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Regular Article

Adsorption of dyes on the surface of polymer nanocomposites modified with methylamine and copper(II) chloride

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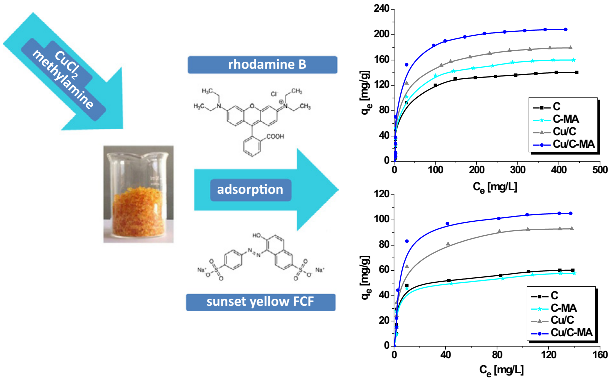
GRAPHICAL ABSTRACT



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ABSTRACT

Polymer nanocomposite was prepared by the conventional sol-gel method using formaldehyde and resorcinol. The surface of the nanocomposite was functionalized with methylamine. Some of the samples were additionally impregnated with copper(II) chloride. All the materials obtained were characterized by FT-IR spectroscopy, low-temperature nitrogen sorption, thermal and elemental analysis. The samples modified with amine groups had lower surface areas and smaller pore volumes than the pure nanocomposite. The modification with methylamine and copper(II) chloride led to increased content of both acidic and basic oxygen functional groups.

All materials were tested for the removal of rhodamine B and sunset yellow FCF from the liquid phase. The sorption capacities of the samples studied towards rhodamine B (140–208 mg/g) were higher than their maximum capacities towards sunset yellow FCF (58–105 mg/g). The most effective adsorbent of the dyes was the material modified with amine groups and copper(II) chloride. Thermodynamic study showed that the adsorption of the dyes was a spontaneous and endothermic process. The character of adsorption of sunset yellow FCF and rhodamine B on the composite materials studied could be described by the Langmuir type isotherm.

1. Introduction

Synthetic dyes make an important class of compounds commonly used in many branches of industry. They are mainly used for coloring of food products, fabrics, textiles and leather products

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[1]. Some of them can be hazardous to human health if eaten in excessive amounts. Removal of dyes from sewage and wastewater has been a challenge since the realization of its necessity for preservation of clean and safe natural environment. Since that time the search for effective methods and procedures for the removal of dyes from water phase has been continued. Different physical and chemical methods have been proposed, including adsorption, coagulation, reversed osmosis, ozonation, oxidation or filtration [1–6]. Removal of dyes from sewage and wastewater by conventional methods such as flocculation is little effective. Dyes are difficult to remove in such processes because of their large molecular mass and high solubility in water [7]. The use of coagulation entails the problem of generation and utilization of sediments [8]. A relatively often used process is adsorption, which is highly effective and non-toxic, moreover, adsorbents are readily available and show high sorption capacity. It should be noted that after adsorption, thanks to sorbents regeneration, the quality of water is unchanged. The course and effectiveness of adsorption processes depend significantly on pH and temperature of the medium [9].

Literature provides many reports on the use of a variety of materials as sorbents in the treatment of wastewater contaminated with dyes. From among them nanocomposites and polymer gels have been successfully applied as adsorbents of dyes from aquatic media [10,11]. Although a number of new materials have been found to be effective adsorbents in sewage and wastewater purification, many of them show too low sorption capacities towards large molecular stable pollutants. Therefore, in continuation of the search for more effective adsorbents of organic dyes, many composite materials based on such compounds as starch [12], starch/polyaniline [13], silica [14], guar rubber [15], chitosan [16], nanocellulose and polyvinylamine [17] have been proposed. Other commonly used adsorbents are composites modified with oxides and metals, e.g. TiO_2 [18], Fe_2O_3–Al_2O_3[19], Co, Cu and Ni [20]. Relatively rare are literature reports on polymer nanocomposites modified with organic functional groups and metal ions. Functionalization of nanocomposites with amines and copper ions is an interesting direction of studies and can lead to extension of the range of their potential applications. Amines endow the composites with basic properties and change their hydrophilic-hydrophobic status. The $-NH_2$ groups are strong electron donors thanks to a free pair of electrons at the nitrogen atom, so they can facilitate adsorption of cationic compounds [21]. Moreover, these groups show a high affinity to acidic dyes [22]. The introduction of copper ions on the nanocomposites surface can enhance electrostatic interactions and donor-acceptor ones with the dye molecules [23,24]. The use of these modifiers can increase the sorption capacities of the nanocomposites towards pollutants with respect to those of unmodified samples.

The aim of the study presented was synthesis and characterization of composites modified with methylamine and copper(II) chloride and their use for adsorption of sunset yellow FCF (SY, Fig. 1A) and rhodamine B (R, Fig. 1B) from water solutions. The effect of pH of dye solution, its temperature and time of contact with the adsorbent on sorption capacities of the synthesized nanocomposites and thermodynamics of dye sorption was also determined.

2. Materials and methods

2.1. Sample preparation

Polymer nanocomposite (C) was synthesized by polycondensation of resorcinol (Aldrich) and formaldehyde (Chempur) [25]. The amount of 25 g of resorcinol was dissolved in 40 mL of distilled water upon stirring by a magnetic stirrer. After dissolution a few drops of 2 mol/L solution of sodium hydroxide (Chempur) were added so that the pH value of the mixture was 5.3. Then, to this solution 34 mL formaldehyde was added followed by the amount of 0.1 mol/L solution of hydrochloric acid (POCh) chosen to ensure that the pH value of the mixture was 5.3. All the additions were made upon continuous stirring of the mixture. Gelation of the mixture was performed at 85 °C for 3 days. After this time, the material was comminuted, dried in a drier for 4 days at 60, 80, 100 and 120 °C.

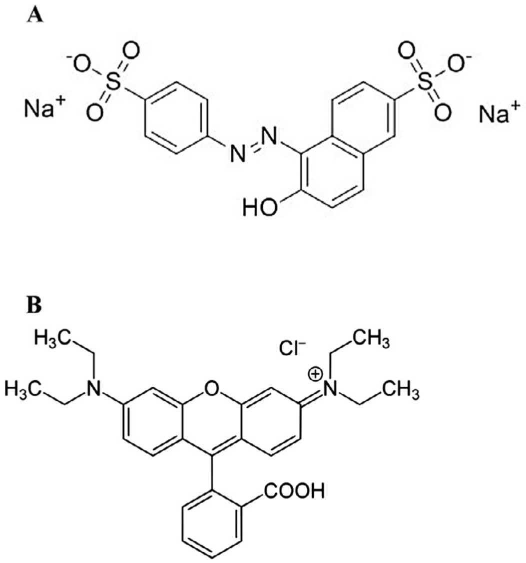

Fig. 1. Chemical structure of sunset yellow FCF (A) and rhodamine B (B).

The polymer nanocomposite (C) was subjected to modification with a solution of methylamine (MA) (Aldrich). For 30 min 2 g of amine were stirred with 30 g of methanol (POCh) and then 2 g of the composite were added. The mixture was stirred for 6 h at 40 °C. After filtration the material was dried at 70 °C. The sample functionalized with methylamine was labelled as C-MA.

At the subsequent stage, samples C and C-MA were impregnated with dihydrate copper(II) chloride ($CuCl_2$ $2H_2O$, Aldrich). The samples were annealed of at 100 °C in order to remove water. Then weighted 2 g portions of each material were flooded with a solution of copper(II) chloride prepared by dissolving 0.0534 g of $CuCl_2$ $2H_2O$ in 3 mL of water, in order to equally fill the pores. Then the samples were dried for 5 h at 100 °C and the unmodified sample (C) was additionally annealed in a tube furnace at 400 °C for 3 h. The adsorbents modified with dihydrate copper(II) chloride were labelled as Cu/C and Cu/C-MA.

2.2. Analytical procedures

Low-temperature nitrogen adsorption/desorption experiments were realized on AutosorbiQ made by Quantachrome in order to determine the surface area, diameter and volume of pores in the samples. Prior to measurements the samples of about 0.2 g were outgassed in vacuum at 300 °C for 3.5 h. The volume of the adsorbed nitrogen was normalized to standard temperature and pressure (STP). The surface area was determined by the BET method. The total pore volume (V_t) was found on the basis of the amount of nitrogen adsorbed at the relative pressure (p/p_0) of 0.99. The area and volume of micropores were found by the t-plot method.

Elemental analyses of pure nanocomposite (C) and that modified with methylamine (C-MA) were made on a Vario EL III analyzer.