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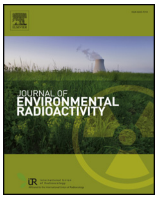

Dried powder of corn stalk as a potential biosorbent for the removal of iodate from aqueous solution

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ABSTRACT

Removal of IO_3^- from environmental samples with low-cost methods and materials is very useful approach for especially large-scale applications. Corn stalk is highly abundant agriculture residual, which is employed as useful biosorbent in many studies. In the present work, dried powder of corn stalk is applied for the removal of IO_3^- under various conditions. The results indicate that the K_d is 49.73 ml g^{-1} under general conditions ($m/V = 8\,g\,L^{-1}$, $t = 5$ day, equilibrium pH = 7 ± 0.3, $T = 298$ K and $C_0 = 15\,mg\,L^{-1}$). The sorption kinetics follows the pseudo-second-order equation, and the isotherm is well described by the Langmuir model. The sorption reaction was non-spontaneous and endothermic. Hydroxyl and carbonyl groups of the corn stalk contribute to IO_3^- sorption by ion-exchange, electrostatic attraction and redox reactions. Spectroscopic analyses and the effect of equilibrium pH prove that corn stalk was not only removed IO_3^- from aqueous solution but also reduced IO_3^- into I_2 and I^-. These results demonstrate that corn stalk is a promising biosorbent for the environmental remediation of radioactive iodine pollution.

1. Introduction

Radioactive iodine isotopes (radioiodine), originated from the atomic energy and nuclear medicine industries, cause a serious hazard to human health as their high toxicity and mobility in environment. Approximately 80–150 mg of iodine is required per day for synthesis of various thyroid hormones and optimum health. Consequently, when radioiodine is taken up by the body, it will be concentrated in the thyroid and potentially induce cancer and other serious illnesses (Radiation Protection, 2018; Atkins et al., 1990). The speciation of iodine determines its migration and sorption behaviors. Elemental iodine in its diatomic form (I_2) is not particularly soluble in water; however, iodine is able to form more soluble anion species including iodate (IO_3^-) and iodide (I^-) (Kulyukhin et al., 2007). A number of valuable studies exist on the migration and sorption behaviors of I^-. However, there are surprisingly few studies on IO_3^- (Lin et al., 2015). Iodate is an important by-product of industrial disinfection, and it is irritant to eyes, mucosa, skin and upper respiratory tracts (Silva et al., 2008). Radioactive iodine from nuclear facilities can be present as IO_3^- in the wastewater (Lin et al., 2015). Therefore, from the perspectives of public health and environmental protection, removing IO_3^- from aqueous solutions is of significant importance.

Various processes have been developed to remove IO_3^- from wastewater, including (i) sorption both in batch and column operations, (ii) coagulation, electrocoagulation and flocculation, (iii) ion-exchange and membrane filtration (Lin et al., 2015). Among these methods, sorption has proved to be a promising technique for treatment processes because of its convenient operation, low cost, low energy consumption, minimal pollution and extensive sources. A wide range of materials has been used to adsorb IO_3^-, such as hydrotalcite (Toraishi et al., 2002), hydrous γ-Al_2O_3 (Szczepaniak and Koscielna, 2002), activated carbon (Mahmudov and Huang, 2011), CeO_2/SiO_2 (Lin et al., 2017), layered double hydroxide (Theiss et al., 2017),organic, loam, sand (Vidal et al., 2009), hematite, humic acid, corundum, quartz sand (Muramatsu et al., 1990) and sterilized soil (Evans and Hammad, 1995). However, corn stalk has been seldom applied to IO_3^- sorption.

Biosorption process using a biomaterial has three important advantages: 1) this process is carried out using natural waste materials, which does not require any material synthesis. 2) biosorption is a generally more eco-friendly and low-cost method since the process does not require chemical synthesis. 3) biosorption has advantage of being of simple, easy to operate and handle as well as being a sludge-free process (Yi et al., 2016).

The most important evaluation parameters of adsorbents are selectivity and capacity of sorption. The type of functional group essentially affects the selectivity of the adsorbent (Chen et al., 2014a). Agricultural residue with abundant cellulose is a well-known low-cost adsorbent of toxic pollutants. Corn is widely cultivated as a major food

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Fig. 1. Dried corn stalk (a); dried powder of corn stalk (b).

crop in China. Therefore, a large number of corn stalk is co-generated as an agriculture residual with the grain each year. It is estimated that approximated 47,097 million tons of corn stalk are generated each year in China (Chen et al., 2014b). Corn stalk is made up of a cortex and a core. The cortex is comprised mostly of cellulose and lignin; the corn stalk pith is comprised mostly of hemi-cellulose (Cao et al., 2017). At present, most of the corn stalk residual is not adequately used. Burning of corn stalk residual in the farmland is a usual disposal exercise of crop waste and land preparation in China, which releases a mass of pollutions into the environment and causes severe environmental problems (Zhang et al., 2013). For the sake of abundant availability, corn stalk residual can be used as a biosorbent for the treatment of polluted wastewater. Wang et al. used modified corn residue to remove phosphate and nitrate from aqueous solutions. The maximum sorption capacities were 40.48 and 80.84 mg g^{-1}, respectively (Wang et al., 2007a, 2008). Hasan et al. investigated the removal of Cr(VI) from aqueous solution by agricultural waste 'maize bran'. The maximum sorption capacity was 312.52 mg g^{-1} (Hasan et al., 2008). Therefore, it is novel to treat corn stalk as adsorbent for IO_3^- removal by sorption.

In this study, dried powder of corn stalk was used to remove IO_3^- from aqueous solutions by a batch method. Non-living biomass has many advantageous over living biomass, because non-living organism can endure toxic wastes, require no nutrient supply and be easily regenerated (Abbaszadeh et al., 2016). Additionally, dead biomass normally accumulates more pollutants than living organisms in a shorter time (Tang et al., 2011). The characterization of corn stalk was measured by Brunauer-Emmett-Teller (BET), scanning electron microscopy and energy dispersive spectrometer (SEM-EDS), Fourier transform infrared spectrometer (FTIR) and X-ray photoelectron spectroscopy (XPS). The effect of the experimental parameters such as equilibrium pH, contact time, initial concentration, temperature and coexisting anions were studied. The sorption process was analyzed using various kinetic and isotherm models. To our knowledge, this is the first characterization of IO_3^- sorption by corn stalk, which might have implications for the environmental remediation of radioactive iodine pollution.

2. Materials and methods

2.1. Reagent and characterization

All of the chemical reagents used in this experiment were analytically pure and purchased from Beijing Chemical Factory, Beijing, China.

The specific surface area and the pore size distribution of dried powder of corn stalk was determined from the conventional analysis of nitrogen adsorption-desorption isotherms measured at 77K using automated surface area and pore size analyzer (TriStar II3020, Georgia, The United States). The surface morphology, energy dispersive spectroscopy and elemental mapping of the biosorbent were analyzed by a field emission scanning electron microscope with a SDD (Model S4800 Hitachi, Tokyo, Japan). The chemical composition and surface state of the biosorbent were determined by Fourier transform infrared spectra in the range of 400–4000 cm^{-1} (IRPrestige-21, Tokyo, Japan) and X-ray photoelectron spectroscopy at 0–1200 eV using Al K_α radiation (Escalab 250xi, Massachusetts, The United States).

2.2. Biomass preparation

The corn stalk used in the present investigation was collected in autumn 2016 from Xingtai, Hebei province, China. The corn stalk was washed repeatedly with deionized water to remove extraneous materials and salts. The cleaned corn stalk was dried in an oven at 60 °C until no variation in the sample weight observed, then crushed to powder by a mortar. The particles, with diameters between 125 and 187.5 μm, were placed in a desiccator to use in the sorption experiments. The dried corn stalk and dried powder of corn stalk are shown in Fig. 1.

2.3. Batch sorption experiment

The IO_3^- sorption of dried powder of corn stalk was investigated under various conditions: equilibrium pH (5–11), contact time (0.25–8 d), initial concentration (5–120 mg L^{-1}), temperature (293–323 K) and coexisting ions (Cl^- and SO_4^{2-}, 0.1, 0.01, 0.001 mol L^{-1}). The pH of the solution was monitored by adding 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH solution as required. Necessary amount of the biosorbent was mixed with IO_3^- solution in a plastic centrifuge tube, and then the mixed samples were shaken for a desired contact time in an thermostatic shaker at 150 rpm. The suspension was separated by centrifuge at 5000 rpm for 30 min. The supernatant was collected and passed through an ultrafiltration membrane (0.45 μm) for the concentration measurement. The IO_3^- concentration was measured by UV-vis spectrophotometry (UV2900, Shanghai, China). In the acid medium (pH = 1.4–3.4), IO_3^- reacts with I^- as follow: $8I^- + IO_3^- + 6H^+ \leftrightharpoons 3\ I_3^- + 3H_2O$. The I_3^- has a characteristic ultraviolet adsorption peak at 350 nm, while I_2, IO_3^- and I^- have no ultraviolet adsorption above 300 nm. The IO_3^- concentration can be calculated according to the amount of I_3^- and their stoichiometric coefficients (Liu et al., 2003). All the sorption experiments were carried out in triplicate. The distribution constant (K_d, ml g^{-1}) was calculated by Eq. (1) (Meng et al., 2017):

$$K_d = \frac{(C_0 - C_e) \times V}{m \times C_e} \tag{1}$$

where C_0 is the initial IO_3^- concentration in the solution (mg L^{-1}), C_e is the residual IO_3^- concentration in the supernatant at equilibrium (mg L^{-1}), V is the volume of solution (L), and m is the mass of the biosorbent (g).