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Adsorption of nitrate and nitrite ions onto carbonaceous material produced from soybean in a binary solution system

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ABSTRACT

In this study, soybean (SB) was treated with calcium chloride, hydrochloric acid, and calcination (400, 600, 800, and 1000 °C) to introduce chloride ions onto the SB surfaces (SB400, SB600, SB800, and SB1000, respectively). The properties of the adsorbents (pH of the solution, acidic functional group, and basic functional group) were investigated. The adsorption of nitrate and nitrite ions onto SB surfaces at different temperatures was evaluated. SB600 had the highest concentration of acidic functional groups (3.34 mmol/g). The amount of nitrate and nitrite ions adsorbed onto SB600 in a binary solution system was lower than that in a single solution system. The amount of nitrate and nitrite ions adsorbed was closely related to the chloride ions. The adsorption mechanism of nitrate and nitrite ions onto SB600 mainly involved an ion exchange (correlation coefficient = 0.993). Moreover, chloride ions affected the adsorption process. The adsorption isotherm data using SB600 were fitted to both the Langmuir and Freundlich equations. The amount of nitrate and nitrite ions adsorbed increased with increasing temperature. The adsorption equilibriums of nitrate and nitrite ions onto SB600 were obtained after 24 and 16 h, respectively. The experimental data fit the pseudo-second-order model better than the pseudo-first-order model. Thus, SB600 is useful for the adsorption of nitrate and nitrite ions in a binary solution system.

Introduction

Several nitrogenous compounds, including ammonia, nitrate, and nitrite, are frequently found in drinking water and various types of agricultural, domestic, and industrial wastewater [1]. A significant increase in the nitrate levels of groundwater has been observed in many countries [2,3]. Nitrate is a potential human health hazard, especially to infants, causing the condition known as methemoglobinemia, also called blue baby syndrome. The US Environmental Protection Agency (US EPA) has set a maximum concentration level (MCL) of 10 mg/L of nitrate–nitrogen (NO_3–N) in drinking water. Therefore, it is necessary to remove excess nitrogen from the aquatic environment.

Several physicochemical and biological processes have been used for the removal of dissolved nitrate in drinking water and wastewater. Among these, the adsorption method has become popular since it allows for simple and economical operation and results in less sludge production [4–6]. A number of materials, including biosorbents, natural sorbents, miscellaneous adsorbents, and agricultural wastes, have been tested for the removal of nitrates from wastewater [5–13]. Afkhami et al. [5] reported the effect of acid treatment of carbon cloth on the adsorption of nitrite and nitrite ions. This study showed that acid treatment caused a significant increase in the adsorption rate of ions and the adsorption capacity of the adsorbent. Chatterjee et al. [8] or Jaafari et al. [9] reported nitrate removal from aqueous solutions by protonated cross-linked chitosan or cross-linked chitosan beads conditioned with sodium bisulfate. These results indicated that removal mechanism was to an acid–base reaction involving amino groups or due to the strong electrostatic interactions between its adsorption sites and the nitrate. Moreover, Mena-Duran et al. clarified that calcium montmorillonite activated by hydrochloric acid showed a better nitrate removal capacity, up to 22.28% [10].

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However, these methods are either time-consuming, inefficient or cumbersome. Development of simple and low-cost anion exchangers could help facilitate the practice of better and less time-consuming water treatment in the world.

Sustainable development is important in the modern world because of the concerns over many global environmental problems such as global warming and incineration of waste. For instance, concern has been raised on the use of agricultural wastes such as soybean as adsorbents for the removal of nitrate and nitrite ions from an aqueous solution. The amount of soybean waste produced per year is around 2.3 million ton, which is ~20% of the global food waste. These wastes are not recycled [14]. Yokoyama et al. [15] reported on the nitrate ion adsorption property of Ca-containing charcoal and suggested that a useful adsorbent for the adsorption of nitrate ions could be produced from waste biomass (soaking wood) treated with calcium chloride and hydrochloric acid. Moreover, our research group applied this technique to other waste biomass (i.e., coffee grounds and soybean), and found that this material can adsorb nitrate and nitrite ions from an aqueous solution in a single solution system [14,16].

However, nitrate ions and nitrite ions are usually mixed in the field rather than found in single solution systems. Moreover, Yokoyama et al. [15] did not investigate the adsorption capability of waste biomass (soybean) for nitrate and nitrite ions in complex solution systems. Therefore, the adsorption capacities of nitrate and nitrite ions onto treated waste biomass (soybean) need to be studied. The object of this study is to investigate the adsorption behavior of nitrate and nitrite ions onto carbonaceous material produced from soybean in a binary solution system. The effects of temperature, contact time, initial concentration, and chloride ion on the adsorption kinetics of nitrate and nitrite ions were investigated.

Materials and methods

Materials

Soybean (virgin SB) was purchased from Akamatsushubyou Co., Ltd. (Japan). The solutions of nitrate ions, nitrite ions, and chloride ions were prepared using potassium nitrate, sodium nitrite, and potassium chloride, respectively (Wako Pure Chemical Industries, Co., Ltd., Japan).

Carbonaceous material produced from soybean

Carbonaceous material was produced according to the method reported by Yokoyama et al. [15]. Virgin SB (40 g) was added to 1 mol/L calcium chloride solution (500 mL, Wako Pure Chemical Industries, Co., Ltd., Japan) and stirred for 24 h at room temperature. The suspensions were filtered using a 0.45 μm membrane filter (Advantec MFS, Inc., Japan) and then the SB residues were dried for 5 h at 110 °C. The SB samples (SBs) were then carbonized in a muffle furnace by heating for 2 h at 400, 600, 800, or 1000 °C under a nitrogen gas flow. Following carbonization, they were decomposed by hydrochloric acid treatment, in which the carbonized SB samples were added to 6 mol/L hydrochloric acid solution (100 mL). The suspensions were filtered and subsequently dried for 5 h at 110 °C to obtain the samples, which are hereafter referred to as SB400, SB600, SB800, and SB1000, respectively, where the numeral indicates the carbonization temperature. The surface functional groups were measured by the titration method [17]. The pH of the solution was measured by JIS K 1474.

Adsorption isotherms of nitrate and nitrite ions

SBs (0.05 g, virgin SB, SB400, SB600, SB800, and SB1000) were added to the binary solution (nitrate and nitrite ions) at different initial concentrations (50 mL). The suspensions were shaken at 25 °C for 24 h at 100 rpm, and then filtered using a 0.45 μm membrane filter. The concentrations of nitrate, nitrite, and chloride ions were measured using an ion chromatograph (Fig. 1, Prominence HIC-NS, Shimadzu, Japan). The measurement was performed using the following: column: Shim-pack IC-A3 (Shimadzu, Japan); mobile phase: 8.0 mmol/L *p*-hydroxylbenzoic acid, 3.2 mmol/L bis–tris, and 50 mmol/L boric acid (1:1:1); flow rate: 1.2 mL/min; temperature: 40 °C; detector: CDD-6A conductivity detector (Shimadzu, Japan); and sample volume 50 μL. The ion concentrations were calculated using Eq. (1) :

$$q = (C_0 - C_e)\frac{V}{W} \quad (1)$$

where q is the amount adsorbed (mg/g), C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the solvent volume (L), and W is the weight of the SB sample (g). Moreover, the pH of the solution was measured by a digital pH meter (Mettler-Toledo International Inc., Japan).

Effect of temperature on the adsorption of nitrate and nitrite ions

SB600 (0.05 g) was added to the binary solution (nitrate and nitrite ions) at different initial concentrations (50 mL). The suspensions were shaken at 5 °C or 45 °C for 24 h at 100 rpm, and then filtered using a 0.45 μm membrane filter. The concentrations of nitrate and nitrite ions were measured using an ion chromatograph. The amounts adsorbed were calculated using Eq. (1).

Effect of contact time on the adsorption of nitrate and nitrite ions

Moreover, SB600 (0.05 g) was added to 50 mL of binary solution (nitrate and nitrite ions) at 50 mg/L. The samples were collected at elapsed time intervals. Subsequently, the suspensions were filtered using a 0.45 μm membrane filter. The concentrations of nitrate and nitrite ions were measured using an ion chromatograph. The amounts adsorbed were calculated using Eq. (1).

Effect of chloride ions on the adsorption of nitrate and nitrite ions

The chloride ions solution (10 mg/L) was added to the binary solution (nitrate and nitrite ions) at 50 mg/L. SB600 was added to the prepared solution. The suspensions were shaken at 25 °C for

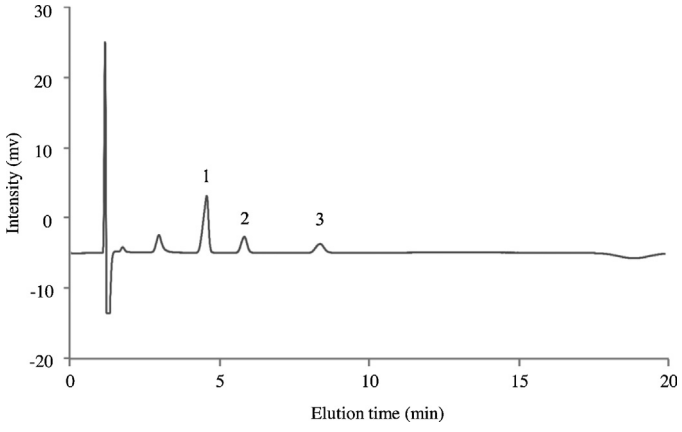

Fig. 1. Chromatograph of anions.