Chemical Engineering Journal 320 (2017) 222–231

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Adsorption of radioactive iodine and krypton from off-gas stream using continuous flow adsorption column

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HIGHLIGHTS

- Sorption of radioactive iodine and krypton on C@ETS-10 sorbent using continuous column.
- Multicomponent experiments were performed to investigate sorption capacity of the sorbent for iodine and krypton.
- Sorption of iodine on sorbent was confirmed by EDS and XPS spectra.
- Langmuir and Freundlich models were fitted for iodine and krypton contaminants.
- C@ETS-10 was found to be remarkable sorbent for adsorption of iodine and krypton from the gas stream.

ARTICLE INFO

Article history:
Received 9 December 2016
Received in revised form 7 March 2017
Accepted 7 March 2017
Available online 10 March 2017

Keywords:
Adsorption
C@ETS-10 porous sorbent
Capacity of sorbent
Iodine
Krypton
Continuous flow
Off-gas stream

ABSTRACT

A novel Engelhard Titanosilicate – 10 (ETS-10) supported 10 wt% hollow carbon nano-polyhedron (10 wt % C@ETS-10) sorbent developed in our laboratory was investigated for adsorption of the radioactive iodine and krypton from off-gas stream using a continuous flow adsorption column. Adsorption experiments were performed to determine the capacity of 10 wt% C@ETS-10 sorbent for iodine and krypton in multicomponent mixture system by varying operating parameters, such as inlet concentration of iodine (I_2) and krypton (Kr), and adsorption column temperature. Pristine and used sorbents were characterized by scanning electron microscopy-energy dispersion spectroscopy (SEM-EDS), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy to identify the morphology, elemental and vibration analysis of the sorbent before and after the experiments. EDS and XPS spectra of the used samples clearly indicate the presence of iodine on the sorbent. Multicomponent sorption capacities of I_2 and Kr of 10 wt% C@ETS-10 sorbent calculated from the breakthrough curves at 20 °C at 25 ppm I_2 and 70 ppm Kr balanced with nitrogen were found to be 41.5 and 0.0323 mg g^{-1}, respectively. Sorption data was found to be best fitted by the Langmuir as well as Freundlich isotherm model. Experimental data were analyzed by Thomas, Yoon-Nelson, and Bohart-Adams sorption kinetics models to predict the breakthrough curves and calculate the characteristic parameters of the column that are useful for process design for the multicomponent system. Results show that 10 wt% C@ETS-10 sorbent has potential sorbent for adsorption of multicomponent (I_2 and Kr) from off-gas stream.

1. Introduction

During the aqueous reprocessing of used nuclear fuel (UNF) several radioactive volatile compounds, such as ^{129}I, ^{85}Kr, ^{3}H, ^{14}C, and Xe are released into the atmosphere via the process off-gas stream [1]. ^{129}I is a primary concern for removal due to its high mobility, and when released into the environment it can collect in 'hot spots' in the earth's atmosphere [2]. It has a long half-life of 1.52×10^7 years and a tendency to bioaccumulate, concentrating in the thyroid glands and affecting metabolism in humans [3,4]. ^{85}Kr is a chemically inert radioisotope with a half-life of 10.7 years. The emission of ^{85}Kr has been neglected in the past; however, it has accumulated in the atmosphere with the concentration increasing

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http://dx.doi.org/10.1016/j.cej.2017.03.020
1385-8947/

from 0.1 Bq m^{-3} in 1959 to 1.2 Bq m^{-3} in 2001, raising concerns about its potential impact. Thus, the EPA released new restrictions regarding its release in 1983 (40 CFR 190) [5]. Therefore, it is essential to remove these contaminants from the off-gas stream before emitted to the atmosphere.

Many studies have been reported on the removal of the radioactive contaminants from the off-gas stream. Iodox, Mercurex, and alkaline scrubbing are well-known wet processes to trap the radioactive iodine and have proven effective removal capacities [6]. However, use of these processes generates alkaline liquid and solid waste containing organic nitrates which are corrosive, and further reprocessing is needed. Currently, the separation of krypton (Kr) and xenon (Xe) is operated via cryogenic distillation, however, it is an energy intensive technique that requires low temperature and high pressure [7]. Selective removal of noble gases and iodine on porous solid sorbents is one of the alternative techniques that is powerful, inexpensive, and reliable – but the development of economical and effective sorbents for practical industrial application is a key challenge.

Numerous sorbents have been studied for the removal of single components, ^{129}I and ^{85}Kr from the reprocessing off-gas stream. Activated carbon is considered a benchmark sorbent for removal of both contaminants due to its several advantages, such as high surface area, cost-effectiveness, and availability. However, nitrogen oxides generated during aqueous reprocessing undergo explosive reactions with the carbon and it cannot be used as a sorbent for off-gas streams [8,9]. To circumvent this issue, thermally stable sorbents, such as zeolites, metal-organic frameworks (MOFs), and graphene materials have been tested [10–14]. Zeolites are porous alumina-silicate materials, of which over 40 have been discovered, making a wide range of materials available. Nevertheless, sorption capacities have typically been small in comparison with activated charcoal. Silver impregnation of zeolites has been used to increase iodine sorption by forming stable and insoluble AgI [10,11]. However, this sorbent is comparatively expensive due to use of silver metal. Zeolitec imidazolate framework-8 (ZIF-8), Hofmann-type structure $Ni^{II}(pz)[Ni^{II}(CN)4]$ (pz = pyrazine) and Cu-BTC were also reported as sorbents for the capture of iodine [3,12,13]. Graphene powder was investigated as a sorbent in static adsorption experiments The sorbent exhibited over an 85 mass% capacity for iodine at 298 K due to the high surface area of the graphene powder (1272 $m^2 g^{-1}$) [14].

MOFs have garnered considerable interest as adsorbents because of their unprecedented set of properties: high surface area, microporosity, and modular nature. Specifically, the synthetic flexibility of MOFs has been applied to the separation of Xe and Kr to reduce the overall volume of high-level waste by separating out Xe, which has a limited half-life [7,15–19]. An exemplary study of MOFs was carried out by Liu et al. by performing Kr and Xe adsorption studies on two MOFs, HKUST-1 and Ni/DOBDC, which exhibited sorption capacities comparable to, and Xe/Kr selectivity higher than activated carbon at 1 bar and 25 °C [15]. The effect of silver deposition in a later study on Ni/DOBDC showed an enhanced sorption capacity (thus selectivity) of Xe, increasing capacity 15% [7]. Though MOFs such as these present an exciting development in the field of adsorption, their synthesis remains expensive and complex.

As the date of this article, the study of combined iodine and krypton sorption in an adsorption column has not been reported. Our previous research on the removal of single component iodine and krypton from a continuous stream on hollow carbon nanopolyhedrons (C) supported on Engelhard Titanosilicate – 10 (ETS-10), C@ETS-10, and studied the effect of carbon loading, empty bed contact time, and temperature of single component sorption to find optimal conditions, and demonstrated that it is a remarkable porous solid sorbent for capture of single species i.e. iodine and krypton at ambient temperature and low partial pressures [20,21].

In the present article, we have studied the adsorption of mixtures of I_2 and Kr on 10 wt% C@ETS-10 sorbent from off-gas streams using a continuous sorption system. Optimal conditions from single component experiments were determined to apply to multicomponent sorption. EDS and XPS spectra were used to confirm the captured contaminants on the sorbent. The capacity of the sorbent was investigated under different process variables, such as inlet concentration of contaminates, and temperature of adsorption column. Adsorption isotherm models were applied to determine the maximum sorption capacity of the sorbent for the multicomponent system. Experimental data for different inlet concentrations of I_2 and Kr sorption were fitted to three different models such as Thomas, Yoon-Nelson, and Bohart-Adams, to estimate the kinetic rate constants.

2. Methods

2.1. Synthesis of C@ETS-10 sorbent

A 10 wt% C@ETS-10 was prepared via wet-impregnation method using the two main materials: hollow carbon nanopolyhedrons (C) and Engelhard Titanosilicate-10 (ETS-10). The detailed procedure for the synthesis of 10 wt% C@ETS-10 sorbent has been described previously [20,21]. The synthesis of the two components of the sorbent is based on the techniques reported in literature [22,23].

2.2. Continuous sorption experiments

Fig. 1 shows the schematic diagram of apparatus that was designed to carry out the experiments. Several parts of the system such as gas flow lines, jacketed adsorption column (1″ I.D. and 12″ height) and jacketed iodine vaporizer (25 mL) were made of Pyrex glass to avoid adsorption of iodine on metal surfaces and corrosion. For each adsorption experiment, 3 g elemental iodine (Fisher Scientific, USA) was packed into the jacketed iodine vaporizer where Kr balanced with nitrogen (1000 ppm, Airgas, USA) was introduced from the gas cylinder using a digital mass flow controller (MFC, Aalborg, USA) and flowed through to carry the iodine vapor. The concentration of iodine and krypton in the combined flow was adjusted by controlling the temperature (35–45 °C) of the iodine vaporizer by circulating heated water through the glass jacket, and the flow of nitrogen balanced krypton (10–30 mL min^{-1}). The resulting stream containing iodine and krypton in nitrogen was mixed with another stream of nitrogen gas to yield a total flow rate of 180 mL min^{-1}. The final resulting gas contained iodine and krypton at concentrations of 15–50 ± 3 and 70–150 ± 5 ppm, respectively, was then passed through the adsorption column.

The 10 wt% C@ETS-10 sorbent was preheated into the oven for 1 h at 120 °C to release any adsorbed moisture and impurities. Approximately 2.5 g of 10 wt% C@ETS-10 sorbent was packed into the adsorption column, forming a 1.5 cm high packed bed in the column. The temperature of the adsorption column was varied using a temperature controlled water bath circulated through the jacket surrounding the column. The removal efficiency of the prepared sorbent was calculated by analyzing the inlet and outlet concentrations of streams over time. Iodine analysis was performed by trapping iodine in de-ionized water by passing the gas streams through bubblers (bubbler-1 for inlet and bubbler-2 for the outlet), followed by the analysis of the iodine trap water by the Leuco Crystal Violet (LCV) method using a Thermo Scientific Evolution 60S UV–Visible Spectrophotometer [24]. Outlet samples were collected for krypton analysis after trapping iodine in de-ionized water and