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Research Paper

Removal of emerging contaminants daidzein and coumestrol from water by nanozeolite beta modified with tetrasubstituted ammonium cation

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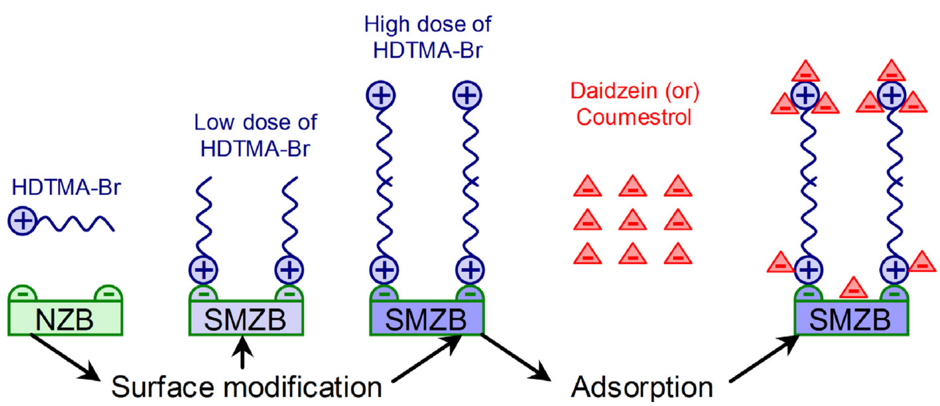
HIGHLIGHTS

- Modified nanozeolite beta showed excellent adsorption capacity for two EDCs.
- Electrostatic interactions and acidic pH caused adsorption.
- Admicelle formation on nanozeolite surface enhanced the percentage removal.
- Experimental data followed Freundlich isotherm and fractional order model.

GRAPHICAL ABSTRACT



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ABSTRACT

In present research, a simplistic hydrothermal method was adopted for one-step synthesis of nanozeolite beta (NZB) having an average particle size of 18 nm with Si/Al ratio 46.67, surface area 328 m^2/g, pore volume 0.287 cm^3/g, and pore diameter 3.5 nm. The surface of the synthesized NZB was modified with 0.5 wt% hexadecyltrimethylammonium bromide (HDTMA-Br) and used as an adsorbent for the removal of two phytoestrogens daidzein and coumestrol from aqueous solutions. The surface properties and surface charge of NZB considerably changed after modification with HDTMA-Br, which resulted in enhanced removal of daidzein (92–98% from 7 to 27%) and coumestrol (93.5–99% from 5 to 9.2%). The surface modified zeolite beta (SMZB) has similar physical characteristics as of NZB with an average particle size of 20 nm, surface area 299.8 m^2/g, pore volume 0.263 cm^3/g, and pore diameter 3.51 nm. The influence of various parameters was examined by conducting a sequence of batch experiments. The adsorption equilibrium was achieved in less than 3 h with saturation capacity of 40.74 mg/g and 42.87 mg/g for daidzein and coumestrol, respectively. The Freundlich isotherm and fractional order kinetic models represented the adsorption data very closely. The thermodynamic parameters indicated that sorption of both phytoestrogens onto SMZB is spontaneous and exothermic.

1. Introduction

Phytoestrogens are plant-derived chemicals, found in legumes such as beans, peas, alfa alfa, wheatberries, wine, beer, grains and

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nuts and most abundantly in soybeans [1,2]. Phytoestrogens have certain binding affinity with cell membrane receptors due to structure similarity with natural hormone and their active metabolites, to mimic estrogenic mediated processes [3]. Therefore, they have also been cited as endocrine disrupting compounds (EDCs) [4]. The accumulation of phytoestrogens in the environment has become a major threat in recent years [5–8]. The phytoestrogens considered in the present study are daidzein and coumestrol. Numerous studies reported that continuous exposure to daidzein and coumestrol leads to various reproductive problems in aquatic species and humans like gene mutations, chromosome aberrations, aneuploidy, DNA adducts, disturbance of lactation, premature reproductive senescence, infertility, glandular metaplasia in prostate and bulb urethral glands [9,10]. Following the approval of the US Food and Drug Administration (FDA) in 1999 for the daily consumption of soya products, phytoestrogens have been detected at certain concentrations (<1 ppm), mainly in the effluents from various soy processing industries, paper and pulp mills, food industries, biodiesel refineries, and wastewater sewage treatment plants [11,12]. Therefore, complete removal of phytoestrogens from surface water has been taken into consideration [13,14].

A variety of physical and bio-chemical methods have been used to remove phytoestrogens from water including enhanced biofilm system, photocatalytic degradation, chemical advanced oxidation process [15–17], biological treatment [4], reverse osmosis, nanofiltration [18] adsorption-separation and ultrasonic atomization [19,20]. Removal of daidzein and coumestrol by physical means is difficult due to their high stability, low solubility and low concentrations in water [11]. Separation of these phytoestrogens by nanofiltration (NF) and reverse osmosis (RO) has been found unsuccessful because of membrane fouling [21]. Some studies reported that biological treatment (trickling filter, activated sludge, etc.) is effective to remove these compounds [22,23]. The adsorption separation is considered as the most suitable method due to its simple theoretical design, ease of operability, relatively low costs and comparatively lesser amounts of toxic by-products [24]. Previously, many adsorbents such as cellulose based materials [25], carbon nanotubes [26], metal organic frameworks [27], and molecular sieves [19] have been employed for the removal of various EDCs from aqueous solutions. However, many of them have low surface area, and incompatible surface charge responsible for less amount of mass transfer [28].

Nowadays, it has been demonstrated that hierarchically nanozeolites can be used for various applications, especially, for the adsorption of organic pollutants and water purification due to their high surface-to-volume ratio, reusability and functionalized surface sites of large pore size (3.5 nm) which is greater than organic molecules so that organic contaminants can infuse through the pores [29–33]. For enhancing the adsorption capacity of nanozeolites towards organic contaminants, various surface modification techniques have been used including physical modification (e.g., heating) and chemical modification such as protonation, impregnation of metal oxides and organic modification [33,34].

In this paper, a nanozeolite beta was synthesized and modified with HDTMA-Br to enhance the removal of daidzein and coumestrol from their aqueous solutions. The adsorbent samples were characterized in detail using XRD, SEM, EDS, TEM, FTIR and BET. The influence of pH, temperature, adsorbent dose, stirring rate, contact time, initial adsorbate concentration and surfactant dose on the adsorption of phytoestrogens was investigated. In addition, the possible mechanism involved in sorption process of phyoestrogens onto nanozeolite beta has been proposed. This study will be useful to develop effective treatment processes for removal of emerging contaminants from wastewater.

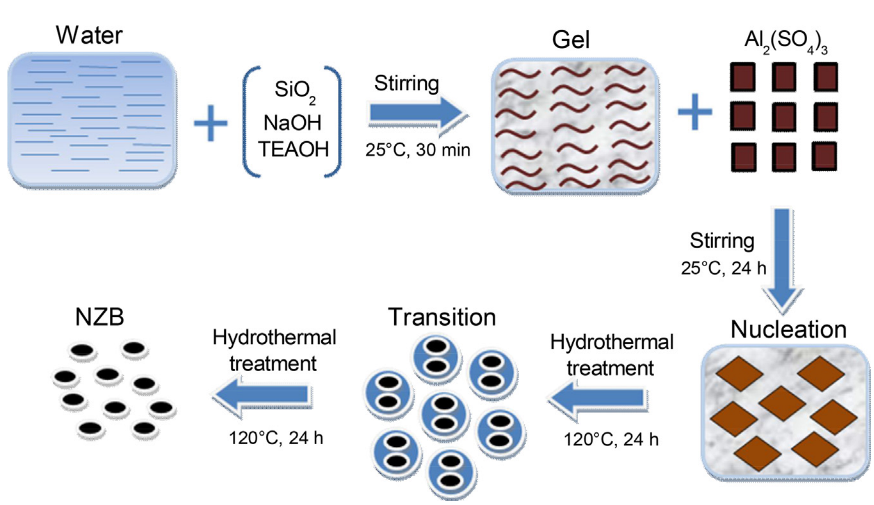
2. Materials and methods

2.1. Procurement of materials

Fumed silica (SiO_2, MW 60.08 g/mol), aluminum sulphate ($Al_2(SO_4)_3$, MW 342.15 g/mol), and sodium hydroxide (NaOH, MW 40.0 g/mol), were used as standard precursors and base medium. Tetraethylammonium hydroxide, 35% dissolved in aqueous solution ($(C_2H_5)_4N(OH)$, MW 147.26) was used as structure directing agent. Hexadecyl-trimethyl-ammonium bromide ($C_{19}H_{42}BrN$, MW 364.4 g/mol), was used for the modification of nanozeolite beta. Methanol (CH_3OH, MW 32.04 g/mol), and distilled water were used to prepare the stock solutions of daidzein ($C_{15}H_{10}O_4$, MW 254.23 g/mol) and coumestrol ($C_{15}H_8O_5$, MW 268.22 g/mol). All these chemicals (analytical grade) were procured from Sigma Aldrich, MO, USA.

2.2. Synthesis of nanozeolite beta

Nanozeolite beta with an average particle size of 20 nm was prepared (shown in Scheme 1) by mixing of fumed silica (3.27 g) and sodium hydroxide (0.2693 g) with tetraethylammonium hydroxide (5.49 g) in 50 mL de-ionized water thoroughly for about half an hour at high stirring speed (300 rpm) until the formation of a clear gel [35]. Then, aluminum sulphate (0.5 g) was added to



Scheme 1. Synthesis of nano-zeolite beta (NZB).