 min) were optimized using design of experiments. The optimum removal efficiency of crystal violet onto adsorbent was determined as 99.82% at pH 7.0, 0.025 g adsorbent dosage, 24 mg/L initial crystal violet concentration and 5.0 min sonication time. Analysis of variance showed a high coefficient of determination ($R^2 = 0.992$). The present analysis suggests that the predicted values are in good agreement with experimental data. Also, the artificial neural network model was used for predicting removal (%) of crystal violet dye based on experimental data. Equilibrium data was fitted well with the Langmuir model having maximum adsorption capacity of 113.64 mg/g. The adsorption of crystal violet followed the pseudo-second order kinetic model. This study clearly showed that response surface methodology was one of the appropriate methods to optimize the operating conditions.

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1. Introduction

Crystal violet (CV) dye is widely used in animal and veterinary medicine as a biological stain and for identifying the bloody fingerprints. It bears triphenyl methane group in its structure and harmful by inhalation, ingestion and skin contact. The dye is also responsible for cancer and severe eye irritation to human beings [1,2]. It is poorly degraded as recalcitrant molecule by microbial enzymes, and can persist in a variety of environments. Very few reports are there for the degradation of crystal violet by microbial organism. Yatome et al. [3] reported the degradation of crystal violet with bacterial cell of Nocardia coralline IAM 12121 at a low concentration (about 2 mg/L). A maximum of 66.60% decolorization rate of crystal violet at the concentration of 0.10–0.28 g/L was reported by Annadurai et al. [4].

Metal nanoparticles are currently getting attention due to their wide application in electrical, optical, mechanical, magnetic and chemical field. Because of their large surface area to volume ratio, the properties of the nanoparticles are different from its bulk materials. Different noble metals are used to prepare the nanoparticles among which zinc nanoparticle plays a significant role due to its wide application in various biological system, living organism and medicine [5–7]. Conventional dye containing wastewater treatment technologies were mainly based on physicochemical, chemical and biological process. These are coagulation and flocculation [8], adsorption [9], biosorption [10], electrochemical [11] and fungal decolonization [12]. Among these procedures, adsorption is the cheapest and applicable for large scale operation [13]. This technique is also beneficial as the design is too simple and uses nontoxic adsorbents with high removal efficiency. Selection of appropriate adsorbent is based on mainly removal capacity, operating conditions and treatment cost [14,15]. Regeneration of adsorbent by chemical treatment or biodegradation may generate toxic by-products.

Use of nanoparticles is a good approach that distinguishes and distinct them in terms of large surface area and high exchange
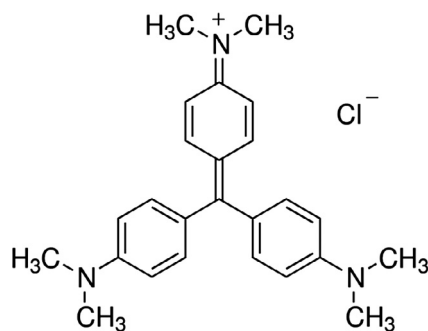
Fig. 1. Chemical structures of crystal violet.

capacity. This study reports the feasibility of applying nanorods loaded activated charcoal as an efficient adsorbent for CV removal from aqueous solution. The use of low-cost, non-toxic, high surface area and eco-friendly adsorbent has been investigated to remove crystal violet from wastewater.

In this work, the zinc oxide nanorods loaded on activate carbon (ZnO-NRs-AC) was synthesized and subsequently characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) analysis. The prepared sorbent was used as an adsorbent for the removal of CV from aqueous medium. Influence of important variables (sonication time, pH, initial CV concentration and adsorbent dosage) 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.

2. Experimental

2.1. Chemicals and instruments

The chemical structure of CV or gentian violet dye with chemical formula $C_{25}H_{30}N_3Cl$ is shown in Fig. 1. The maximum absorption was observed at wavelength of 584 nm. All chemicals including crystal violet, Zinc acetate dihydrate, NaOH, and HCl with the highest purity available were purchased from Merck (Darmstadt, Germany). Activated carbon was purchased from Chem Lab Company and used as a support material for the preparation on ZnO-NRs-AC. 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 CV concentration was determined using Perkin Elmer Lambda 25 spectrophotometer at a wavelength of 584 nm using a quartz cell with an optical path of 1 cm. X-ray diffraction (XRD, Philips PW 1800) was performed to characterize the phase and structure of the prepared nanoparticles using $Cu_{k\alpha}$ radiation (40 KV and 40 mA) at angles ranging from 30 to 60º. The morphology of the nanorods were observed by field emission scanning electron microscopy (FE- SEM: Hitachi S- 4160) under an acceleration voltage of 15 KV. A Fourier transform infrared (FT-IR) spectrum was recorded using a Perkin Elmer-Spectrum RX-IFTIR spectrometer in the range of 400–4000 cm^{-1}. The stock solution (100 mg/L) of CV was prepared by dissolving 10 mg of solid dye in 100 mL double distilled water and the working concentrations daily were prepared by its suitable dilution.

2.2. Ultrasound assisted adsorption method

The removal of CV was studied using ultrasound assisted method to adsorb dye using ZnO-NRs-AC. The sonochemical adsorption experiment was carried out in a batch mode as follows:

specified amounts of CV dye solution (50 mL) at known concentration (24 mg/L) and pH 7.0 with a known amount of adsorbent (0.025 g) were loaded into the flask and desired sonication time (5.0 min) at the room temperature were maintained. At the end of the adsorption experiments, the sample was immediately centrifuged and analyzed. The concentration of the CV in the solution after equilibrium adsorption was quantified at 584 nm. The efficiency of CV removal was determined at different experimental condition according to CCD method. The CV removal percentage was calculated with the following equation [16]:

$$R\%_{CV} = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

where C_0 (mg/L) and C_t (mg/L) are the concentration of purpose at initial and after time t, respectively. The adsorbed CV amount (q_e (mg/g)) was calculated using following relationship [17]:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_0 (mg/L) and C_e (mg/L) are the initial dye concentration and equilibrium dye concentration in aqueous solution, respectively. V (L) is the solution volume and W (g) is the adsorbent mass. The kinetic studies were performed in a series of flask containing 0.025 g of ZnO-NRs-AC and 50 mL of CV of 11 and 15 mg/L at room temperature. After fixed time intervals (1–8 min), adsorbent were separated and the concentration of CV remaining in the supernatant solution was determined by a UV–visible spectrophotometry at 584 nm. The thermodynamic parameters were investigated in 50 mL of solution of 0.025 g adsorbent and 24 mg/L CV at pH 7.0 for 5.0 min sonication time. The solution temperature was varied in the range of 10–60 °C.

2.3. Synthesis of ZnO-NRs-AC

Activated carbon was purchased from Chem Lab Company and used as a support material for the prepared ZnO-NRs. Zinc acetate dihydrate ($Zn(CH_3COO)_2$, $2H_2O$) was purchased from Merck company and used as-received without further purification. This was employed as the source of Zn^{2+} ions. Ammonia solution (NH_4OH) was purchased from Chem Lab Company and used as a hydroxide source as well as a complexing agent for Zn^{2+} ions. The preparation of precursor solution for fabrication of the ZnO nanorods was carried out as follows: 0.02 mol zinc acetate solution was mixed with 40 mL of a fresh ammonia solution (25% w/w) at pH 11.0. Distilled water was then added to the mixture to make a total volume of 500 mL in a volumetric flask. In the next step, 5 g activated-carbon (AC) was added to 250 mL of the prepared reaction solution in an Erlenmeyer flask stirred for 1 h at room temperature. The mixed reaction solution with AC was transferred to a microwave oven with power of 540 W. The reaction solution was kept in the microwave oven for cycles of 4×15 min. After 4×15 min cycles, the reaction solution was removed from microwave oven and strongly stirred for 5 h at room temperature to obtain a homogenous deposition of ZnO-NRs on activated carbon. The obtained ZnO-NRs-AC was filtered, washed several times by deionized water. The product is dried in a microwave oven with power of 360 W for 12 min. Finally, these were used as an absorbent for adsorption experiments.

2.4. Central composite design

Central composite design (CCD) was used to study the individual and synergetic effect of the four factors toward one response. This method can reduce the number of experimental trials required to evaluate main effect of each parameter and their interactions [16]. In general, CCD is characterized by three operations namely: 2k axial runs, 2^k factorial runs and central runs. The CCD in present research