Per- and Polyfluoroalkyl substances (PFAS): Ubiquity, levels, toxicity and their removal from aqueous media using novel agro-based adsorbents

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are organic compounds whose hydrogen atoms are replaced with fluorine, thereby making them fluorinated organic substances. They find applications in aqueous film firefighting foams (AFFF), stain repellents, surface-active agents and metal plating parts, textile products and food packaging materials. Consequently, they have become ubiquitous, and are extremely persistent and have the tendency to be accumulative within biotic systems [6]. Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are two most abundant PFAS. Because of the aforementioned properties, their use and dissemination have been restricted under the Stockholm Convention for persistent organic pollutants. Potential health effects associated with the ingestion of PFAS include kidney and liver diseases, thyroid hormonal effects, low birth weight and systemic effects. Based on the toxicological concerns that PFASs pose, their removal from water systems is, therefore, of essence. In the present study, maize tassel powder (MT) and chemically activated maize tassel (CAMT) are applied as adsorbents for the adsorption of PFAS from aqueous media. Maize tassel has been shown to have the potential to remove toxic metals from aqueous media [7]. The objective of this research was to evaluate the efficacy of MT and MT-derived composite materials in removing PFASs from aqueous media.

Materials and Methods

The MTs were sampled from a maize farm in the North West Province, South Africa. This was followed by washing, drying, grinding, milling and sieving using analytical sieves of variable sizes. In order to produce the CAMT powder, 10g of MT powder was added to 10 mL of phosphoric acid (H_3PO_4) (85% by weight) (1:1) in a beaker. The coffee-brown mixture was stirred manually for 10 min and then left to dry for 24 h, and thereafter was oven dried for 2 h at 110°C to ensure the total removal of moisture. This was followed by carbonization and activation, respectively, of the dried CAMT powder at 500°C for 1 h using a tubular furnace (Carbolite-Labotec, South Africa). Batch adsorption experiments were performed in triplicates using the prepared adsorbents. The PFAS-water was prepared using standards of analytical grade. Polypropylene (PP) centrifuge tubes were used and different variables were investigated. The mixture (adsorbent + PFASs) was subsequently filtered after shaking; through a 0.45 µm filter and then the filtrate was analysed for residual PFAS concentrations using a Liquid Chromatography-Mass Spectrometry (LC-MS 8030, Shimadzu) instrument. As a precautionary step, glass wares were first rinsed with methanol to prevent the adsorption of PFAS onto their walls. PFASs have the tendency to adsorb to plastic and more to glass. Therefore, both negative (solution without spiked PFASs) and positive (solution with known concentration of PFASs but without adsorbent) blanks were used. The positive blanks were then used to quantify the PFAS loss to the tube. A correction factor was subsequently calculated and applied for the experiment.

Results and Discussion

Per- and polyfluoroalkyl substances are ubiquitous. They are found in different environmental matrices. Loos et al. [4] reported PFOS and PFOA levels of (10 and 1.3) ng/L, respectively, in River Po in Northern Italy. Llorca et al [3] recorded a PFOA range of (21-907) ng/L in eight breast milk samples from women in Barcelona, Spain. The PFOS and PFOA levels (0.11 and 0.95) ng/g, respectively, were found in the Ariake sea sediments, off the coast of Japan, in the studies by Nakata et al. [5]

Effects of pH and adsorbent mass

The pH range investigated was (2-9). This range was selected to ensure that the adsorbents (MT and CAMT) were in their positively charged state. It has been reported that the point of zero charge (pzc) for MT is 10.4 and most agro-based-activated carbons (5.03), below this pzc, MT and CAMT are positively charged [1, 7]. Simultaneously, this pH range allows the PFASs molecules to be in their deprotonated (ionized) state, whereby there are negatively charged. This is because pH values of 2 and above are higher than the acid dissociation constant (pKa) (below 1) for perfluorinated sulphonates and carboxylates. The effect of pH using MT and CAMT as adsorbents for PFAS removal is shown in Figs. 1 and Fig 2. The effect of pH was more conspicuous when CAMT was applied as an adsorbent than with MT. The optimum pH was found to be pH 2 for both MT and CAMT materials. The long chained PFASs were readily removed by MT across the pH values in the range of (68-88) %; with the highest (88.30%) recorded at pH 2. The PFASs removal using MT was in this order; PFDA>PFNA>PFOS>PFHxS>PFOA for the long chained PFASs and PFHxA>PFHpA>PFPeA>PFBA>PFBS for the short chained PFASs. The PFASs percentage removal recorded using CAMT (Fig.2.) was in the range of 83-88%, a seemingly higher range than the (68-88) % recorded using MT (Fig. 1). Figs. 3 and 4 show the effect of adsorbent dosage (0.02, 0.05 and 0.1g) on the PFASs using MT and CAMT. It can be observed that the PFASs % removal decreases as the adsorbent mass increases using MT (Fig3.). A decrease in chromium ion removal from aqueous media using raw maize tassel was similarly reported in a study by Zvinowanda et al [7]. The reverse is the case for CAMT (Fig.4), where the PFAS % removal increases with increase in the mass of the activated carbon sample. This is similar with several studies on the use of activated carbon derived from agricultural waste. For instance, Fagbayigbo et al. [2] reported an increase in PFAS removal with increase in adsorbent dosage using grape leaf litter-activated carbon.
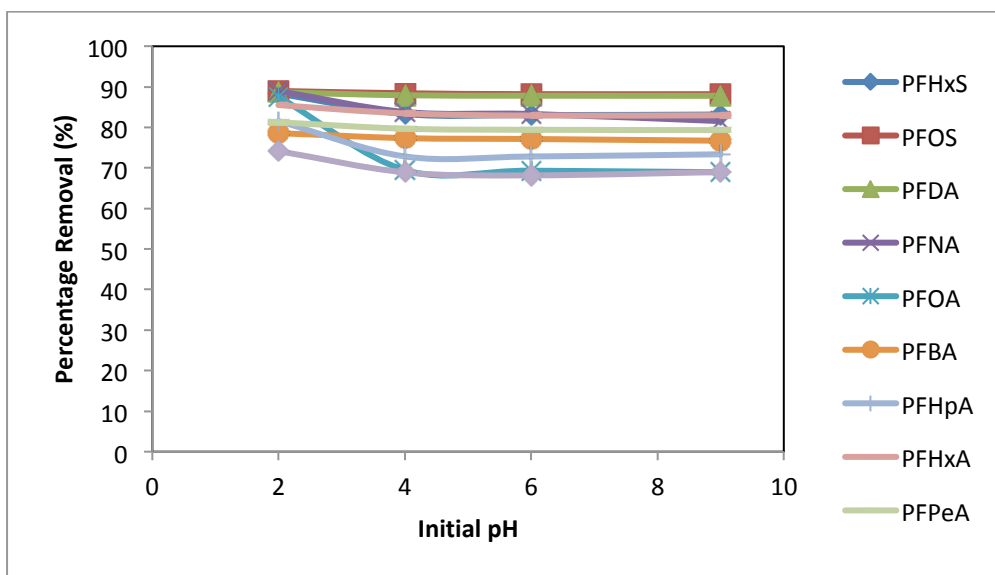

Fig.1: Effect of solution pH using MT (Temp 25°C, duration 24 h, initial PFASs concentration 100 µg/L and adsorbent mass 0.05 g)
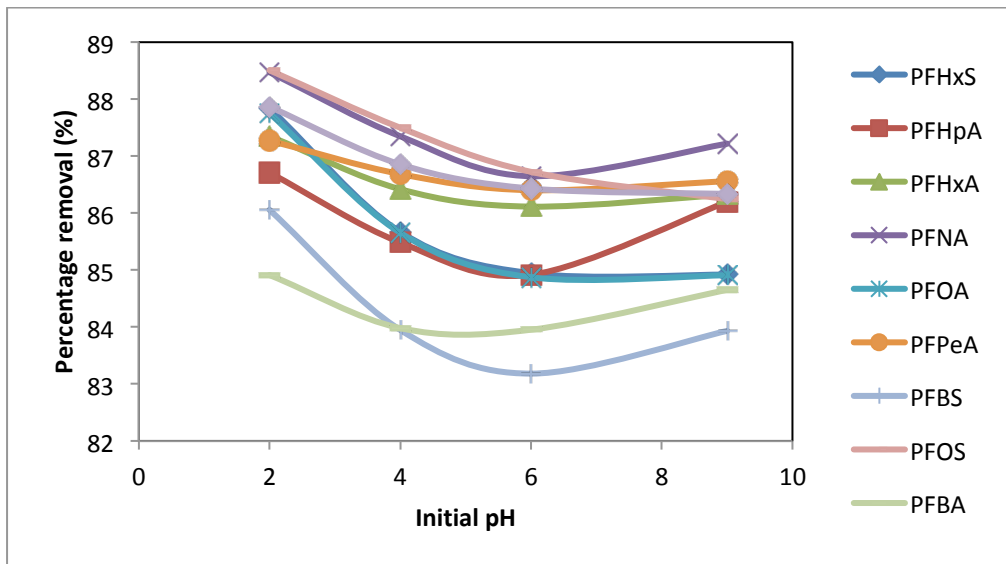
Fig.2: Effect of solution pH using CAMT (Temp 25°C, duration 24 h, initial PFASs concentration 100 µg/L and adsorbent mass 0.05 g)
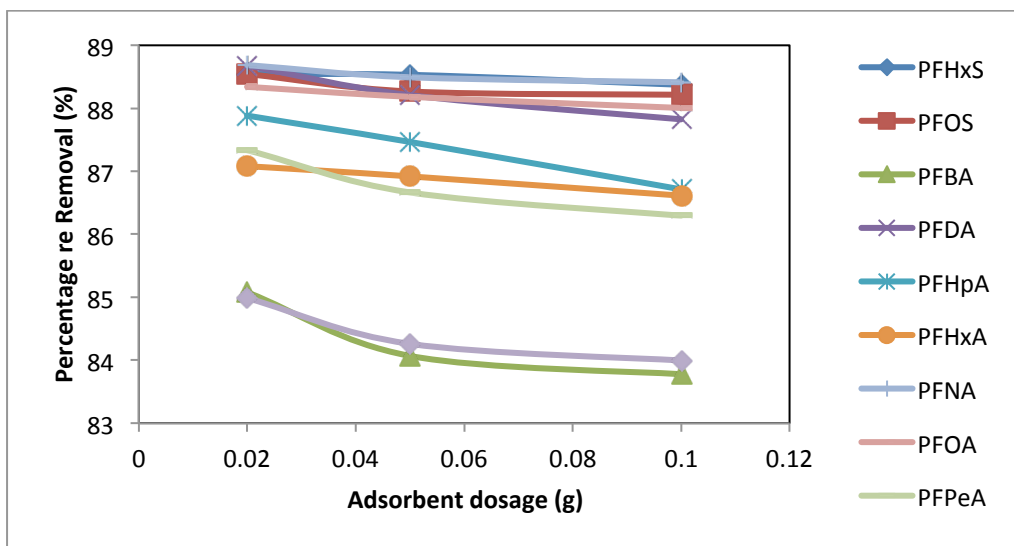

Fig.3: Effect of adsorbent dosage using MT (Temp 25°C, duration 24 h, initial PFASs concentration 100 µg/L and optimum pH of 2)
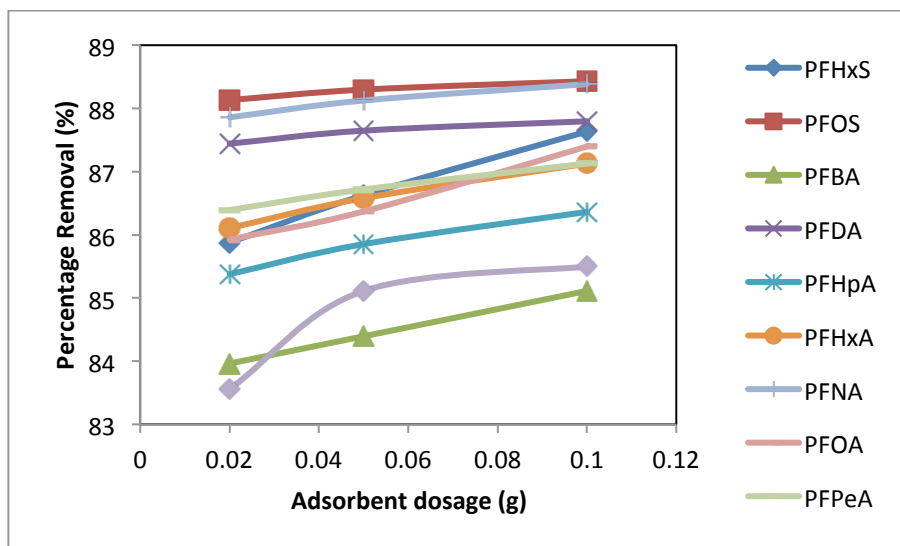
Fig.4: Effect of adsorbent dosage using CAMT (Temp 25°C, duration 24 h, initial PFASs concentration 100 µg/L and optimum pH of 2)

Effect of initial PFAS concentration

The PFAS % removal decreased from (88.2 to 85.3) µg/L for MT and also decreased from (88.9 to 85.6) µg/L for CAMT; as the PFAS concentration was increased from 25 to 100 ug/L.

The presence of functional groups in the maize tassel such as hydroxyls, amides, carboxylic acids and carbonyls is closely associated with the efficacy of maize tassel as an adsorbent [7]. The high PFAS % removal recorded using both adsorbents could be due to electrostatic interaction occurring between the anionic PFASs (negatively charged) and the positively charged adsorbents. Hydrophobic interaction also played a role, especially in alkaline medium whereby there might be little or no electrostatic interactions occurring. This is evident in the pattern observed where the more hydrophobic (less soluble) PFASs (PFDA, PFNA, PFOS) adhered more readily to the adsorbents than remaining in solution; hence the higher % removal rates. This is in agreement with similar studies by [2]. Both adsorbents investigated in the present study performed reasonably well. The need to achieve relatively high PFAS % removal for short chained PFASs, as well as long chained PFAS could be a motivation for the utilization of CAMT over MT. Research on the adsorption process isotherms and kinetics using the investigated agro-based adsorbents is still underway.

Acknowledgements

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