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Removal of a cationic bisbiguanide using Functionalized Activated Carbons (FACs)

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A B S T R A C T

Functionalized Granular Activated Carbons (FACs) are used as adsorbents for treating pharmaceutical wastewaters containing Chlorhexidine Gluconate. Chemical modifications of Granular Activated Carbons (GACs) using functionalizing agents like HCl and HF produce FACs. The adsorption capacity of each of FAC-HCl and FAC-HF is found to be higher than GAC. The modelled maximum adsorption capacity for FAC-HCl is 1.02 g/g of adsorbent, 3.49 g/g of adsorbent for FAC-HF and 0.0682 g/g of adsorbent for GAC. This is mainly due to the additional chemisorptions by surface complexation at the functionalized surface sites of the modified GACs. This is also supported by the well-known pseudo-second-order kinetic model. Formation of surface complexes with the functional groups and weakly polar Chlorhexidine Gluconate is well supported by the physical characterization using Energy dispersive X-ray spectroscopy (EDAX), Brunner–Emmett–Teller (BET) test and Fourier Transform Infrared spectroscopy (FTIR) analysis after adsorption. The adsorption capacity of GAC and the FACs increases in the order of FAC-HF > FAC-HCl > GAC conforming to the proportion of the total acidity of the carbon surfaces. Intra-particle diffusion is not the sole rate-controlling factor. An agreement to pseudo-second-order kinetic model, Elovich kinetic model and Boyd's film diffusion model proves that chemisorption is the rate-controlling parameter in this adsorption study.

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Keywords: Pharmaceutical wastewater; Chlorhexidine Gluconate; Adsorption; Functionalized Activated Carbon; Batch equilibrium analysis; Kinetics

1. Introduction

Chlorhexidine Gluconate, on its own and in mixture, constitutes the composition of various antiseptic and antibacterial solutions used as oral rinses, skin cleansers, surgical scrub, etc. Chlorhexidine can strongly bind to skin and the mucous membrane. It is a cationic bisbiguanide companionable with other cationic materials like quaternary ammonium compounds. The negatively charged surface of bacterial cell is neutralized with the application of an adequate amount of Chlorhexidine causing a fast rate of destruction of the bacterial cells. Even if it is effective for human cells, Chlorhexidine Gluconate is very much toxic to aquatic organisms.

Some of the emerging chemical contaminants like the polar organic pollutants have raised concerns among researchers, regulating authorities and the public due to their ecotoxicological property. Toxicity of Chlorhexidine Gluconate towards fish (*Brachydanio rerio*) is correlated to lethal concentration (LC₅₀) (96 h) = 10.4 mg/l and LC₀ = 10.0 mg/l (OECD Test Guideline 203). Its toxicity towards crustaceans (*Daphnia pulex*) by half maximal Effective Concentration (EC₅₀) (48 h) ≥ 0.05 mg/l < 0.10 mg/l (DEV, DIN 38412) and towards algae (*Scenedesmus subspicatus*) by half maximal Inhibitory Concentration (IC₅₀) (72 h) = 0.011 mg/l (OECD Test Guideline 201) (OECD Guidelines for the Testing of Chemicals, Section 2: effects on Biotic Systems). Sub-acute toxicity of Chlorhexidine

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Nomenclature

q	amount adsorbed (g/100 ml solution/g of adsorbent)
q_{\max}	maximum amount adsorbed (g/100 ml solution/g of adsorbent)
C	equilibrium concentration (g/100 ml solution)
k	Langmuir isotherm constant
n	heterogeneity factor
K	Halsey isotherm constant
n	Halsey isotherm exponent
q_s	theoretical isotherm saturation capacity (mg/g)
K_{ad}	Dubinin–Radushkevich isotherm constant (mol^2/kJ^2)
ε	Dubinin–Radushkevich isotherm constant.
R	gas constant (8.314 J/mol K)
T	absolute temperature (K)
C_e	equilibrium concentration (g/100 ml)
K_E	Elovich equilibrium constant
q_m	Elovich maximum adsorption capacity
α	initial adsorption rate (mg/g min)
β	adsorption constant (g/mg)
ψ	mass transfer coefficient (m/s)
S	surface area of the adsorbent per solution volume (m^{-1})
C	concentration in the solution (mgL^{-1})
C_s	concentration at the surface (mgL^{-1})
q_e	amount of Chlorhexidine Gluconate adsorbed at equilibrium (g adsorbate/L/g of adsorbent)
q_t	amount of Chlorhexidine Gluconate adsorbed at time t (g adsorbate/L/g of adsorbent)
k_1	Pseudo first-order rate constant (min^{-1})
k_2	pseudo-second-order rate constant (g adsorbate/L/g adsorbent min)
k_{id}	intraparticle diffusion rate constant (g adsorbate/L/g adsorbent $\text{min}^{1/2}$)
C	constant which indicates the boundary layer thickness (g adsorbate/L/g adsorbent)
$F(t)$	fractional attainment of equilibrium, at different times
Bt	mathematical function of $F(t)$

Gluconate towards green algae is IC_{50} (10 days) = 4.4 mg/l. Its COD value is 219,000 mg/l and BOD_5 value is 0 mg/l. Considering these eco-toxicological effects it is recommended treating pharmaceutical waste water containing Chlorhexidine Gluconate prior to discharge into the inland surface water body. Adsorption, using activated carbon is a cost-effective and versatile process for the treatment of various organic contaminants and is used in some water-treatment plants.

The specific objective of the work is to analyze the batch equilibrium adsorption of Chlorhexidine Gluconate by granular activated carbon (GAC) and by some of its functionalized forms (FAC). Various authors have studied the adsorption of polar organic compounds by activated carbon and Functionalized Activated Carbons (FACs). Adsorption on activated carbon depends on factors like specific surface area, pore-size distribution, pore volume, surface charge and presence of surface functional groups. Oxidation with suitable oxidizing agents brings changes in the physicochemical properties (Moreno-Castilla et al., 1998). After modification of Granular Activated Carbon (GAC) with HCl and HF, a large amount of

oxygen-containing functional groups like $-\text{COOH}$, $-\text{OH}$, or $-\text{C}=\text{O}$ gets attached on the surface of GAC. Oxygen-containing functional groups are commonly hydrophilic in nature, and these can easily adsorb the polar species from the solution (Xiao and Thomas, 2005). Along with acidic groups, some basic and neutral surface groups can also be introduced by oxidation (Bansal et al., 1988; Mattson and Mark, 1971). The acidic and the basic oxygen functional groups can show the properties of ion exchange and coordination with polar species (Jia and Thomas, 2006). These functional groups tend to increase the quantity of negative charges on the carbon surface, and the oxygen atoms in functional groups donate a single pair of electrons and consequently, increase their cation exchange capacity. Jia and Thomas (2006) showed that chemical modification could increase the adsorption power of activated carbon and modify its selectivity towards various ion species in solution. Therefore, specific modification of activated carbon is required in order to enable the activated carbons to develop affinity for respective polar compounds in aqueous solution and remove them effectively.

In this study, the adsorption capacity of Granular Activated Carbon (GAC) and Functionalized Activated Carbons (FACs) are compared. The morphology and other physical characteristics of Functionalized Activated Carbon (FAC) and GAC are also discussed with the help of Energy dispersive X-ray spectroscopy (EDAX) images, Nonlocal density functional theory (NLDFT) and Brunner–Emmett–Teller (BET) tests. Fourier Transform Infrared (FTIR) spectroscopy analysis examined the existence of specific functional groups on GAC. Further, batch equilibrium analysis is done with the help of standard physical as well as chemisorption isotherms. The parameters of various isotherms are estimated. A kinetic study is undertaken, and pseudo kinetic schemes are explored with respect to standard pseudo-first and pseudo-second order kinetics. An intra-particle diffusion model, Elovich model and Boyd's film diffusion model are also analyzed to support chemisorption.

2. Experimental

2.1. Preparation of Functionalized Activated Carbon (FAC)

Various researchers modified the activated carbon with acids (HCl and HF) (Nevskaia et al., 2004; Li et al., 2009; Derylo-Marczewska et al., 2011; Pakuła et al., 2005; Derylo-Marczewska et al., 2008). The analytical method followed by Nevskaia et al. (2004) and Moreno-Castilla et al. (1998) is followed in the present study. LR grade Granular Activated Carbon (Make: S.D. fine-CHEM Ltd., India; IMDG Code: 4.2/III; UN: 1362 IATA: 4.2), which has a bulk density of 40 gram per 100 ml and particle size ranging from 2.0 mm to 5.0 mm, is used for the study. The ratio of GAC: acid (HCl/HF) is 1:10. For the preparation of FAC-HCl, GAC immersed in HCl acid is heated at 333 K (60 °C) until all the acid from the beaker is evaporated. The treated GAC is then washed with de-ionized water and dried in an air oven for 5 to 6 h. For preparation of FAC-HF, GAC along with HF acid is kept in a magnetic stirrer for 1 h at a temperature of 333 K (60 °C).

2.2. Physical characterization of Functionalized Activated Carbon

The textural characterization of activated carbon samples is done using Energy dispersive X-ray spectroscopy (EDAX)

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