

Chemical Activation of Recycled Carbon Fibres for Application as Porous Adsorbents in Aqueous Media

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Abstract — The carbon fibre reinforced polymer (CFRP) industry has rapidly expanded over recent due to a range of benefits, including high mechanical strength and low weight. However, issues arise when the products reach their end-of-life (EoL). At present, pyrolysis is the only method for recycling CFRPs at scale. The process is still relatively new, resulting in stigma around the reapplication of recycled fibres within many industries due to the compromised mechanical stability. In order to increase the sustainability of the industry, alternative EoL pathways must be identified.

Virgin carbon fibres (vCFs) have been successfully applied as adsorbents; however, there appears to be a gap in the literature when considering their recycled counterparts. In this study, chemical activation of industrial-grade recycled carbon fibres (rCFs) using NaOH has been investigated, together with vCF as proof of concept. The adsorption capacity of methylene blue (MB) was investigated to determine the degree of *activation*. The UV-visible spectrometry results indicated a maximum MB removal efficiency of 21.83 % and 21.80 % for activated-vCF (AvCF) and activated-rCF (ArCF), respectively; indicating that rCF are a promising precursor for applications as adsorbents in aqueous media, despite the higher levels of impurities when compared to the virgin counterpart.

I. INTRODUCTION

Polyacrylonitrile (PAN)-based CFRPs boast a range of attractive properties, including low weight, while maintaining high tensile strength, durability, temperature tolerance and chemical resistance. This has led to the rapid expansion of their application within a range of industries, some examples being aviation, aerospace, automotive, wind turbines and more, with the former two contributing the largest portion of over 55 kt in 2018 [1]. Over a 12-year period from 2006 – 2018, the production of carbon fibres (CFs) has increased by 180.36%. However, sustainability issues arise when the materials reach their EoL with waste projected to reach 20 kt annually by 2025 [2–4]. This issue has been accelerated by the Coronavirus pandemic, with many aircraft retirement programs being brought forward; it has been predicted that approximately 6000 – 8000 commercial aircraft will reach their EoL by 2030 [2].

At present CFs are classified as *chemical waste* by the EC Waste Landfill Directive leading to sizeable disposal costs [4]. Although, in recent years, there has been significant research into the recovery of CFs from CFRP matrix using a range of methods, namely mechanical, thermal (pyrolysis), chemical, microwave, and fluidised bed recycling. Currently, pyrolysis is the only commercial recycling method that leaves CFs intact. The method involves heating (450 – 700 °C) CFRPs in an inert atmosphere to thermally decompose the resin. Gen 2 Carbon (formerly ELG), based in the West Midlands, UK, is an example of where this method has been commercialised, with the recycling plant being capable of processing 5 tons of waste per day [5]. However, the process causes a reduction of mechanical stability and fibre length, an increase of approximately 5 % in weight and the introduction of impurities. Therefore, even Gen 2 Carbon has stated that their products require new processes and designs rather than directly replacing vCFs.

In recent decades the application of carbonaceous adsorbents in environmental remediation has received great attention due to their high specific surface area, tunable pore size distribution and surface functionalities, leading to high removal efficiencies against both organic and inorganic pollutants [6–8]. These characteristics are achieved using activation and modification to achieve the desired properties to attract target pollutants.

vCFs have been widely activated using physical or chemical methods for application as adsorbents in both liquid and gas media [9–15]. Physical activation typically involves heating (700 – 1200 °C) the CFs with a gaseous activation agent such as CO₂ or steam [16]. Whereas chemical activation involves heating (400 – 850 °C) with a chemical agent, for example, sodium hydroxide or nitric acid [16–18]. Chemical activation presents several advantages over physical activation, such as lower activation temperatures and reaction times, higher yields, and controlled porosity development. However, the method also comes with some disadvantages, including expensive and often corrosive reagents and an additional washing stage, resulting in secondary pollutions. Overall, it

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was decided that the advantages of chemical activation outweighed the disadvantages, leading to the application of chemical activation methods.

At present, very few studies have investigated the activation of rCF. Nahil et al. recovered CFs from the CFRP resin using pyrolysis methods on a laboratory scale [4]. After which, they successfully activated the rCF using thermal activation methods, achieving a maximum specific surface area of $803 \text{ m}^2\text{g}^{-1}$, which is comparable with SSA achieved for physically activated PAN-based vCFs in the current literature [6, 18]. The aim of this study is to determine the “proof of concept” as whether industrial-grade rCFs are potentially suitable precursors to produce activated carbon fibres using chemical activation methods for application as adsorbents in aqueous media.

II. MATERIALS AND METHODS

The rCF precursor was obtained from Gen 2 Carbon (West Midlands, UK). The rCFs were chemically activated by heating in an inert atmosphere (N_2) with NaOH to $700 \text{ }^\circ\text{C}$ for 1 h, using a 1:1 impregnation ratio. After activation, the fibres were neutralised using HCl (2 M), followed by washing with $80 \text{ }^\circ\text{C}$ deionised water until the filtrate was free of chloride ions [17]. The resulting fibres were dried at $110 \text{ }^\circ\text{C}$ overnight. vCF were activated using the same conditions as proof of concept.

Both rCF and vCF were characterised before and after activation using Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDS, LEO 1455VP), Fourier Transform Infrared Spectrometry (FTIR, Perkin Elmer Spectrum One).

The *potential* adsorption capacity of ACF was assessed by determining the corresponding MB number. 50 ml of MB (21.5 mg/L) was placed in a sealed container with ACF (40 mg) and left at room temperature ($20 \text{ }^\circ\text{C}$), with shaking (200 rpm) for 24 h [20]. After which, the solution concentration was determined using a UV-vis spectrophotometer (Shimadzu UV-1800) with a wavelength of 664 nm; the λ_{max} of MB. The final concentration of MB was determined using two calibration curves ranging in concentrations from 5 – 25 mg/l.. The total amount adsorbed was determined using Equation 1:

$$q_{\text{eq}} = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

where, q_e is the maximum adsorption capacity, C_0 is the initial starting concentration, C_e is the concentration of the MB at equilibrium time, V is the solution volume, and M is the dosage of adsorbent used in this work.

III. RESULTS AND DISCUSSION

A. Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS)

The surface morphology of the ACFs is shown in Figures 1A and 1B. The images show a smooth fibrous structure with no defects on the surface (Figure 1); this is consistent with images of chemically activated PAN-based CFs in the current literature [10]. The average diameter of the fibres was approximately $7.5 \text{ }\mu\text{m}$ and $7.75 \text{ }\mu\text{m}$ for AvCF and ArCF,

respectively. The difference in diameter can be attributed to increased impurities within the ArCF structure resulting in larger interlayer spacing between the CF planes, which is confirmed by the EDS data (Table 1), where ArCF showed a larger content of Na, Mg and other impurities, including Si, K and Ca. Another difference observed between the two types of fibres was the presence of impurities. AvCFs appeared to have very few, small amounts of impurities, whereas ArCFs typically displayed larger ($> 10 \text{ }\mu\text{m}$) impurities on the surface, shown in Figure 1B.

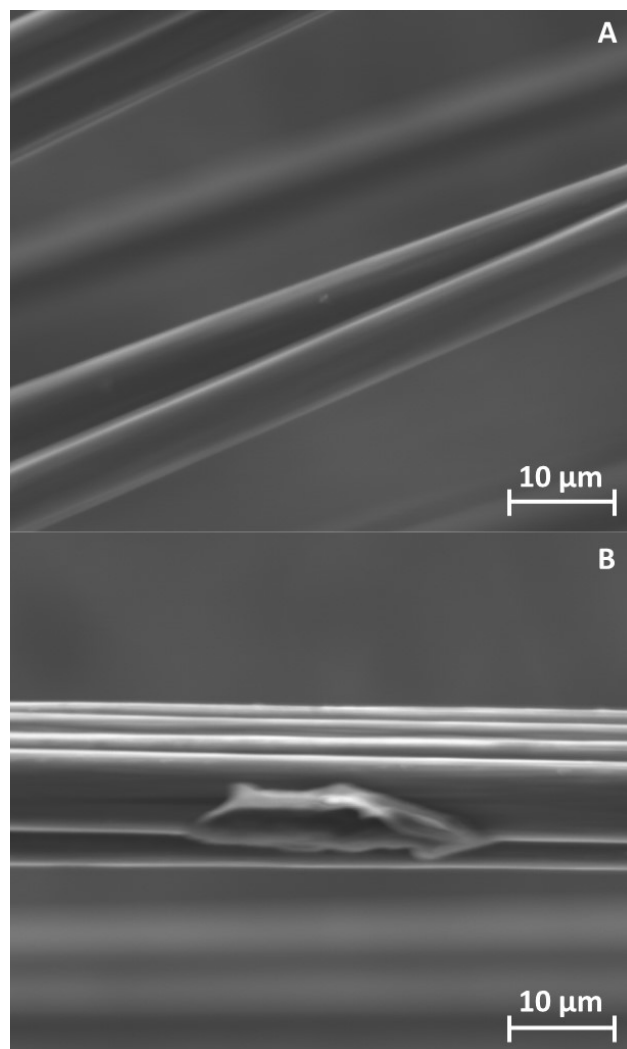


Figure 1. SEM images of AvCF (A) and ArCF (B).

Moreover, the EDS data showed a very low carbon content for both ACFs, which could be attributed to a considerable number of oxygen groups added to the surface of ACFs.

Table 1. Percentage composition of AvCF and ArCF

Element	Composition (wt%)	
	AvCF	ArCF
C	24.13	22.72
O	69.76	65.78
Na	0.14	2.35
Mg	0.03	0.15

Others	5.94	9
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B. Fourier Transform Infrared Spectroscopy

Figure 1 depicts the FTIR spectra for both rCF and vCF; displaying some of the typical bonds expected for activated carbonaceous adsorbents [22, 23]. Both materials show prominent peaks at 3500 and 1122 cm^{-1} , corresponding to O-H and C=O stretching vibrations, respectively. The peaks observed at 1632 cm^{-1} indicate the stretching vibrations of C=C, C=N and C=O in heteroaromatic ring systems [23]. Additional peaks are observed at 974 and 807 cm^{-1} which can be attributed to the C=C and C-H bending vibrations, sequentially.

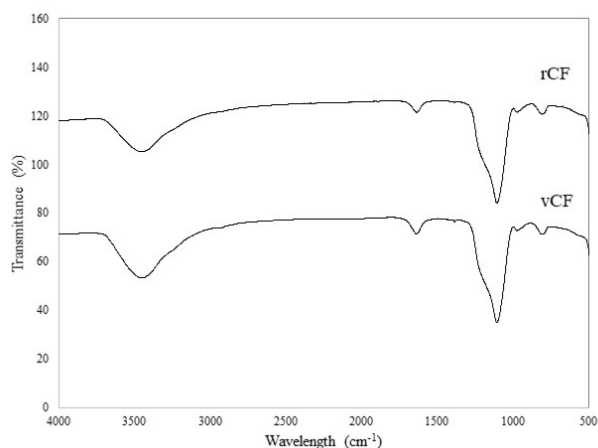


Figure 2. FTIR of activated rCF (top) and vCF (bottom).

C. Adsorption of Methylene Blue

After adsorption, the remnant concentration of MB was determined using UV-visible spectroscopy (Table 2). Both ACFs had a maximum experimental adsorption capacities of > 5.75 mg/g, which is greater than values achieved in other studies [24]. However, the value remains lower than the adsorption capacities observed when applying experimental methods such as design of experiment [22], indicating the necessity of further optimisation of experimental variables in the next phase of our study. Overall, ArCF had a fractionally lower removal efficiency when compared AvCF, which was attributed to the higher levels of impurities within the structure resulting in pore blocking and, potentially, the presence of repulsive electrostatic fields.

Table 2. UV-vis absorbance of AvCF and ArCF at 664 nm.

Sample	Absorbance	C_e (mg/l)	q_e (mg/g)	Removal (%)	Ref
MB	2.70	-	-	-	
AvCF	2.36	16.83	5.77	21.83	
ArCF	2.36	16.84	5.76	21.80	
AC	-	-	4.80	-	[24]

IV. CONCLUSION

In this study, both vCFs and rCFs have been successfully

activated using chemical methods. It was found that rCFs are promising precursors for the synthesis of environmentally friendly adsorbents for applications in aqueous media, achieving a similar MB removal efficiency to vCFs, of > 21.80 %. However, in order to make this material comparable to other current carbonaceous adsorbents in literature, our pre-treatment, activation and adsorption methods will be further improved in the next phase of this research to achieve the optimum adsorption capacity.

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