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Principal component analysis-artificial neural network and genetic algorithm optimization for removal of reactive orange 12 by copper sulfide nanoparticles-activated carbon

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ABSTRACT

In this study a green approach described for the synthesis of copper sulfide nanoparticles loaded on activated carbon (CuS-NP-AC) and usability of it for the removal of reactive orange 12 (RO-12). This material was characterized using instruments such as scanning electron microscopy (SEM) and X-ray diffraction (XRD). The effects of variables were optimized using Principal component analysis-artificial neural network (PCA-ANN). Fitting the experimental equilibrium data shows the suitability of the Langmuir isotherm. The small amount of proposed adsorbent (0.017 g) is applicable for successful removal of RO-12 (RE > 95%) in short time (31.09 min) with high adsorption capacity (96.9 mg g^{-1})

1. Introduction

Different industries (textile, leather, paper and plastics) consume and generate large amounts of polluted water. The biological activity and abundance of dye molecules greatly depend to variables such as pH, electrolyte and metal ions levels. The dyes significant, importance and associated environmental problem come from their high visibility and recalcitrance. Therefore, their removal from such industrial effluents is challenging requirement to produce a safe and clean environment [1–4]. Reactive orange 12 (Fig. 1) is an azo dye and widely used to color the cellulosic textiles which may cause toxicity of ecosystems and may lead to skin cancer due to photosensitization and photodynamic damage [5,6]. Concentrated treatment techniques of dyes contaminated wastewaters are flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation and biosorption [7]. Among them, the adsorption based procedure associated with advantages including high efficiency, capacity and large scale ability with 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 oppose 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 applied for removal of various toxic materials [14,15]. Activated carbon (AC) generally has porous structure and high surface area is one of the most popular low cost and general material as support for loading nanomaterial [16,17]. AC is widely used as adsorbents in a variety of processes for removal of dyes from water and wastewater [18,19]. In this technique application of nano scale materials with high surface area enhance the removal percentage and adsorption capacity of AC based adsorbent. Metal based nanoparticles such as copper sulfide has great importance in the analytical chemistry, catalytic applications, electromagnetic devices, etc.

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. For optimization section and model construction such techniques including multiple linear regression (MLR), partial least squares (PLS), principal component regression (PCR), support vector regression (SVR), adaptive network-based fuzzy inference system (ANFIS) and artificial neural networks (ANNs) can be applied [20–24]. Artificial neural network (ANN) as non-linear approach is

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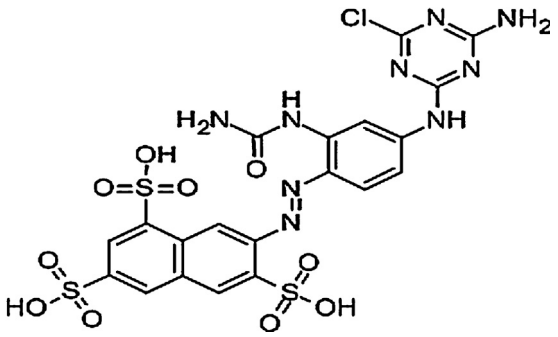

Fig. 1. Chemical structure of RO-12.

suitable for modeling complex nonlinear systems. This model based on alternative formulas (mathematical or physical relationships) is able to solve problems in various areas [25]. Yetilmezosy and Demirel [26] developed a three layer artificial neural network model for prediction the removal of Pb (II) ions from aqueous solution using Antep pistachio.

Genetic algorithm (GA) according to evolutionary algorithms is used for optimization of objective function by means of the parameters space coding. This technique applied in complex spaces of various scientific disciplines following admit to maximize or minimize objective function [27]. The GA can obtain acceptable results using operators namely reproduction, crossover and mutation. The theory and application of ANN and GA to chemical problems can be found in the literature [28].

In this study, PCA-MLR and PCA-ANN have been utilized for inspection of linear and nonlinear relationships exist among variables while GA used to optimize the effect of variables concern to the adsorption of RO-12 by CuS-NP-AC. The results obtained from the presented models were compared with the experimental values. The CuS-NP-AC was synthesis and subsequently characterized via different techniques such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. Then the adsorption kinetics and isotherms of RO-12 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 RO-12 with high sorption capacities in short time.

2. Experimental

2.1. Instruments and reagents

The stock solution (100 mg L^{-1}) of RO-12 (formula weight: 739.98 g mol^{-1} and molecular formula: $C_{20}H_{23}ClN_9O_{10}S_3$ 3Na) 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. The pH measurements were carried out using pH/Ion meter model-686 (Metrohm, Switzerland, Swiss) and the RO-12 concentration was determined using Jusco UV–vis spectrophotometer model V-530 (Jasco, Japan) at a wavelength of 395 nm. The morphology of the CuS-NP-AC was observed by scanning electron microscopy (SEM; Hitachi S-4160) under an acceleration voltage of 15 kV. X-ray diffraction (XRD) pattern was recorded by an automated Philips X'Pert X-ray diffractometer (40 kV and 30 mA) for 2θ values over 10–80°. All chemicals including NaOH, HCl and KCl with the highest purity available were purchased from Merck (Darmstadt, Germany).

2.2. Measurements of dye uptake

The dye concentrations were determined according to general traditional photometry method at maximum wavelength over working concentration. The efficiency of RO-12 removal was determined at different time intervals (in the range of 2–30 min) and the equilibrium was established after 12 min of contact time. The effect of initial pH on the removal of RO-12 was evaluated in the pH range of 1–6, by contacting 50 mL of 40 mg L^{-1} of initial dye concentration with 0.02 g of CuS-NP-AC for 20 min of contact time. The experiments were also performed in the initial RO-12 concentration range of 20–70 mg L^{-1} to obtain adsorption isotherms. The RO-12 removal percentage was calculated using the following equation:

$$\%\,\text{RO-12 removal} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

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 RO-12 amount (q_e (mg g^{-1})) was calculated by the following mass balance relationship:

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

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.

The pH corresponding to the point of zero charge (pH_{ZPC}) for the CuS-NP-AC was determined by the pH drift method according to our previous publication [29,30]. The charge of adsorbent surface significantly depends to pH [31,32]. At pH < pH_{ZPC} it has positive charge, while at higher value it has negative charge.

2.3. Preparation of copper sulfide nanoparticle

The CuS nanoparticles was prepared according to the following pathway by the reaction of copper acetate ($Cu(CH_3COO)_2$) with thioacetamide (CH_3CSNH_2) in an oxygen free water under nitrogen as follow: 10 mL of freshly prepared 0.1 mol L^{-1} thioacetamide solution was added into 40 mL mixture of 0.05 mol L^{-1} $Cu(CH_3COO)_2$ and 0.5 mol L^{-1} trisodium citrate at pH of 7.0 and stirred vigorously. Heating the mixture till 40 °C cause the growth of citrate-stabilized CuS nanoparticles after about 10 min and the solution color turned milky white that is attributed to the formation of CuS nanoparticles. The maintenance of the mixture at 40 °C for 6 h lead to change in color of the reaction solution to milky white mixed with light yellow. After rapid centrifugation, the CuS nanoparticles were settled and all its impurity was removed by addition of water and ethanol. Finally, the CuS nanoparticles were dried in a vacuum oven (ca. 0.1 MPa) for 6 h prior to being characterized.

2.4. PCA-ANN

The Matlab R2009a Neural Network Toolbox was applied to forecast the adsorption efficiency. A three layer PCA-ANN (Fig. 2) with a tangent sigmoid transfer function (tansig) at hidden layer, a linear transfer function (purelin) at output layer and Levenberg–Marquardt back-propagation algorithm with 1000 iterations were applied. The data were randomly divided into three groups (70% for training, 15% for the testing and 15% for the validation set). Therefore 184, 40 and 40 samples were applied for training, testing and validation subsets, respectively. Three neurons (concentration (mg L^{-1}), adsorbent dosage (g) and contact time (min)), 1 to 25 neurons in the hidden layer and one neuron (removal percentage)