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Original Research Paper

Removal of methyl orange by multiwall carbon nanotube accelerated by ultrasound devise: Optimized experimental design

M. Ghaedi [a,*], S. Hajati [b], M. Zaree [a], Y. Shajaripour [a], A. Asfaram [a], M.K. Purkait [c]

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

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ABSTRACT

This study investigates the methyl orange (MO) removal from aqueous solution through the application of ultrasound onto multiwalled carbon nanotubes (MWCNTs). Characterization of MWCNT was carried out using scanning electron microscopy (SEM) and tunneling electron microscopy (TEM). The influences of various parameters on the removal percentage were studied and optimized by a central composite design (CCD) and response surface methodology (RSM). Results indicate that a small amount of proposed adsorbent (0.025 g) is responsible for successful removal of 15 mg L^{-1} of MO (RE > 99%) in a short time (3.4 min) and pH of 1–2. Adsorption kinetic data are fitted well with pseudo second order model. Equilibrium data followed Langmuir isotherm model with maximum adsorption capacity of 53.76 mg g^{-1}.

1. Introduction

Dyes with adverse effects on human body [1] applied in textile, dyeing, printing, and related industries led to large amounts of dye-containing wastewater and their subsequent discharge into environment associated with generation of hazards for human health [2,3]. Methyl orange (MO, a water-soluble azo dye in addition to above activities widely used in research laboratories as an acid base indicator [4]. This dye is entering the body through ingestion metabolizes into aromatic amines by intestinal micro-organisms. Liver reductive enzymes catalyze the reductive cleavage of the azo linkage to produce aromatic amines and generation of cancer [5,6]. Therefore, the MO removal before discharging to environment is necessary and accomplished via photocatalytic degradation [7], advanced oxidation [8], electrochemical oxidation [9], ultrafiltration [10] and adsorption [11–13]. Adsorption process due to remarks viz. simplicity in operation, high adsorption capacity is good applicable approaches for dye removal from various systems [14–16]. Application of MWCNT cause achievement of high adsorption capacity and fast removal using small amount of adsorbent in short time [17,18]. Ultrasound irradiation accelerate the rate of chemical process by formation of acoustic cavitations that facilitate mass transfer following propagation of pressure wave through liquid [19,20]. The ultrasound radiation led to increase in rate of mass transfer through migration and diffusion [21,22]. Optimization based experimental design help the researchers to ascertain interactions among the operating variables for the simultaneous optimization and investigation of the effects of variables with least number of experiments [23,24].

From the above literatures it is envisaged that the use of multiwall carbon nanotube as an adsorbent for the removal of Methyl orange dye has not been investigated. Present work explored the possibility of MWCNT application as an adsorbent for MO removal from aqueous medium. The adsorption performance was enhanced by applying sonication. Influence of important variables (pH, amount of adsorbent, initial MO concentration and contact time) were investigated and optimized by central composite design (CCD) combined with response surface methodology (RSM). The proposed technique might be of useful and cost effectives for quantitative adsorption of MO as effective adsorbent.

2. Experimental

2.1. Instruments and reagents

The methyl orange (Fig. 1) dye concentration was determined using Jusco UV–visible spectrophotometer model V-530 (Jasco, Japan) at a wavelength of 473 nm while the pH/ion meter

* Corresponding author. Tel./fax: +98 741 2223048.
E-mail addresses: m_ghaedi@yu.ac.ir, m_ghaedi@mail.yu.ac.ir, m_ghaedi@yahoo.com (M. Ghaedi).

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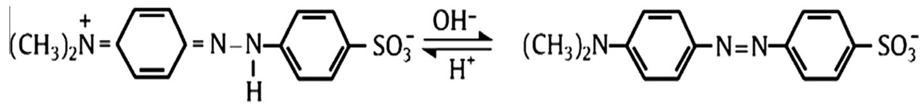

Fig. 1. Chemical structure of MO.

(Metrohm, model-686, Switzerland, Swiss) was used for the measurement of pH of solution. The morphology of the multiwalled carbon nanotube (MWCNT) was observed by scanning electron microscopy (SEM; Hitachi S-4160, Tokyo, Japan) under an acceleration voltage of 15 kV. The morphology and the size distribution of the MWCNTs were determined by a Hitachi H-800 TEM (Hitachi, Japan) at an operating voltage of 200 kV. An ultrasonic bath with heating system (Techno-GAZ SPA Ultra Sonic System, Bologna, Italy) at frequency 40 kHz and power 130 W was used for the ultrasound-assisted adsorption procedure. All chemicals including NaOH, HCl, KCl and methyl orange (MO) with the highest purity available were purchased from Merck (Dermasdat, Germany). The stock MO solution was prepared by dissolving appropriate amount of solid dye in double distilled water and the desired concentrations of test solutions were prepared by diluting the stock solution. 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 10–90°. Fourier transform infrared spectroscopy (FTIR in the range of 400–4000 cm^{-1}) of the adsorbent was recorded using FTIR spectrophotometer (Model: FT-IR JASCO 460 Plus). The spectra obtained were analyzed.

2.2. Ultrasound assisted adsorption method

The MO removal experiments were performed under ultrasound using MWCNT as adsorbent. The sonochemical adsorption experiment was carried out in batch mode as follows: specified amounts of MO dye solution at known concentration (15 mg L^{-1}) and initial pH of 1 with a known amount of adsorbent (0.025 g) were poured into the flask and maintained the desired sonication time (3.4 min). At the end of the adsorption experiments, the sample was immediately centrifuged and analyzed. Details of experimental procedure and calculation are reported in our earlier work [3].

2.3. Multiwalled carbon nanotubes

Multiwalled carbon nanotubes (MWCNT) were purchased from Merck. The purity of the as-received MWCNTs material was >95% and its outside and inside diameters were 10–20 nm and 5–10 nm, respectively. The length of these MWCNT was 10–30 μm. These specification details were given by the manufacturer. The surface area (BET) of MWCNT was measured around 200 $m^2\,g^{-1}$.

2.4. Central composite design (CCD)

The CCD was used to investigate the significance of the effects of parameters including pH, amount of adsorbent, initial MO concentration and contact time. A five-level CCD was performed to evaluate the variables influence (sole and interaction) on removal percentage (Table 1) that leads to 31 runs for the optimization process. Table 2 shows the experimental design points consists of 2^n factorial points with $2n$ axial points ($\alpha = 2$ distance from center), Nc central points (to estimate experimental error and the reproducibility of the data) and the test results for the response variables. The mathematical relationship between the four independent variables was approximated by the second order polynomial model [25,26].

Table 1
Experimental factors and levels in the central composite design.

Factors	Levels			Star point $\alpha = 2$	
	Low (−1)	Central (0)	High (+1)	$-\alpha$	$+\alpha$
(X_1) pH	2.5	4.0	5.5	1.1	7.0
(X_2) Adsorbent dosage (g)	0.015	0.025	0.035	0.005	0.045
(X_3) MO concentration (mg L^{-1})	10	15	20	5	25
(X_4) Contact time (min)	2.0	35	5.0	0.5	6.5

Table 2
Data statistics of model variables.

Runs	X_1	X_2	X_3	X_4	Removal (%)
29	4.0	0.025	15	3.5	73.39
13	2.5	0.015	20	5.0	77.19
24	4.0	0.025	15	6.5	69.10
6	5.5	0.015	20	2.0	63.26
16	5.5	0.035	20	5.0	70.27
19	4.0	0.005	15	3.5	40.73
12	5.5	0.035	10	5.0	64.86
26	4.0	0.025	15	3.5	83.02
14	5.5	0.015	20	5.0	59.10
4	5.5	0.035	10	2.0	65.75
20	4.0	0.045	15	3.5	85.99
8	5.5	0.035	20	2.0	80.79
30	4.0	0.025	15	3.5	82.73
15	2.5	0.035	20	5.0	91.18
2	5.5	0.015	10	2.0	69.86
3	2.5	0.035	10	2.0	98.13
31	4.0	0.025	15	3.5	76.85
22	4.0	0.025	25	3.5	73.12
10	5.5	0.015	10	5.0	67.12
5	2.5	0.015	20	2.0	60.29
28	4.0	0.025	15	3.5	76.78
9	2.5	0.015	10	5.0	97.24
27	4.0	0.025	15	3.5	79.46
21	4.0	0.025	5	3.5	82.17
18	7.0	0.025	15	3.5	64.60
1	2.5	0.015	10	2.0	87.50
11	2.5	0.035	10	5.0	99.17
25	4.0	0.025	15	3.5	75.89
7	2.5	0.035	20	2.0	88.24
23	4.0	0.025	15	0.5	66.96
17	1.0	0.025	15	3.5	91.75

Response surface methodology (RSM) allows the determination and evaluation of the relative significance of parameters on the process. The modeling was performed to estimate first or second order polynomials equations following analysis of variances (ANOVA). Results were plotted in tridimensional graph and allow surface response corresponds to a response function that always used for prediction of real optimum points.

3. Results and discussion

3.1. Characterization of MWCNTs

The Field Emission Scanning Electron Microscopy (FESEM) image of the MWCNTs is shown in Fig. 2(a). It can be seen that