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Adsorption of carbamazepine on sludge/fish waste derived adsorbents: Effect of surface chemistry and texture

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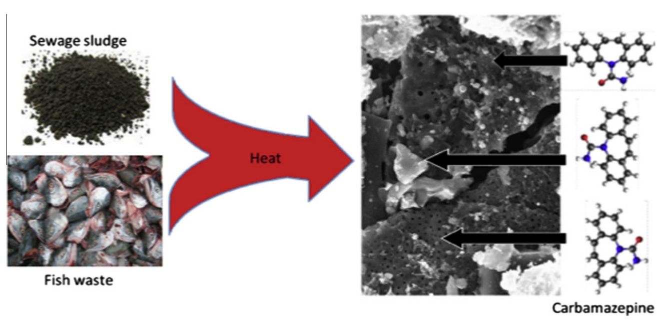
HIGHLIGHTS

- Adsorbents were produced from sewage sludge/fish waste by carbonization at 650/950 °C.
- Adsorption capacity for carbamazepine was measured.
- Surface chemistry (complexation and/or acid–base mechanisms) governed performance.
- Adsorption mechanisms includes dispersive and specific interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

Sewage sludge, fish waste and their homogenized mixtures (90:10, 75:25, or 50:50) were carbonized at two temperatures (650 and 950 °C). The obtained materials were extensively characterized in terms of their chemistry and porosity, and tested as adsorbents of carbamazepine from an aqueous phase. The content of a carbon phase was between 26% and 45% and the main components of an inorganic phase were oxides and salts of such metals as Si, Ca, Al, and Fe. The materials were predominantly mesoporous, with pore sizes larger than 30 Å. The high carbonization temperature led to better performing materials. Moreover, for the composites a synergistic effect of the component mixture was observed. An addition of a small amount of the fish waste increased the content of the carbon phase. A high carbonization temperature improved the level of carbonization and thus resulted in the favorable dispersion of the polar inorganic phase. While the former increased the adsorption of carbamazepine in the small pores via dispersive interactions, the latter contributed to the specific adsorption in mesopores via complexation and/or acid–base interactions.

1. Introduction

During recent decades concerns about the contamination and pervasive detection of pharmaceuticals in wastewater effluents have intensified [1,2]. Adsorption on activated carbon has long been used as a technique for water purification. It has proven effective in removing contaminants such as heavy metals [3], dyes [4], phenols [5], and some pharmaceuticals [6]. However, despite activated carbon's efficiency and ease of use in water purification, its cost is considered as one of the draw-backs [7], especially in developing countries [8].

In the search for low-cost alternatives, diverse arrays of waste materials have been pyrolized to produce activated carbon adsorbents. The list of applied materials/waste include rice hulls [9], fly ash [10], coirpith [3], fruit stones and nut shells [11], PET

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[12], and used tires [13]. Essentially any carbon-rich material can be pyrolized and treated/activated to form a carbon-based adsorbent. As such, another raw material under consideration is sewage sludge, a by-product of the biological treatment of wastewater. Previous applications of pyrolized sewage sludge-based adsorbents, although not activated carbons in the traditional meaning of this word, have proven effective in removing pollutants such as H_2S [14], dyes [15], phenols and heavy metals [16], and pharmaceuticals [17].

Another raw material of interest in adsorbent production/waste recycling is fish waste, including bones, shells and scales. Fish waste consists of 30 wt.% organic compounds (mainly keratin) and 70 wt.% inorganic compounds (mainly hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$) [18]. This waste material has been successfully employed in the removal of pollutants such as heavy metals [19–21] and dye [22]. Thus the production of carbon-based adsorbents from pyrolized sewage sludge and fish waste is a promising way not only to generate adsorbents for water purification, but also to re-purpose a rapidly accumulating disposal problem of industrial/municipal by-products. In this way these environmentally detrimental wastes can be minimized and be converted into materials contributing to environmental remediation. Moreover, mixing sewage sludge and fish waste may result in beneficial synergistic effects of the adsorbents' compositions. This might include a combination of carbonaceous and polar phases, which is a unique feature of this kind of adsorbents and not found in typical activated carbons. Such surface heterogeneity might increase the diversity of these adsorbents' applications.

It is well known that the effectiveness of activated carbon as an adsorbent is linked to its high surface area and porosity [23]. The challenge is to develop a substitute with comparable adsorption capacity. Sewage sludge-based carbonaceous adsorbents have a rather low volume of micropores [24], therefore physical (selective oxidation of atoms from the carbon structure) or chemical (mixing the precursors with an activation reagent) activation have been employed to increase the porosity and surface area [24,25]. It has been shown that high carbonization temperatures cause aromatization/condensation of the carbon containing phase, leading to an improved surface area and also to an increased porosity (particularly micropores, <2 nm in diameter), due to dehydroxylation of the inorganic material [25].

Besides porosity, another feature that is developed during the adsorbent synthesis and is of paramount importance for the selectivity of the adsorption process, is the surface chemistry [26]. The surface groups of the carbon adsorbent can be modified by a thermal or chemical treatment. The atmosphere (oxygen or inert) during heating affects the populations of carboxylic, lactone, phenol, carbonyl, anhydride, ether and quinone groups on the carbon surface [27]. Acidic and basic functional groups can be added or eliminated from the surface [28], thus governing the adsorption/removal capacity of either polar or nonpolar species.

Carbamazepine (CBZ) is often used as a model adsorbate to study the removal of pharmaceuticals from the water phase [29–31]. CBZ ($C_{15}H_{12}N_2O$) is an anti-epileptic medication, which is common in wastewater, and it is known of its ineffective removal during wastewater treatment [32–35]. In fact, in the effluent from one wastewater treatment plant, the removal rate of CBZ was found to be a mere 7% [32]. With such a low efficiency of pharmaceuticals' removal, aqueous environments are experiencing accumulations of these undesired compounds. Deleterious effects on aquatic organisms (fish, amphibians) have been found [36] even at lower concentrations than those utilized in this current study. Based on the harmful effects of the pharmaceuticals' exposure, it is imperative to find an effective and affordable method for their removal.

Taking into account the above, the objective of this paper is to investigate the effects of the surface features of sewage sludge/fish waste-derived adsorbents on the removal of low concentrations of carbamazepine from an aqueous phase. Such features as surface chemistry and porosity, which might play an important role in surface interactions, are analyzed and their effects on the adsorption mechanism are elucidated. The results might throw new light on desired features of waste-derived adsorbents, and on the means leading to their incorporation to adsorbent surfaces.

2. Experimental

2.1. Materials

2.1.1. Adsorbent preparation

Anaerobically digested and dewatered sewage sludge (New York City Department of Environmental Protection) and fish waste (local fish market), were dried (120 °C), homogenized and carbonized individually, as well as in composites with ratios of sewage sludge to fish waste 50:50, 75:25, or 90:10. The precursor are water unstable materials and cannot be used in the untreated form as adsorbents from an aqueous phase. To stabilize them, a high temperature treatment has to be applied. Thus the precursor materials and their mixtures were carbonized at two distinct temperatures, 650 °C and 950 °C, in a nitrogen atmosphere at a heating rate of 10 °C/min, with a holding time of 1 h. The final yield of the adsorbents was about 40%. A previous study [37] was conducted with these composites, carbonized only at 950 °C, activated with CO_2, and used as hydrogen sulfide adsorbents. Since activation decreased the content of carbon phase that might be beneficial for the removal of organic compounds from the aqueous phase, the current study focuses on the carbonized composites. The names of the adsorbents, their composition and preparation temperatures, are summarized in Table 1. To guide the readers, in the names of the samples chosen, F and S refer to the fish and sludge derived adsorbents, respectively. A, B, C represent an increase in the fish waste content in the composites (10%, 25%, and 50%, respectively; the increase follows the alphabetical order). Roman numbers I and II represent 650 °C and 950 °C carbonization temperatures, respectively.

2.1.2. Adsorbate

Carbamazepine (CBZ) was obtained from Sigma–Aldrich (St. Louis, MO), with a purity of $\geqslant$98% (Fig. 1).

2.2. Methods

2.2.1. Elemental analysis

The samples were oxidized/burned in a furnace at 950 °C, and ash was fluxed with 1 g $Li_2B_4O_7$ in a platinum crucible at 950 °C, then diluted to 200 mL with 5% HCl. Elements in ash were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) on Varian Vista-MPX ICP-OES, and the percentage of detected oxides was calculated.

2.2.2. Determination of porosity

Nitrogen adsorption isotherms were measured at −196 °C using an ASAP 2020 (Micromeritics, Norcross, GA). Initial and spent samples were outgassed at 120 °C in a constant vacuum (10^{-4} Torr), and the surface area (S_{BET}), total pore volume (V_t), micropore volume (V_{mic}), and mesopore volume (V_{mes}) were calculated. The volume of micropores was obtained from the Dubinin–Astakhov equation [38]. The BJH method [39] was used to calculate the pore size distributions.