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ORIGINAL ARTICLE

Removal of permethrin pesticide from water by chitosan–zinc oxide nanoparticles composite as an adsorbent

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Abstract Synthesis of chitosan–ZnO nanoparticles (CS–ZnONPs) composite beads was performed by a polymer-based method. The resulting bionanocomposite was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) spectroscopy and infrared spectroscopy (FT-IR). Adsorption applications for removal of pesticide pollutants were conducted. The optimum conditions, including adsorbent dose, agitating time, initial concentration of pesticide and pH on the adsorption of pesticide by chitosan loaded with zinc oxide nanoparticles beads were investigated. Results showed that 0.5 g of the bionanocomposite, in room temperature and pH 7, could remove 99% of the pesticide from permethrin solution (25 ml, 0.1 mg L^{-1}), using UV spectrophotometer at 272 nm. Then, the application of the adsorbent for pesticide removal was studied in the on-line column. The column was regenerated with NaOH solution (0.1 M) completely, and then reused for adsorption application. The CS–ZnONPs composite beads appear to be the new promising material in water treatment application with 56% regeneration after 3 cycles.

1. Introduction

Nowadays, existing commercial sorbents including, activated carbon, zeolites, activated alumina, and silica gels play important roles in adsorptive separation and purification. However, innovative technological developments are needed in the new economy and under the stringent environmental regulations. Despite of very promising features of the newly developed nanostructured sorbent materials, basically exploring and

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systematic investigations are needed on both synthesis methods and adsorption characteristic studies [1].

Chitosan, poly[β-(1→4)-2-amino-2-deoxy-D-glucopyranose], is a natural cationic, cellulose biopolymer of high molecular weight obtained commercially from deacetylation of chitin by thermochemical reaction. As a natural polymer, it is in abundance and has many qualities such as non-toxicity, non-allergenic, biodegradability, biocompatibility, inexpensiveness and hydrophilicity, with ability of the biological activity and fiber and film formation [2–8].

Chitosan contains high units of two functional groups, hydroxyl (—OH) and amino (—NH_2), which are responsible for the reactivity of this polymer as an excellent natural adsorbent and give chitosan its powerful adsorptive capacity [9–11]. Due to the highly reactive amino groups and carboxyl groups, chitosan has been regarded as a useful material for various purposes such as treatment of wastewater, ion-exchanger and functional matrixes [2]. Because of its multi-functionality, in the field of water and wastewater treatment applications, chitosan has been used as an absorbent as well as primary coagulant or flocculent [12–14].

The goal of nanotechnology is to make nanostructures or nanoarrays with special properties, which do not exist in their bulk or single particle types. Oxide nanoparticles can present unique physical and chemical properties, because of their limited size and a high density in their corner or edge surface sites [15,16].

In recent years, chitosan based metal particles composites have been studied increasingly as an alternative adsorbent in water treatment, such as using metals [17], metal oxides [18], and bimetals [19]. Saifuddin et al. [20] have embedded silver nanoparticles in chitosan by using microwave irradiation for the removal of pesticides from water. The main goal of our last study was to develop an adsorbent with chitosan–silver oxide nanoparticles composite. It was demonstrated that the AgO nanoparticles-chitosan beads could be used for the adsorption of permethrin as the model pesticide [21].

In this paper, the application of chitosan beads modified with ZnO nanoparticles to remove Permethrin (Fig. 1), (3-phenoxyphenyl)-methyl(+)cistrans-3-(2,2-dicloroethenyl)-2,2-dimethylcyclopropanecarboxylate, a neurotoxin widely used in agriculture [22], has been proposed. The main goal of this study is to develop an on-line filter, by using a column of CS–ZnONPs beads and also its application in pesticide adsorption in 3 cycles.

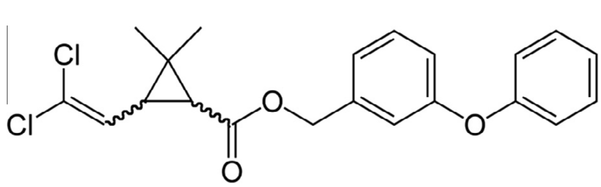

Figure 1 Structure of permethrin.

2. Experimental

2.1. Chemicals and reagents

Chitosan with medium molecular weight was purchased from Sigma Chemical Company. Zinc Oxide was purchased from Merck. Permethrin (25%, Moshkam Fars) was used in order to prepare the stock solution of pesticide. Other chemicals were chemical grade from Merck.

2.2. Preparation of CS–ZnONPs composite

Typically, 0.75 g of ZnO powder was dissolved in 100 ml of 1% acetic acid by adding 10 ml of 65% Nitric acid. Then, 1 g of chitosan was added to this solution. After that, sonication process was performed for 30 min. This step was followed by adding drop by drop NaOH solution until the pH reached about 10. The solution was kept in water bath at 60 °C for about 3 h. The mixture was filtered and washed with deionized water a few times; then it was dried in an oven at 50 °C for 1 h. The preparation procedure employed has been reported elsewhere with some modification [23].

2.3. Dissolution and swelling study

A solubility study was performed on both the chitosan and CS–ZnONPs beads. The beads were tested with regard to their solubility in each of 5% (v/v) acetic acid, distilled water and 0.1 M NaOH solution. A value of 1.0 g of each of the beads, using analytical balance, was weighted accurately. The samples were kept in each solution for about 24 h at room temperature under stirring using mechanical stirrer (100 rpm). After that, the mixture was filtered, washed with distilled water and dried for 24 h at room temperature. Then, the dried samples were weighted using the analytical balance.

The swelling study of chitosan and CS–ZnONPs beads was carried out in distilled water at room temperature for about 24 h. Then, the swollen beads were removed from water, dried and weighed as soon as possible. The swelling percent ($S\%$) of beads was calculated from the following equation [20]:

$$S(\%) = \frac{W_s - W}{W} \times 100\% \quad (1)$$

where, Ws and W represent the weight (g) of swollen beads and dry beads, respectively.

2.4. Characterization methods

Fourier transform infrared spectroscopy (FT-IR) of nanocomposite samples was recorded on a Thermo Nicolet FTIR spectrometer (America) using KBr powder. Surface morphology was studied by scanning electron microscope (EM3200, KYKY) at a voltage of 25.0 kV. The surfaces of sample were gold coated before the analysis. The crystallinity of nanocomposite in powder form was studied by the X-ray diffraction method (*STOE Stadi P*), using Cu Kα radiation generated at 40 kV and 30 mA in the region of 2θ from 10 to 90.

2.5. Adsorption experiments

To obtain a preliminary assessment of the performance of the sorbent materials, batch experiments were carried out by using a mechanical shaker at a speed of 150 rpm and 25 °C for 45 min with specified amount of adsorbents (the dosage varied from 0.01 to 1.5 g) in contact with 25 ml of synthetically prepared Permethrin solution (0.1 ppm). The pH of the adsorbate solution was adjusted to around 7 at the beginning of the