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Regular Article

Removal of salicylic acid as an emerging contaminant by a polar nano-dendritic adsorbent from aqueous media

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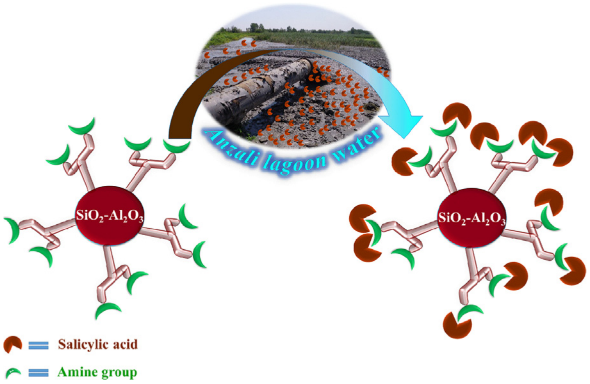
GRAPHICAL ABSTRACT



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ABSTRACT

A polar nano-dendritic adsorbent containing amine groups (SAPAMAA) was synthesized onto the nanoparticles of $SiO_2—Al_2O_3$ and its uptake of salicylic acid (SA) from the synthetic and real water was investigated. The synthesized nanomaterials were fully studied by nuclear magnetic resonance spectrum (^{1}H NMR and ^{13}C NMR), Fourier transform infrared spectroscopy (FT-IR), zeta potential (ζ), inductively coupled plasma atomic emission spectroscopy (ICP-AES), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) and elemental analysis. Various parameters such as the effect of the contact time, adsorbent dosage, initial SA concentrations, effect of solution's temperature, interfering ions, the hydrophobicity of the nanoadsorbent and initial pH were assessed. The contact time to approach equilibrium for higher adsorption was 15 min (252.8 mg g^{-1}). The isotherms could be fitted by Sips model (with the average relative error of 6.6) and the kinetic data could be characterized by pseudo-second-order rate equation (with the average relative error of 13.0), implying chemical adsorption as the ratelimiting step of uptake process which was supported by the experimental data from the effect of interfering ions, zeta potential, and altering of the adsorbent's hydrophobicity. The uptake capacities decreased with temperature increasing, and showed that the uptake of SA was chemically exothermic in nature between 15 and 80 °C. In addition, the spent SAPAMAA could be regenerated by the removal of adsorbed SA with NaOH and ethanol to regain the original SAPAMAA, the regenerated SAPAMAA also exhibited the high adsorption capacity after 10 runs. Moreover, SAPAMAA could also be applied to uptake SA from a real water (*Anzali lagoon* water). We envisage that the prepared nano-

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dendritic with remarkable characteristics such as environmentally friendly, low-cost, easy preparation in large quantity, high mechanical and chemical stability will play a significant role in developing a new generation of emerging contaminants adsorbent.

1. Introduction

The appearance of pharmaceutical drugs as emerging contaminants in aquatic ecosystems has been frequently considered in the recent years. Salicylic acid (SA) is mainly consumed in human medicine as an analgesic and antipyretic drug, being active in preventing platelet aggregation [1]. SA is available in the forms of ointments, cream, gel, transdermal patches, liquids, and plaster. Salicylic acid is soluble in water, boiling water, alcohol, ether, and chloroform. SA has keratinolytic characteristics and is used topically in the therapy of hyperkeratotic and scaling conditions such as dandruff, ichthyosis and psoriasis and also in the form of paint and collodion basis (10–17%) or as a plaster (20–50%) to destroy warts and corns [2].

The existence of SA in wastewater effluents and potable water origin is now a global challenge [3,4] and this compound has been identified as a contaminant of emerging concern. Unfortunately, traditional water purification techniques are not efficient for the removal of such pollutants [5–7]. Although the last influence of these type of contaminants on population health remains up to this time a field of intense study, their uptake from wastewater and aquatic media is definitely an important challenge for world-wide government agencies and scientists. Indeed, numerous attempts including physical and chemical technologies comprising advanced oxidation processes (AOPs) such as oxidation, TiO_2 photocatalysis, perozonation, ozonation, direct photolysis, solar photocatalysis, Fenton reactions and ultrasonic irradiation, electrochemical oxidation, electrocoagulation, membrane separation, and adsorption have been made to improve adsorbents in order to uptake emerging contaminants from drinking water [8–14]. However, the high-cost of the systems, the uncontrolled reaction conditions, limitation on being used in large scale and the production of secondary contaminants are the main drawbacks of the considered techniques. The adsorption techniques have been mentioned to be the economically promising alternatives for the sequestration of organic compounds from the wastewater [15,16].

Adsorption data confirmed that the organic based adsorbent showed excellent uptake potential toward emerging contaminants (aromatic compounds), especially those with nonpolar and also weakly polar characteristic. If the functional group is hydrophilic and specially partitions at the end of framework of the adsorbent, more reaction can take place. The generation of the dendritic structure could further alter the hydrophilic environment leading, to increase in the rates of interaction and eventually increasing uptake ability of the adsorbent in water. In fact, loading of amine groups onto at the end on stabilised organic branches help us to improve the polarity and adsorption capacity of the adsorbent through an acid-basic interaction and a weak chemical bond formation between SA and the functional groups [17,18].

In this study, a polar nano-dendritic adsorbent containing amine groups has been immobilized onto the nanoparticles of $SiO_2—Al_2O_3$ and fully characterized for uptake of SA from aqueous media. Several complementary methods such as zeta potential, measuring the hydrophobicity of the adsorbent, kinetics, adsorption isotherm and effect of interfering ions were utilized to evaluate the uptake mechanisms of SA.

2. Experimental section

2.1. Materials and characterization

All reagents were purchased and used from Fluka, Merck and Aldrich without further purification, except that solvents were treated according to standard methods [19].

$SiO_2—Al_2O_3$ was prepared and used as the supporter of the dendrimer. This inorganic support was prepared by a sol–gel procedure using; 13.0 mmol of aluminum tri–*sec*–butylate and tetraethyl orthosilicate were dissolved in 50 ml of *n*–butanol and the solution's temperature was increased to 60 °C whilst continuously stirred and then it was cooled to 25 °C before slowly adding H–acac. The resulted clear mixture was hydrolyzed with deionized water (11.0 mol H_2O/mol alkoxide). The solution was left overnight to hydrolyze the alkoxides, resulting in a transparent gel. The gel was then dried at 110 °C to evaporate the solvents, and finally, it was calcined at 500 °C for 5 h in order to remove the organic materials.

Bis(phthaloyl)diethylenetriamine was prepared based on the procedure described in the literature [20]. A mixture of diethylenetriamine (10.3 g, 0.10 mol) and phthalic anhydride (33.2 g, 0.20 mol) in 160 g of glacial acetic acid was refluxed for 2 h. The solvent was evaporated on a rotary evaporator by boiling water bath and was replaced with 160 g of hot ethanol (95%) with stirring until a solid appeared. The product was collected and washed with cold ethanol: yield 151 g (83%); m.p. 182–183 °C. ^1H NMR (DMSO-d_6), δ 2.76 and 3.59 (t, $^3J_{HH} = 6.3$ Hz, 2 × 4H, CH_2), 7.80 (m, 8H, arom). ^{13}C NMR (DMSO-d_6), δ 37.14 and 46.10 (NCH_2CH_2N), 122.70, 131.59 and 134.07 (arom), 167.81 (CO).

The propyl amine functionalized $SiO_2—Al_2O_3$ (S-A) by refluxing 5.2 g of $SiO_2—Al_2O_3$ (SA) that was activated at 550 °C for 6 h under air with 3.5 mL (0.0195 mol) of 3-aminopropyl-trimethoxy silane (3–APTMS) in dry dichloromethane (100 mL) for 24 h. The solid was filtered and washed off with methanol, dichloromethane and dried at 100 °C under vacuum for 6 h. The functionalized S-A (1:1) that was prepared with the linker, is identified hereafter by SAPA. Eight gram of SAPA was dispersed in 250 mL of methanol and 70 mL of methyl acrylate. The suspension was ultrasonicated and was refluxed for 2 h. The obtained nanoparticles were washed with methanol 3 times (SAPAMA), and then the suspension was refluxed for 12 h after 3 g bis(phthaloyl)diethylenetriamine (BPA) was added (SAPAMABPA). Methyl acrylate and bis(phthaloyl)die thylenetriamine were added for dendrimer branches to be linked onto the modified mixed-oxides surface. In the next step deprotection of amine groups was performed with hydrazine hydrate. The resultant nanoadsorbent was separated, washed with methanol, CH_2Cl_2 and DMF sequentially and is identified hereafter by SAPAMAA (Scheme 1). The prepared nanomaterials were stored in a dark and dry place.

The prepared materials were characterized by the following technique. Diffuse reflectance spectra were recorded on a JASCOV-550 UV–Vis spectrophotometer. Fourier transform infrared spectroscopy (FT-IR) was measured using a JASCO FT/IR (680 plus) spectrometer. The spectra of solids were obtained using KBr pellets. Approximately 40–50 mg of material with 10–15 times KBr was pressed into a self-supporting wafer of 0.9 mm diameter. The FT-IR spectra of the synthesized materials were recorded at