

# Carbon adsorbents for the uptake of radioactive iodine from contaminated water effluents: A systematic review

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## ABSTRACT

The need to remove radioactive iodine from water extends beyond the liquid radioactive waste treatment in the nuclear industry, as it can also be found in hospital wastewater and reach wastewater treatment plants. However, it remains a challenge affected by diverse iodine speciation, which includes anions and neutral forms. Recent developments in new carbon materials are offering new opportunities to capture radioactive iodine species from aqueous and gas phases. But how are they made, how feasible is their use, and how effective can they be? Do they outperform traditional carbon materials such as activated carbon?

This review, for the first time, assesses current developments in preparing adsorbents for removing iodine species, including nanocarbons. Specifically, their synthesis, properties, maximum extraction capacity, and sorption mechanisms are discussed. The most effective biomass-based carbon for iodine removal was found to be chemically activated (with KOH) sunflower hydrochar with highly developed porosity and a surface area >2000 m<sup>2</sup>/g. Its capacity achieved 6.46 g of I<sub>2</sub>/g adsorbent. A similar level of uptake was demonstrated by KOH-activated hydrochar made from cellulose diacetate. The range of nanocarbons studied for this application did not outperform biomass-activated carbons. The regeneration of adsorbents, their scalability, current gaps in understanding the mechanisms of iodine species uptake, and the need to achieve their practical application have been discussed. The purpose of the review is to extract new knowledge from relatively new carbon nanomaterials, nanocomposites as well as traditional carbon sorbents that will inform the preparation of effective sorbents for upscaled applications such as the treatment of radioactive effluents from hospitals or liquid radioactive waste produced in the nuclear fuel cycle.

## 1. Introduction

Nuclear energy provides ~10 % of global electricity, with about 440 nuclear power reactors in 32 countries. There are also research reactors (~220 across 50 countries), and a further 55 are under construction, which is equivalent to ~15 % of the existing nuclear capacity [1]. The growth in nuclear energy capacity is expected to replace energy production by coal plants. Coal plants produce ~35 % of the global electricity and emit carbon dioxide (CO<sub>2</sub>) as a major by-product, according to a report from the International Energy Agency. There is a global trend

to commit to strategies aimed at reducing carbon emissions [1] [2]. The production of electricity from nuclear energy has advantages as well as disadvantages. Main disadvantages are the need to store nuclear waste and the risk of releasing radionuclides from nuclear waste or from used nuclear fuel (off-gas) during spent fuel reprocessing. <sup>85</sup>Kr, <sup>133</sup>Xe and <sup>131</sup>I<sub>2</sub> are among the most volatile radioactive species, the latter being the most reactive one. Furthermore, radioactive iodine is especially important because of its high toxicity [3], penetration into the environment [4] and long-term impact on public health [5]. The most common of them, <sup>131</sup>I, is produced commercially and generated in large

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amounts in nuclear reactors, thus presenting a serious source of radioactive contamination.

Radioactive iodine is a by-product of uranium fission in the nuclear fuel cycle. During normal operation of nuclear plants, iodine is transferred to the Reactor Coolant System (RCS) as a metal iodide, where it is partly emitted in volatile form in the containment building [6]. Most metal iodides, except silver iodide, are easily retained in the water recirculation circuit used for core cooling, where iodine remains in the ionic form [7]. However, iodide ions ( $I^-$ ) can be thermally [8] and radiolytically [9] oxidised to volatile molecular iodine ( $I_2$ ).

The International Atomic Energy Agency (IAEA) identifies four release routes of radioactive iodine into the atmosphere. The first one is due to accidental uncontrolled leaks in the containment vessel that is used to retain radioactive material during transport. The containment vessel is the receptacle on which principal reliance is placed to retain the radioactive material during transport. The leaks can also take place via the nuclear venting system. The third path is due to the penetration of iodine into reinforced concrete in the reactor building. The fourth pathway is via a bypass release of gas following an accident [7]. The main radioactive iodine isotopes in the nuclear industry are  $^{129}I$  and  $^{131}I$ . Both are harmful and have very different half-lives ( $t_{1/2}$ ): 8.04 days for  $^{131}I$  and  $1.57 \times 10^7$  years for  $^{129}I$ . Other main iodine radioisotopes are short-lived; they form in the nuclear reactor fuel and can be released during accidents; these are  $^{132}I$  (2.3 h),  $^{133}I$  (20.8 h),  $^{134}I$  (0.9 h) and  $^{135}I$  (6.6 h), with half-lives indicated in brackets. The nuclear waste from nuclear energy production is highly controlled globally by governmental agencies; it commonly contains iodine radioisotopes [10].

Besides emissions from the nuclear industry, radioactive iodine can migrate to the environment from low-level radioactive waste from hospitals. Radioactive iodine (specifically the isotopes  $^{124}I$  and  $^{131}I$ ) is widely used in diagnosis, research, and medical treatment of cancer of the thyroid gland [11,12]. In the case of thyroid cancer treatment, a dose of 4.14 GBq of  $^{131}I$  is required, and for hyperthyroidism, 414 MBq are administered per treatment [13]. In a study where urine samples from 244 patients with hyperthyroidism and 23 thyroid cancer patients were collected, the estimated direct activity discharged to the sewage for both thyroid cancer and hyperthyroidism treatment was 14.57 GBq and 1.27 GBq, respectively, per week. The treatment of 79 thyroid cancer cases and 187 hyperthyroidism cases throughout the year 2009, generated radioactivity between 2 and 15 GBq in liquid waste [14]. Hospitals are estimated to produce daily ~400–1200 L wastewater per bed in developed countries and ~200–400 L, in developing countries [15]. Some of these effluents can be contaminated with radioactive iodine from thyroid treatment or radiographic iodinated contrast media. Beyond the hospital premises, patients go home after radiotherapy, which risks unwanted radioisotopes to be released and reach municipal wastewater treatment plants. Unlike in facilities designed to work with radioactive effluents, hospital waste is not controlled in many regions of the world. In contrast, there are stringent regulations in the European Union, US and UK [16]. To avoid the release of radioactive iodine into the environment, there is a need to remove it from wastewater. Low-cost materials, such as modified bentonite, could be part of the solution for removing iodine from radioactive effluents [17]. The tertiary treatment in hospitals and nuclear facilities includes adsorption in activated carbon columns. Indeed, functionalised activated carbons are considered a suitable option for the removal of uranium (VI) from radioactive wastewater [18]. A recent review assessed porous organic frameworks, specifically Covalent Organic Frameworks (COFs), Porous Organic Polymers (POPs), and Porous Organic Cages (POCs) for the removal of  $I_2$  [19]. Nevertheless, a broader range of materials that can efficiently capture the wider family of radioactive iodine species, including anions, from aqueous effluents is needed. These could be used as tertiary treatment media and, therefore, be scalable as required for particular industrial applications. This review assesses technologies for removing radioactive iodine, paying special attention to new developments in carbon materials because activated carbon is used among traditional

tertiary methods in water treatment plants and new carbons would have lower entry barriers for adoption by the nuclear and healthcare industries. Fig. 1 illustrates the layout of the review and the specific areas it covers.

Recently published reviews of methods used for the removal of noxious pollutants, e.g. [20], have been published, yet the assessment of carbon materials for the uptake of radioactive iodine and its species has not been addressed. This paper will discuss new directions for preparing effective carbon sorbents for radioiodine uptake.

## 2. Source of radioactive iodine

The diameter of molecular iodine in the gas phase ( $I_2$ ) is estimated to be 0.56 nm [21]. In the liquid phase, iodine can be found in the form of  $I_2$ , inorganic anions ( $I^-$ ,  $IO_3^-$ ,  $IO_4^-$ ) and organic molecules such as  $CH_3I$  and  $C_4H_9I$ . Of 37 known iodine isotopes, from  $^{108}I$  to  $^{144}I$ , only  $^{127}I$  is non-radioactive and is used in most research studies. Most radioactive iodine isotopes are short-lived; nevertheless, all are reactive and have debilitating effects on human health and can impact the environment [22]. Iodine isotopes tend to accumulate in the thyroid gland, and this can cause cancer. Two isotopes of iodine, namely  $^{131}I$  ( $t_{1/2}$ : 8 days) and  $^{129}I$  ( $t_{1/2}$ :  $1.57 \times 10^7$  years), are generated in considerable quantities in the nuclear fuel during fission; it has been estimated that  $1.8 \text{ EBq} = 1 \times 10^{18} \text{ Bq}$  of  $^{131}I$  was emitted during the Chernobyl incident. [23]. Radioactive iodine is not released to the atmosphere during the normal operation of a nuclear plant, but it is present when reprocessing the spent fuel [24].

Nuclear medicine widely uses  $^{129}I$  and other isotopes such as  $^{127}I$ , (stable isotope),  $^{123}I$  ( $t_{1/2}$ : 13.2 h) in imaging;  $^{125}I$  ( $t_{1/2}$ : 59 days) in biological assays, imaging and radiotherapy; and  $^{131}I$  for thyroid cancer treatment [25–27]. The extensive use of these isotopes makes it imperative to control their discharge to the atmosphere and the aqueous environment. Approaches to remove iodine radioisotopes have been based on physisorption [28], chemisorption [29], electrodialysis [30], ion exchange [31], precipitation and dry dedusting. In this review, we focus on evaluating carbon materials for the extraction of radioactive iodine.

## 3. What is known from the interaction of iodine with carbon?

Granular activated carbon (GAC) and ion exchange resins are the industry standard to control the emissions of radioactive elements during nuclear plant operations. Activated carbons (AC) are part of the ventilation network of the nuclear plant in the form of filter beds. Radioactive iodide is also removed from liquid effluents; this is commonly done with ion exchange resins or entrapment in salts [32]. An alternative to these methods is removal by physisorption, for instance, using Granular Activated Carbon (GAC). Commercial GACs (from bituminous coal, coconut shell and sub-bituminous coal) were used to remediate groundwater contaminated with radiological waste [33]. Their contamination occurred by leaching from radioactive waste storage facilities where short-lived low-level nuclear materials were contained. Iodine was found in the form of three species in the groundwater: mainly  $IO_3^-$  (60.5 % to 86.7 %), followed by organo-iodine originating from the organic matter of soil (12.3 % to 28.7 %) and as  $I^-$  (0.4 % to 10.8 %) [33]. The initial pH of the water source was 8.2. Compounds with lower oxidation degrees were oxidised to  $IO_3^-$ , followed by a reduction to  $I^-$  prior to attempting their adsorption with GACs originating from bituminous coal and coconut shell. This step was taken to ensure that the concentration of iodine did not change during the oxidation treatment. The GACs studied exhibited  $I_2$  uptakes of 0.92–1.1  $\text{g g}^{-1}$  of the adsorbent when incubated with water containing  $\sim 3.5 \text{ pCi L}^{-1}$  of  $^{129}I$ . The most effective of them was coconut shell-based activated carbon. In contrast, iodine removal was only 2.75 to 5.90  $\mu\text{g/g}$  when  $I_2$  was converted to  $I^-$ . Therefore, various factors need to be considered to achieve optimal results when utilising GAC. Firstly, the performance

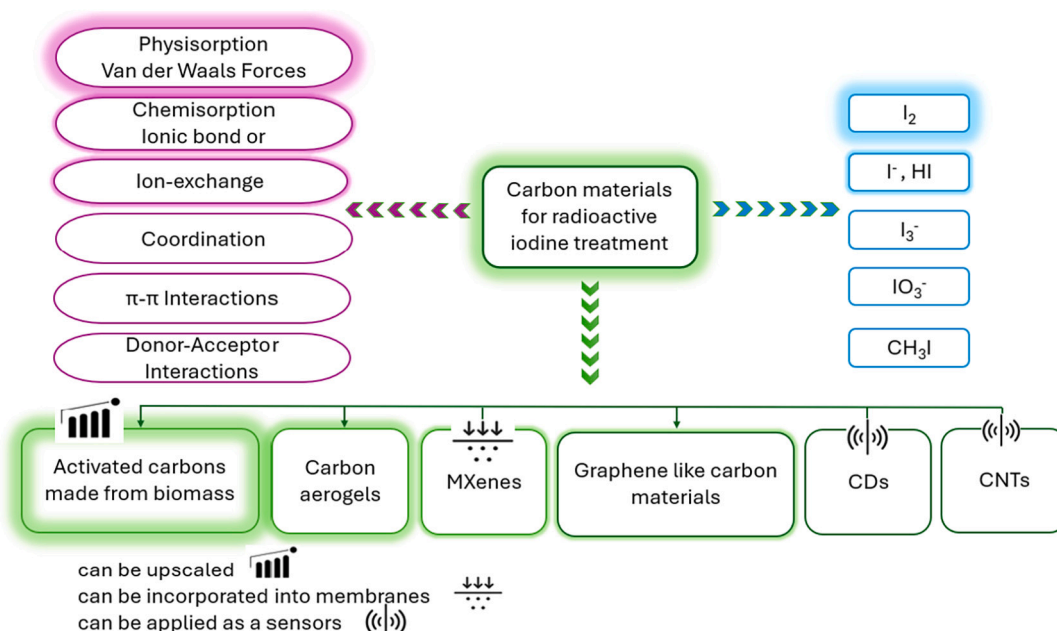


Fig. 1. Application of carbon materials for radioactive iodine sensing and capturing.

specifications provided by the manufacturer may differ from the characteristics of the effluents to be treated. Secondly, the pH of the effluent has to be monitored as it could impact the iodine speciation and uptake. Additionally, it is important to ensure that all forms of iodine are converted into a single form, such as iodide ( $I^-$ ) in order to achieve the desired outcome. By considering these important factors, one can maximise the efficacy of GAC treatment.

The typical approaches for removing halides from water are based on (i) membrane separation, which include reverse osmosis (RO), nanofiltration (NF) and electrodialysis (ED); (ii) electrolysis: electrodialysis reversal (EDR), capacitive deionisation and membrane capacitive deionisation; (iii) adsorptive techniques using layered double hydroxides, impregnated activated carbons, carbon aerogels; (iv) ionic extraction using exchange resins; and (v) coagulation [34]. Among all, RO was the most effective approach for both organic and inorganic iodine removal (up to 99.4 %) [33]. However, it involves high running costs, needs pre-treatments and has energy intensive high operating pressures. Currently, adsorptive techniques are commonly used in water treatment facilities [35,36]. Therefore, this review focuses on assessing carbon adsorbents for capturing radioactive iodine, which could be adopted in large-scale water treatment facilities.

The interaction of radioactive iodine with carbon materials usually exhibits high adsorption capacity due to the sorption mechanism, which involves physisorption, including van der Waals forces. Additionally, surface functional groups—such as positively charged N or S groups—improve the carbon surface affinity for iodine through hydrogen bonding, dipole interactions, or covalent bonding. Iodine molecules can be retained by carbon materials such as graphene or carbon nanotubes via  $\pi$ - $\pi$  interaction. Moreover, carbons can function as electron donors and iodine as an acceptor of electrons, which increases iodine adsorption onto the carbon surface.

#### 4. Natural porous materials - derived activated carbon for radioactive iodine capture

The removal of iodine radioisotopes from large volumes of industrial or wastewater effluents would benefit from using low-cost materials [37]. It would be favourable that these were abundantly available, locally sourced, and prepared to reduce  $CO_2$  emissions and minimise supply chain issues [38]. The capacity of reusing the sorbents is also

important to make the process more sustainable and affordable for its applications. In addition, avoiding the spent sorbents becoming a second type of waste and maximising their reuse also contributes to the sustainability of the water treatment process. Activated carbons made from agricultural waste are well-known as effective adsorbents of pollutants both from liquid [39,40] and gas [41,42], and can contribute to local economies attaining sustainable development goals. Biomass-derived carbons manufactured from common raw materials such as bamboo, wood, coal, petroleum pitch, walnut shell, coconut shell, rice straw and husk residue [39] can be used as efficient adsorbents of organic and inorganic contaminants from water [43], and some of them can capture iodine [44–47].

A comparison of the sorption of iodine species by biomass-derived ACs is in Table 1, which includes information about these sorbents' maximum adsorption capacity, synthesis, and characterisation. The ACs with greater iodine uptake had been chemically activated with KOH (see Table 1). Superior iodide uptakes of  $>6$  g  $I_2$ /sorbent were achieved. Interestingly, such high recoveries came from orange peel biomass doped with urea [48], sorbents from industrial waste [49], biomass from rice husk [50]. Both hydrochar and biochar underwent KOH activation. When comparing these two methods, the hydrochar was more sustainable because of its lower processing temperature requirements. The KOH activation involved the first step of melting KOH and spreading it into the biomass, which led to the generation of  $K_2CO_3$ . The reaction in Eqs. (1)–(4) describes the processes taking place [52]. In addition, biomass can also be activated with substances such as urea. Eq. (5) describes the activation process for carbons modified with urea, where the basic conditions led to the formation of  $NH_3$ , favouring pore formation. To understand in which form N is bound to biomass, the XPS analysis of N-doped hydrochar obtained from orange peel doped with urea (Fig. 2) reveals three types of N-groups, attributed to amine, pyridinic, pyridonic, and graphitic structures at different ratios (Fig. 3).



**Table 1**

Removal of iodine species by the biobased carbonaceous adsorbents.

| Biobased precursor                                                                   | Pore volume, cm <sup>3</sup> g <sup>-1</sup> | Surface area, m <sup>2</sup> /g | Carbonisation conditions                                                                    | Pyrolysis conditions                                                 | Activation conditions                                                                                     | Iodine uptake, g/g sorbent                                                                                                                                          | Additional information                                                                                     | Reference |
|--------------------------------------------------------------------------------------|----------------------------------------------|---------------------------------|---------------------------------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|-----------|
| Uptake of I <sub>2</sub> in gas phase                                                |                                              |                                 |                                                                                             |                                                                      |                                                                                                           |                                                                                                                                                                     |                                                                                                            |           |
| Cigarette butts                                                                      | 0.80–1.34                                    | 1634–2751                       | 600 °C in Ar for 2 h.                                                                       | 800 °C in Ar for 2 h                                                 | Raw material/KOH ratio of 1:5                                                                             | 2.62 g/g at 353 K and ambient pressure (initial concentration of I <sub>2</sub> not reported)                                                                       | Micro and mesopores prevail                                                                                | [60]      |
| Orange peel waste                                                                    | 1.67                                         | 3053                            | Hydrothermal method at 210 °C in Ar                                                         | 800 °C in Ar for 2 h                                                 | Hydrochar to KOH (mass ratio of 1:2). Urea to char (ratio of 1:2)                                         | 2.25 g/g (initial concentration of I <sub>2</sub> not reported)                                                                                                     | Micro and mesopores prevail. N-doped with urea                                                             | [48]      |
| Receptacle and stalk of sunflower                                                    | 0.46–1.77                                    | 3072                            | Powdered and heated to 500 °C in Ar, heating rate 2.5 °C·min <sup>-1</sup> and kept for 2 h | 800 °C in Ar, heating rate 2.5 °C·min <sup>-1</sup> and kept for 2 h | Biochar to KOH ratio (1:5)                                                                                | 6.46 g/g (initial concentration of I <sub>2</sub> not reported)                                                                                                     | Micropores prevail, very low bulk density (0.033 g cm <sup>-3</sup> )                                      | [49]      |
| Rice husk                                                                            | 0.97                                         | 1930                            | 450 °C in N <sub>2</sub> for 1 h.                                                           | 750 °C, for 1 h                                                      | Hydrochar/KOH (ratio of 1:4) pre-calcination at 400 °C, for 25 min                                        | 13.75 mmol/g (3.49 g I <sub>2</sub> /g) from initial concentration of 21 mmol/L of I <sub>2</sub>                                                                   | Micropores prevail. HNO <sub>3</sub> and H <sub>2</sub> O <sub>2</sub> to oxidise the carbon surface       | [50]      |
| Uptake of iodide (I <sup>-</sup> and IO <sub>3</sub> <sup>-</sup> ) in aqueous phase |                                              |                                 |                                                                                             |                                                                      |                                                                                                           |                                                                                                                                                                     |                                                                                                            |           |
| Sacha inchi shells and hazelnut shells                                               | –                                            | –                               | –                                                                                           | –                                                                    | Washed with water before drying in oven, ground, sieved (0.5–0.711 mm particle size)                      | 0.0484 g/g (sacha inchi shells); 0.0189 g/g (hazelnut shells). initial concentration 10 mg I <sup>-</sup> /L pH 3, 5, 7, and 11. T 5, 15, 25, 45, and 65 °C         | pH range 3, 5, 7 and 11. T range 5, 15, 25, 45, and 65 °C. pH-dependent, most effective at pH 3 and 25 °C. | [55]      |
| Pomegranate peels and mangosteen pericarps                                           | –                                            | –                               | –                                                                                           | –                                                                    | Washed with water, ground by a grinder. Dried at 40 °C in an oven, they were sieved 0.5–0.711 mm fraction | Remove IO <sub>3</sub> <sup>-</sup> from the water, pomegranate peels 0.00959 g/g, mangosteen pericarps 0.00231 g/g, initial concentration 10 mg/L contact time 2 h | Most effective at pH 1                                                                                     | [61]      |



The main difference between physical and chemical activation is that only steam or gas is used in physical activation. Activation agents such as salts, acids, alkali compounds or impregnates are added for their chemical activation [51]. The rise in temperature affects the formation of pores. During activation at moderate temperatures (usually <600 °C), KOH had a low effect on the biomass. However, it had a more significant impact during chemical activation, which involved the decomposition of K<sub>2</sub>CO<sub>3</sub> at higher temperatures (usually >700 °C), leading to the pore widening and the formation of micropores. New mesopores were also generated from the space occupied by the KOH during the carbonisation at higher temperatures. [52].

The porosity of the materials is very important for both the filtration and adsorption performance of ACs during water treatment. The sorbent porosity can be, to some extent, tailored towards the desired application [49], although the intrinsic structure of the precursor biomass puts some limitations on it. For example, in case of the milky and spongy stalk of sunflower yielded a porous carbon material with casing-like morphology (Table 1) [53]. The final surface properties of activated carbon are also affected by the additives used for chemical activation, such as KOH and N-doping agents. An effective way of nitrogen doping into the structure of activated carbon is a hydrothermal method (HTM) involving high pressure and temperature. Specifically, there is a process using 10 % (w/w) of urea H<sub>2</sub>NCONH<sub>2</sub> as the N-doping agent, by autoclaving carbonized biochar and urea at 210 °C and 5 MPa [54].

The sorbent' surface chemistry also contributes to removing radioactive iodine. However, the assessment of this factor cannot be

discerned easily from the effect of the porosity. Biomass-derived activated carbons had a high affinity with radioiodine (I<sub>2</sub>). The sorption achieved was 6.44 g I<sub>2</sub> g<sup>-1</sup> from the gas phase in dry conditions and 2.44 g I<sub>2</sub> g<sup>-1</sup> under high humidity, which is close to actual conditions of nuclear fuel reprocessing (created via saturated salt solutions, 26.9 ± 0.3 % (MgCl<sub>2</sub>), 50.3 ± 1.3 % (NaBr) and 74.0 ± 0.9 % (NaCl). Their high sorption capacity for iodine could be partly attributed to the oxygen-containing functional groups on the activated carbon surface and van der Waals interaction with its benzene rings. This phenomenon has been explained by Density Functional Theory (DFT) calculations where the energy of I—I (isolated molecular I<sub>2</sub>) was compared with C—I in the C<sub>24</sub>H<sub>12</sub>–I<sub>2</sub> and optimised structures of the C<sub>24</sub>O<sub>12</sub>H<sub>6</sub>–I<sub>2</sub> system. The latter was the most stable system. The high uptake of iodine in the pores may be thus attributed not only to pore-filling mechanisms, which is boosted by a large surface area (1830–3000 m<sup>2</sup>/g) and high pore volume, but also due to the enhanced interaction of iodine molecules with surface oxygen functional groups [46].

Combining the hydrothermal carbonisation (HTC) technology and pre-pyrolysis impregnation methods with N-compounds significantly improved the adsorption capacity of porous carbon for weakly polar pollutants such as molecular iodine. Thus, the adsorption capacity of up to 2.25 g I<sub>2</sub>/g of carbon was achieved, indicating that it was competitive among other biochar-based carbon sorbents. The use of HTC has only been reported in a few recently published papers (compiled in Table 1). In comparison with the commonly used pyrolysis treatment, HTC does not require the pre-drying procedure, and it is performed at a lower temperature range of 180–250 °C. Finally, activated carbons offer numerous advantages over other sorbents: high surface area, porosity,

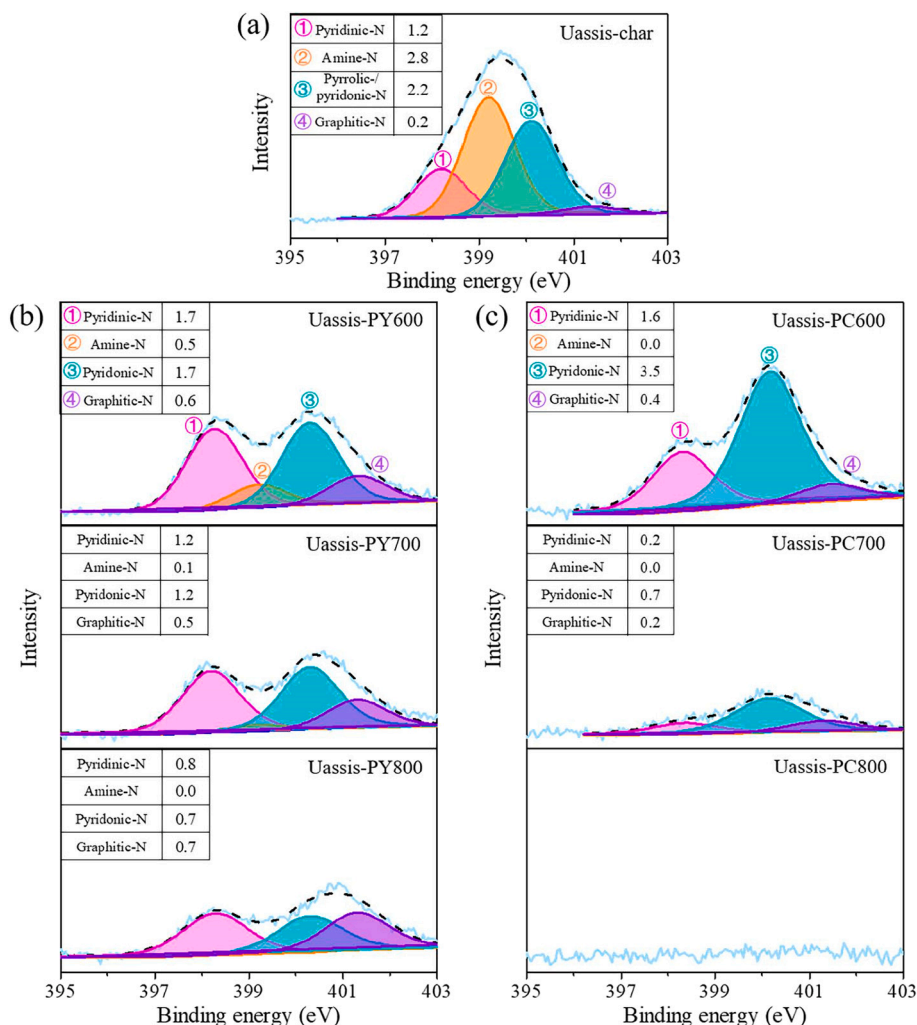


**Fig. 2.** N 1s spectra and relative contents (%) of different nitrogen groups in carbon materials at different stages of activation, where PY-obtained by pyrolysis without activation. PC – obtained by activation with KOH at a 1:2 ratio (hydrochar to KOH). 600, 700 and 800 indicate the pyrolysis/activation temperature, °C. Uassis means urea-assisted hydrochar.

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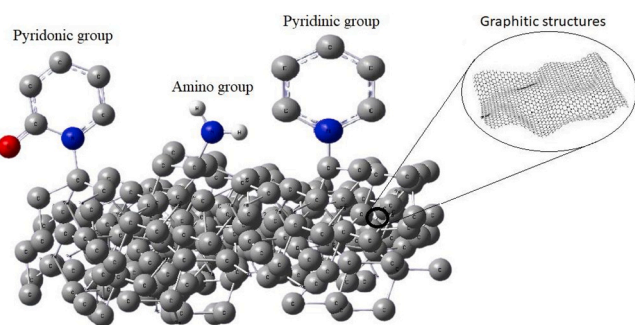


**Fig. 3.** Gaussian model of N-containing functional groups of AC after N-doping.

tunable surface chemistry, chemical stability, low toxicity, mechanical strength, thermal stability, reusability and regeneration, environmental compatibility, cost-effectiveness, a wide range of pollutants adsorbed, and the ability to be applied in large-scale applications.

Notably, N-doping had a minor effect on the pore structure of hydrochar, but it greatly promoted the development of its pore structure during activation [48]. When analysing the chemistry of N-doped activated carbons, the pyridinic and pyridonic nitrogen groups are prevalent

after high-temperature pyrolysis (<700 °C) and become less visible after activation at around 800 °C (see Fig. 4). Therefore, N-containing groups did not take part in the uptake of iodine species. However, they still affected the surface chemistry of the initial carbon biomass and facilitated the formation of highly porous carbon with developed micropore and mesopore structures. The hydrophobicity of the carbon surface contributed to the increase of molecular iodine ( $I_2$ ) adsorption. The heat treatment (~800 °C) used during pyrolysis caused the partial loss of some surface functional groups, such as oxygenated ones, reducing the overall hydrogen content. For instance, the data for rice husk derived carbons in Table 1 show that the degree of hydrophobicity of the graphite surface can increase the adsorption of iodine molecules by reducing the amount of polar carboxylic, carbonyl and phenolic groups on the carbon surface [50].

The mineral composition of the original biomass also contributes to iodide ( $I^-$ ) sorption. For instance, Sacha Inchi shells contain magnesium ( $Mg^{2+}$ ), potassium ( $K^+$ ), and calcium ( $Ca^{2+}$ ) cations in the original biomass, which are transformed as active sites into activated carbon after pyrolysis. Sacha inchi shells and hazelnut shells are effective adsorbents of the iodide anion (Table 1). Although the charge of cationic species present in the adsorbent is important, nevertheless, the main factor driving the uptake of  $I^-$  species is understood to be physisorption [55].

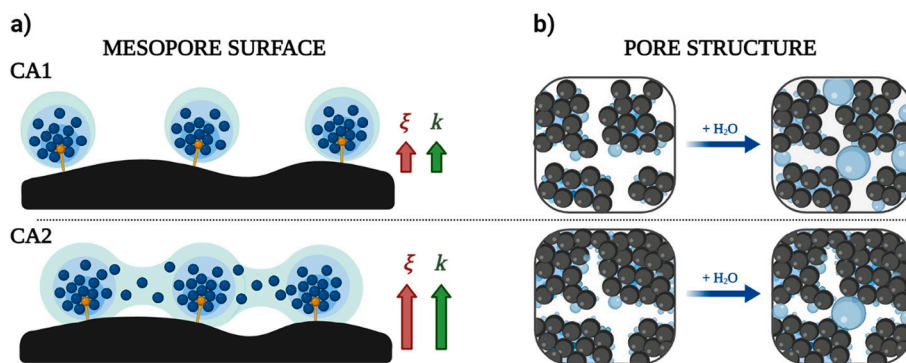


**Fig. 4.** Wetting process of the mesopores of CA1 and CA2 carbon aerogels as seen by NMR a) on the pore surface and b) in the pore system. The carbon aerogel skeleton is signed with black colour, the functional groups are yellow, while blue colour shows the water in the pore system. a) on the pore surface and b) in the pore system. Where ( $\xi$ ) surface relaxivity and ( $k$ ) layer thickness.

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When assessing the surface charge of materials and the speciation of radioiodine, the pH of the media affects their sorption capacity: the maximum adsorption of  $I^-$  by bio-based adsorbents is achieved at pH 3 [55]. The adsorption of the iodine species tends to decrease with increasing pH. For example, sorption of  $I^-$  by saccharin shells was 0.0468 g/g at pH 3, 0.045 g/g at pH 7 and 0.0379 g/g at pH 11, respectively. Besides the pH dependence of the iodine speciation, the increase of  $OH^-$  concentration competes with  $I^-$  anions and reduces adsorption of the latter from water [55].

The adsorption capacity of biomass-derived ACs for iodine is high (up to 6.46 g/g of  $I_2$ , Table 1) and very similar to that of synthetic microporous carbons, 7.39 g/g (Table 2). It mainly depends on the amount of micropores and the hydrophobicity of the carbons, and it is linked with the type of biomass precursor and the activation technique. Chemical activation with KOH tends to be preferred to potassium salts because KOH starts reacting with carbon at lower temperatures [56].

The effectiveness of biomass-derived carbons for capturing volatile iodine from the gas phase (Table 1) is increased with temperature. In contrast, their performance deteriorates at high humidity or in the presence of nitrogen oxides ( $NO_x$ ), which are present in the off-gas of nuclear plants. [35]. The application of ACs for pollution control of nuclear power plant emissions creates new challenges, such as explosion risks in the case of nitrate sorption (the saturation of carbon beds with  $NO_x$  can lead to explosion because of low ignition point [57]) which also can release the adsorbed radioiodine at high temperatures ( $CH_3I$  at 400 °C) [47]. To overcome this, ACs are usually co-impregnated with potassium iodide (KI) and triethylenediamine (TEDA) because of partial pore blockage phenomena [58].

The reusability of the spent biomass AC is a challenge [59], and it needs to be addressed in the development of carbons for uptaking  $I_2$  (Table 1). Its regeneration is not attempted because of the economic costs involved in its thermal regeneration, usually carried out off-site, or the additional chemical treatment, which may be superior to preparing a new sorbent. Furthermore, works related to the preparation of carbons do not generally address energy demand and  $CO_2$  emissions related to the preparation or regeneration of the carbons, which is an important shortcoming given the importance of these factors for their applicability and sustainability.

## 5. Synthetic carbon materials for radioactive iodine capture

### 5.1. Carbon aerogels

Aerogels are a unique class of 3D air-filled materials (consisting of 90–99 % air) that have a highly structured porous network and high surface area (~400–800  $m^2/g$ ). Their surface chemistry is controllable [62]. The use of porous aerogels for water treatment has been recently

discussed: their porosity makes aerogels efficient in the removal of radioactive pollutants from air and water [63,64] [57,65]. There are aerogels based on silica, graphene, AC and composites [66] Table 2 compares the maximum iodine extraction capacity of synthetic AC and a carbon aerogel: the extraction of iodine is of the same order of magnitude across aerogels (~1 g  $I/g$  sorbent).

The carbon aerogels prepared from resorcinol-formaldehyde aerogels were applied to absorb pollutants in aqueous solutions. It was proven that the pore size distribution affects the sorption mechanism, as the pore structure facilitates the wetting of aerogels (Fig. 4) [59].

The interaction of diffused iodine with the sorbent is influenced by its surface chemistry. The density functional theory (DFT) method is commonly used for theoretical calculations and simulation of surface chemistry. The DFT applied for carbon aerogels made of graphene doped with sulfur and nitrogen (SN-GA) showed a high iodine adsorption capacity of 0.999 g  $I_2 g^{-1}$  at the initial  $I_2$  concentration of 0.200 g  $L^{-1}$  after 72 h [68]. A different approach was used to prepare a carbon aerogel from leather waste, the latter being a source of tannins, including catechin. The resulting carbon adsorbent, designated Catechin@3DCF, demonstrated the iodine adsorption capacity of 0.323 g/g. Iodine adsorption in that sorbent was affected by its mesoporous interconnectivity and catechin-doping on the aerogel surface. Regarding reusability, the Catechin@3DCF aerogel could be regenerated and showed stable adsorption capacity during five regeneration cycles with ethanol [69]. The impact of pH has been checked for biomass-derived aminated carbonaceous aerogel synthesised from watermelon peel waste to capture iodide from water. Its adsorption capacity was 0.85 mmol  $I^-/g$  (0.141 g  $I^-/g$ ) at pH 2.0 when the starting concentration of iodide was 8 mmol/L (1.328 g  $I^-/g$ ). The low pH promoted protonation of the iodide anions. Notably, the adsorption was fast, and the adsorption equilibrium was reached within 2 h [70]. Two carbon aerogels produced from resorcinol-formaldehyde (RF) precursor, designated RFac (790  $m^2/g$ , cylinder-shaped pores, with dominance of acidic groups), and from RF with melamine and graphene oxide, designated RMF-GO (375  $m^2/g$ , slit/cylinder-shaped pores, dominated by basic groups) showed iodide extraction capacity of 0.082 g/g and 0.097 g/g under acidic conditions (pH 2.5) from the solution with 500 mg/L initial concentration of iodide. The adsorption mechanism usually involves the interaction of a positively charged carbon surface comprising either pyrone or amino groups with the negatively charged iodide anions [71]. Large surface areas (2630  $m^2 g^{-1}$ ) and the graphene monolayers mostly promote physical adsorption compared to the chemical affinity. In this case, it can be seen from graphene aerogel, which demonstrated a maximum iodine uptake of 0.510 g/g of  $I_2$  [72].

Similarly, nitrogen-rich silk fibroin aerogel has been recently reported as a sorbent for  $I_2$  and  $CH_3I$  extraction. It showed an adsorption capacity of 0.724 g  $CH_3I/g$  and 0.348 g  $I_2/g$ . The main mechanism of

**Table 2**

Comparison of synthetic carbons for removal of iodide in gas and water phases.

| Type of carbon                                                              | Porosity, $\text{cm}^3 \text{g}^{-1}$                                                     | Surface area, $\text{m}^2/\text{g}$                                                 | Preparation method                                                                                                                                                                                                                                          | Iodine sorbed                                                                                                              | Additional information                                                                                                                                                                                                                | Reference |
|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| <b>Gas phase (<math>\text{I}_2</math>)</b>                                  |                                                                                           |                                                                                     |                                                                                                                                                                                                                                                             |                                                                                                                            |                                                                                                                                                                                                                                       |           |
| Oxygen-rich microporous carbon named CDA4T                                  | 0.88–1.40                                                                                 | 1829–2998                                                                           | Hydrothermal reaction, cellulose diacetate (CDA) and deionised water at 250 °C for 2 h at 600, 700, 800 and 900 °C in $\text{N}_2$ hydrochar and KOH activation ratio of 1:4 (LC-K) lignin and KOH ratio: 1:2 at 900 °C for 1 h under a nitrogen atmosphere | Up to 6.44 g/g in dry conditions (75 °C under ambient pressure) 2.44 g/g at high humidity ( $74.0 \pm 0.9 \%$ )            | Oxygen content 19.32–26.14 %                                                                                                                                                                                                          | [46]      |
| Lignin-based porous flower-like carbon nanosheets named LC-K, LFC-K, LFC-KN | 0.92 (LC-K)<br>1.14 (LFC-K)<br>1.69 (LFC-KN)                                              | 1746(LC-K)<br>2282 (LFC-K)<br>1994 (LFC-KN)                                         | Carbonisation at 500 °C in $\text{N}_2$ for 1 h<br>For (LFC-K)<br>lignin + KOH (ratio of 1:2) + MgO templates<br>For (LFC-KN) lignin + KOH/NaOH (ratio 1:1:0.83) MgO template                                                                               | Iodine vapour<br>4.06 g/g (LFC-K)<br>3.83 g/g (LFC-KN)<br>In presents of humidity<br>1.16 g/g (LFC-K)<br>1.30 g/g (LFC-KN) | Interconnected 3D graphitic shell network.<br>MgO template.<br>Adsorbent can be regenerated                                                                                                                                           | [97]      |
| Synthetic microporous carbons (HPNs) hypercrosslinked polynaphthalenes      | Pore sizes<br>0.5–1.2 nm, pore diameters<br>0.56 nm–1.14 nm                               | 944–2754                                                                            | Heated to 800 °C in $\text{N}_2$ and kept for 2 h. C activation with KOH (1:4)                                                                                                                                                                              | 0.003 g/g                                                                                                                  |                                                                                                                                                                                                                                       | [98]      |
| <b>Water phase (<math>\text{I}^-</math>)</b>                                |                                                                                           |                                                                                     |                                                                                                                                                                                                                                                             |                                                                                                                            |                                                                                                                                                                                                                                       |           |
| Boron and nitrogen-doped fluffy carbon composite form tapioca root B-N@CS   | 1–50 nm                                                                                   | 130                                                                                 | Mix boric acid, melamine, tapioca root powder and deionised water, at 100 °C for 3 h dehydrated using 0,022 L of conc. $\text{H}_2\text{SO}_4$                                                                                                              | 0.47 g/g<br>$[\text{I}_2]_0 (\text{aq})$ 200 ppm                                                                           | Incorporation of boron nitrogen in the carbon matrix.<br>Suitable for large-scale production<br>1/3 Of this capacity attributed to physical adsorption, while 2/3 was chemically reacted with nano-Bi particles on the carbon fibres. | [96]      |
| Bismuth-decorated electrospinning carbon nanofiber Bi@ESCNF                 | Pore size 15 nm                                                                           | 537                                                                                 | Pre-oxidation at 260 °C for 2 h<br>Pyrolysis at 800 °C for 2 h in $\text{N}_2$ and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$                                                                                                                     | 0.56 g/g                                                                                                                   |                                                                                                                                                                                                                                       | [99]      |
| Nanoporous carbon materials named Z11–700, Z11–800 and Z11–900              | 0.37 nm–0.44 nm, and total micropore volumes<br>0.085–0.124 $\text{cm}^3 \text{g}^{-1}$ , | 377, 260 and 157 $\text{m}^2/\text{g}$ for the samples Z11–700, Z11–800 and Z11–900 | Pyrolysis at 700, 800 and 900 °C                                                                                                                                                                                                                            | 3.78 g/g                                                                                                                   | Adsorbent can be regenerated.                                                                                                                                                                                                         | [100]     |
| Sulfur and nitrogen co-doped graphene aerogels SN-GA                        | 1–10 $\mu\text{m}$                                                                        | 180                                                                                 | SN-GA synthesised by a hydrothermal method 180 °C for 12 h<br>thiourea and GO mass ratio 10:1<br>AC fibre (ACF) was procured from Nantong Senyou Company Limited (Jiangsu, China)<br>Hydrothermal method at 80 °C for 24 h                                  | 0.999 g/g at 298 K                                                                                                         | Iodine can be released from adsorbents by immersion in ethanol for 12 h. Active sites are S and N.                                                                                                                                    | [68]      |
| Silver-loaded activated carbon fibre (Ag@ACF)                               | 0.30                                                                                      | 700                                                                                 |                                                                                                                                                                                                                                                             | 0.372 g/g at pH 2 initial concentration 400 mg/L                                                                           | Silver concentration of 4 %. equilibrium was achieved after 4 h.                                                                                                                                                                      | [101]     |

adsorption involved the formation of the charge transfer complexes between diverse N-groups and the iodine molecule and lipophilic nature and stronger affinity of aliphatic amines in case of  $\text{CH}_3\text{I}$  sorption [73].

Overall, the sorption mechanism of iodine species comprises chemisorption and physical sorption, which takes place via weak supramolecular interactions through S, N-doping and electrostatic interactions, respectively. Aerogel ageing should be an issue that needs to be addressed in future works: aerogels may not be applicable for a long-time iodine capture because of the deterioration of their mechanical and interlaminar properties [74,75]. Carbon aerogels suffer from a complex and multistep synthesis involving resorcinol and formaldehyde polycondensation followed by pyrolysis, making them impractical for large-scale applications due to cost constraints.

## 5.2. Carbon nanotubes

Carbon nanotubes (CNTs) are rolled layers of  $\text{sp}^2$ -hybridized carbons. CNTs can be single-walled carbon nanotubes (SWCNTs), or multi-walled carbon nanotubes (MWCNTs) [76]. Their diameter of 0.4–40 nm is suitable for  $\text{I}_2$  capture, and their length and chirality can be adjusted. However, they only have a minor effect on the iodine sorption [77]. SWCNTs can be divided into those to detect  $\text{I}_2$  (sensors) and those to capture  $\text{I}_2$  vapour and iodine ions from solutions. While both types of SWCNTs interact with iodine species, not all of them are intended to maximise iodine capture. The development of CNT-based sensors for the detection and separation of halogen gases ( $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$ ) has been assayed, and the size of pore vacancies (1, 2, 3 and 4 atoms) can selectively sensor different types of halogen gases. The mechanism of molecular iodine incorporation into the CNT structure is shown in Fig. 5.

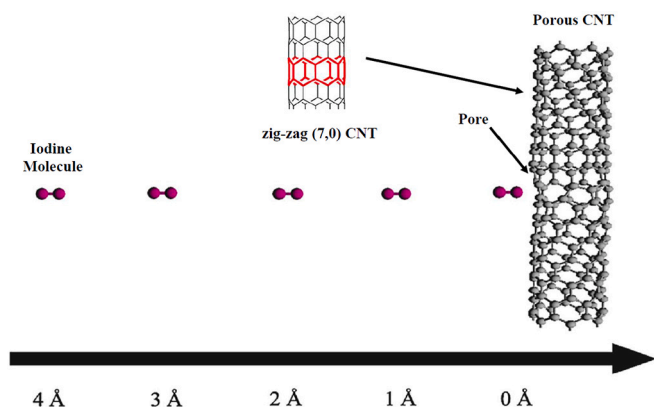


Fig. 5. Schematic representing the migration of  $I_2$  towards the CNT channel at various distances from the pore.

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As shown in Fig. 5, the zig-zag (7,0) CNT system was based on introducing pores of various sizes into the CNT surface by removing the host carbon atoms and creating vacancies (bigger holes in a CNT structure). However, creating a suitable vacancy to capture iodine species in the CNT structure was not enough for  $I_2$  attraction, and further modification was required to create an electrostatic interaction between halogen molecules and atoms with the CNT's pore rim. This has been achieved by the functionalisation of the pore vacancy with hydrogen atoms, which are more selective towards iodine molecules. In this case, H–I electrostatic attraction is greater than the I–I electron cloud repulsion [78].

One of the best choices to detect iodine vapour can be Ag-modified MWCNT. MWCNTs (Ag filled and coated) demonstrated a sensing response of 45 % in just ~60 s at room temperature, but a significant disadvantage of this material was the prolonged duration needed to recover the sensor itself (400 s with heating at 100 °C in the air) [79]. The analysis of the iodine removed from the solution by sorption to the CNTs can be done with inductively coupled plasma-mass spectrometry (ICP-MS) after sample preparation using pyro-hydrolysis with a relatively low limit of detection (LOD) of  $0.004 \mu\text{g I}^- \text{g}^{-1}$  [80].

From the latest research papers on  $I_2$  detection by CNTs [77–79], it has been found that CNTs are effective for detecting iodine, but they are not practical for extracting it from air or water due to high costs. Moreover, most studies aimed at sensing  $I_2$  are theoretical simulations. The issue of toxicity is a common concern with CNTs and requires further examination [81].

### 5.3. Graphene/pyrene/fullerene

Graphene, which consists of two-dimensional carbon sheets, can be used in membranes that can adsorb micropollutants [82]. Graphene materials are not commonly used for iodine adsorption. In particular, there are only a few studies on graphene aerogels showing capability for iodine uptake, as compiled in Table 2. In addition, a co-doped graphene aerogel (SN-GA), which contains both sulfur and nitrogen active sites that enable having well-developed porosity and surface area for adsorption, retention and storage of iodine has been proposed [83]. The role of graphene in this material was the creation of  $\text{sp}^2$  carbon framework and  $I_2$  binding, which occurred through the pyrrolic N and thiophene-S. With the same approach, a 2D nanomaterial, mono-sheet pyrene-alkaline framework, the structure of which has similarities with graphene, has been recently tested towards the capture of radioactive  $I_2$ . Its structure is similar to graphene but has regular standardised porosity contrasting with ACs. 2D layered poly-1,3,6,8-tetraethynylpyrene (PTEP) was obtained from 1,3,6,8-tetraethynylpyrene (TEP) by solid-phase thermal polymerization promoted by flame

heating. The pyrene groups are quadruple-linked via the alkynyl groups of TEP (Fig. 6a).

Molecular iodine was adsorbed from gas and aqueous phase by pyrene groups of PTEP. It had an adsorption capacity of 3.380 g/g (at 75 °C, gas phase) and 2.570 g/g (at 25 °C, aqueous phase), respectively. PTEP has hydrophobic surface, which makes it capable of adsorbing iodine in both water and humid air. Furthermore, PTEP could be restored to >85 % of its initial adsorption capacity after 5 adsorption/desorption cycles, but no more information is known beyond this initial feasibility study regarding its regeneration. The adsorption of  $I_2$  in gas phase mainly occurs through the  $I_2$ -pyrene charge-transfer mechanism, and unsaturated PTEP bonds (including those in acetylene ( $\text{C}\equiv\text{C}$ ), alkadiene ( $\text{C}=\text{C}-\text{C}=\text{C}$ ) and cumulene of the alkadiene transformation ( $\text{C}=\text{C}=\text{C}=\text{C}$ )) also contributing to iodine adsorption. Moreover, intraplanar pores (~1.2–1.6 nm), and interlamellar structure, with 2D interspace sizes from 2.1 to 6.4 Å, also contribute to the diffusion and adsorption of  $I_2$ . The adsorption of  $I_2$  in an aqueous solution is explained by the high density of homogeneously distributed pyrene groups and the monolayer structure. A possible mechanism of  $I_2$  uptake by PTEP from water, proposed based on UV–Vis measurements can be seen in Fig. 6b [84].

A new method has been used to understand how iodine adsorption works. This method involves a computational study of the interaction between  $I_2$  and S-doped fullerenes. Since the C–S bond length is greater than that of C–C, the S atom is positioned on top of the fullerene surface. This creates a potential interaction between the lone pairs of I atoms and  $\sigma$ -bond of C–S bonds in p configurations [85] graphene-like materials; the adsorption of iodine is attributed to the charge transfer between  $I_2$  and pyrene groups, as well as N. Research on planar graphene-like materials has shown that the adsorption of iodine is attributed to the charge transfer between  $I_2$  and pyrene groups and N- and S-containing groups. To conclude, a graphene-like structure has the potential to be applied in membrane filtration. Modifications with S and N containing groups enhance sorption capacity of graphene like sorbents towards radioactive iodine.

### 5.4. MXenes

MXenes are 2D materials that consist of atomically thin layers of transition metal carbides, nitrides or carbonitrides with weak bonding between the layers. Their structure and mechanical properties are similar to other 2D materials such as graphene and can be tuned with various functional groups. Their structural complexity and chemical diversity make them multifunctional materials [86]. The 10th anniversary of MXenes was celebrated in 2022 [87]. Despite MXenes being a young group of materials, their potential for sorbing radionuclides has been shown by sorbing  $I_2$  from non-polar solvents. That is especially challenging due to the stability of  $I_2$  in the solution. Sun et al. [88] developed a polyimidazole functionalised MXene (MXene-PIL) that can adsorb iodine from a cyclohexane solution through the interaction of the imidazole ring with iodine. MXene-PIL adsorbed up to 0.170 g/g of iodine when the initial concentration of iodine was 1.0 mmol/L in cyclohexane. Other MXene based composites were also found to absorb iodine dissolved in cyclohexane. Other composites based on MXene were also found to absorb iodine that was dissolved in cyclohexane. MXene modified with polydopamine (PDA) and nano-mixed silver oxide (MXene-PDA-Ag<sub>2</sub>Ox) can adsorb up to 0.080 g/g. In comparison, nano-mixed bismuth oxide MXene-PDABi6O7 can absorb up to 0.065 g/g of iodine when incubated with  $I_2$  at a starting concentration of 1 mmol/L [88]. Adding ionic liquids can improve the extraction of organics by MXenes. As an example, a MXene coated with polydopamine (PDA) and further immobilised with ionic liquid (IL), called MXene-PDAIL, extracted iodine from cyclohexane effectively. Its extraction capacity was  $0.695 \text{ g I}_2 \text{ g}^{-1}$ , achieved with a starting concentration of 1 mmol/L of iodine in cyclohexane [89]. A silver-modified MXene called PDA-Ag<sub>2</sub>Ox had an adsorption capacity of only 0.080 g/g towards iodine in

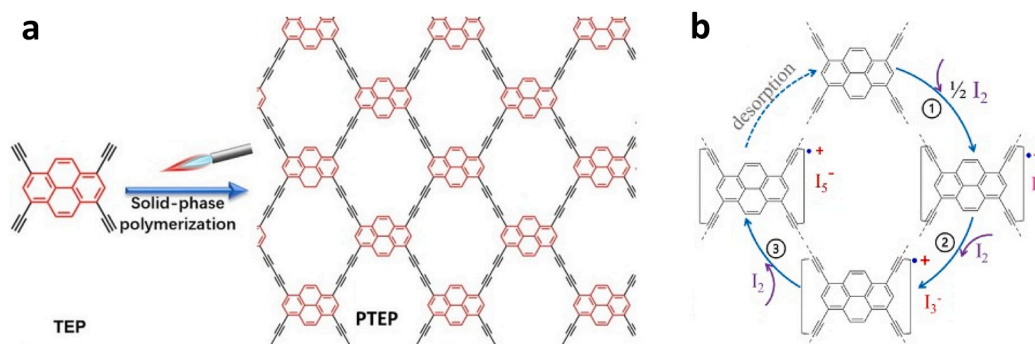


**Fig. 6.** (a) Schematic of solid-phase thermal polymerization of TEP to PTEP, (b) mechanism of  $I_2$  uptake by PTEM. (Reprinted with permission [84]. Copyright 2024, Elsevier).

aqueous solution with an initial concentration of 20 mg/L [90]. The iodide was sourced from potassium iodide.

MXenes can be applied for the extraction of  $I_2$  and  $I^-$  from both aqueous and organic solvents. However, only MXenes doped with silver have been studied for their ability to remove  $I^-$ . Future studies would need to determine whether it is possible to upscale the modification of their surface removal of  $I_2$  and  $I^-$ . When comparing MXenes with ACs the latest have demonstrated to be more efficient in extracting iodine.

### 5.5. Carbon dots (CDs)

Carbon dots (CDs) are spherical nanomaterials with a radius of  $\leq 10$  nm. They can be classified as graphene quantum dots, carbon quantum dots, or polymer dots. CDs have been effectively used in the detection of metal ions such as Fe(III), Cu(II) and Hg(II) [91]. Although the use of CDs for the detection of  $I^-$  has been studied, their application for the removal of  $I^-$  has not been widely implemented due to their low extraction capacity of  $I^-$  [92]. Instead, CDs found their application as turn-off-on detectors of iodine due to the fluorescence effect of electron transfer from  $Hg^{2+}$  to  $Hg-I$  complex, where CDs are quenched by  $Hg^{2+}$  and then recovered after the addition of  $I^-$ , with LOD 46 nmol  $I^-$  L $^{-1}$ . Amphiphilic CDs (A-CDs), which have both hydrophilic and hydrophobic properties, were prepared for the detection of main iodine species ( $I_2$ ,  $I^-$  and  $IO_3^-$ ) in highly saline water. The high selectivity response of CD $_2$  to  $I_2$  was attributed to its amphiphilic properties, which brought  $I_2$  closer to the A-CDs and quenched their fluorescence (LOD 3.5 nmol  $I_2$  L $^{-1}$ ) [93]. A similar approach has been applied for iodide detection with  $Hg^{2+}$  assembled nitrogen-doped fluorescent carbon dots (NCDs- $Hg^{2+}$ ) [94].

A new approach to iodine sorption was suggested through the creation of a hydrophobic surface on natural cotton fibres (n-CF). Organic-soluble carbon dots (OCDs) were physically adsorbed to the surface of cotton fibres, which acted as a hydrophobic interface compatible with  $I_2$ . This material exhibited 0.190 g  $I_2$  g $^{-1}$  adsorption capacity with initial 400 ppm concentrations of  $IO_3^-$  and  $I^-$ . Here,  $IO_3^-$  and  $I^-$  anions were converted to  $I_2$  by a redox process at low pH before their removal [95]. Finally, CDs can effectively sense  $I_2$ ,  $I^-$  and  $IO_3^-$ , but efficient approaches to enhancing the iodine species affinity with CDs and their exploitation as adsorbents in large-scale applications are not yet known.

### 5.6. Carbon nanocomposites

Carbon nanocomposites made of nanomaterials which cannot be clearly identified as carbon aerogels, MXenes, graphenes, CDs or CNTs, are discussed here. The removal of iodine from water with boron- and nitrogen-doped carbon nanocomposite (B-N@CS) achieved sorption capacity of 9.92 g/g of (Table 2). The carbon source was tapioca root, with boric acid and melamine used as the doping agents. An advantage of this sorbent is its fast synthesis, which can be completed in 15 min and

carried out in one-step dehydration that did not involve heating. The final unmodified carbon had irregular thin 2D flakes with cavities that could capture  $I_2$  from water (capacity  $\sim 71.3$  % from initial concentration 0.200 g L $^{-1}$  solution of  $I_2$ ). In contrast, when it was modified by boron and nitrogen, leading to the so-called B-N@CS material (Table 2), the iodine removal increased up to  $\sim 94.6$  % within 21 min from the same  $I_2$  initial concentration in water. The adsorption mechanism involved the interaction of the lone pair of electrons of the iodine in aqueous solution, which had three forms:  $I^-$ ,  $I_2$  and tri-iodide ( $I_3^-$ ), with nitrogen atoms via van der Waals interactions [96].

The introduction of a templating agent can be applied to control porosity. For example, lignin-based flower-like porous carbon (LFC) doped with MgO as a templating agent was carbonized and activated with KOH (schematized in Fig. 7), also included in Table 2. LFC material adsorbed large iodine amounts from both the gas phase (4.060 g  $I_2$  g $^{-1}$ ) and water (1.295 g  $I_2$  g $^{-1}$ ) [96]. Rich microporous structure of the LFC composite was created by MgO templating and chemical activation by KOH, which contributed to its high iodine adsorption capacity.

Overall carbon nanocomposites can extract  $I_2$  from water and gas phases. Templating methods and B and N doping can provide additional binding through ionic and van der Waals interactions. When analysing the compositions of the sorbents in Table 2, it can be concluded that oxygen-rich carbons, templating, S- and N-doping enhance the sorption of iodine species in both water and gas phases.

## 6. Conclusions

The recovery of radionuclides from water effluents is a growing need due to increasing volume of contaminated water. Tertiary treatment with carbon materials can be a solution for recovering toxic radioactive iodine, as ion exchange and RO treatments have higher operating costs. The assessment of the literature clarifies that the most effective, and with possibilities to be adopted beyond bench scale applications, are carbons from biomass. A wide variety of biomass (orange, sunflower, rice, hazelnut, pomegranate)-based carbons led to uptakes  $>1$   $I_2$ /g sorbent. These are expected to be competitive for treating water effluents. Hence, locally sourced biomass could be a greener option than RO for preparing effective sorbents with high value, given its specialised application. The most effective carbons from biomass were hydrochars that were activated with KOH or urea. Hydrochars prepared with an HTM process conducted at 180–250 °C need milder thermal treatment than biochars, and therefore, they offer a greater opportunity. While KOH contributes to achieving suitable porosity and high surface area, the hydrothermal treatment leads to an oxygen-rich surface, both contributing features favouring iodine recovery. HTM has not yet been widely used for iodine uptake, although its value has been demonstrated by its performance of 2.25 g of  $I_2$ /g of orange peel biomass. Modified activated carbons with urea can have superior performance from that achieved with HTM, although their properties, energy requirements,

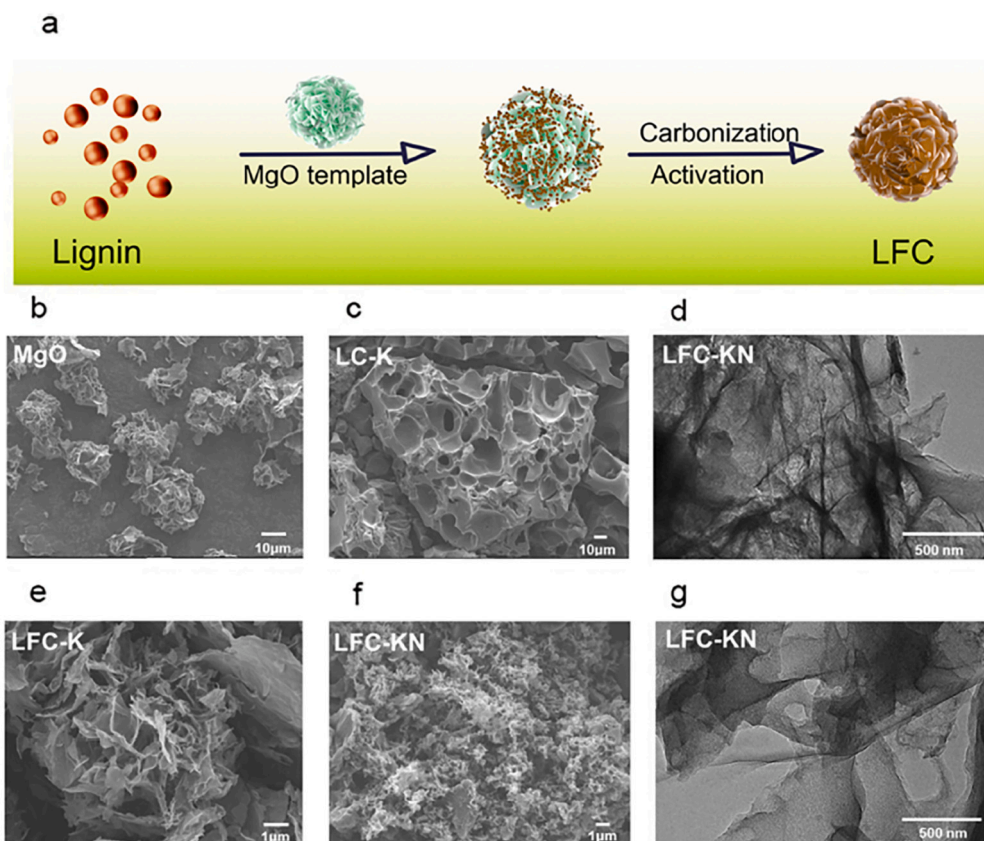


**Fig. 7.** (a) Schematic of lignin-based porous carbon (LFC) synthesis from lignin. (b)–(g) SEM and TEM micrographs of (b) MgO template, (c) lignin-based KOH AC (LC-K), and (d)–(g) lignin-based KOH/NaOH AC (LFC-KN) at different magnifications. (Reprinted with permission [97]. Copyright 2024, Elsevier).

and CO<sub>2</sub> emissions make it less green.

Unlike the adoption of activated carbons for treating effluents, the adoption of nanocarbons, potentially integrated in membranes will require changes in the industrial infrastructure. With the development of new carbon nanomaterials and preparation procedures in the last decade, the assessment of carbon sorbents for the removal of iodine radioisotopes is needed to inform manufacturers as well as the design of water treatments. Comparing ACs from either natural or synthetic origin with aerogels, both types can achieve a similar order of magnitude in iodine uptake ( $\sim 1$  g I<sub>2</sub>/g sorbent). Carbon aerogels prepared from biomass are competitive; some have even outperformed those produced from resorcinol–formaldehyde. The introduction of nitrogenated and sulfur groups results in enhanced chemisorption and physisorption of I<sub>2</sub>. The adsorption of iodine can also be enhanced by creating positively charged carbon surface, which at low pH promotes interaction of the sorbent with HI and I<sup>−</sup> anions. Aerogels have complex preparation procedures, change over time and have fragile structure that deteriorates, factors that will hinder their use for upscaled water treatment applications. The regeneration of aerogels has been addressed and showed stable adsorption capacity during five regeneration cycles with ethanol.

CNTs can uptake I<sub>2</sub> via lateral vacancies in hydrogenated pore edges of CNTs and are useful for the detection of I species with fast response. However, the recovery affected by the desorption of I<sub>2</sub> can be slow and is an aspect to improve. CNTs' application as an adsorbent for extracting iodine from contaminated water is questionable due to noncompetitive sorption capacities and their toxicity. The highest uptake of I<sub>2(aq)</sub> was reported by B and N doped carbon nanocomposite from CNTs (9.92 g I<sub>2</sub>/g carbon), where the nitrogen groups participated in ionic interactions. Like CNTs, carbon dots can be used for the detection of I<sub>2</sub> (even from several of its species I<sub>2</sub>, I<sup>−</sup> and IO<sub>3</sub><sup>−</sup>) with high sensitivity (LOD 3.5 nmol

I<sub>2</sub>/L). However, as sorbents to remediate water, they had low performance ( $<0.2$  g I<sub>2</sub>/g removal).

MXenes derivatised with Ag, the only ones prepared and tested for the removal of iodine from water, took up to 0.7 g I<sub>2</sub>/g. Hence, their cost/effectivity does not justify using them for the large-scale applications.

The number of regenerable carbon adsorbents is increasing, yet many studies neglect addressing their regeneration and end-of-life. The main gaps in knowledge that deserve further research due to the increase in demand for the removal of iodine are 1) alternatives to activation with KOH, currently a main activating agent which is corrosive and harmful to the environment; 2) Improvements in the sustainability of the preparation of carbons and their composites. That would reduce energy consumption by eliminating the carbonisation step and compensating this with B and N or S and N doping under moderate temperatures (170–210 °C); using hydrothermal method (HTM); capturing CO<sub>2</sub> emissions; and studying cost/effective ways to prolong the use and re-use the sorbents to avoid generating a new type of radioactive waste. Carbons that can be incorporated in membranes may hold the future of the removal of iodine species and warrant further research.

#### CRediT authorship contribution statement

**M. Kunarbekova:** Visualization, Formal analysis, Data curation. **R. Busquets:** Supervision, Resources, Methodology. **Ye. Sailaukhanuly:** Writing – original draft. **S.V. Mikhlovsky:** Supervision, Conceptualization. **K. Toshtay:** Visualization, Validation, Software. **K. Kudaibergenov:** Writing – review & editing, Project administration. **S. Azat:** Supervision, Resources, Methodology, Funding acquisition,

Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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Views and opinions expressed are however those of the authors only and do not necessarily reflect those of the European Union or Research Executive Agency (REA). Neither the European Union nor the REA can be held responsible for them.

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