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

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ABSTRACT

A novel Engelhard titanosilicate - 10 (ETS-10) supported 10 wt% hollow carbon nanopolyhedron (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 (I₂) 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 I₂ and Kr of 10 wt% C@ETS-10 sorbent calculated from the breakthrough curves at 20°C at 25 ppm I₂ 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.

Keywords: Adsorption, C@ETS-10 porous sorbent, capacity of sorbent, iodine, krypton, continuous flow, off-gas stream

1. Introduction

During the aqueous reprocessing of used nuclear fuel (UNF) several radioactive volatile compounds, such as ^{129}I , ^{85}Kr , 3H , ^{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 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. Zeolite imidazolate framework-8 (ZIF-8), Hofmann-type structure $\text{Ni}^{\text{II}}(\text{pz})[\text{Ni}^{\text{II}}(\text{CN})_4]$ (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 ($1272 \text{ m}^2 \text{ g}^{-1}$) [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 nano-polyhedrons (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 I₂ 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 contaminants, 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 I₂ 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 nano-polyhedrons (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 drying the gas with a moisture trap. The outlet sample was analyzed in a Clarus SQ 8T GC/MS (PerkinElmer) using Restek Crossbond 5% diphenyl/ 95% dimethyl polysiloxane (60 m long and 0.25 mm ID) column kept at 80°C with a 15 min elution time. Helium was used as a carrier gas at a flow rate of 1.0 mL min⁻¹.

The following equation was used to determine the I₂ and Kr sorption capacities of the sorbent.

$$q = \int_0^V \frac{(C_0 - C_e)}{M} dV \quad (1)$$

where q is the adsorption capacity of sorbent (mg kg⁻¹); C_0 (mg L⁻¹) and C_e (mg L⁻¹) are the inlet and outlet concentrations of multi-contaminant in gas stream, respectively; V is the total volume processed at breakthrough (L), and M is the mass of sorbent (g).

2.3 Characterization techniques

The surface morphology and chemical elements of samples were obtained using LEO SUPRA 35VP, SEM-EDS. Raman spectra of samples were measured using a WITec alpha300 Raman microscope (Ulm, Germany) with excitation at 532 nm. Photoelectron spectroscopic analysis of the pristine and used C@ETS-10 was performed in a custom built ultra-high vacuum (UHV) chamber with a base pressure of 1.5x10⁻¹⁰ Torr. The chamber is equipped with an Omicron model EA 125 hemispherical electron energy analyzer, a dual anode X-ray source, and a He UV lamp. Both the X-ray source and the UV lamp are at the so-called magic angle of 54.7 ° relative to the axis of the electron analyzer. The Mg K α emission line (1253.6 eV) was used for all XPS data acquisition.

3. Results and discussion

3.1 Characterization of pristine and used sorbents

Surface morphology of 10 wt% C@ETS-10 sorbent before and after sorption is shown in Fig. 2. The morphology of the used sample showed globular deposits not present on the fresh

sample, which may be adsorbed iodine. No differences were noticed between the morphology of the single (I_2) contaminant [21], and multicontaminant (I_2 & Kr) adsorbed samples. The presence of I_2 on the sorbent was confirmed by EDS analysis. The spectrum of the unused sorbent was collected with expected constituents such as Ti, Si, Na, K, Cl, C and O, consistent with the sorbent composition. Identical spectra were recorded with the used sorbent, and iodine abundance was noticed in the sample at 3.9 keV, indicating that iodine was present on the surface of the sorbent at about 3.4 wt%. However, krypton presence cannot be detected in the EDS spectra, indicating a limitation of EDS to detect small amounts of krypton molecules on the C@ETS-10 sample (Fig. 3).

Displayed in Fig. 4 are survey XPS spectra of pristine and used C@ETS-10. As expected, core level states corresponding to the Si 2p (103.3 eV) and Si 2s (157.2 eV), C 1s (284.6 eV), and O 1s (532.6 eV) are observed in the spectra for both samples [25]. Iodine 3p_{1/2} and 3p_{3/2} core level states at 931.2 eV and 876.4 eV, respectively, are observed for the used C@ETS-10 sample. Also observed in the used C@ETS-10 spectrum are the Ti 2p_{3/2} (458.4 eV) and the Na 1s (1072 eV) core level states, which is due to using a crushed pellet of used C@ETS-10, thereby exposing Ti and Na in the ETS-10. The I 3d_{3/2} and 3d_{5/2} core level states for the used C@ETS-10 consist of doublets. The low binding energy shoulders of the I 3d_{3/2} and 3d_{5/2} core level states at ~619 eV and ~631 eV, respectively, of the used C@ETS-10, correspond to I_3^- [26]. The higher binding energy shoulders at ~622.5 eV and ~634.5 eV are typically assigned to I 3d shakeup satellite peaks [26], but their intensities are too strong to be shakeup peaks and have lower binding energies than observed for I doped TiO₂ [27]. Tentatively we have assigned these to core level states to a yet to be identified as either an I-C or I-C-O complex [28]. No evidence of Kr

was observed in the used sample i.e. no evidence of Kr capture, possibly due to the release of adsorbed Kr molecules from the sorbent when exposed to the atmosphere.

Fig. 5 displays the Raman spectra of the pristine and experimentally used sorbent. The pristine C@ETS-10 sample showed an intense peak for ETS-10 at 723 cm^{-1} , due to the stretching vibration of Ti-O-Ti of the TiO_6 structural group [29]. The weak band observed in the range of $300 - 400\text{ cm}^{-1}$, may be attributed to bending vibration of Si-O-Si and Ti-O-Ti fragments [30]. Three major carbon peaks were observed in the sample for D-band (1332 cm^{-1}), G-band (1579 cm^{-1}), and 2D (2690 cm^{-1}) [31]. The original sample of carbon nanoparticles presents the peak of D-band was more intense than G-band and 2D, indicating a long-range disorder in the carbon nanomaterial [20]. The spectra of iodine and krypton adsorbed/used sample were completely different than the pristine sample. Only a small peak of ETS-10 was observed. Other peaks of ETS-10 and carbon were reduced/disappeared due to adsorption of iodine and krypton on the sorbent. No other evidence was found in the used sample related to sorption of iodine and krypton.

3.2 *Effect of inlet concentration of contaminants (I_2 and Kr)*

The effect of inlet concentration of I_2 (15 – 50 ppm) on iodine sorption capacity of 10 wt% C@ETS-10 sorbent was studied at 20°C while maintaining the Kr inlet concentration constant at 70 ppm during the operation. The outlet concentration of I_2 was plotted against time as a breakthrough curve (Fig. 6). In a continuous adsorption column, the maximum adsorption takes place at the initial period of the experiment. As the duration of the experiment progresses, the sorbent saturates until equilibrium is reached between the adsorbed and gaseous phases and the outlet concentration is equal to the inlet concentration. The obtained curve (S-shape) is called a breakthrough curve. The capacity of the sorbent was calculated from integrating the area above

the breakthrough curve using equation 1. It was seen from Fig. 6, the breakthrough time was decreased with increase in inlet concentration iodine and the iodine sorption capacity of sorbent increased. The increase in sorption capacity is expected, as an increase in the inlet concentration drives more iodine into the adsorbed phase and follows Henry's Law. The decrease in breakthrough time may be explained by an increase in the mass transfer driving force from the bulk gas to the sorbent surface. The minimum and maximum capacities of sorbent were found to be 39 and 49 mg g⁻¹ at 15 and 50 I₂ concentration, respectively.

Iodine sorption capacity of 10 wt% C@ETS-10 sorbent was also examined by varying krypton concentration from 70 to 150 ppm, keeping 25 ppm I₂ inlet concentration constant during the experiments at 20°C (column temperature). Increasing the krypton inlet concentration from 70 to 150 ppm was shown to decrease the iodine sorption capacity from 41.5 to 34.8 mg g⁻¹ (graphs are not shown). This decrease in iodine capacity of the sorbent with added krypton in the inlet stream may be due to a competition of the iodine and krypton for active sites on the surface of the sorbent. However, affinity of the sorbent for krypton is much lower than that of iodine, the inhibitive effect on the sorption capacity for iodine is limited.

Fig. 7 shows the breakthrough curves for the Kr sorption capacity of 10 wt% C@ETS-10 sorbent at different inlet concentration of Kr (70-150 ppm; I₂ concentration – 25 ppm constant in gas stream). It was observed that the capacity of the sorbent was elevated with an increase in inlet concentration of Kr. 0.0323 and 0.0617 mg g⁻¹ Kr adsorption capacities of sorbent were found at 70 and 150 ppm, respectively. The breakthrough of krypton occurred quickly in the initial period (20 min) of the multicomponent experiments, while iodine breakthrough took around 60 - 70 h. The breakthrough curves from Fig. 6 & 7 clearly shows that both the contaminants were adsorbed on 10 wt% C@ETS-10 sorbent at 20°C column temperature.

3.3 *Effect of temperature on sorption of I₂ and Kr*

The effect of adsorption column temperatures (20 – 60°C) on the adsorption of I₂ and Kr were studied using 10 wt% C@ETS-10 sorbent with the inlet gas stream containing 25 I₂ and 70 ppm Kr. Fig. 8a & b show the breakthrough curves of multicomponent (I₂ and Kr) sorption with the column temperature varied. The capacity of the sorbent decreased with an increase in column temperatures, as expected from the exothermic nature of adsorption. Sorbent capacities reduced from 41.5 to 27.9 mg g⁻¹ for iodine and 0.0323 to 0.0245 mg g⁻¹ for krypton from 20 to 60°C.

Table 1 compares the krypton sorption capacities of some MOFs, zeolites, and carbon materials at different conditions to benchmark the results found in this work. The first three entries in Table 1 show results from the study carried out by Liu et al., and show that the MOFs Ni/DOBDC and HKUST-1 possess krypton sorption capacities comparable to activated carbon under pure gas conditions [15]. Multicomponent gas adsorption (40 ppm Kr and 400 ppm Xe balanced with air) on Ni/DOBDC at 298 K yielded a krypton sorption capacity of 0.0055 mg g⁻¹. Comparison shows that 10 wt% C@ETS-10 is comparable to Ni/DOBDC. The suitability of C@ETS-10 for krypton sorption is further supported by the study performed by Greenhalgh et al. of hydrogen activated mordenite (H-mordenite), a zeolitic sorbent shown to have a high capacity for krypton [32]. H-mordenite exhibited quite a good capacity for krypton when sorption was performed with a 150 ppm krypton stream balanced with helium of 8.40 mg g⁻¹, but capacity dropped by two orders of magnitude when the stream was modified to include 79% nitrogen to about one half the capacity of 10 wt% C@ETS-10 under similar conditions. Though the removal properties of individual sorbents are difficult to compare, as the literature studies lack uniform conditions, the previous comparisons clearly indicate that 10 wt% C@ETS-10 is a viable sorbent for the removal of krypton and iodine from off-gas streams.

3.4 Adsorption isotherms

To determine the isotherm equilibrium of the multicomponent system, experiments were performed holding the concentration of each contaminant constant while varying the concentration of the other. Each experiment was conducted at 20°C. Because the krypton reaches equilibrium within 30 minutes of the experiment initiation and occupies much less of the sorbent than iodine, it is reasonable to assume that iodine and krypton sorption in the multicomponent system is similar to that of the single component system. Therefore, the two well-known single component adsorption isotherm models such as Langmuir and Freundlich can be used to calculate the maximum sorption capacity of the sorbent. Sorption capacities of the sorbent were determined separately for both the contaminants. The mathematical forms of these models can be expressed as follows [35, 36]:

$$\text{Langmuir: } q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

$$\text{Freundlich: } q_e = K_F C_e^{1/n} \quad (3)$$

where q_e and C_e are the amount of contaminant on sorbent at equilibrium and equilibrium concentration of species in the gas stream (mg g⁻¹) respectively; K_L and Q_m are the Langmuir constant and maximum sorption capacity, respectively; K_F and n Freundlich model parameters which represent the capacity of sorbent and intensity of adsorption, respectively.

Table 2 shows isotherm constants obtained for I₂ and Kr at 20°C. The experimental data for multicontaminant (I₂ & Kr) adsorption were fitted to the Langmuir isotherm, yielding large correlation coefficients (< 0.953). The maximum I₂ and Kr sorption capacities (Q_m) of sorbent were found to be 57.77 and 0.2933 mg g⁻¹ from the Langmuir isotherm at 20°C. The iodine and krypton experimental data also fitted the Freundlich isotherm with R² value > 0.9925 (Appendix

A - S1). It is clear that both Langmuir and Freundlich models approximately describe the adsorption isotherm of I₂ and Kr in the concentration range used experimentally.

3.5 Kinetic modelling of breakthrough data

Kinetic models for the adsorption of mixtures of I₂ and Kr were studied using different inlet concentrations of the contaminants. Three well-known models – Thomas, Yoon-Nelson, and Adams-Bohart models – were applied to predict the breakthrough curves and determine the characteristic parameters of the column that would be useful for process design of the continuous column [37]. As the gas phase concentrations of the contaminants are quite low (ppm range), it was assumed that models could be applied to each component separately, reducing the complexity of the system.

3.5.1 Thomas model

This model is widely used as a kinetic model to predict the performance of the continuous adsorption operation. It assumes that sorption of gases is not limited by chemical interaction but by the mass transfer at the interface. The linear expression is given by the following equation [38]:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{q_0 k_{TH} M}{Q} - k_{TH} C_0 t \quad (4)$$

where C_0 and C_t are the inlet and outlet concentration of contaminant (mg L⁻¹); Q is the flow rate of gas (mL min⁻¹); t is the total gas flow time (h); k_{TH} is the Thomas kinetic coefficient (L h⁻¹ mg⁻¹); M and q_0 are the mass of sorbent (g) and adsorption capacity of operation (mg g⁻¹). The values of k_{TH} and q_0 were calculated using the slope and intercept obtained from the linear plot of $\ln(C_0/C_t - 1)$ versus t , and are shown in Table 3. It was observed that correlation coefficient (R^2) values were higher than 0.92 for multicomponent, indicating Thomas model well fitted with the breakthrough experimental data. The values of rate constants (k_{TH}) were decreased with increase

inlet concentration of contaminants and q_0 values were increased from 37.09 to 50.76 mg g⁻¹ for I₂ and 0.0343 to 0.0551 mg g⁻¹ for Kr contaminant.

3.5.2 Yoon-Nelson model

Yoon-Nelson model was also applied to quantify the behaviour of the adsorption process using experimental data. The model is expressed by the following equation [39]:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}t - \tau k_{YN} \quad (5)$$

where τ is the time required for 50% adsorbate breakthrough; k_{YN} is the Yoon-Nelson rate constant (h⁻¹), these two value can be determined by plotting the graph between $\ln(C_t/(C_0 - C_t))$ against time (t) and are listed in Table 3. R² values were clearly indicates that the Yoon-Nelson model also fitted well with the experimental data.

3.5.3 Adams-Bohart model

In this model, it is assumed that rate of adsorption was proportional to the concentration of residual adsorbent. Consequently, the rate of adsorption was directly proportional to the fraction of adsorption capacity remains same on the adsorbent [40]. The behaviour of continuous adsorption column is given by the following equation:

$$\ln\left(\frac{C_t}{C_0}\right) = C_0 k_{AB}t - N_0 k_{AB}(Z/F) \quad (6)$$

where k_{AB} is the Adams-Bohart rate constant (mL mg⁻¹ min⁻¹); N_0 is the saturation concentration (mg L⁻¹); F is the linear flow rate calculated by dividing the flow rate by the cross-section area of the column; Z is the height of bed in adsorption column (cm). A plot of $\ln(C_t/C_0)$ verse t gives the unknown values of k_{AB} , N_0 and R² (Table 3). The value of k_{AB} was decreased with increase in inlet concentration of contaminants. R² values widely varied from 0.7646 - 0.9389 for I₂ and 0.8520 – 0.9887 for Kr, which were not a good fit with the experimental data (Appendix A - S3 and S4).

The correlation coefficient values of Thomas and Yoon-Nelson models are higher than the Adams-Nelson for the obtained experimental data. Thus Thomas and Yoon-Nelson models are found to be best suited to represent krypton and iodine adsorption system.

4. Conclusion

In summary, we have successfully investigated the capacity of 10 wt% C@ETS-10 sorbent for adsorption of mixture of I₂ and Kr using continuous flow adsorption system. XPS and EDS results confirm that the iodine was adsorbed on the sorbent, however, Kr peak was not detected in any spectra. Langmuir and Freundlich isotherms appropriately fitted the sorption of I₂ and Kr with high correlation coefficients. The maximum sorption capacities of sorbent were found to be 57.77 and 0.2933 mg g⁻¹ for iodine and krypton contaminants, respectively for the Langmuir isotherm. Thomas and Yoon-Nelson kinetic models were good agreement with experimental data with a large value of correlation coefficient. The results of this study indicate that C@ETS-10 sorbent has potential to be used in nuclear industrial operations for the adsorption of radioactive I₂ and Kr from the gas stream to protect the environmental pollution.

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Tables Caption

Table 1. Krypton sorbent capacities of various sorbents.

Table 2. Isotherm parameters for capture of multicomponent on 10 wt% C@ETS-10 sorbent at 20°C column temperature.

Table 3. Kinetic parameters for I₂ and Kr adsorption using continuous adsorption column at different inlet concentration of contaminants.

Figures Caption

Fig. 1. Schematic diagram of the experimental set-up for adsorption of I₂ and Kr contaminants.

Fig. 2. SEM images of 10 wt % C@ETS-10 sorbent (a) before, and (b) after I₂ and Kr sorption at 20°C.

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Fig. 4. XPS spectra of samples (a) pristine (b) used C@ETS-10 sorbent for I₂ and Kr sorption at 20°C, XPS of I 3p_{1/2}, I 3p_{3/2}, I 3d_{3/2} and I 3d_{5/2} peaks (inset).

Fig. 5. Raman spectra of (a) pristine and (b) used 10 wt% C@ETS-10 for I₂ and Kr sorption at 20°C.

Fig. 6. Breakthrough curve of iodine adsorption of different iodine concentration on 10 wt% C@ETS-10 at 20°C (Experimental conditions: Total gas flow – 180 mL min⁻¹; Kr concentration at inlet - 70 ppm; amount of sorbent – 2.5 g).

Fig. 7. Breakthrough curve of krypton adsorption of different krypton concentration on 10 wt% C@ETS-10 at 20°C (Experimental conditions: Total gas flow – 180 mL min⁻¹; I₂ concentration at inlet - 25 ppm; amount of sorbent – 2.5 g).

Fig. 8. Effect of column temperature on (a) iodine and (b) krypton adsorption from multicontaminant gas stream (Experimental conditions: Total gas flow – 180 mL min⁻¹; iodine concentration – 25 ppm; Kr Concentration - 70 ppm; carbon loading – 10 wt% C@ETS-10; amount of sorbent – 2.5 g).

Tables

Table 1. Krypton sorbent capacities of various sorbents.

Sorbent	q_{Kr} (mg g ⁻¹)	T (K)	Partial Pressure Kr (Pa)	Feed Gas Composition	Ref.
Activated Carbon ^a	2.20E+02	298	1.00E+05	Kr	Liu et al. [7]
Ni/DOBDC ^b	1.42E+02	298	1.00E+05	Kr	
HKUST-1 ^b	1.61E+02	298	1.00E+05	Kr	
Ni/DOBDC ^b	5.54E-03	298	4.05E+00	400 ppm Xe/ 40 ppm Kr/ Balance air	
HKUST-1 ^b	1.68E-01	298	1.01E+02	1000 ppm Kr/ Balance air	
H-Mordenite ^c	8.40E+00	190	1.52E+01	150 ppm Kr/ Balance He	Greenhalgh et al. [32]
	4.78E-02	190	1.52E+01	150 ppm Kr/ 79 % N ₂ / Balance He	
Molecular Sieve-5A	4.46E-02	298	9.98E+01	Kr	Kitani and Takada [33]
Molecular Sieve-13X	5.72E-02	195	1.04E+01	Kr	
Molecular Sieve-AW500	3.91E-01	195	5.42E+00	Kr	
Takeda-L ^a	1.15E+00	195	5.11E+00	Kr	
Takeda-G ^a	1.20E+00	195	7.88E+00	Kr	
Ambersorb 563 ^a	6.35E-01	273	1.57E+01	155 ppm Kr/ Balance He	Munakata [34]
Ryujou-Shirasagi G2x4/6- 3 ^a	1.05E+00	273	1.73E+01	170 ppm Kr/ Balance He	
Molsievon X2M4/6	1.27E+00	273	2.03E+01	200 ppm Kr/ Balance He	
10 wt% C@ETS-10	3.23E-02	293	7.09E+00	70 ppm Kr/ 25 ppm I ₂ / Balance N ₂	This Work
	6.17E-02	293	1.52E+01	150 ppm Kr/ 25 ppm I ₂ / Balance N ₂	

a – carbon, *b* – MOF and *c* - zeolite

Table 2. Isotherm parameters for capture of multicomponent on 10 wt% C@ETS-10 sorbent at 20°C column temperature.

Models	Constants	Species	
		Iodine	Krypton
Langmuir	Q_m (mg g ⁻¹)	57.33	0.2933
	K_L (L mg ⁻¹)	10.7	0.52
	R ²	0.9973	0.9526
Freundlich	K_F (mg g ⁻¹ ppm ⁻¹)	20.72	0.0009
	n (mg ² g ⁻¹ L ⁻¹)	4.572	1.19
	R ²	0.9925	0.9992

Table 3. Kinetic parameters for I₂ and Kr adsorption using continuous adsorption column at different inlet concentration of contaminants.

Model	Parameters	I ₂				Kr		
	Concentration (ppm)	15	25	40	50	70	100	150
Thomas	k_{TH} (L h ⁻¹ mg ⁻¹)	0.6834	0.3255	0.4703	0.3082	260.0	113.2	82.34
	q_o (mg g ⁻¹)	37.09	38.72	41.00	50.76	0.0343	0.0318	0.0551
	R ²	0.9207	0.9306	0.9345	0.9863	0.9805	0.9524	0.9749
Yoon-Nelson	k_{TH} (h ⁻¹)	0.1255	0.0850	0.1833	0.1609	64.72	39.82	43.50
	τ (h)	46.79	34.31	24.36	22.57	0.0319	0.0209	0.0242
	R ²	0.9207	0.9306	0.9345	0.9863	0.9805	0.9524	0.9749
Adams-Bohart	k_{AB} (L mg ⁻¹ h ⁻¹)	0.4067	0.1660	0.2263	0.1682	42.26	23.90	17.22
	N_o (mg L ⁻¹)	4345	5278	6173	6456	5.66	8.36	12.38
	R ²	0.8622	0.9389	0.7646	0.8522	0.9887	0.8238	0.8520

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