# Chemical oxidation of mesoporous carbon foams for lead ion adsorption

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## ARTICLE INFO

## ABSTRACT

Acid treated mesoporous carbon foams, with surface areas ($S_{BET}$) as high as 2207 $m^2 g^{-1}$, were synthesised by the carbonisation of fructose over $ZnCl_2$ templates and tested as adsorbents of Pb(II) ions from aqueous solutions. Whilst the oxidising acid treatment disrupted the morphology of the foams, it also led to a proliferation of oxide moieties on the surface of the material which acted as binding sites for Pb(II) ions. Characterisation of the oxidised surfaces by IR spectroscopy and measurement of the zero point charge ($pH_{pzc}$) showed that the number of acidic surface sites increased with increasing acid concentration and temperature. The oxidised carbon foams were tested for their efficiency at removing Pb(II) ions from aqueous solutions, using batch adsorption techniques. The concentration dependence of Pb(II) ion uptake by the mesoporous carbon adsorbents could be fitted to Langmuir, Freundlich and Dubinin–Kaganer–Radushkevich (DKR) isotherms, from which the maximum adsorption capacity ($Q_m$) and the energy of adsorption ($E_a$) was derived. $E_a$ values obtained for the mesoporous carbon adsorbents were associated with weak adsorption (<8 kJ mol$^{-1}$), ion exchange adsorption (8–16 kJ mol$^{-1}$) and chelation (>16 kJ mol$^{-1}$) depending on the surface oxidation conditions used.

## 1. Introduction

Lead (Pb(II)) ion contamination in drinking water is a major source of concern due to its detrimental effect on human health when ingested. Chronic exposure to Pb(II) ions, even at low levels, can cause long term health effects as the ions are not easily excreted from humans and build up in their bones, lymphatic system and digestive tracts [1,2]. Elevated levels of Pb(II) ions in the human body have been shown to cause a number of ailments such as fatigue, a decrease in male reproductive ability, digestive problems and anaemia [3–5]. Children are particularly susceptible to the effects of Pb poisoning as extensive research has proven abnormal levels can effect brain development and depress cognitive skills, causing learning and behavioural difficulties [6–8]. Sources of Pb intoxication include ingestion, through contaminated food or drinking water [9], occupational exposure [3,4], inhalational of contaminated dust [7,10] and even obscure means as shown by a relationship between a child's play habits in mud and Pb intoxication [10].

The partial solubility of Pb in wastewater makes remediation and purification of drinking water problematic. Adsorption by activated carbons is the most commonly used method to reduce the amount of Pb(II) ions in drinking water to levels acceptable for consumption. Several methods have been employed for removing

Pb(II) ions from wastewater, such as their adsorption onto zeolites [11], clays [12] and phytoremediation [13]. Activated carbons are ideal candidates for adsorbing Pb(II) ions from aqueous solutions as they can be prepared easily from abundant and low cost raw materials, ranging from coconut shells [14] to car tyres [15], have large surface areas of over 2000 $m^2 g^{-1}$, vast pore networks and readily oxidised surfaces through pre- or post-modification processes [14–16]. Pre-treatment of activated carbons can be carried out by chemically oxidising carbon biomass prior to pyrolysis. Zhang et al. impregnated sugar cane with $ZnCl_2$, $MgCl_2$ and $CaCl_2$ before heat treatment, showing that $ZnCl_2$-treated samples yielded high surface area carbons (1353 $cm^2 g^{-1}$) compared to similar treatments using $MgCl_2$ and $CaCl_2$, which recorded surface areas in the range between 54 and 180 $m^2 g^{-1}$ [17]. When tested as adsorbents of Pb(II) ions it was found the highest and lowest uptake were recorded for $CaCl_2$ and $ZnCl_2$ modified carbons respectively, indicating the importance of the oxidation strength of the metal chloride in modifying Pb(II) ion adsorption, even if it is to the detriment of the pore structure of the carbons [17]. Chemical oxidation using strong oxidising acids (namely nitric and sulphuric acids) is known to be highly effective in modifying the surfaces of carbon materials for the adsorption of Pb(II) ions. Nitric acid treatment of activated carbons results in a collapse of their surface area (from 1245 to 1053 $m^2 g^{-1}$) but an exponential increase (from 17 to 40 mg $g^{-1}$) in their capacity for the adsorption of Pb(II) ions as the temperature and the acid strength used in the surface modification process is increased [18]. Highest reported uptake of Pb(II)

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ions, 444 mg g$^{-1}$, was reported for nitric acid modified crushed corn cobs, and therefore nitric acid surface modification was be used for the purposes of this study [19]. Sulphuric acid is commonly used in the pre-treatment of biomass (such as tamarind wood) before pyrolysis to create activated carbons with high adsorption capacities for Pb(II) ions (134.2 mg g$^{-1}$), and a similar process used on wheat bran gave uptakes of 55.6 mg g$^{-1}$ [20,21]. Post-treatment of activated carbon by hydrogen peroxide, producing oxidised activated carbon surfaces, results in an increased capacity for Pb(II) ion uptake, but is less effective than nitric acid treatments using parallel conditions [18]. Li et al. used nitric acid oxidised carbon nanotubes (CNTs) as Pb(II) ion adsorbents, giving an uptake as high as 97.1 mg g$^{-1}$ [22]. In a separate study, the same group showed that the dimensions of CNTs greatly affected the uptake of Pb(II) ions [23]. Other novel carbon nanostructures such as carbon nanocages (CNCs), offer much higher surface areas and porosities when compared to their CNT counterparts and also excellent dispersion in aqueous solution compared to activated carbon [24].

Activated carbons are generally synthesised by the pyrolysis of biomass with limited control over morphology, resulting in carbons with broad pore volume distributions and extensive macroporous regions, limiting the high surface areas that can be achieved [25]. Carbon foams are prepared by nanocasting the carbonisation of a carbon precursor over a well-defined template. These templates are varied and can be chosen selectively to establish a certain morphology and porosity in the resulting carbon matrix. Mesoporous silicas, silica spheres, zeolites and metal chlorides have all been utilised to nanocast carbon foams [26–29]. Following dissolution of the hard template pure carbon structures are obtained with monodisperse nanoscale pore structures, which greatly improves the overall surface area of the carbon materials. Silica is commonly used as a hard template as its pore structure can be effectively transferred to a carbon replicate, as silica has the strength and flexibility to sustain the pressures exerted by nanocasting [27,30,31]. Aggressive dissolution methods are often needed (such as treatment with HF) to fully remove the silica template [31]. Zeolite templates allow for the formation of carbons with high surface areas (in the region of 2000 m$^2$ g$^{-1}$), with narrower pore diameters than are achievable using silica templates [29,32]. Micropores in zeolite-templated carbons contribute to the high surface area and much like silica, aggressive treatment with HF acid is necessary to completely remove the zeolite template [29]. Huang et al. previously demonstrated that nanocasting of carbohydrates on metal chlorides (ZnCl$_2$) allows for the development of carbons with surface areas up to 2047 m$^2$ g$^{-1}$. The metal chloride template was easily washed out using mild hydrochloric acid (1 M HCl) [26]. Nanoporous carbons generated using organic colloids eliminates the need for dissolution of the template, as the colloids depolymerise during the carbonisation process [33]. However, control over the pore structure in such porous carbons diminishes with the colloid soft templating method and the highest surface area achieved was 765 m$^2$ g$^{-1}$ [33,34]. Gogotsi et al. demonstrated that the chlorination of SiC at 1000 °C generated microporous carbon foams with surface areas greater than 1000 m$^2$ g$^{-1}$ without any post-treatment, as the non-carbon by-products were removed as gaseous chlorides (SiCl$_4$) [35]. The properties of nanoporous carbon, such as electrical conductivity and high surface areas, make them ideal candidates for a multitude of applications including hydrogen storage [29,36], lithium ion battery electrodes [37] and catalyst supports [38].

This article describes the use of nitric acid-treated, high surface area nanoporous carbon materials as adsorbents of Pb(II) ions from aqueous solution, providing an insight into how surface oxidation can promote the uptake of metal ions. In particular, the uptake of Pb(II) ions on the porous carbon surfaces was found to differ according to the acid treatment used.

## 2. Experimental

### 2.1. Synthesis of mesoporous carbon foams

Mesoporous carbon foams were synthesised using a previous method described by Huang et al. [26]. Briefly 10 g of fructose was mixed with 10$n$ g of ZnCl$_2$ (where $n$ = 1,2,4) and dissolved in 10$n$ ml of deionised H$_2$O to form a clear solution. The samples were labelled CF$n$, where $n$ denotes the ratio of ZnCl$_2$ to fructose. The solution was then heated at 85 °C for 3 h to form viscous slurry, which was cured by further heating in an oven at 130 °C for 90 min to form a black sponge like solid. The black solid was then carbonised in a tube furnace at 450 °C (heating ramp rate = 5 °C min$^{-1}$) for 2 h under a flow of Ar (200 ml min$^{-1}$) before cooling to room temperature. To remove ZnCl$_2$, the product was stirred in 1 M HCl for 1 h before filtering, to yield a granular black solid before washing with boiling deionised H$_2$O. The samples were then dried in a 100 °C oven for 24 h.

#### 2.1.1. Regeneration of ZnCl$_2$ precursor
The ZnCl$_2$ precursor was isolated and recycled through a number of cycles. The filtrate from the 1 M HCl acid purification was collected and reduced in volume by boiling until a precipitate was formed. The precipitate was then stirred with 50 ml of 37% HCl for 4 h to form the ZnCl$_2$ phase, before evaporation to reduce the mixture in volume. As ZnCl$_2$ is hygroscopic, the mixture was dried by evaporating any residual liquid by mixing with liquid N$_2$. The isolated ZnCl$_2$ could subsequently be used as a precursor in the formation of CF2 as described in the previous section and is labelled as CF2*.

### 2.2. Chemical oxidation of CFn mesoporous carbons

Oxidation of the carbon surfaces was carried out using various concentrations of HNO$_3$ over a range of temperatures. In the preparation of samples denoted as CF$n$–$x$M–$y$C, 0.5 g of CF$n$ carbon foam (where $n$ is the type of pristine mesoporous carbon used ($n$ = 1,2,4), $x$ is the molar strength (M) of nitric acid used ($x$ = 1, 4, 6, 8, 10) and $y$ is the temperature (°C) at which the chemical oxidation of mesoporous carbons was undertaken ($y$ = 20, 50, 80, 105)), was mixed with 80 ml of HNO$_3$ and heated for 3 h in a partially closed solvent bottle at a set temperature. The mixture was then filtered in a fume hood and washed with deionised H$_2$O until the run off was at a neutral pH. All prepared samples were dried in a 100 °C oven for 24 h.

### 2.3. Characterisation

Transmission electron microscopy (TEM) of the carbon foams was performed on a JEOL 2000FX microscope operating at 200 kV. Samples were prepared for TEM analysis by dispersing the material in ethanol and dropping onto copper grids. Scanning electron microscopy (SEM) analysis of carbon foams, to identify their morphologies, was conducted on a JEOL 5510 SEM. The powder samples were placed on carbon tape and then adhered to a brass stub. The surface areas of the carbon sorbent materials were measured using a Micromeritics TriStar II 3020 volumetric analyser. Each sample was degassed for 5 h at 200 °C prior to measurement. The surface area was calculated using the Brauner Emmett Teller (BET) method based on the adsorption data in the relative pressure ($P/P_0$) region of 0.01–0.99 and single-point pore volume