Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 171 (2017) 268–279

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Application of linear and non-linear methods for modeling removal efficiency of textile dyes from aqueous solutions using magnetic Fe_3O_4 impregnated onto walnut shell

Motahare Ashrafi, Mansour Arab Chamjangali, Ghadamali Bagherian *, Nasser Goudarzi

College of Chemistry, Shahrood University of Technology, Shahrood, P.O. Box 36155-316, Iran

ARTICLE INFO

Article history:
Received 2 April 2016
Received in revised form 9 July 2016
Accepted 31 July 2016
Available online 03 August 2016

Keywords:
Artificial neural network
Dye removal
Multiple linear regression
Non-linear model
Random forest

ABSTRACT

The performance of the Nano-magnetite Fe_3O_4 impregnated onto walnut shell (Fe_3O_4-WNS), which possessed the adsorption features of walnut shell and the magnetic property of Fe_3O_4, was investigated for the elimination of the methyl violet and Rhodamine 6G from contaminated aqueous solutions. The effects of different experimental variables on the removal efficiency of the cited dyes were examined. Then these variables were used as the inputs to generate linear and non-linear models such as the multiple linear regression, random forest, and artificial neural network to predict the removal efficiency of these dye species at different experimental conditions. The validation studies of these models were performed using the test set, which was not present in the modeling procedure. It was found that ANN had a higher ability to predict the adsorption process under different experimental conditions, and could be applied for the development of an automated dye wastewater removal plant. Also the maximum adsorption capacity (q_{max}) indicated that the q_{max} value for Fe_3O_4-WNS for removal of cationic dyes was comparable or better than that for some reported adsorbents. Also it should be cited that exhausted Fe_3O_4-WNS was regenerated using dishwashing liquid, and reused for removal of the cited dye species from aqueous solutions.

1. Introduction

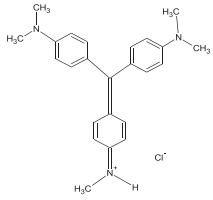
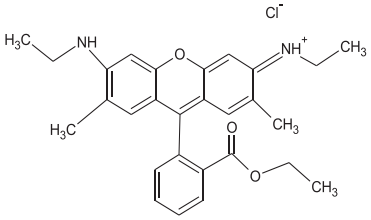
Dyes are extensively used in different industries such as textiles, leather, paper, plastics, food, and rubber for coloring their products [1,2]. Annually more than 10,000 tons of dyes are utilized, and approximately 100 tons are released into water streams [3]. Dyes have been recognized as the first water contaminants [4], and their concentration in water streams usually varies from 10 to 200 mg L^{-1} [5]. These pollutants can have considerable ecological impacts on the ecosystem [6]. For example, most dyes produce mutagenic and carcinogenic intermediates via different reactions [7], and also decrease sunlight diffusion and exhaust dissolved oxygen [6,7]. As a result, elimination of these pollutants from contaminated effluents is a critical problem, and it is required to find suitable treatment techniques for this aim. Among the different methods used for purification of wastewater, adsorption has appeared as a simple, an eco-friendly, and an efficient technique [8,9]. Using this process, the pollutants (as dyes) are transformed to the solid phase from a contaminated liquid or gaseous environment [5,10], and consequently, the adsorbent can be recovered or burned or even reserved in a dry place without a direct contact with the surroundings [10]. Nevertheless, in order to reduce the amount of adsorbent used, and to decrease the disposal issues, significant consideration has been made to employ cost-effective adsorbents with high capacities. In this regard, much attention has been given to the agricultural wastes [5]. Walnut shell (WNS), an abundant agricultural residue (with a production rate of 290,000 tons per year in Iran) [11] with a large specific surface area and a good chemical stability [12], has been successfully used for the removal of single-component aqueous solutions such as malachite green and Lanaset Red [12,13]. Unfortunately, one problem that limits the application of these low-cost adsorbents is the separation of adsorbent along with adsorbate from the solution. The separation is usually made by filter or centrifuge, which are time-consuming and may lose the solid phase or block the filters [14]. Magnetic filtration has been appeared as an alternative method in the recent years. The low-cost magnetic adsorbents can adsorb the pollutant and then be magnetically separated even if the solid phase has a high concentration [15].

It should be noted that the output of an adsorption process, which is the removal efficiency or adsorbed amount of dye per unit mass of the adsorbent [16], is closely related to the experimental factors involved such as the initial pH, dye concentration, temperature, ionic strength, and contact time. Solving this complex problem and modeling the adsorption process can be achieved by computational intelligence systems

* Corresponding author.
E-mail address: Gh_Bagherian@shahroodut.ac.ir (G. Bagherian).

http://dx.doi.org/10.1016/j.saa.2016.07.049
1386-1425/

Table 1
Information about MV and Rh 6G dyes.

	MV	Rh 6G
Color index number	42535	45160
Type	Cationic	Cationic
Class	Triarylmethane	Xanthene
Molecular weight	407.99	479.02
Chemical formula	$C_{24}H_{28}N_3Cl$	$C_{28}H_{31}N_2O_3Cl$
Maximum wavelength (nm)	586	526
Molecular structure		

i.e. least squares support vector machine (LS-SVM) [17], multiple linear regression (MLR) [18], and artificial neural network (ANN) [16,19].

Therefore the objectives of the present study were as follow. (1) Synthesis of Fe_3O_4 nanoparticles impregnated onto walnut shell (Fe_3O_4-WNS) by the co-precipitation method and their characterization using various techniques namely FT-IR spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD). (2) Evaluation of the applicability of Fe_3O_4-WNS for the adsorption of two textile dyes from different classes (methyl violet (MV) and Rhodamine 6G (Rh 6G)), and studying the effects of different experimental variables such as the initial pH, dye concentration, temperature, ionic strength, and contact time in a batch mode on the removal efficiency of the cited dyes. (3) Assessment of the feasibility of the linear and non-linear models (MLR, RF, and ANN) for prediction of the removal efficiency of the MV and Rh 6G dyes using Fe_3O_4-WNS at different experimental conditions. (4) Investigation of the isotherms and kinetics of the adsorption process involved. (5) Evaluation of the reusability of Fe_3O_4-WNS.

2. Material and methods

2.1. Chemicals, apparatus, and software

WNS was separated by hand from walnut fruit, purchased from a supermarket in Shahrood (Iran), and was used as the adsorbent. The cationic dyes MV and Rh 6G, whose characteristics are listed in Table 1, were purchased from Merck to investigate the adsorption behavior of the prepared adsorbent. The stock solution of each dye (0.4 g L^{-1}) was prepared by dissolving 0.1000 g of the dye in distilled water and dilution to the mark in a 250-mL volumetric flask. The working solutions were prepared by diluting a known volume of the stock solution. Hydrochloric acid and sodium hydroxide, purchased from Merck, were used for adjustment of the solution pH using a Metrohm 744 pH-meter with a calomel combined electrode. All the other chemicals used for the synthesis of Fe_3O_4 were of analytical grade, and were used without further purification.

Absorption of the cited dyes at their maximum wavelengths was recorded on a Rayleigh UV-2601 spectrophotometer using a pair quartz cell of 1 cm path length. The nature of the functional groups was specified using a Fourier transform-infrared (FT-IR) spectrophotometer (WQF-520) in the scanning range of 4000–400 cm^{-1}. The XRD patterns for Fe_3O_4-WNS were taken on a Siemens D5000 diffractometer (Germany). The random forest (RF) and feed-forward ANN programs were written in the MATLAB software using the corresponding toolbox, and were run on a personal computer (PC). Also the MLR model was constructed using the SPSS 20 statistical software.

2.2. Preparation of Fe_3O_4-WNS and its characterization

Fe_3O_4-WNS was prepared by the in situ co-precipitation of Fe^{3+} and Fe^{2+} ions with a molar ratio of 2:1 in the presence of a base [20]. According to this method, 4.24 g of $FeCl_3 \cdot 6H_2O$ and 2.16 g of $FeSO_4 \cdot 7H_2O$ were dissolved under nitrogen atmosphere in 100 mL of distilled water with mechanical stirring to obtain a homogeneous solution. Afterwards the solution was heated to 80 °C, and ammonium hydroxide (25%) was added drop wise in 30 min to adjust the solution pH to 11. Then 10 g of powdered WNS was added to the suspension, and the reaction was continued for a further 30 min under vigorous stirring. The final magnetic composite was separated using an external permanent magnet, and frequently washed with doubly distilled water for neutralization. The oven-dried adsorbent was then stored for further use.

The FT-IR spectra for pure WNS, Fe_3O_4, and Fe_3O_4-WNS were shown Fig. 1. The broad band at around 3390 cm^{-1} (Fig. 1a) is related to the O—H stretching vibration of the hydroxyl groups present in cellulose [20–22]. The peak observed in the region of 2889–2920 cm^{-1} is characteristics of the C—H bond stretching vibrations in the methyl and methylene groups [21,23]. The peak around 1655 cm^{-1} is indicative of the presence of COO [20,23,24]. The peak around 1454 cm^{-1} is referred to

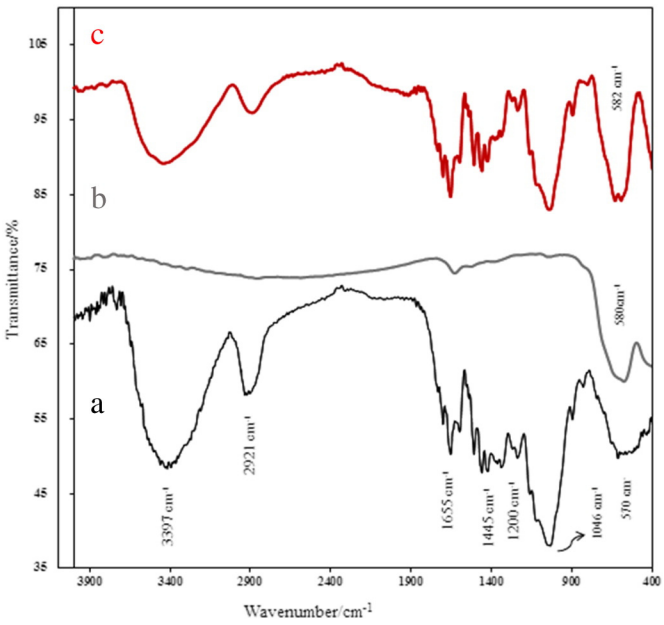


Fig. 1. FT-IR spectra for (a): WNS, (b): Fe_3O_4 NP, and (c): Fe_3O_4-WNS.