On the adsorption mechanisms of diethylamine by medically-certified activated carbons: Investigation of critical parameters controlling sorption properties

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A B S T R A C T

This study investigates the adsorption mechanisms and reaction pathways involved in the adsorption of diethylamine (DEA) by medically-certified activated carbons (ACs). DEA is used as a model of amines secreted during healing process of chronic wounds. DEA adsorption kinetics/isotherms were performed in liquid phase. Based on a preliminary assumption of a sorption favoured by surface chemical functions, it was found that the sorption kinetics followed accurately a pseudo-second order model. In addition, our analysis revealed that surface diffusion strongly influenced DEA sorption. If Langmuir and Redlich–Peterson models provided the most accurate fit of the adsorption isotherms, the Freundlich isotherm gave a fair representation of experimental data as well. L-type isotherms supported the occurrence of strong surface interactions. Also, a negative correlation was drawn between the micropore volume percentage and adsorption capacity at equilibrium. Further, acid/base reactions were believed to occur, along with the establishment of numerous H-bonds between the sorbent and DEA. This study is ended by a discussion of the effect of AC entrapment within a polymeric matrix on the adsorption properties. If DEA removal was still observed, a serious decrease of sorption properties was measured. We concluded that AC must be treated during the activation process in order to possess a high BET surface, an important mesopore/macropore content and a high content of acidic surface functions, in order to balance the decreasing of adsorption properties owed to its entrapment.

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1. Introduction

Activated carbon (AC) is a well-known and efficient adsorbent. The creation of internal porous structure during the activation process enables AC to develop a high specific surface, up to 2000 m^2 g^{-1} [1]. In addition, the presence of acidic and basic surface functional groups may significantly influence the overall efficiency of the adsorption process [2–4]. Concerning organic substances, removal of low molecular weight aromatics such as phenol or naphthalene has been widely investigated [5–13]. Moreover, sulphur compounds constitute another important class of molecules that can be removed using AC. In particular, removal of hydrogen sulphide [14–16], sulfur dioxide [17] or diethyl sulphide [18] has been explored over the past decade. Without being totally overlooked, a literature survey shows that removal of amines by ACs has been much less investigated [19–21]. Still, amines may also be responsible for environmental pollution since their biodegradability strongly depends on their chemical structure [22].

If the focus is now laid more specifically on the wound healing field, emission of malodours amine-based volatiles molecules – cadaverine (pentamethylenediamine) and putrescine (tetramethylenediamine) – from chronic wounds represents a serious discomfort for both patients and medical staff [23]. These amines arise from putrefaction of tissue during healing process. Only few strategies have been proposed up to now to reduce volatilization of amines synthesized during healing, without sacrificing essential properties of dressings [23,24]. Importantly, very little is known regarding the mechanisms of amine adsorption. The adsorption of diethylamine (DEA) has been performed using different kind of composite dressings [23,24], made of mineral matters such as

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Nomenclature

AC	activated carbon
DEA	diethylamine
a_R	Redlich–Peterson isotherm constant $[(\text{L mg}^{-1})^{\beta}]$
C	constant of the intraparticle diffusion model $[\text{mg g}^{-1}]$
C_o	initial concentration of DEA in solution $[\text{mg L}^{-1}]$
C_e	equilibrium concentration of DEA in solution $[\text{mg L}^{-1}]$
D	percent deviation error [dimensionless]
h	constant of the pseudo-second order kinetic model $[\text{mg g}^{-1}\text{ h}^{-1}]$
k_i	intraparticle diffusion rate constant $[\text{mg g}^{-1}\text{ h}^{-1/2}]$
k_I	rate constant of first-order kinetic model $[\text{h}^{-1}]$
K_F	Freundlich isotherm constant $[\text{mg}^{1-1/n}\text{ L}^{1/n}\text{ g}^{-1}]$
K_L	Langmuir isotherm constant $[\text{L mg}^{-1}]$
K_R	Redlich–Peterson isotherm constant $[\text{L g}^{-1}]$
n	Freundlich exponent related to adsorption intensity [dimensionless]
N	number of experimental data points
q_c	constant of the pseudo-second order kinetic model $[\text{mg g}^{-1}]$
q_{eI}	theoretical (calculated) amount of DEA molecules adsorbed from Lagergren model $[\text{mg g}^{-1}]$
q_{eth}	theoretical amount of DEA molecules adsorbed $[\text{mg g}^{-1}]$
q_t	amount of DEA molecules adsorbed at time t $[\text{mg g}^{-1}]$
Q°	Langmuir monolayer adsorption capacity $[\text{mg g}^{-1}]$
Q_e	experimental/calculated amount of adsorbed DEA at equilibrium $[\text{mg g}^{-1}]$
R^2	squared regression determination coefficient [dimensionless]
t	duration of adsorption test [h]
V	volume of solution [L]
W	weight of activated carbon [g]
β	Redlich–Peterson exponent [dimensionless]

alpha sepiolite or charcoal cloth, or arising from a combination of a polymer and a mineral material. The goal of these previous studies was to evaluate the sorption capacity of dressings in a gaseous environment. The choice of diethylamine relied on its molecular properties that mimic those of cadaverine and putrescine. If important insights were provided on the efficiency of dressings to reduce DEA partial pressure, nothing was mentioned regarding the adsorption properties of materials in liquid phase and related mechanisms. Yet exudates are constituted of a complex liquid fluid circulating in the areas of wound inflammation.

Considering the outstanding adsorption performances of AC powder, it is believed that their use in a wound-healing polymer matrix could constitute an important strategy to explore in order to effectively address this issue. Nonetheless, before considering entrapping AC within a polymer matrix to form a composite as reported earlier in various applications [25,26], it is essential and critical to first assess the adsorption properties of "free" AC towards these amines. The body of knowledge on sorption mechanisms and potential rate controlling steps has grown importantly and has been reviewed [27]. It is therefore possible to intend using this knowledge to describe DEA adsorption by ACs.

Also, because potential changes in adsorption behaviour may arise from entrapment of AC in a matrix, it is first essential to identify the righteous mechanisms responsible for DEA adsorption onto AC, as well as it is critical to determine the important physicochemical parameters favouring DEA adsorption by ACs. Results of such an analysis could provide key information on the essential parameters controlling the amine adsorption by ACs and would help in the design of composite matrices intended as being used in wound healing. Further, such a study in liquid environment would provide complementary data on the fate of the malodour molecules right from their starting emission point.

Therefore the scope of the present study is to address these concerns regarding the adsorption of amines by ACs. We aimed at identifying the reaction pathways and adsorption mechanisms, as well as determining which parameters control and promote amine adsorption. To do it, the focus will be principally laid on the adsorption properties towards DEA of several kinds of activated carbon powders certified for medical use by the European Pharmacopoeia. These ACs will be analyzed in details considering their structural and chemical properties. In particular, adsorption kinetics and isotherms are presented, and their simulation performed using previously published models. From these results, conclusions and correlations will be drawn regarding the mechanisms controlling DEA adsorption. To finish this study, we will also present and discuss the adsorption of diethylamine by a composite hydrogel made of chitosan polymer and AC entrapped within the polymeric chains.

2. Materials and methods

2.1. Materials

The activated carbon powders used in this study were commercial products from Pica Co. (St Maurice, France) and Norit Co. (Amersfoort, The Netherlands) certified for medical use by the European pharmacopoeia. Chitosan (Mw: 180,000 g mol^{-1}) produced from shrimp shell wastes (batch N° 342) was supplied as flakes by France Chitine Co. (France). It has a 20% degree of acetylation (producer data and Proton Magnetic Nuclear Resonance measurement). Diethylamine (Mw: 73.14 g mol^{-1}, reagent grade) was purchased from Aldrich and used without further purification.

2.2. Methods

2.2.1. Characterization of AC powders

Pore characteristics of AC were determined through N$_2$ adsorption isotherms at 77 K, performed with a Micromeritics 2010 analyzer after degassing for 48 h at 300 °C. The theories of Brunauer et al. [28], Barrett et al. [29] and Horvath and Kawazoe [30] were used to calculate their specific surface area, pore size distribution and micropore volume, respectively. Physical characterization of the different AC is provided in Table 1. In addition, the surface acidity and basicity of AC particles were quantified using the Boehm methodology [31]. As the similar procedure as that presented by Boehm was applied in this work, one is invited to refer to literature for further details. Results of this chemical characterization are displayed in Table 1 as well. It is clear that there were 3–4 times more acidic functions than basic ones. In addition, no phenolic functions could be found and most of the acidity of the surface oxides was due to compounds belonging to the second group, that is to lactones and weak carboxylic acids. Concerning the first group, results were disseminated (from 0.02 to 0.13 meq g^{-1}) but still low compared to the second group. Such a distribution arose from a concomitant effect of the origin of the active carbon samples and their activation treatment.