BENZOIC ACID REMOVAL FROM AQUEOUS SOLUTIONS BY ACTIVATED CHARCOAL

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Benzoic acid has a wide use primarily in food but it is also used in cosmetic, pharmaceutical and other products. Because of noted carcinogenic and toxic characteristics under certain concentration it is considered a pollutant that becomes an important environmental problem. In this study, commercial activated charcoal was tested for the removal of benzoic acid from aqueous solutions. Removal of benzoic acid was investigated in a batch and column system under various values of pH, temperature, activated charcoal granulation and mass. The analysis of all samples was performed by visible absorption spectrometry. The optimum conditions for benzoic acid removal in a batch system were found to be pH 3, contact time of 60 min, the temperature of 273.65 K and adsorbent dose of 10 g L⁻¹. The benzoic acid removal can be performed in a column system as well in which the highest quantity of benzoic acid is removed during the first 20 min (70%) and saturation occurs after 70 min. The used benzoic acid removing methods can be characterized as simple, economical and fast and requiring no chemical treatment.

Keywords: benzoic acid, activated charcoal, adsorption, pollution.

Introduction

Benzoic acid, C₇H₆O₂, is aromatic acid naturally present in many plants. Benzoic acid (BA) has a wide use primarily in food but it is also used in cosmetic, pharmaceutical and other products. BA and its salts and esters known as benzoates are used as food preservatives (E210 and E211). As a food preservative BA is commonly used in the concentration of 0.05-0.1% [1]. The highest allowed BA concentrations in food are 0.1% in the USA, and between 0.15% and 0.25% in other countries [1]. The use of BA is reasonably brought into question because of numerous investigations that point to the negative BA effects. It is considered to be a pollutant as well, because of its toxic and carcinogenic characteristics. BA can cause allergic reactions in people with asthma who are sensitive to salicylic acid [2]. Some studies have reported the hyperactive behavior in children population after consuming benzoic acid [3]. After oral uptake, BA is rapidly absorbed from the gastrointestinal tract and metabolized in the liver. Gardner and Lawrence [4], discovered a mechanism of BA and ascorbic acid reacting in food, where benzene is formed as a main reaction product that further causes severe damage of the bone marrow, aplastic anemia, leukemia, cancer, the immune and nervous system disorders, liver cirrhosis or neuronal death in Parkinson's disease [4,5]. BA applied dermally can also penetrate through the skin. BA is slightly irritating to the skin and eye in contrast to the Na-benzoates [1]. Some mortality cases in animals with about 0.450 g kg⁻¹ body weight were reported. For example, LD50 for

mouse and rat is 1.94 g kg⁻¹ and 1.70 g kg⁻¹, for oral intake, respectively. By WHO, the maximum daily intake of BA that has no detrimental effect on health is 5 mg kg⁻¹ [1,6,7].

BA is also present in the wastewaters of coking plants, fertilizer, pharmaceutical, plastics, organic chemical, steel, and petroleum industries, dye manufacturing and paint-stripping operations. Increasing concern for public health and environmental quality has led to the establishment of rigid limits on the acceptable environmental levels of specific pollutants. Thus, the removal or destruction of BA from process or waste streams has become an important environmental problem. Several methods are popular for BA removal of this material such as photocatalytic degradation, combined photo-Fenton and biological oxidation, advanced oxidation processes, aerobic degradation, nanofiltration membranes, ozonation and adsorption [8-9]. Chitosan and β-cyclodextrin (β-CD) are well investigated as feedstock for preparing polysaccharide-based toxic compounds removing adsorbents that have excellent ability to adsorb benzoic acid [10]. Single-walled carbon nanotubes (SWNTs), synthesized by direct thermal decomposition of ferrocene (Fe(C₅H₅)₂), can also remove BA from water with high efficiencies [11]. Adsorbents as zeolites and bentonites are also used for BA adsorption [12,13].

Activated charcoal (AC) can be considered as a safety barrier in case of pollution. Wastewater treatment by activated charcoal is considered to be an effective

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and the best available environmental control technology based on the phenomena of adsorption. Its widest use is in the production of carbonated and non-carbonated juices and the preparation of drinking water. Although AC can be used to adsorb inorganic and organic substances, organic substances are better adsorbed by dissociation forces and hydrophobic interactions. Nevertheless, in addition to the properties of the pollutants, it is necessary to take into account the characteristics of the adsorbent, including the specific surface area, the pore size distribution, as well as the physico-chemical properties of aqueous solutions.

Considering previously published studies, we investigated AC potentiality for BA adsorption at various conditions from water solutions in batch and column systems. Due to significant releases of benzoic acid into the environment, primarily into water and soil from food preservatives, mouthwashes, dentifrices, and cosmetics, and considering the optimum tolerable BA intake of 5 mg kg^{-1} body weight per day for humans and animals (300 mg kg^{-1} body weight), this study can help in resolving the problem of BA removing or reducing from the contaminated water and food [1]. The conclusions about AC potential use for this purpose are given based on the obtained laboratory results.

Experimental

Methods

Adsorption in a batch system

The study of adsorption was carried out at a constant temperature (295.15 K) under continuous stirring (100 rpm). The contact time was 0-100 min (Figure 1a).

Adsorption in a column system

The study of adsorption was carried out at a constant temperature (295.15 K) under continuous BA solution flow (5 mL min^{-1}). Two types of column are used: plastic column and porous plastic column with pores of 1 mm (Figure 1b). A porous column has higher flow resistance in the center of the column compared to the plastic column. The column with granular activated charcoal fill was 2 cm high and with diameter of 2 cm.

Figure 1. Schematic illustration of the BA removal process in batch (a) and column system (b)

Materials

Adsorbent

The adsorbent used in the experiments was AC of two different sizes (2 and 2.5 mm). Granulated AC is supplied from Miloje Zakić- Kruševac, Serbia.

Adsorbate

Benzoic Acid (BA–Zorka Pharma-Hemija” DOO) was used as an adsorbate. The aqueous solutions were prepared by dissolving benzoic acid in distilled water (Fisher Chemical-HPLC grade). The calibration plot of benzoic acid was prepared by using $2.5 \times 10^{-3} \text{ M}$ to $9.5 \times 10^{-6} \text{ M}$ BA solution.

Experiments on the effect of adsorbent dose, pH and contact time on BA removal by AC in the batch and column systems were performed with the BA concentration of $1.23 \times 10^{-3} \text{ M}$.

Optimization of adsorbent mass

Adsorption of BA by AC with different masses of 0.01-1 g (and AC granulation) was carried out by 100 ml of BA investigated solution. The adsorption was carried out by shaking the solution using a magnetic stirrer for 100 min (100 rpm). The solutions were analyzed at different periods (0-100 min) for the amount of BA adsorption, which was quantitatively determined by the difference between initial and final concentrations of BA by using the calibration plot.

Optimization of pH

In order to optimize the pH of BA adsorption at $1.23 \times 10^{-3} \text{ M}$ and 1 g of AC for maximum adsorption, solutions of BA with different pH 2-11 were prepared. The adsorption was carried out by shaking (100 rpm) the investigated solution for 100 min.

Optimization of adsorption temperature

Adsorption of BA by AC was studied at different temperatures (273.65, 295.15 and 323.15 K) for 1g of AC with 100 ml BA solution ($1.23 \times 10^{-3} \text{ M}$), and analyzed by measuring absorbance on the spectrometer and the concentrations were calculated by the calibration plot.

Apparatus

A double-beam Varian Cary-100 Conc UV-VIS spectrometer connected to the computer and loaded with Cary WinUV software was used for all absorbance measurements and data treatment. The instrument has an automatic wavelength accuracy of 0.1 nm and matched quartz cells of 10 mm cell path length. Before the measurements, all investigated samples were filtered through the $0.45 \text{ }\mu\text{m}$ filters.

In addition, the removed (adsorbed) BA amount was determined from the following formula:

$$\% \text{ adsorption} = (C_i - C_f) \times 100 / C_i$$

- where C_i and C_f are the initial and final BA concentrations.

Results and discussion

Research in a batch system

Effect of AC mass and granulation

In water treatment, AC has multiple effects on water: it neutralizes taste and smell, removes dyes and toxic substances, reduces the content of free chlorine, etc. The study of BA adsorption in the batch system showed AC adsorption activity, which varied at different AC masses and granulation. Figure 2 shows the adsorption results of BA at room temperature of two different AC granulations (Figure 2a-b). The results imply that the optimal AC weight for removing BA is 1 g.

Figure 2. BA adsorption by AC of lower (a) and higher (b) granulation, under different AC mass (g) in a batch system. BA concentration in water solution was 1.23×10^{-3} M and the pH of the solution was 6.5

The most important physical property of AC is its surface. In special applications, the surface layer on which adsorption can be carried out depends on the size of the adsorbent molecule and the pore diameter of the AC [14]. In general, most of the adsorbents have a diameter of 3 nm or less. AC has a very large specific surface area ($>500 \text{ m}^2 \text{ g}^{-1}$), good porosity and tunable surface-containing functional groups [15], giving the material

with important adsorptive properties. Based on these facts, it can be justified to claim that a higher degree of BA removal can be obtained by a higher adsorbent dose (1 g) compared to the smaller masses (0.01-0.2 g), as shown in Figure 2 a-b. However, the system with an adsorbent of higher granulation (Figure 2b) of mass 1 g did not achieve the greatest efficiency. This result can be explained by the fact that adsorption is not only dependent on the weight of an adsorbent, but also on the pore size [16]. Adsorption on AC mostly takes place on the surface of pores. When the pores are larger the diffusion of liquids takes place quickly. If the size of the AC particles is smaller they reach the surface more easily and the adsorption kinetics is faster. Therefore, effective adsorbents should have a large volume of micropores (which makes up over 95% of the total pore area), with a width of about 1.3 to 1.8 times larger than the kinetic diameter of the target adsorbate [16]. As can be seen from the presented results (Figure 2), the best BA removal was achieved at the AC mass of 1 g for the AC granulation of 2 mm. For a longer contact time, the larger size and aggregation of BA molecules make it almost impossible to diffuse deeper into the adsorbent structure at highest energy sites [17]. Also, at longer contact times, the mesopores are almost filled up and begin to resist the diffusion of aggregated molecules into the AC, which may explain the fact that the highest BA removal is achieved in the first 20 minutes of removal in the batch system, after which AC saturation is achieved.

Effect of pH

The adsorption of organic compounds from aqueous solutions is usually largely pH dependent. The adsorption of BA was investigated at different pH values at a constant temperature of 295.5 K during different adsorption times (0-60 min).

Figure 3. BA adsorption by AC at varied pH and constant room temperature. The AC mass and granulation used in the batch system were 1 g and 2 mm, respectively. BA concentration in water solution was 1.23×10^{-3} M

The amounts of adsorbed BA decreased with increasing pH of the solution as shown in Figure 3. Generally, the chemical nature of the adsorbent surface affected by the pH of the solution plays an important role in the adsorption of adsorbates from aqueous solutions. A lower adsorption at higher pH may be due to the abundance of OH⁻ ions and consequent ionic repulsion between the negatively charged surface and the ionic organic compounds [9]. The optimal pH at which the maximum adsorption of BA was obtained was 3 (Figure 3). Previously published results indicated that the AC adsorption capacities increase with decreasing pH value and increasing temperature [12]. Also, adsorption of BA by modified bentonites from aqueous solution has already been investigated and results showed the optimum pH of 3.5 [18], as in the case of the Ayranci et al. [19] study where they found 3.7 as the optimal pH for benzoic acid removal by AC cloth.

Effect of temperature

The adsorption of organic compounds from an aqueous solution is usually not highly dependent on the temperature. Lower temperatures favored physical adsorption and higher temperature achieved a significant enhancement in capacity under oxic conditions [20]. In some cases, the adsorption increases with increasing temperature due to easier diffusion of molecules from the solution to the adsorbent [12,18].

Figure 4. BA adsorption by AC at varied temperatures. The AC mass and granulation used in the batch system were 1 g and 2 mm, respectively. BA concentration in water solution was 1.23×10^{-3} M

However, adsorption is generally an exothermic process. Therefore, it is expected that an increase in temperature of the BA system would result in decreased sorption capacity of AC [17]. This fact was supported by the findings of Maqsood and Benedek [21]. In this study, better adsorption of BA was achieved at lower temperatures (273.65 and 295.15 K) which is also in agreement with the claim of Nakhl et al. [20]. In the process of removing BA by AC at different temperatures, two phases can be observed: the first phase of 0-20 min, when the

maximum adsorption of BA is 60%, and the second of 20-100 min, when the adsorbent becomes almost saturated (after 40 min). In the first phase, it can also be noticed that the removal of BA increases with increasing temperature (Figure 4). At the temperature of 323.15 K saturation is reached after 20 minutes. For the temperatures of 273.65 and 295.15 K, results are showing reverse change so that in a second phase the better adsorption is achieved at the lower temperature.

Research in a column system

Further research was directed towards the research of BA removal in a AC column system. The research was done with two types of columns - a plastic and a porous plastic column in order to examine the possible effect of fluid flow. The test results are presented as the percentage of BA adsorption over time at constant flow and column height (Figure 5).

Figure 5. BA adsorption by AC in column system at room temperature. The AC granulation used in the column system was 2 mm. The column height in both cases was 2 cm, and flow was constant - 5 mL min^{-1} . BA concentration in water solution was 1.23×10^{-3} M

The full plastic column, in contrast to the plastic porous column, does not allow contact with ambient air, while the porous column allows contact of the adsorbent and the fluid along the entire length of the column. Also, the full plastic column has the highest flow resistance at the perimeter, and the porous plastic column has the highest flow resistance in the center of the column. For industrial applications, this can have a significant impact [22]. In this way, enhanced oxidation processes in the porous column can be expected, which can have an impact on the final adsorption capacity of AC. The results presented in Figure 5 showed that the column type did not significantly affect the adsorption of BA. The maximum achieved BA removal was 80% for both column types after 100 min. The saturation of AC column occurred after 40 min. Compared to the results presented in Figure 2, higher BA adsorption was achieved in column after one hour. Although higher adsorption of BA was achieved in the column systems, it should be noted that the final AC mass used in the column system was higher (3.7 g) than

in the batch system (1 g). Also, differences in the adsorption capacity of BA between porous and non-porous plastic columns that are not obvious were not fully confirmed due to the small laboratory systems of the columns as well as the short time period.

Conclusion

Presented results indicate that activated charcoal can be used for the removal of benzoic acid from aqueous solutions. The used batch and column methods can be characterized as simple, economical and fast, requiring no chemical treatment. The results indicate that the amount of benzoic acid in a solution decreases over time. Namely, the largest percentage of BA was adsorbed in the first 20 min. AC reached the maximum value of adsorption (82%) in the batch system within an hour. The process of BA removal also depended on the mass of AC, granulation of AC, pH value of the solution and temperature. The optimal AC mass was found to be 1 g for the batch system. The most suitable pH value for BA adsorption was 3. The best BA removal was achieved at the temperature of 273.65 K. The BA removal can be performed in a column system as well in which the highest quantity of benzoic acid is removed during the first 20 min (70%) and saturation occurs after 70 min. Differences in column type (porous and full plastic) do not make large differences in the removal of BA from the tested solutions.

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Izvod

UKLANJANJE BENZOEVE KISELINE AKTIVNIM UGLJEM IZ VODENIH RASTVORA

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Benzojeva kiselina se široko koristi prvenstveno u hrani, ali i u kozmetičkim, farmaceutskim i drugim proizvodima. Zbog zapaženih kancerogenih i toksičnih karakteristika pri određenoj koncentraciji, smatra se zagađivačem koji postaje važan ekološki problem. Iz tog razloga, komercijalni aktivni ugalj je testiran za uklanjanje benzojeve kiseline iz vodenih rastvora. Uklanjanje benzojeve kiseline u šaržnom i kolonskom sistemu je ispitano pri različitim vrednostima pH, temperature, granulacije i mase aktivnog uglja. Analiza svih uzoraka izvršena primenom vidljive apsorpcione spektrometrije. Utvrđeno je da su optimalni uslovi za uklanjanje benzojeve kiseline u šaržnom sistemu pH 3, vreme kontakta od 60 min, temperatura od 273.65 K i doza adsorbenta od 10 g L⁻¹. Uklanjanje benzojeve kiseline može se izvršiti i u sistemu kolona u kome se najveća količina benzojeve kiseline uklanja tokom prvih 20 minut (70%), a zasićenje kolone ispunjene aktivnim ugljem javlja nakon 70 min. Korišćene metode uklanjanja benzojeve kiseline mogu se okarakterisati kao jednostavne, ekonomične, brze i ne zahtevaju hemijsku obradu.

Ključne reči: benzojeva kiselina, aktivni ugalj, adsorpcija, zagađenje.