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Synthesis of MnO_2/cellulose fiber nanocomposites for rapid adsorption of insecticide compound and optimization by response surface methodology

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ABSTRACT

The MnO_2/Cellulose fiber Nanocomposites have been prepared via the microwave-assisted hydrothermal method. The characteristic structure of MnO_2/Cellulose fiber Nanocomposites was analyzed using X-ray diffraction, photoluminescence and UV–vis spectra, Transmission electron Microscopy, N_2 adsorption-desorption and Scanning electron microscopy instrumental techniques. BET surface area and crystallite size values of MnO_2/cellulose fiber nanocomposites have been found as 87.064 m^2/g and 70.0 nm, respectively. Response Surface Methodology (RSM) has been used for adsorption of Insecticide compound such as Toxaphene by prepared adsorbent. MnO_2/Cellulose fiber Nanocomposites shows maximum removal of 96.5% at initial Toxaphene concentration of 5.0 mg/L, pH 3 and adsorbent dose of 5.0 g/L. Kinetic and equilibrium data follow pseudo-second order and Langmuir isotherm model, respectively. Adsorption capacity of MnO_2/Cellulose fiber Nanocomposites has been found to be 5.465 mg/g.

1. Introduction

Toxaphene is a major nonsystemic insecticide that is applied on cereal grains, cotton, fruits, and vegetables. Also, Toxaphene has been used to control ticks and mites in livestock. Toxaphene has hazard health influences in humans. Food, drinking water, and breathing contaminated air are main sources of Toxaphene exposure. Toxaphene can cause damage to several body members, may even cause death probably. It has a potential carcinogen in humans [1]. At present, the techniques used for its removal may be broadly divided into four categories: i.e., membrane-separation, ion exchange, precipitation-coagulation and adsorption [2–5]. Adsorption process is economically effective and ultimate fate of many contaminants in aquatic environment [6]. Adsorption is basically a mass transfer driven process and the adsorbate is adsorbed on the surface of adsorbent due to affinity of the adsorbent surface for a particular substance. Nowadays, most of the studies are made to synthesize the high efficiency adsorbents, for the removal of pollutants [7]. Nanostructured materials with high specific surface area and active sites, have been in the center of attention as an emerging water treatment methods [8]. Cellulosic fibers materials have traditionally been used in different technology. Cellulose used as hydrophilic materials to fabricate nanocomposites has been reported in several studies due to its natural characteristics and properties [9–11]. Cellulose is considered as a unique biopolymer which holds significance properties such as bio-compatibility and degradability, thermal-chemical stability. The cellulose functionalized can present many active sites to bonding and growth of metal oxides nanoparticles, which could make the nanomaterials with high specific-surface area and excellent properties in different technology. The conventional technique to optimize multivariable systems requires a lot of experiments to determine the optimum level which is a time consuming process [12–14]. Such problems can be diminished by changing a number of variables at a time. This is possible by designing experiments statistically using statistical techniques such as Response Surface Methodology (RSM) [15–17]. Therefore, in the present work, we have synthesized MnO_2/Cellulose fiber (MnO_2/CF) nanocomposites and characterized by using several instrumental techniques. The application of

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MnO_2/Cellulose fiber (MnO_2/CF) nanocomposites was investigated by through the removal of Insecticide from aqueous solution.

2. Materials and methods

2.1. Materials

All the chemicals were obtained from Sigma-Aldrich Ltd, USA. Cellulose fibers (UF 500) (Tensile strength >750 MPa) with diameter of 10–30 μm were purchased from Beijing Ronel Engineering Materials Co. Ltd., and washed with distilled water before use.

2.2. Synthesis of MnO_2/cellulose fiber nanocomposite

A facile microwave-assisted hydrolysis method was used to synthesize the MnO_2/CF composites. Initially, 1.0 g of cellulose fibers was added to a mixture of distilled water (150.0 mL) and HNO_3 (1.0 mL) in a round bottom flask under constant stirring. The flask was placed into the microwave oven (650 W, 2.45 GHz) for further hydrothermal treatment. The suspension was put into the microwave oven for 30 min. Then 0.6 mL of $MnCl_2{\cdot}4H_2O$ and 0.1 g PVP were dissolved and $KMnO_4$ solution (0.2 M) was added to the flask, and microwave irradiation was applied again for 30 min. So, the MnO_2/CF nanocomposite formed were collected and processed by filtering, thorough washing with distilled water and drying at 50 °C under vacuum for 12 h.

2.3. Characterization instruments

The morphology of the adsorbent was investigated by using A field emission scanning electron microscopy (SEM-Hitachi SU8000) and X-ray diffractometer (XRD) Philips X'Pert. The particle size was measured using Transmission Electron Microscope (TEM) (Zeiss EM-900). The surface area was analyzed by nitrogen adsorption instrument in an ASAP2020 surface area. Zeta potential measurements of the dilute dispersions (0.1 mg mL^{-1}) of the various the nanocomposites were performed with a Brookhaven NanoBrook Omni Instrument at 25 °C.

2.4. Toxaphene removal study using MnO_2/CF nanocomposite

2.4.1. Kinetic study

Toxaphene solutions of desired initial concentration were prepared by diluting stock solution using requisite amount of water. Several influences such as initial concentration of Toxaphene, dose of adsorbent, pH, and temperature generally affect the kinetics of adsorption process [17] and the success of adsorption process depends on the proper selection of key parameters and their ranges. Therefore, in the present study, pH of solution was considered as key parameter and before going to elaborate kinetic study, optimum pH of Toxaphene removal was ascertained. Furthermore, to compare the adsorption capability of MnO_2/CF nanocomposite, definite amount of both of these adsorbents (0.3 g) were contacted with simulated Toxaphene solution of 10 mg/L at different pH condition. pH of solution was maintained by adding 0.1 N HCl or 0.1 N NaOH and varied in the range of 1–9. Volume of solution was 50 mL. The samples were collected after 45 min of operation. The solution containing spent MnO_2/CF nanocomposite were centrifuged and collected for tested residual toxaphene concentration in solution using 2D Gas Chromatography (Kimia Shangarf Pars Research CO., Iran). The column set used a first column 30m × 0.25 mm i:d: × 0.25 μm film thickness 5% phenyl-methyl siloxane phase serially coupled to a second column 1m × 0.1 mm i:d: × 0.1 μm film thickness 50% phenyl equivalent phase. Both columns which were temperature programmed from 70 to 320 °C. The injector temperature was 250 °C (injection volume of 1 mL) was employed in the split less mode. Helium was used as the carrier gas (2 mL/min). Maximum removal was obtained at pH 3. Therefore, kinetic study was carried out at pH 3. The operating parameters varied during kinetic studies include adsorbent dose (2–6 g/L).

2.4.2. Equilibrium study

The adsorbate has been distributed between the solid phases and liquid during adsorption reaction and attains maximum value on solid phase at equilibrium condition and the adsorbate concentration in solution becomes constant at such condition. In the present investigation, equilibrium study was done by varying initial toxaphene concentrations (2.0–22.0 mg/L) keeping other variables such as adsorbent dose, volume of solution, pH and temperature constant at of 4 g/L, 50 mL, 3 and 25 °C, respectively. Samples were collected after 45 min and analyzed for residual toxaphene concentration. In next set of experiments, temperature was varied from 25 to 35 °C, keeping other variables constant.

2.4.3. Optimization of removal of toxaphene using RSM

RSM was also used to distinguishe the optimum condition for removal of toxaphene. The (−1) and (+1) values of three input factors namely initial concentration of toxaphene, pH and adsorbent dose were 2.0 and 20.0 mg/L, 2 and 9, and 1 and 6 g/L, respectively. The percentage removal of toxaphene was considered as response. Since equilibrium was attained after only 25 min operation as seen from kinetic and equilibrium studies, 'time' has not been considered as input factor during optimization of such process.

3. Results and discussion

3.1. Characterization of the MnO_2/cellulose fiber nanocomposites

Fig. 1 represents the SEM images of cellulose fiber and MnO_2/CF nanocomposites. As can be seen, nanocomposites look like heterogeneous lamellar form. The surfaces of material have been obtained to be rough with many small pores. EDX study of MnO_2/CF nanocomposites has been shown in Fig. 1B. MnO_2/CF nanocomposites contains carbon (C), oxygen (O), and manganese (Mn). BET surface area of MnO_2/cellulose fiber nanocomposites has been found as 87.064 m^2/g. Fig. 2A image indicated MnO_2 particles anchored onto the pores of cellulose fiber to form raspberry-like structure. The MnO_2 particle coverage demonstrates strong contact with the cellulose fiber. The average size of the MnO_2/cellulose fiber nanocomposites is about 72.5 nm (Fig. 2B). Fig. 3 represents the XRD patterns of cellulose fiber and MnO_2/CF nanocomposites prepared. The diffraction peak at $2\theta = 22.9^\circ$ is ascribed to the plane of cellulose fiber, and the characteristic diffraction peaks at other angles correspond to the (310), (211) and (301) crystal planes of polymorph phase of manganese. The crystallite size from the Scherrer equation [18] is distinguished to be 70.0 nm for MnO_2/CF nanocomposites. Fig. 4a indicates UV–vis spectra of surface modified cellulose materials. The MnO_2/CF nanocomposites have one absorption band at 316 nm, attributed the absorption of MnO_2 nanoscale. In addition, the absorption band of MnO_2/CF nanocomposites demonstrated new absorption band at 525 nm that due to the surface plasmon resonance (SPR) absorption of the MnO_2 on nanofibers. Fig. 4b indicates a photoluminescence spectrum for MnO_2/CF nanocomposites. Blue luminescence is associated with the excitonic emission (465 nm). In the green emission, a sharp band at 509 nm was detected. This behavior is favored by the synthesis of the MnO_2 nanoparticles under the condition of excess of atoms of the metal that enter in the lattice. Finally, the red band of PL is typically observed at 530 nm which contain a certain concentration of intrinsic defects of the manganese and oxygen vacancies.