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Microwave-assisted hydrothermal synthesis and adsorption properties of carbon nanofibers for methamphetamine removal from aqueous solution using a response surface methodology

Q1 Vinod Kumar Gupta[a,*], Shilpi Agarwal[a], Inderjeet Tyagi[b], Maryam Sohrabi[c], Ali Fakhri[d,*], Sahar Rashidi[e], Nima Sadeghi[f]

[a] Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa
[b] Department of Chemistry, Indian Institute of Technology Roorkee, 247667, India
[c] Department of Chemistry, Shahr-e-Qods Branch, Islamic Azad University, Tehran, Iran
[d] Young Researchers and Elites Club, Science and Research Branch, Islamic Azad University, Tehran, Iran
[e] Department of Chemical Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran
[f] Department of Environmental Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

Carbon nanofibers have been synthesized by simple facile microwave-assisted hydrothermal route and applied as adsorbent for the fast adsorption of methamphetamine. The topological property of CNF was analyzed using XRD, SEM, TEM, and nitrogen adsorption–desorption instrumental techniques. The significance of the independent variables and their interactions were tested by the analysis of variance (ANOVA) and *t*-test statistics. Influential parameters are optimized using BBD implemented with RSM, and the optimized value of pH, adsorbent dose and temperature was found to be 8.0, 0.1 g and 298 K, respectively. Under optimal conditions, the removal efficiency of methamphetamine was found to be 55.25 mg/g.

Introduction

Methamphetamine is controlled drug and routinely dispensed from pharmacies and hospitals. However, it used for curing various medical disorders in addition to this it sometimes often ill-treated [1–3]. In past few years, the occurrence and rapid distribution of pharmaceutical and personal care products (PCPs) including controlled drugs have gained much attention due to their potential risk to the aquatic ecosystem and food chain particularly through bioaccumulation and bio magnification [4,5]. These controlled substances enter the natural waterways through various subways including human metabolic wastes and pharmaceutical companies waste effluents in to nearby aquatic sources. This waste disposal in to the aquatic ecosystem causes irreversible damage to the aquatic flora and fauna.

Methamphetamine (MA) is an addictive stimulant drug that strongly activates certain neurological activities in the brain. Methamphetamine is chemically closely related to amphetamine, but the effect of methamphetamine on central nervous system is greater than that of amphetamine. The ill effects of the methamphetamine include several short term and long term health hazards, excessive dose of this noxious methamphetamine results in increased wakefulness and physical activity, decreased appetite, tachycardia, irregular heartbeat, insomnia, paranoia, hallucinations, intense itching leading to skin sores, premature delivery, separation of placenta from the uterus, lethargy, hepatitis and other infectious diseases. The molecular structure along with the basic physicochemical characteristics of MA drug is listed in Table 1.

Several traditional techniques like coagulation, ion selective electrodes, biosorption, photo degradation, electrochemical oxidation, ozonation, reverse osmosis and adsorption are reported for the removal of hazardous impurities. But among them adsorption was envisioned to be a favorable approach to remove trace

Q2 * Corresponding authors.
E-mail addresses: vinodg@uj.ac.za, vinodfcy@gmail.com, vinodfcy@hotmail.com, vinodfcy@iitr.ac.in (V.K. Gupta), shilpi.agarwal2307@gmail.com (S. Agarwal), indertyagi011@gmail.com (I. Tyagi), msohrabi734@gmail.com (M. Sohrabi), ali.fakhri88@yahoo.com (A. Fakhri), srashidi05@gmail.com (S. Rashidi).

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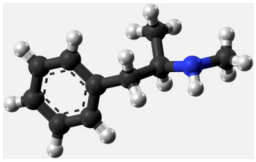
Table 1
Physicochemical properties of MA. Q7

	Molecular weight ($g\,mol^{-1}$)	Molecular formula	Chemical structure
Methamphetamine	149.24	$C_{10}H_{15}N$	

pollutants from aqueous solution by virtue of low energy cost, environmental friendliness and ease of operation [6–8].

Response surface modelling (RSM) is an empirical statistical technique that uses quantitative data obtained from appropriately designed experiments to determine regression model and operating conditions [9–33].

Carbon nanofibers (CNFs) represent a new form of carbon adsorbents, which are microporous materials in the form of woven fabrics with large specific surface area and narrow pore size distribution. Since the adsorption energy could be enhanced by low-size pores [34], CNFs are considered as a promising material for highly efficient adsorption [35,36]. Furthermore, the exposure of micropores on the large surface could potentially benefit and help in increasing the adsorption rate [37]. CNFs have been used for toluene and activated dyes adsorption [38,39].

In the present work, the rapid adsorption of drug methamphetamine with the help of CNFs is well evaluated and studied. The investigation and optimization of combined effect of various process parameters like adsorbent dose, temperature and pH of the solution on removal of MA from aqueous medium by CNFs were carried out using Box–Behnken model experimental design incorporated with Response Surface Methodology (RSM) through Design Expert Version 6.0.10 (Stat Ease, USA).

Experimental

Material

In this study, raw materials and reagents like ethoxy ethyl, ($C_2H_5OC_2H_5$), zinc (Zn), iron (Fe) powder, and HCl were purchased from Sigma–Aldrich Ltd. The structure of CNFs particle was characterized by nitrogen adsorption–desorption isotherm (77.4 K using Micro meritics ASAP2010) and X-ray diffractometer (XRD) Philips X'Pert.

Preparation of carbon nanofibers

In a typical synthesis process of CNFs, $C_2H_5OC_2H_5$ (7.5 mL) and a mixture of 1.00 g Zn and 0.500 g Fe powder were performed by the microwave-assisted hydrothermal system. The apparatus is equipped with a series of stirred and hermetically sealed Teflon reaction vessels and a microwave heating system. Pressurized reactions were performed for 2 h autogenously and reached at 400 °C. The oven power source was fixed at 400 W. After the hydrothermal reaction, samples were washed with diluted HCl solution and dried in vacuum at 150 °C for 1 h.

Characterization and analyses

The surface topology and anatomy of CNFs were characterized with the aid of scanning electron microscope (SEM; JEOL JSM-5600) and transmission electron microscopy (TEM; JEM-2100F HR, 200 kV). The structure of CNFs particle was characterized by nitrogen adsorption–desorption isotherm (77.4 K using Micro meritics ASAP2010) and X-ray diffractometer (XRD) Philips X'Pert.

Adsorption experiment

The adsorption of MA onto CNFs was investigated using batch experiments. In these studies 1000 mg/L stock solution was prepared by dissolving 1 g of MA in 1000 mL distilled water. Different concentrations (30, 60 and 90 mg/L) of MA solutions were prepared by this stock solution. Solutions were evacuated to flasks of 100 mL. Then adsorbent in the range of dosage 0.02–0.1 g was added and placed in the water bath shaker after pH adjustments made in the range of 2–12. The suspensions were shaken at 2000 rpm for 5 min at room temperature. Samples from shaker were filtered with filter paper, and then remaining MA levels were measured using the aid of a two dimensional Gas Chromatography (GC × GC). The equilibrium adsorption capacity was calculated from the relationship Q3

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

where q_e (mg/g) is the equilibrium adsorption capacity, C_e is the MA concentration at equilibrium (mg/L), V is the volume of solution (L) and w is the weight of adsorbent (g).

Optimization of adsorption process using Response Surface Methodology

Optimum condition for the adsorption of MA by CNFs was determined by means of Box–Behnken design (BBD) incorporated with response surface methodology (RSM). The RSM consists of a group of empirical techniques devoted to the evaluation of relationship existing between a cluster of controlled experimental factors and measured responses according to one or more selected criteria. Optimization studies were carried out on studying the effect of three variables including adsorbent dose, temperature and pH of the solution [40]. The chosen independent variables used in this study were coded according to Eq. (2):

$$x_i = \frac{X_i - X_0}{\Delta X} \quad (2)$$

where x_i is the dimensionless coded value of the ith independent variable, X_0 is the value of X_i at the center point and ΔX is the step change value. The behavior of system is explained by the following empirical second-order polynomial model Eq. (3):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1 \le i \le j}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where Y is the predicted response, x_i, x_j, . . . , x_k are the input variables, which affect the response Y, x^2_i, x^2_j, . . . , x^2_k are the square effects, x_ix_j, x_ix_k and x_jx_k are the interaction effects, β_0 is the intercept term, β_i ($i = 1, 2, \ldots, k$) is the linear effect, β_{ii} ($i = 1, 2, \ldots, k$) is the squared effect, β_{ij} ($i = 1, 2, \ldots, k$; $j = 1, 2, \ldots, k$) is the

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