Removal of tartrazine from aqueous solution by carbon nanotubes decorated with silver nanoparticles

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A B S T R A C T

Multi-walled carbon nanotubes (CNTs) were decorated with silver nanoparticles, characterised, and used for the removal of anionic tartrazine dye from aqueous solution. Adsorption experiments were carried out as batch studies at different contact times, pH and initial dye concentrations. The dye adsorption equilibrium was rapidly attained after 60 min of contact time. Removal of the dye from acidic solutions was better than from basic ones. The equilibrium data were analysed by the Langmuir and Freundlich models, which revealed that the Langmuir model was more suitable to describe the azo dye adsorption than the Freundlich one. Kinetics of the adsorption processes was studied using pseudo-first and second-order models and the intra-particle diffusion model. It was found that the kinetics followed a pseudo-second-order equation. The adsorption capacities of carbon nanotubes modified with silver nanoparticles decrease in the following order: 5 Ag/CNTs (84.04 mg/g) > 3 Ag/CNTs (72.33 mg/g) > 1 Ag/CNTs (62.07 mg/g) > CNTs (52.24 mg/g).

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1. Introduction

Dye-containing wastewater discharged from factories producing paper, plastic, textiles, food and cosmetics is a major source of environmental pollution [1–5]. The residual coloured compounds in the wastewater are hazardous to fish and other organisms, they also restrain photosynthesis by absorbing sunshine which adversely affects the natural aquatic systems. Organic dyes are usually difficult to degrade because of their high molecular weight and complex structure. Different technologies for their removal have been proposed, including adsorption [1–5], coagulation and flocculation [6], oxidation [7,8] and membrane separation [9]. Among these techniques, adsorption has been considered an attractive process, because of its many advantages such as high flexibility, simplicity of design, ease of operation, insensitivity to toxic pollutants and small amounts of harmful substances [5,10,11].

Different adsorbents have been found to show potential for pollutant removal in processes of wastewater treatment, although the large specific surface area, low density, chemical stability, variety of structural forms, and the ability to modify the pore structures make activated carbon by far the most widely used [4,12]. However there are still some disadvantages such as, high costs of activated carbon regeneration, long adsorption time and the inconvenience of separation, as each process causes some loss in carbon content and thus a decrease in the adsorption capacity. Commonly used activated carbons are microporous materials that are efficient in removing molecules of size smaller than the width of micropores (typically below 2 nm) [13], but they are not attractive adsorbents of dyes, because the adsorption equilibrium is slowly established as large molecular weight compounds are characterised by low diffusion within the internal pores [5,14].

Therefore, many research teams have been working to develop alternative adsorbents which may replace activated carbon in the use for pollution control. In comparison with activated carbons, carbon nanotubes (CNTs) are more attractive because of their favourable thermal/chemical stabilities, high selectivity and structural diversity [3,11]. Also the recent progress in their large-scale production makes them better for use as ideal organic and inorganic contaminants adsorbents [15]. Extensive experimental work has been conducted on the adsorption of different dyes onto CNTs, such as methyl orange [3,11], methylene blue [16–18], crystal violet [18], thionine [18], direct yellow 86 (DY86) [19], direct red 224 (DR224) [19], procion red MX-5B [20], reactive red M-2BE [21], sudan [22], and congo red [23]. It should be added that although carbon nanotubes are interesting materials, they must be modified with metals, metal oxides or salts [18,24,25] to increase their sorption capacity towards dyes.

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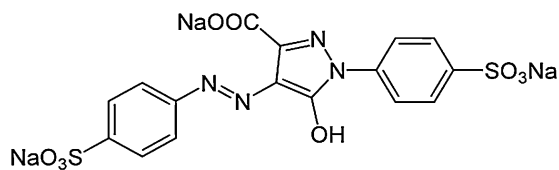 *E-mail address:* pietrob@amu.edu.pl (R. Pietrzak).

Fig. 1. Structure of tartrazine azo dye.

The main objective of the present work was to determine the potential of multi-walled carbon nanotubes modified with silver nanoparticles as adsorbent materials for the removal of tartrazine dye from aqueous solutions. The effect of contact time, pH and initial concentration on adsorption characteristics of carbon nanotubes was studied, and the experimental data obtained from the equilibrium studies were fitted to the Langmuir and Freundlich adsorption models. In addition, kinetics of the adsorption process was also studied. Tartrazine, whose IUPAC name is trisodium 1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-5-pyrazolone-3-carboxylate (Fig. 1) is a typical synthetic, water-soluble anionic dye. This substance appears to cause the most allergic and intolerance reactions of all the azo dyes, particularly among asthmatics and those with aspirin intolerance. Consequently, the wastewater containing tartrazine with various concentrations should be treated before discharge.

2. Materials and methods

2.1. Sample preparation

Multi-walled carbon nanotubes obtained by a catalytic chemical vapour deposition method were commercial CNTs (purity > 98%) supplied by Sigma–Aldrich. They have outer diameter in the range 6–9 nm and lengths up to 5 μm.

Wet impregnation was applied to modify multi-walled carbon nanotubes with an aqueous solution of silver nitrate (V) (Aldrich). The amounts of AgNO$_3$ used for modification were calculated to achieve the loading of silver equal to 1, 3 or 5 wt.%. After impregnation the adsorbents were successively dried at 105 °C for 5 h (temperature ramp 10 °C min^{-1}) and heated in argon for 3 h at 400 °C (2 °C min^{-1}). The samples obtained were denoted as: 1 Ag/CNTs, 3 Ag/CNTs, 5 Ag/CNTs.

2.2. Sample characterisation

The prepared materials were characterised by powder X-ray diffraction using a D8 Advance Diffractometer made by Bruker with the copper $K_{\alpha 1}$ radiation (λ = 1.5406 Å).

Surface areas, pore diameters and pore volumes were calculated from low-temperature nitrogen adsorption–desorption isotherms measured on a sorptometer Quantachrome Autosorb iQ. The materials were pre-treated in situ under vacuum at 300 °C.

For transmission electron microscopy measurements (TEM), powdered samples were deposited on a grid with a perforated carbon film and transferred to a JEOL 2000 electron microscope operating at 80 kV.

The content of the surface oxygen functional groups, both acidic and basic, was determined by standard neutralisation, titration with HCl and NaOH, according to the Boehm method [26]. To establish the content of acidic groups, a portion of 0.25 g of dry sample powder was shaken for 24 h in 25 mL of the 0.1 M NaOH solution. After that the suspension was filtrated through a membrane filter and titrated with 0.1 M HCl solution. To establish the content of basic groups the converse procedure was applied.

2.3. Adsorption studies

To evaluate the adsorption properties of multi-walled carbon nanotubes modified with silver nanoparticles, a series of adsorption experiments was conducted. Typically, 50 mL of tartrazine solution were added into a set of 100 mL stoppered flasks that contained 25 mg solid adsorbent. The flasks were kept in a shaker at a speed of 250 rpm. After predetermined time intervals, the sample solutions were filtered after equilibrium using 0.45 μm filter paper to determine the residual concentrations. The azo dye concentrations in the initial and final aqueous solutions were measured by using UV–vis spectrophotometer at 427 nm. The equilibrium adsorption capacities (q_e) were determined according to the following formula:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

wherein C_0 is the initial concentration, C_e is the residual concentration, V is the volume of the solution, m is the mass of the adsorbent.

The effect of pH on dye removal was studied over the pH range of 3–11. The initial pH of the dye solution was adjusted by the addition of 1 mol/L solution of HCl or NaOH.

2.4. Mathematical modelling

2.4.1. Adsorption isotherms models

When the adsorption process reaches the equilibrium state, it is advisable to describe the interaction of the adsorbate with adsorbents. The adsorption isotherm data were fitted by the Freundlich and Langmuir models, which are the most frequently used. The best-fit model was selected on the basis of the linear regression correlation coefficient values (R^2). The Langmuir model assumes that there is no interaction between the adsorbate molecules, and that the adsorption takes place in a monolayer. The Langmuir isotherm [27] is represented by the following linear equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{2}$$

where q_m is the theoretical maximum adsorption capacity, K_L is the Langmuir constant [mg/g], C_e is the equilibrium concentration and q_e is the equilibrium adsorption amount [mg/g]. The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface, and assumes that different sites with several adsorption energies are involved [11]. The linear form of Freundlich equation is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

where q_e is the amount of tartrazine adsorbed at equilibrium [mg/g], C_e is the equilibrium concentration of dye. K_F and n are the Freundlich constants: n giving an indication how favourable is the adsorption process and K_F [mg/g (L/mg)$^{1/n}$] is defined as an adsorption or distribution coefficient representing the amount of adsorbate adsorbed on an adsorbent for a unit equilibrium concentration.

2.4.2. Kinetic models

Adsorption is a physicochemical process that involves mass transfer of a solute from liquid phase to the adsorbent surface. In order to investigate the mechanism of tartrazine adsorption onto multi-walled carbon nanotubes modified with silver nanoparticles, three kinetic models, namely, pseudo-first-order [28], pseudo-second-order [29] and intra-particle mass transfer diffusion equation models were considered.