

1. Introduction

Aerogel is a light weight, porous solid material having low density, high porosity, low thermal conductivity, high specific surface area, and good mass transfer capabilities. According to IUPAC (International Union of Pure and Applied Chemistry), “aerogel are non-fluid networks composed of interconnected colloidal particles as dispersed phase in a gas (typically air)” (White et al., 2014). Almost nine decades ago, aerogel comes into use however, its application was limited in ancient time. Recently, aerogel have gained huge interest from the researcher due to their unique characteristics (porous network, low density, light weight, mechanical strength, etc.). Aerogel possess some interesting characteristics like low thermal conductivity (as low as $0.015 \text{ W m}^{-1}\text{K}^{-1}$), low density (as low as 1 kg m^{-3}), high specific surface area (as high as $1000 \text{ m}^2\text{g}^{-1}$), and excellent mass transfer properties with coherent porous (porosity more than 95 % and pore diameter is in the range from 2 nm to 50 nm) solid structure (Wang et al., 2019; Wu et al., 2018; Zhang et al., 2017; Zhao et al., 2018; Zheng et al., 2020). Due to these aforementioned characteristics, aerogel grabs the attention of food researchers for the application in food.

In 1931, Steven Kistler first developed aerogel (silica gel as precursor material) by increasing the pressure and temperature of the jellies beyond its critical point to replace the liquid of jellies with gas (Kistler, 1931). A series of aerogels (silica, stannic oxide and cellulose) have been synthesized by Steven Kistler since first development (Zheng et al., 2020). Silica based aerogel are available since last nine decades (approximately). Traditionally, inorganic compounds are used to prepare aerogels. Poly vinyl alcohol (PVA), polysaccharides, proteins, seed mucilage, etc. based aerogel are quite common nowadays. Mainly, the trend is going towards bio-based aerogel as these are biodegradable, environment friendly, non-toxic and less hazardous (Nita et al., 2020). Protein (Kleemann et al., 2018; Plazzotta et al., 2020; Selmer et al., 2019), starch (Ubeyitogullari & Ciftci, 2016; Zhao et al., 2018; Zhu, 2019), and mucilage (Comin et al., 2015; Falahati & Ghoreishi, 2019; Ubeyitogullari & Ciftci, 2020) based aerogel are some of the examples of food grade aerogel. Starch is one of the popular precursor materials of bio-based aerogel preparation. Various kinds of starches (corn, wheat, rice, etc.) are used for aerogel preparation due to their functional properties like, chemical component carrier (Fonseca et al., 2021; Goimil et al., 2017), carrier and filler of bioactive component in food

preparations (Ubeyitogullari & Ciftci, 2016), functional food ingredient (Ubeyitogullari et al., 2018), etc. The crucial steps involved in the development of aerogel are (i) making hydrogel, (ii) turning hydrogel into alcogel, and (iii) turning alcogel into aerogel. Most hydrogels are made using either the sol-gel method (Chen & Zhang, 2019) or the emulsion gelation method (Kleemann et al., 2018; Selmer et al., 2019). However, some other gelation method like gelatinization retrogradation (Ubeyitogullari et al., 2018), ionotropic gelation (Plazzotta et al., 2019), heat set (Kleemann et al., 2020; Plazzotta et al., 2020), cold set gel (Ahmadi et al., 2016) and enzymatic cross-linking (Kleemann et al., 2020) can be followed to form hydrogel. Substitution principle [water (present in hydrogel) with alcohol (methanol, ethanol, etc.)] is used to form alcogel from hydrogel. Alcogel are dried [super critical CO₂ (SCCO₂), freeze drying, vacuum drying, hot air oven drying, etc.] to form aerogel. It is noteworthy mentioning that freeze drying can convert hydrogel into aerogel directly without converting it into alcogel. Since last few years super critical fluid (CO₂) extraction has become a well adopted and well established technology in food industries, which indicates a potential to set up a food grade aerogel industry (Selmer et al., 2015). Moreover, direct evaporation of the liquid is avoided to preserve the connected structure from shrinkage. Depending upon the treatment and preparation procedure aerogels possess all the three types of porosity (micro-, meso-, and macroporosity). As the physicochemical characteristics is highly dependent on fabrication process (specially the drying process), still the definition of aerogel is ambiguous (Ganesan et al., 2018; Zheng et al., 2020). To the best of our knowledge aerogels can be prepared by substituting the liquid of the gels into three dimensional network with gas and extended to various kind of porous solid materials having low weight, large inner surface area, high porosity and low density.

In the recent times, corn starch has grabbed the attention of researchers as it is having broader range of application potential. However, structural collapse, poor mechanical strength, high stiffness etc. restricts the use of biopolymer-based aerogel in the food systems (Abdullah et al., 2022). Glycerol, which is having similar glucose unit to starch is very often used as plasticizer in starch. Starch molecule's intermolecular interaction is reduced due to addition of glycerol thereby results in increased intermolecular spacing which promotes flexibility and reduces fragility to the entire structure (Aghazadeh et al., 2018). Presence of glycerol also increases starch molecules affinity towards water due to increase in number of hydroxyl groups and it also helps in developing strong hydrogen bonds with water because of reduction in O-H band stretching (Aghazadeh et al., 2018; Nordin et al., 2020).

Aerogel are applied mainly for oil water separation (Li et al., 2017; Meng et al., 2017), adsorption (Chen et al., 2017; White et al., 2014), chromatography (White et al., 2014), thermal insulation (Shang et al., 2017; Yang et al., 2017), ion exchange materials (Keshipour & Khezerloo, 2017; White et al., 2014), air filtration (Zeng et al., 2019), food and drug delivery systems (Bhandari et al., 2017; de Oliveira, Bruni, el Halal, et al., 2019), food packaging (de Oliveira et al., 2020b; de Oliveira, Bruni, Fabra, et al., 2019b; Wang et al., 2019), glucose detection (Ma et al., 2020) and sensing of NO_x and aldehyde species for the detection of glutaraldehyde (Wu et al., 2019).

Active nanomaterials like quantum dots (QDs), carbon dots (CDs), and others are being used to make functional aerogel. CDs as nanomaterials (quasi-zero-dimensional materials) are very interesting because they have some unique and great properties, such as a nano size (10 nm), high dispersibility in water and other polar solvents, high photostability, high biocompatibility, low photobleaching, low cytotoxicity, low chemical toxicity, and high fluorescence quantum yield (QY). Moreover, versatile surface chemistry (through surface passivation) and tuneable fluorescent behaviour (based on excitation wavelength) of CDs extends its range of application (De Medeiros et al., 2019; Pappalardo et al., 2020) like, detection and adsorption of heavy metals (Cr³⁺, Cr⁶⁺, actinide, lanthanide ions etc.) in water, volatile organic compounds detection, solar energy conversion system (Zhang et al., 2019), solar water evaporation system (Xu et al., 2022), photocatalyst (Han et al., 2020; Lu et al., 2018), photosensitizer (Lu et al., 2016), adulterant detection in food, smart packaging material, etc. However, some limitations like, cheap source of biomass, too much by-products during synthesis (top-down), narrow range of absorption and emission wavelength, upconverting emission, chance of heterogeneity, etc. are there for bio-derived CDs which restricts its application (Zhang et al., 2018). Recent trend is towards the incorporation of nanomaterials (QDs, CDs, etc.) inside different carrier media like the aerogel. Nowadays CDs are used inside the aerogel matrix to make a functional aerogel.

In present days consumers are paying attention to their diet and they become more health conscious ever before. It is worth mentioning that technology related to food processing has improved over time to fit with the trend accordingly with the consumers demand. Food scientists and researchers are working irrepressibly to deliver more hygienic, fresh, safe, nutritious, healthy and tasty food stuffs to the diverse range of consumers. They are working continuously to improve production process by introducing novel technologies (includes encapsulation and slow release of bioactive compounds), packaging by means of active and

intelligent packaging (includes retention of product quality, increased shelf life, preserving and utilizing the characteristics of functional compounds) and safe distribution of food stuffs (de Oliveira, Bruni, Fabra, et al., 2019a; Mikkonen et al., 2013). To conserve and protect the food from extrinsic factors and to provide health benefits to the consumer, food industries are continuously searching for an emerging technology (de Oliveira et al., 2020a). Aerogel is one of the emerging and important material among the others (hydrogel, nano-emulsion etc.).

Formalin (FA) is basically a colourless, transparent solution of formaldehyde (37 – 40 % w/w) which is a highly flammable, extremely sensitive, colorless gas that readily polymerizes in normal temperature and pressure. The consumption of FA causes serious health issues like damage in liver, kidney, lung, neurological systems etc. International Agency for Research in Cancer (IARC) has listed formaldehyde as Group I carcinogen. Generally, FA is widely used for biological preservation purpose (Thepchuay et al., 2022). However, it has been used illegally by the food merchants especially fish merchants to cope with rapid spoilage as fish is highly perishable (Kaur et al., 2024). The conventional analytic detection methods [spectrophotometric, gas chromatography-mass spectrometer (GC-MS), high performance liquid chromatography (HPLC), etc.] of FA are complex, vexatious and costly (Fappiano et al., 2022). Therefore, simple, advance and economic techniques of FA is highly needed to cope with the rising concern of illegal addition of FA in food (fish, meat, vegetables, etc.).

To the best of our knowledge, there is a lack of study on the effect of glycerol on physical, mechanical, functional, textural, and morphological properties of SCCO₂, freeze and microwave dried corn starch based aerogel. The existing drying techniques (SCCO₂ and freeze drying) are expensive, time consuming, complex in operation, and high energy consuming. Additionally, the potentiality of CDs loaded aerogel as a multiresponsive functional aerogel remain inadequately addressed. Further, the applicability of CDs loaded corn starch-based aerogel in the sensing of FA in fish was not thoroughly investigated.

The entire work is organized into the following objectives to achieve the aim of the present research/ thesis:

1. To optimize the processing conditions for development of aerogel using corn starch
2. To study the effect of different drying techniques on functional properties and physicochemical properties of developed aerogel
3. To develop multiresponsive carbon dots based aerogel and its characterization
4. To develop a method for sensing formalin in fish using carbon dots based aerogel