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Adsorption of octylamine on titanium dioxide

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ABSTRACT

Processes of adsorption and desorption of a model active substance (octylamine) on the surface of unmodified titanium dioxide (E 171) have been performed. The effects of concentration of octylamine and time of the process on the character of adsorption have been studied and the efficiency of the adsorption/desorption has been determined. The samples obtained have been studied by X-ray diffraction. The nitrogen adsorption/desorption isotherms, particle size distribution and absorption capacities of water, dibutyl phthalate and paraffin oil have been determined. The efficiency of octylamine adsorption on the surface of the titanium dioxide has been found positively correlated with the concentration of octylamine in the initial solution. The desorption of octylamine has decreased with increasing concentration of this compound adsorbed. For octylamine in low concentrations the physical adsorption has been found to dominate, which is desirable when using TiO_2 in the production of pharmaceuticals.

1. Introduction

The most important and most widely used inorganic pigments are those of titanium dioxide [1]. They are applied in many branches of industry; in pharmaceutical, cosmetic and food industries [2–4]. They are commonly used as pharmaceutical excipients because they are not toxic, are not metabolised and are neutral to human body and its organs [5]. The most desirable features of titanium dioxide from the point of view of applications include: the ability of whitening, covering power, brightness, resistance to environmental factors, chemical neutrality and non-toxicity [6]. In pharmaceutical industry TiO_2 is the pharmaceutical excipient of no pharmacological effect in the amounts used and needed for proper drug formulation [7,8]. Titanium dioxide is used for the production of tablets and dragees [9]. In the production of tablets it might be used as an adsorbing and filling excipient, supplementing the mass of powders when the therapeutic substance is used in low amounts [7,10].

Processes of adsorption and desorption of the active substances on suitable pharmaceutical carriers are of key importance for release of the active substance. The formulations with individual doses of the active substance must ensure its proper release of active substance to maintain a desired concentration of the therapeutic substance in the organism. Painkillers are examples of the formulations expected to have a very fast release of the active ingredient. The formulations of prolonged release ensure a constant and effective level of the drug in the patient blood over a long period (8–12 h). In this way the threat of the appearance of a maximum concentration of the therapeutic substance that may cause a toxic effect and reduction of the accumulated dose [7]. The type of adsorbent or pharmaceutical carrier is chosen to meet particular demands on the time of activity of the therapeutic substance [11–19]. In a considerable number of pharmaceutical recipes the active substances are organic compounds, including amines [20–22].

The aim of the study was the characterisation of the processes of adsorption and desorption of octylamine on and from titanium dioxide surface (E 171, Kronos), respectively, in relation to different factors that could influence the courses of the processes. Selected samples were subjected to XRD study to ascertain their crystallographic structure. The properties of the samples were characterised by the determination of absorbing capacities of water, dibutyl phthalate and paraffin oil, as well as the particle size distributions. The nitrogen adsorption/desorption isotherms were established to get the information on the surface areas (BET), pore volume and pore diameters.

2. Experimental

2.1. Materials

The substrates used in the study included: titanium dioxide E 171, produced by KRONOS (minimum purity of 99%, crystalline form of anatase); octylamine produced by Merck (minimum purity of 98%).

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2.2. Procedure and methods

2.2.1. Adsorption of octylamine on the surface of titania

The process of adsorption on titanium dioxide was conducted from water solutions of octylamine of the following concentrations: 1.0, 3.0, 5.0, 7.5, 10.0 and 20.0 g/dm^3. A portion of 10 g of titan a was placed in a conical flask together with 100 cm^3 of the water solution of octylamine of a given concentration. The system was stirred by a magnetic stirrer for 0.5, 1.0 or 2.0 h. The mixture was filtered off under vacuum. The precipitate was dried in a stationary evaporator for 2 h at 105 °C. The filtrate was subjected to spectrophotometric analysis (Spekol 1200, Analityk Jena).

2.2.2. Desorption of octylamine from the surface of TiO_2

Desorption was performed to recover the adsorbed amine and to estimate the contributions of physical and chemical adsorption. The dried precipitate was introduced into a reactor to which distilled water was added. The system was stirred by a magnetic stirrer for 0.5, 1.0 and 2.0 h. The mixture was filtered off under vacuum. The filtrate was additionally filtered. The solution was subjected to spectrophotometric analysis.

2.2.3. Physico-chemical characterisation

Structure of the TiO_2 samples was determined by the X-ray diffraction method (XRD), on a horizontal diffractometer TUR-M-62 with a goniometer HZW-3.

The absorbing capacities of water, dibutyl phthalate and paraffin oil by the titanium dioxide surface was determined according to the method given in [23]. The size of titania particles as well as the particle size distribution were documented using Zetasizer Nano ZS instrument (Malvern Instruments Ltd.) employing the technique of non-invasive back scattering (NIBS).

In order to characterise adsorptive properties of the product, the nitrogen adsorption/desorption isotherms were determined and specific surface area, pore volume, mean pore size were estimated using ASAP 2020 apparatus (Micromeritics Instrument Co.).

3. Results and discussion

Fig. 1 presents the curves of octylamine adsorption on the surface of titania for the three times considered. Moreover, the efficiency of adsorption versus the concentration of octylamine in the initial water solution is also presented.

For all times of adsorption with increasing concentration of amine the efficiency of its adsorption increases; at the concentration of 20.0 g/dm^3 octylamine in the initial solution the efficiency is close to 80% (0.5 h – 78.6%; 1.0 h – 84.6%; 2.0 h – 81.0%). For lower concentrations of octylamine in the initial solutions, between 1.0 and 5.0 g/dm^3, time of the process has no significant effect on the efficiency of adsorption, however, for the concentration above 5.0 g/dm^3, a slight increase in the adsorption efficiency is observed with increasing process duration.

The adsorption curves for the times of 1.0 and 2.0 h have similar characters, while for the time of 0.5 h the adsorption efficiency was much lower. Thus, the efficiency of adsorption for particular concentrations of octylamine increases with the time of the process only to a certain time, above which it is more or less constant. The optimum time of the process of the times considered proved 1.0 h, for which the maximum efficiency of adsorption of 84.6% was observed.

From the point of view of the use of titania as an adsorbent for pharmaceutical preparations (tablets, dragees) its desirable feature would be high desorption permitting the release of the dose of the therapeutically active substance. The stability of the system adsorbent/adsorbate was tested by desorption of octylamine from the surface of titanium dioxide by water.

Fig. 2 presents the course of octylamine desorption by water from the surface of the samples studied obtained by adsorption of octylamine from water solutions of different concentrations. The process was performed for the three durations considered.

As follows from the plots presented in Fig. 2, desorption of octylamine depends on the concentration of octylamine water solutions used for production of the titania samples with adsorbed amine. The efficiency of desorption decreases with increasing concentration of the water solution of octylamine used. For the water solution of the lowest concentration of octylamine the efficiency of desorption decreased with the time of the process: for 0.5 h it was 69.2%, for 1.0 h – 58.9%, 2.0 h – 58.0%. With increasing concentration of octylamine in the initial water solution the efficiency of desorption decreases reaching the minimum values for the concentration of 20.0 g/dm^3 irrespective of the time of the process (0.5 h – 14.0%; 1.0 h – 40.8%; 2.0 h – 12.7%). The curves of desorption describing the process performed in 0.5 and 2.0 h have similar character and reveal a rapid decrease in the desorption efficiency with increasing concentration of octylamine in the initial water solutions. For the process performed for 1.0 h no rapid decrease in the adsorption efficiency was noted. In view of the above, it was assumed that the optimum time of the process was 1.0 h. The high degree of desorption for low concentrations of octylamine was desirable as the therapeutic substance in any formulation occurs in low concentrations.

For the optimum duration of the processes of adsorption and desorption of 1.0 h, the percentage contributions of the physical

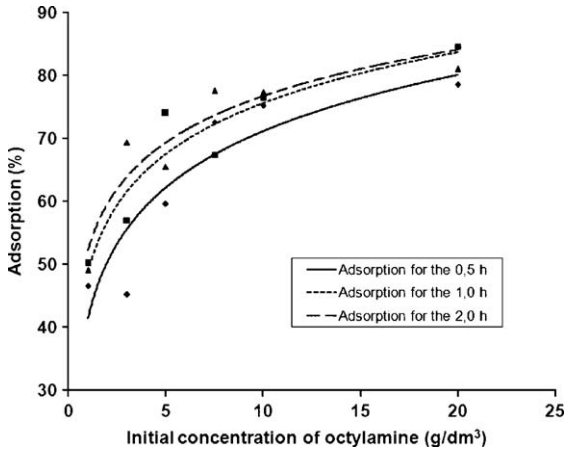

Fig. 1. Kinetics of octylamine adsorption on the surface of titania (E 171, Kronos).

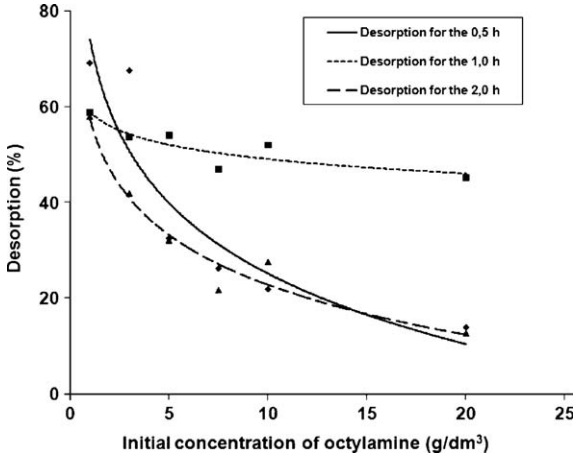

Fig. 2. Kinetics desorption octylamine desorption from titanium dioxide (E 171).