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Removal of microfiber and surfactants from household laundry washing effluents by powdered activated carbon: kinetics and isotherm studies

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ABSTRACT

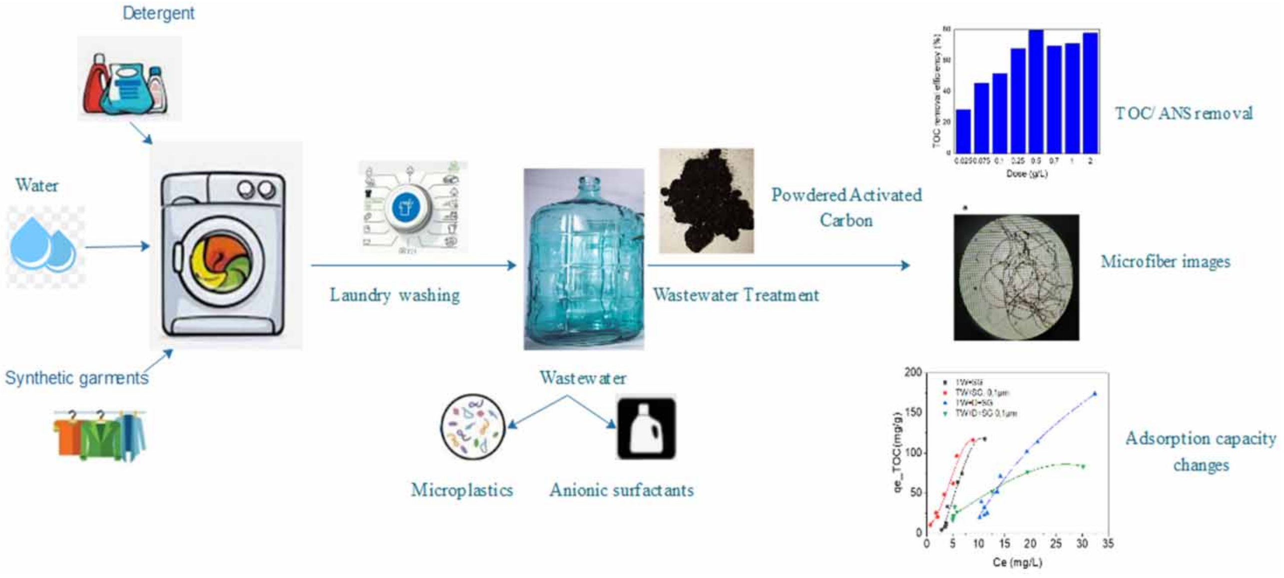
Domestic laundry wastewater discharge contributes significantly to the presence of microfiber and surfactant pollutants in aquatic ecosystems, which have detrimental and toxic effects on humans and the environment. Investigating the efficacy of powdered activated carbon (PAC) in removing micro-/nanofibers with or without surfactant from household laundry effluent is the purpose of the current research. To simulate real-world scenarios, PAC adsorption kinetics and isotherms in laundry effluents under controlled conditions were studied. These studies showed that the kinetics obeyed a pseudo-second-order process and the isotherms varied between Langmuir and Freundlich models depending on the water types. In the results of experiments using distilled water and tap water, it was observed that the adsorption capacity was higher in tap water. When the adsorption of 0.1 μm filtered synthetic garments, detergent, and tap water was compared with the adsorption of the raw sample, it was observed that the adsorption capacity of the 0.1 μm filtered version was higher. Even though this study is preliminary, the results indicate that PAC has the capacity to serve as a viable approach for mitigating micro-/nanoplastic and surfactant contamination from laundry wastewater, thereby offering valuable guidance for advancing eco-friendly laundry techniques.

Key words: adsorption, detergent, household wastewater, laundry, microfiber, nanofiber

HIGHLIGHTS

- The adsorption capacity of PAC is higher for nanofibers than microfibers.
- Surfactants and microfibers can be removed with low dosages of PAC.
- With PAC adsorption, more than 60% of TOC and ANS removal was obtained in the first 30 min.
- The ions in the tap water play a role in increasing the adsorption capacity.

GRAPHICAL ABSTRACT



1. INTRODUCTION

People in developing civilizations are aware of the complexity of environmental pollution management. Domestic activities, especially laundry, release large amounts of contaminants into our water systems. Laundry releases micro/nanoplastics and surfactants, which reduce reusability and pose ecological hazards. Households in urban areas use 23% of their water for laundry (Tony *et al.* 2018). Each washing procedure generates 50–200 liters of wastewater containing these hazardous pollutants (Patil *et al.* 2020; Siyal *et al.* 2020).

Surfactants make up 5–15% of laundry detergents (Bianchetti *et al.* 2015; Ho *et al.* 2021), which are usually anionic surfactants (ANS) (Mohan 2014). Surfactants are a class of compounds that exhibit surface-active properties, which enable them to lower the interfacial tension between two phases. This property enhances their ability to solubilize hydrophobic substances, such as oil and dirt, from various materials. Due to their low cost, ANS molecules constitute a significant portion, approximately 60%, of the global surfactant production (Tripathi *et al.* 2013; Shami *et al.* 2020). They have negatively charged hydrophilic ionic parts and long-chain organic hydrophobic parts (Corona *et al.* 2021). These ANS molecules have toxicity to aquatic habitats due to their lengthy, negatively charged organic structure (Zahoor 2014; Siyal *et al.* 2020). Furthermore, they can decrease dissolved oxygen concentration, increase hazardous substance solubility, and cause taste and odor issues, according to scientific research (Oz *et al.* 2019; Patil *et al.* 2020).

Microfibers, which are classified as microplastics (tiny plastic particulates less than 5 mm in size), are the other major pollutant found in laundry effluent (Dalla Fontana *et al.* 2021; Tripathy *et al.* 2022). It was indicated that these microfibers account for approximately 35% of primary microplastic emissions into global water bodies (De Falco *et al.* 2021; Volgare *et al.* 2021). The long-term presence of microplastics in the environment and their ability to accumulate in living organisms are causes for serious concern. According to the referenced publications, the presence of these particles can disrupt ecosystems, impact the food chain, and potentially pose hazards to human health (Koyilath Nandakumar *et al.* 2021; Liu *et al.* 2021; Kiran *et al.* 2022). Similar to surfactants, microplastics can absorb various organic pollutants, resulting in their transport and ensuing toxic effects (Zhang *et al.* 2021; Sun *et al.* 2022). As microplastics accumulate in aquatic organisms' bodies, they can affect their nutritional and reproductive systems (Bui *et al.* 2020; Zhuang *et al.* 2022). Furthermore, microplastics are present in human tissues and organs (Wu *et al.* 2022) and can even cross the placenta, posing a threat to human health (Singh *et al.* 2021; Zhuang *et al.* 2022). Domestic wastewater treatment plants (WWTPs) have shown the ability to remove a substantial proportion of microplastics, with removal rates ranging from 72 to 98% (Mason *et al.* 2016; Galvao *et al.* 2020; Ali *et al.* 2021). These facilities are not specifically designed with a primary focus on microplastics and lack the capability to effectively manage NPs.

In order to promote sustainable water management practices and mitigate the negative effects on ecosystems and human health, it is essential to resolve the environmental issues associated with laundry wastewater and water consumption. Regarding the simultaneous elimination of surfactants and microfibers in households, the current literature on the treatment of laundry effluent highlights an important absence of research. Additionally, there have been numerous investigations into the management of laundry wastewater. The vast majority of these studies, however, have only examined the elimination of surfactants (Šostar-Turk *et al.* 2005; Bering *et al.* 2018; Ecer Uzun *et al.* 2020; Furtado *et al.* 2020; Mozia *et al.* 2020; Ho *et al.* 2021; Santiago *et al.* 2021). On the other hand, the treatment of microplastics has been investigated in a small number of studies without regard to the presence of surfactants (Tang *et al.* 2020; Rostami *et al.* 2021). A number of studies on microplastics have predominantly focused on quantifying the quantities and types of microplastics released during the washing process (Pirc *et al.* 2016; De Falco *et al.* 2018; Matafonova & Batoev 2018; Galvao *et al.* 2020; Karkkainen & Sillanpaa 2021). Only a couple of studies have investigated the simultaneous removal of microplastics and surfactants (Akarsu & Deniz 2020; Li *et al.* 2022), but none have examined the effect of surfactant removal. There is no study examining microplastic and surfactant removal in domestic laundry wastewater simultaneously. The adsorption process is an excellent option for the on-site treatment of laundry effluent due to its practicality and low cost.

The adsorption process is frequently used in the literature to remove surfactants from laundry wastewater using various materials, including alumina (Adak *et al.* 2005; Nguyen *et al.* 2018), zeolite (Dinmez *et al.* 2022), carbonate rock (Hemmati *et al.* 2017), silica (Li & Ishiguro 2016), and activated carbon (Wu & Pendleton 2001; Gonzalez-Garcia *et al.* 2004; Bindes & Franco 2014). According to Ntakirutimana *et al.* (2019), powdered activated carbon (PAC)'s large surface area, which makes it a popular adsorbent, makes it an attractive research subject. Multiple studies have used PAC to remove ANS (Basar *et al.* 2004; Schouten *et al.* 2007; Valizadeh *et al.* 2016). Schouten *et al.* (2007) evaluated adsorbents to determine the most cost-effective option for the reuse of laundry wastewater. Activated carbon is most effective at removing surfactants from wastewater (Siyal *et al.* 2020). There is limited evidence that activated carbon can remove surfactants and micro/nanofibers (microfibers/nanofibers) from laundry effluent. It is essential to investigate the ability of activated carbon to remove surfactants and microfibers/nanofibers from laundry effluent. The absorbability of surfactants and microplastics/NPs is unknown. Surfactants enhance adsorption due to their properties.

The present investigation represents a preliminary study with the goal of evaluating the efficiency and adsorptive capabilities of PAC through an investigation of its capacity for adsorption, kinetics, and isotherm properties across diverse compositions of laundry wastewater. Using the collected data, the study serves to assess the applicability and efficiency of PAC adsorption techniques for purifying wastewater containing microfibers. Furthermore, the simultaneous presence of microfibers and surfactants provides valuable insights into the adsorbability of these constituents by PAC. This helps to improve our understanding of the practical applications of these methods.

The study initiative was to evaluate the practicality and effectiveness of PAC adsorption techniques in treating microfibers-containing wastewater by utilizing the collected data. This assessment aims to enhance our comprehension of the real-world applications of these methods.

2. MATERIALS AND METHODS

The discharge of washing machine effluent containing surfactants and microfibers into bodies of water has a significant impact on environmental pollution. These substances' interactions can result in a variety of reactions. Adsorption-based treatment of wastewater involves complex physical and/or chemical reactions. In this context, it is essential to investigate the specific interactions between microfibers and surfactants, microfibers and activated carbon (as the adsorbent), and the combined effects of all three components. In adsorption research, investigating isotherms and kinetics provides preliminary insights into the adsorption process and its efficiency. Isotherms assist in comprehending the equilibrium relationship between the adsorbate (microfibers or surfactants) and the adsorbent (activated carbon), thereby determining the adsorption capacity and whether monolayer or multilayer adsorption occurs. Kinetic investigations, on the other hand, give light on the adsorption rate and contribute to identifying the optimal contact time for effective adsorption. By thinking about these factors, a thorough comprehension of the complex interactions and efficacy of the adsorption process can be obtained.

2.1. Materials

Garment: Five pieces of approximately 2.5 kg of synthetic laundry were washed: one of each 90 × 90 cm acrylic blanket, 120 × 170 cm polyester blanket, 130 × 170 cm polyester blanket, 100% polyamide sweater, and 100% acrylic sweater.

Detergent: Ariel brand liquid laundry detergent was used (Procter & Gamble, USA). The detergent consists of 5–15% ANS, <5% non-ionic surfactant, phosphonate, soap, enzyme, benzisothiazolinone, perfume, alpha-isomethyl ionone, and citronellol. *Activated Carbon*: PAC (density 1.8–2.1 g/cm^3, CAS 7440-44-0) obtained from Merck was used for adsorption studies.

2.2. Sample collection

It is possible to conduct a comprehensive analysis of the effects of numerous factors on the composition and behavior of laundry effluent by collecting multiple samples of high-quality washing water. Taking into consideration detergent concentrations, the presence or absence of synthetic laundry, and alterations in water quality, this investigation could reveal a great deal about the individual and combined effects of these elements on the composition of wastewater.

To accomplish this, three distinct samples of laundry wastewater were collected. As the name ‘Tap Water + Detergent’ (TW + D) suggests, the first sample consisted of tap water and detergent alone. The second sample contained a synthetic garment that had been cleansed with tap water and detergent and was labeled ‘Tap Water + Detergent + Synthetic Garment’ (TW + D + SG). The third sample, titled ‘Tap Water + Synthetic Garment’ (TW + SG), consisted of laundering the synthetic garment with only tap water and no detergent. Washing with distilled water and detergent (DW + D) was also performed to understand the effect of ions in water.

The size of each particle determines the classification of plastics and fibers in aquatic environments. Ali *et al.* (2021) define microplastics or microfibers as particles with a size between 0.1 μm and 5 mm, whereas nanoplastics or nanofibers are defined as particles with a size less than 0.1 μm. In order to separate the nanofibers in this study, the three distinct washing machine effluents were filtered through a 0.1-μm membrane filter. The trials then utilized the filtered water.

By developing an increased awareness of the variables determining the composition and behavior of laundry effluent during the adsorption process, we may establish better treatment methods to minimize the detrimental environmental effects of laundry effluent discharge.

2.3. Washing conditions

The laundering process was conducted utilizing a domestic washing machine of Turkish origin, operating at a temperature of 40 °C and a speed of 1,200 revolutions per minute, specifically utilizing a synthetic program for a duration of 64 min. In the process of laundering, a quantity of 45 mL of liquid detergent was utilized for an estimated mass of 2.5 kg of synthetic fabric that did not exhibit any organic dirt. In order to avoid any potential contamination, the machine was run through a cycle of operation without any contents at a temperature of 60 °C and a rotational speed of 1,200 rpm subsequent to each washing procedure. Water samples have been collected from the effluent generated by a washing machine.

2.4. Analytical methods

The pH was determined using a Hach Multimeter (Loveland, CO, USA). The total organic carbon (TOC) was measured using a Shimadzu TOC-V CPN instrument (Kyoto, Japan). Prior to being introduced to the instrument, the samples performed filtration utilizing a cellulose acetate (CA) filter with a pore size of 0.45 μm, manufactured by Sartorius in Germany. The measurement of chemical oxygen demand (COD) was conducted using the titrimetric method described in Standard Methods 5520-C (APHA *et al.* 1999). The researchers of the study conducted a spectrophotometric measurement using methylene blue to measure ANS ranges. The measurement was performed at a wavelength of 650 nm in a DR5000 instrument, using a quartz cuvette. This method was a modified version of the original spectrophotometric measurement method (Jurado *et al.* 2006).

A standardized approach for quantifying microplastics and NPs in aquatic environments has yet to be established. Weight determination is a commonly employed method, nevertheless with a significant margin of error, for quantifying the desired substance. However, in cases where substantial volumes of water require filtration, the microfiber technique, which involves microscopic counting, is preferred (Galvao *et al.* 2020). In this instance, it is unfeasible to attain an outcome for NPs.

A methodology was utilized to comprehend the discharge of microfibers and nanofibers during a standard household washing machine cycle. The evaluation employed the parameter of TOC to approximate the amount of micro and nanofibers that arise from textiles during the process of washing synthetic laundry in the absence of organic soil and detergent. This methodology yielded significant findings related to the efficacy of PAC adsorption in the removal of microfibers. Synthetic fabrics are carbon-rich polymer compositions and microfibers will be similar to chemical structures (Wiśniowska & Włodarczyk-Makuła 2022). A decrease in TOC and COD levels could indicate the removal of various organic contaminants, covering possible reductions in microfibers. It is necessary to consider the limitations of this approach in the analysis of findings, as the direct correlation between the removal of microfibers and TOC and COD cannot be established. They do not provide specific information on individual constituents, such as surfactants or microfibers. Monitoring the levels of surfactants in aqueous solutions allows for a better knowledge of how surfactants, microfibers, and activated carbon interact rationally, allowing for an evaluation of the effectiveness of water treatment techniques.

The utilization of Kern & Sohn light microscopy, based in Balingen, Germany, was also employed for the purpose of microfiber assessment in wastewater samples. The surface was imaged post-adsorption using scanning electron microscopy (SEM) from Philips FEI XL30 SFEG, a facility located in the Netherlands.

2.5. Characterization of laundry wastewaters

In this study, the wastewater generated because of washing solely synthetic clothes in a domestic washing machine using commercial detergent was investigated. Wastewater was characterized to include surfactants as well as microfibers/nanofibers. Here, all organic matter contents were measured by TOC and COD parameters, and the amount of surfactant was also determined separately. The characterization values of tap and various domestic laundry washing effluent waters are given in Table 1.

2.6. Adsorption experiments

Firstly, the system was operated at 250 rpm, 25 °C, and 24 h (sampling at 0, 1, 3, 5, 10, 15, 15, 20, 30, 60, 90, 120, 240, 300, and 1,440 min) at 0.1, 0.5, and 1.0 g/L PAC dosages to find the optimum dose and equilibration time. The samples were diluted after passing through a 0.45 μm cellulose acetate (CA) filter. TOC and ANS measurements were performed, and removal fractions were calculated. In isotherm studies, temperature, stirring speed, and time were kept the same and the system was operated using PAC dosages ranging from 0.01 to 2.0 g/L in 100 mL volume. After reaching equilibrium, phase separation was performed by centrifugation at 4,000 rpm for 5 min and samples were filtrated before analysis.

In isotherms, the amount of pollutant retained in the solid phase in equilibrium state (q_e) is calculated by using the concentration of pollutant remaining in the liquid phase (C_e) (Equation (1)):

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where q_e is the amount of pollutant retained in the adsorbent (mg/g), V is the sample volume (L), C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), and m is the adsorbent mass (g).

2.7. Data evaluation

Many kinetic models are used to determine the degree of reaction of adsorption systems. Among these models, pseudo-first-order and pseudo-second-order or kinetic models are widely used. Kinetic analysis of the results according to these two

Table 1 | Characterization of tap water and laundry wastewater according to various laundry washing scenarios

Parameters	TW	TW + D + SG	TW + D	TW + SG
pH	7.9 ± 0.1	8.3 ± 0.1	8.2 ± 0.1	8.2 ± 0.1
Conductivity (μS/cm)	253.5 ± 0.5	286 ± 4	278.8 ± 1.5	258 ± 0.5
Turbidity (NTU)	0.4 ± 0.1	239.8 ± 16.4	14.3 ± 0.7	56.8 ± 0.1
Color (mg Pt-Co/L)	0.4 ± 0	1,136.2 ± 52.2	68.6 ± 3.2	22 ± 0.5
Temperature (°C)	21.2 ± 0	22.5 ± 0	22.2 ± 0	22.6 ± 0
Alkalinity (mg/L)	130 ± 2	143 ± 1.7	149 ± 1	134 ± 2
Hardness (mg/L)	134 ± 2	120 ± 4	134 ± 4.5	115 ± 1
Suspended Solids (mg/L)	0.5 ± 0	71.7 ± 2.0	42.8 ± 2.6	28.3 ± 3.7
Dissolved solids (mg/L)	122 ± 0	138.3 ± 3.0	131.5 ± 0.5	118.5 ± 0.5
TOC (mg/L)	1.0 ± 0.4	53.2 ± 12.3	67.2 ± 13.7	11.3 ± 1.1
COD (mg/L)	17.2 ± 1.9	323.2 ± 1.9	316.5 ± 3.2	101 ± 5.7
Anionic surfactant (ANS) (mg/L)	0 ± 0	33.4 ± 7.3	60.9 ± 10.5	0 ± 0

models and the model formulas are given in Supplementary Table S1. The experimental data were fitted into each isotherm equation separately. In this study, the suitability of the two most widely used isotherm models, Langmuir and Freundlich isotherms, were examined and the formulas of these isotherms are presented in Supplementary Table S2.

3. RESULTS AND DISCUSSION

3.1. Microfiber in laundry washing effluents

Basically, the study includes adsorption process experimental study steps using washing machine wastewater with different laundry wastewater contents (detergent/non-detergent, synthetic laundry only/non-synthetic laundry) with tap water as the main component. Images of the fibers depending on the content of the laundry wastewater are shown in Figure 1. The reason why fewer fibers appeared on the filter when washed with synthetic garments and detergent (Figure 1(b)) than washed with synthetic garments only (Figure 1(a)) is that the detergent increased friction and caused large fibers to break down.

In Figure 2(a), the PAC structure appeared as a thin layer in the adsorption of tap water, whereas in Figure 2(b), with the addition of detergent to the tap water, large pieces were collected on the surface of the PAC (magnification 10,000×). In the adsorption experiment, only distilled water was used to obtain SEM images of the raw PAC. Figure 2(f) shows the image of the PAC after adsorption with distilled water; this image shows the raw PAC surface at 500 nm scale and 50,000× magnification. Compared to Figure 2(c), the detergent and synthetic garments adsorbed on top of the raw PAC, causing it to be observed as new agglomerates sticking on top of each other. Figure 2(e) shows tap water and synthetic garments, while Figure 2(d) also shows the addition of detergent. In Figure 2(e), the layers formed by the synthetic garments were thinner and sharper, while in Figure 2(d), they were clustered (magnification 20,000×).

3.2. Adsorption process effect

The quantitative evaluation of the adsorption capacity of microfiber adsorption onto activated carbon, surfactant adsorption onto activated carbon, and the simultaneous adsorption of both pollutants onto activated carbon was conducted by utilizing three distinct washing water samples, as explained before. Initially, an investigation was conducted to determine the suitable PAC dosage to be performed.

3.2.1. Effect of adsorbent dosage

This study examines the impact of varying dosages of PAC – ranging from 0.1 to 1.0 g/L – on the adsorption process of laundry washing machine effluent. Numerous experiments were carried out utilizing different doses of PAC, and the elimination parameters of both TOC and ANS were evaluated. The findings, as illustrated in Figure 3(a) and 3(b), offer valuable insights regarding the efficacy of various PAC dosages in eliminating TOC and ANS from the synthetic laundry effluent.

During the first 10 min of contact, the removal efficiencies for both TOC and surfactants were relatively consistent across all three dosage levels. The least effective removal percentages were observed at a PAC dosage of 0.1 g/L, with approximately 20% removal for TOC and 13% removal for surfactants. However, as the dosage level progressively increased, the removal efficiency also increased. The highest dosage of 1.0 g/L resulted in the most effective removal, with TOC removal fractions of 62% and surfactant removal fractions of 71% within a 10-min contact duration. This finding was very good match with

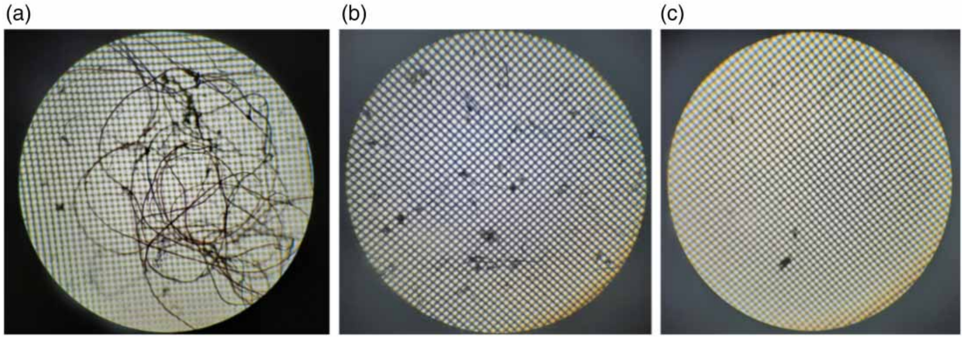


Figure 1 | (a) TW + SG, (b) TW + D + SG, and (c) TW + D microscope images.

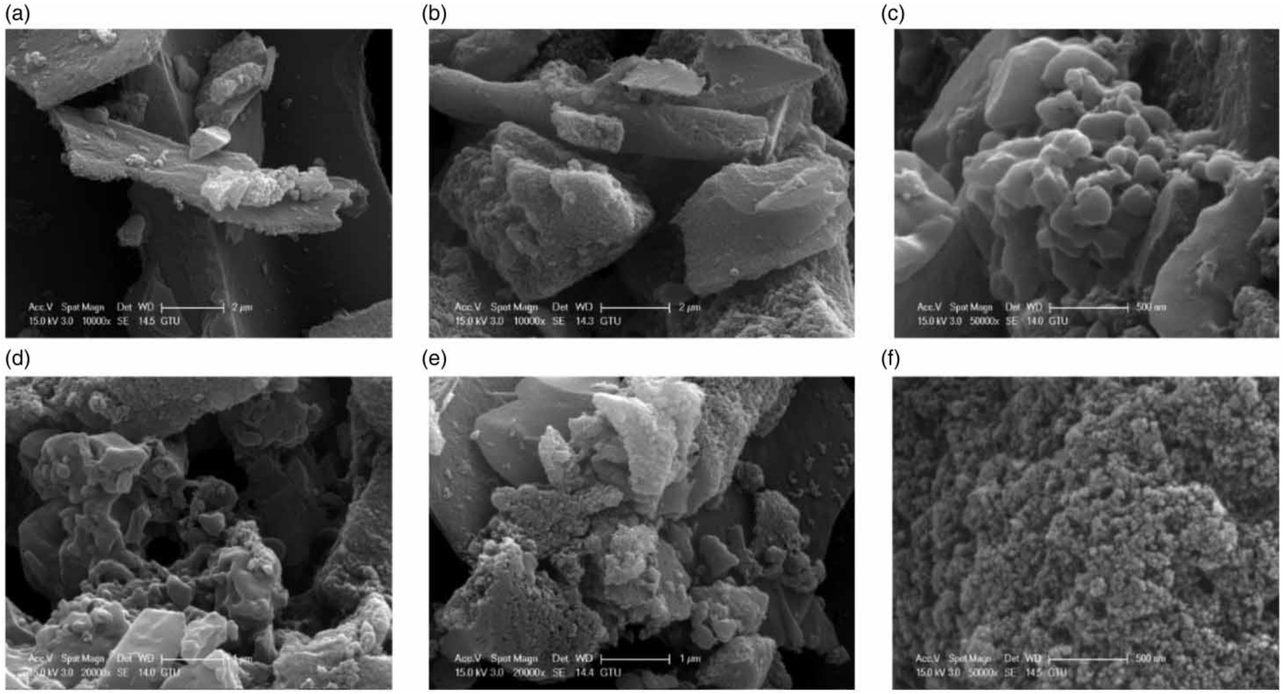


Figure 2 | (a) TW (2 μm scale), (b) TW + D (2 μm scale), (c) TW + D + SG (500 nm scale), (d) TW + D + SG (1 μm scale), (e) TW + SG (1 μm scale), and (f) DW (500 nm scale) SEM images of PAC after adsorption.

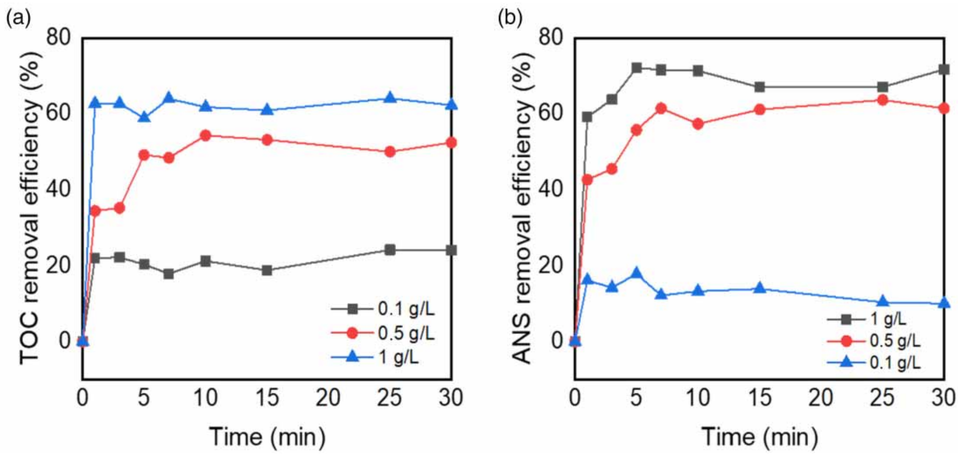


Figure 3 | (a) TOC and (b) ANS removal efficiencies in TW + D water at different PAC doses.

Terechova *et al.* (2014)'s study that aimed to eliminate ANS from laundry wastewater and obtained a removal rate of 71.26%. However, after 10 min, reducing the PAC dosage to 0.5 g/L resulted in a 10% reduction in removal efficiency compared to the dosage of 1.0 g/L. Therefore, it was determined that an ideal concentration of 0.5 g/L for PAC would be most suitable for subsequent tests. The duration of saturation time chosen for the subsequent investigation was established as 30 min, representing a notable expansion from the comparatively brief duration of contact of 10 min. It would be advantageous to carry out more extensive evaluations to track the stability and effectiveness of the adsorption process by lengthening the contact time or carrying out kinetic investigations.

Due to the porous structure and high specific surface area of PAC, it is capable of adsorbing numerous organic compounds. In this study, the laundry wastewater contains acrylic, polyester, and polyamide microfibers/nanofibers in the TW + SG water sample. By increasing the dosage of PAC, the number of microfiber adsorption sites can be increased, as can the adsorption efficiency. In these experiments, synthetic microfiber/nanofiber removals were determined by adding varying concentrations of PAC to TW + SG effluent. The initial TOC value of TW + SG laundry wastewater was measured at 11.3 mg/L. Adding different PAC dosages results in the removal of TOC efficiencies for 60 min, as seen in Figure 4. It can be said that by increasing PAC dosages from 0.025 g/L dose to 0.5 g/L dose, efficiency increased continuously, and the microfiber removal efficiency and max efficiency were about 80% at 0.5 g/L. However, after 0.5 g/L, there was no significant increase in productivity with increasing doses. Adding additional PAC has no effect on adsorption because all PAC adsorption sites can be occupied by microfibers.

3.2.2. Effect of the laundry wastewater characteristics

To generate different varieties of laundry wastewater for this study, non-soil synthetic laundries were washed in a front-loading household washing machine. This procedure utilized a synthetic washing program and commercially available detergent. Tap water, detergent, and microplastics, also known as microfibers/nanofibers, constituted the primary components of this laundry effluent. To comprehend the effect of various components on the adsorption process of activated carbon, however, various waters were produced: (1) TW + D + SG, (2) TW + D, (3) TW + SG, and (4) DW + D.

The presence of microfibers/nanofibers from synthetic laundries and surfactants from detergents in TW + D + SG effluent makes the case more complicated. According to the study's findings, detergent and microfibers/nanofibers increase the rate of adsorption removal in the TW + D + SG wastewater composition. The interaction of TW + D + SG with the microfibers/nanofibers in wastewater synergistically improves the adsorption process, as seen in Figure 5(a), which shows a comparison of findings across different washing water contents. In particular, the coexistence of detergent and microfibers/nanofibers in the TW + D + SG wastewater causes a significant improvement in the adsorption rate, reaching about 63% in a 10-min period. In contrast, the rate reaches a lower peak of 54% in the absence of microfibers/nanofibers, highlighting the synergistic interaction between these elements. As a surfactant, detergents can have the potential to increase capacity through modifying the activated carbon and/or the microfiber/nanofiber surfaces. The only noticeable difference between TW + SG and TW + D + SG wastewater is the addition of surfactant. The effectiveness of TOC removal appears to be significantly impacted by this addition. It has been suggested that the detergent and the microplastics/NPs may have a joint or synergistic effect on the adsorption process. Surfactants are also organic ingredients, which makes it difficult to determine how much of an impact they have on the increase in TOC removal.

Figure 5(b) displays the adsorption and removal efficiency data for detergents by measuring ANS. In TW + D water, only detergent has an adsorption removal efficiency for ANS of 57% at 10 min. On the other hand, in TW + D + SG water that has extra microfiber/nanofiber, by ANS measurement, the adsorption efficiency increases to 64% at 10 min. Here, it may have hydrophobic interactions, and stacking between the hydrocarbon chain of the detergent and the aromatic surface of PAC accounts for the strong affinity between these two molecules. The absence of microfibers/nanofibers in the environment results in a decrease in the efficiency values of ANS adsorption. The findings indicate that both TOC and ANS measurements exhibit a comparable impact on adsorption outcomes.

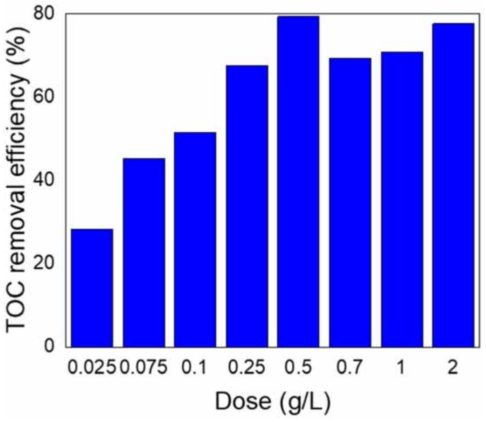


Figure 4 | Removal efficiencies of synthetic microfiber by PAC according to TOC measurements in TW + SG.

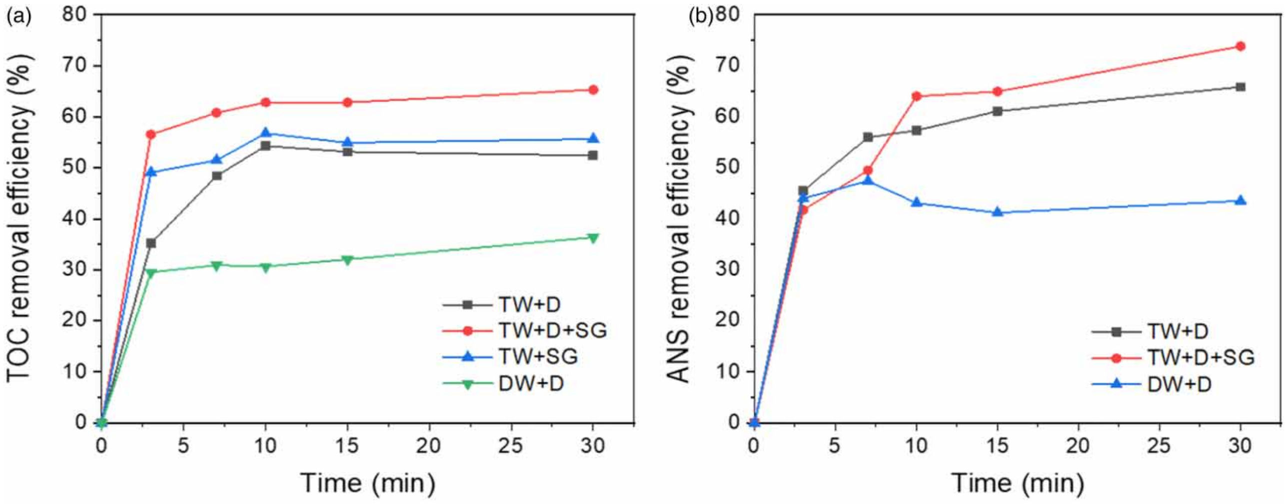


Figure 5 | (a) TOC and (b) surfactant removal efficiencies according to different laundry wastewater types at 0.5 g/L PAC dose.

The DW + D sample, which is made up of distilled water and detergent, exhibits the lowest removal efficiency during the trial. This might be because distilled water does not contain any salts or minerals. On the other hand, TW + D water adsorption removal efficiencies of both TOC and ANS have better results, as seen in Figure 5(a) and 5(b). Tap water contains lots of ions that could help with the adsorption process by altering the surface charge of PAC and improving its interaction with organic materials.

For water with DW + D, the TOC source is only a trademark detergent (Ariel, Procter & Gamble). The activated carbon's TOC capture capacity was found to be 30.0 mg/g within 10 minutes, consistent with the findings of Lee *et al.* (2018). This study found that the amount of surfactant loaded on AC was 32–45 mg TOC/g adsorbent for distilled water solution. It is thought that the adsorbed organics here are mostly detergent-derived surfactants. When Figure 5(b) is examined, it can be seen that the capacity was 66.6 mg/g in 10 min as a result of the measurements of the hydrocarbon chain surfactant, which is hydrophobic and therefore has sorption affinity to AC. While the concentration of ANS in domestic wastewater varies between 1 and 10 mg/L (Siyal *et al.* 2020), it can reach concentrations of 500 mg/L in laundry wastewater (Kim & Park 2021). The low concentrations in domestic wastewater are due to dilution as a result of the mixing of all wastewater. Measuring at the source results in more concentrated water in terms of pollution and the higher the concentration, the more efficient the adsorption process is.

In the study with TW + D, the highest TOC adsorption capacity was 73.3 mg/g over 10 min and it can be determined that the ions in tap water increased the capacity by 2.4 times. Surfactant measurement also showed that tap water ions supported the maximum detergent adsorption of about 85.0 mg/g. For TW + D + SG, it can be said that the presence of microfibers/nanofibers in the washing water caused a gradual increase in the surfactant uptake capacity from 2 to 10 min of 13.23 and 29.60 mg/g, respectively. On the other hand, TOC uptake capacities reached 50.5 mg/g over 10 min.

Zhou *et al.* (2021) showed that the removal performance of polystyrene (PS) and polyethylene (PE) by PAC has better removal efficiency of PS and PE microplastics (PS %80, PE %30, for 500 mg/L). For PE microplastics, the smaller the particle size, the higher the removal efficiency. The laundry wastewater in this study contained acrylic, polyester, and polyamide microfiber.

3.3. Adsorption kinetics

Adsorption kinetic experiments were conducted at 0.5 g/L adsorbent dose for different laundry wastewater types. Initial TOC and ANS concentrations for laundry wastewater, respectively: TW + D as 67.2 ± 13.7 mg/L and 60.9 ± 10.5 mg/L, for TW + D + SG as 53.2 ± 12.3 and 33.4 ± 7.3, for TW + SG as 11.3 ± 1.1 and 0 mg/L, and for DW + D as 64.4 ± 6.6 and 66.1 ± 10.0 mg/L. The decrease in ANS concentration in TW + SG + D in comparison to TW + D can be ascribed to the physical and chemical interplays between the detergent and synthetic microfibers/nanofibers. Surfactant molecules present in detergents exhibit amphiphilic characteristics, possessing both hydrophobic and hydrophilic ends, which enable them to adsorb onto fibers. The detergent molecules' hydrophobic ends demonstrate an attraction to the synthetic fibers that are typically hydrophobic, resulting in the detergent adhering to these fibers. In the process of filtration using a 0.45 μm filter, it is possible for the detergent molecules that have been adsorbed and increased in size due to their association with fibers to be trapped by the filter, leading to a decrease in their transmission into the filtrate. The presence of synthetic fibers (TW + SG + D) in post-filtration water leads to a reduced measured concentration of ANS in comparison to water that lacks such fibers (TW + D). The results of the study were evaluated according to the pseudo-first-order and pseudo-second-order reaction and the graphs obtained are shown in Supplementary Figures S1 and S2. The pseudo-first-order TOC data only achieved a maximum R^2 value of 0.73. The ANS R^2 values varied between 0.24 and 0.88; clearly, the pseudo-first-order reaction fails to model the adsorption process.

When the TOC adsorptions from the waters are analyzed according to the pseudo-second-order, the R^2 value is more than 0.98 in all water types, which indicates that the pseudo-second-order kinetic model was fitted. When the ANS values are analyzed according to the pseudo-second-order kinetic model, R^2 values range between 0.95 and 0.99; this information shows that the ANS values of the waters also fit the pseudo-second-order kinetic model. Tables 2 and 3 were created by summarizing the data obtained from the graphs, and all constants of the equations are also included in the table.

In addition to understanding which kinetic model is more suitable with R^2 control, the closeness of the theoretical and experimental q_e data also provides information about the fit (Corona *et al.* 2021). Considering the pseudo-second-order kinetic model, the experimental and theoretical data are close, so this result can be considered as another indicator of the fit of adsorption to the pseudo-second-order rate model.

Similar results were obtained in studies conducted with different ANS. According to the study of Oz *et al.* (2019), the adsorption of ANS on microplastic was investigated and it was observed that it fits the pseudo-second-order kinetic model. In another study, the adsorption of a different ANS on carbonate rock was studied and it was found to fit the pseudo-second-order kinetics (Hemmati *et al.* 2017). In the studies conducted by Sharma & Krupadam (2022) and Zhu *et al.* (2021), microplastics obeyed pseudo-second-order kinetics. In short, although different interactions have been studied, it can be concluded that ANS and microplastics/microfibers match pseudo-second-order kinetics when it comes to adsorption.

3.4. Adsorption isotherm

Firstly, q_e–C_e plots of the water types were generated for both TOC and ANS (Figure 6). Figure 6 shows the PAC adsorption isotherm results performed using real domestic laundry wastewater containing synthetic garments and/or detergent. Furthermore, tests were also performed using 0.1 μm filtered water containing nanofibers. It was observed that the PAC adsorption capacity increased with the increase of the equilibrium concentration, with non-linear adsorption in all cases.

Table 2 | Pseudo-first-order and pseudo-second-order constants calculated using TOC values

Kinetics	Pseudo-first-order				Pseudo-second-order			
For TOC	q_e – Experimental	q_e – Theoretical	k_1	R^2	q_e – Experimental	q_e – Theoretical	k_2	R^2
TW + D	79.68	28.14	0.048	0.41	79.68	80.00	0.006	0.99
TW + D + SG	53.90	13.39	0.080	0.63	53.90	52.08	0.410	0.99
TW + SG	12.44	14.83	0.297	0.73	12.44	11.63	0.446	0.98
DW + D	31.00	5.05	0.062	0.65	31.00	36.77	0.015	0.99

Table 3 | Pseudo-first-order and pseudo-second-order constants calculated using ANS values

Kinetics	Pseudo-first-order				Pseudo-second-order			
For ANS	q_e – Experimental	q_e – Theoretical	k_1	R^2	q_e – Experimental	q_e – Theoretical	k_2	R^2
TW + D.	82.77	22.19	0.053	0.24	82.76	91.74	0.007	0.98
TW + D + SG	32.96	21.25	0.111	0.88	32.96	37.59	0.007	0.99
DW + D	68.30	18.16	0.079	0.44	68.39	58.82	0.005	0.95

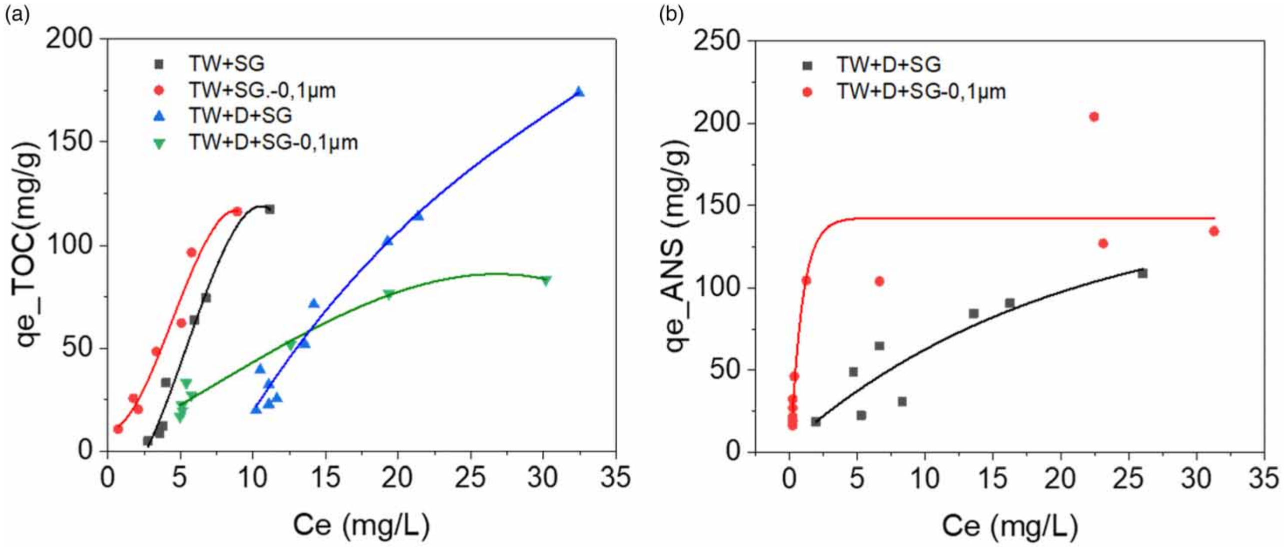


Figure 6 | (a) TOC and (b) ANS values of laundry wastewaters for adsorption isotherms. Please refer to the online version of this paper to see this figure in colour: https://dx.doi.org/10.2166/wst.2023.281.

The change in the adsorption capacity of PAC in the presence of microfibers and/or nanofibers (filtered through 0.1 μm) alone, which may be present in real laundry wastewater, was deduced by monitoring the TOC. The adsorption capacity of PAC for nanofibers is higher than raw TW + SG (Figure 6(a), red and black curves), and small-sized microfibers can be easily retained in PAC macro- and mesopore sites. It can be considered similar to dissolved natural organic matter adsorption on an activated carbon (Abdurahman *et al.* 2020). NPs are predicted to have higher adsorbability than microplastics because of their smaller size and higher mobility (Wang *et al.* 2021).

When the continuation of the graph is examined, it is seen that at low concentrations, the 0.1 μm filtered form of TW + D + SG has a better capacity and after a certain concentration, the capacity of the unfiltered form is higher (Figure 6(a), blue and green curves). This situation can be explained by microfiber, detergent competition. After a certain point, the detergent might clog the pores of the activated carbon and cause a capacity reduction. Figure 6(b) shows that the maximum capacity of ANS on PAC is 120 mg/g at an equilibrium concentration of approximately 25 mg/L in filtered TW + D + SG, as the adsorbent surface increased with the reduction of microfiber size by filtration, and consequently the amount of ANS adsorbed on the surface increased.

The presence of ions in solution can lead to an increase in the charge sites of the surfactant on the activated carbon surface and hence an increase in the adsorption of ANS onto negatively charged surfaces (Figure 7). Azam *et al.* (2013), in a study on the adsorption of ANS, increased the ion content of the solution with the addition of NaCl and determined that the adsorption capacity increased as a result. They stated that the addition of NaCl reduces the functional group electrostatic repulsion in the adsorbed layer and the electrical double layer is strongly compressible, thus increasing the adsorption of the ANS. According to the results of the activated carbon adsorption experiment with distilled water detergent and tap water detergent, it can be said that the ions in tap water increase the adsorption capacity of the surfactant of activated carbon by approximately two times. Figure 7 shows that the adsorption capacity of activated carbon for 25 mg/L surfactant concentration is approximately 66 mg/g in the study with distilled water and 130 mg/g in the study with tap water. Since the contents of the produced waters are different, the C_e values also differ; the aim here is to try to express how the differences in water affect the adsorption capacity rather than just performing isotherm studies.

In the case of the isotherm study, C_e–C_e/q_e graph for Langmuir isotherm and log C_e–log q_e graph for Freundlich were created for each water type from these graphs obtained, thus determining which isotherm the waters comply with, and equations and R^2s were obtained from the graphs obtained. In addition to this information, constants were also calculated, and all data are given in Tables 4 and 5.

When the isotherm models according to TOC values are examined, only distilled water + detergent follows the Langmuir isotherm; all other water types are found to comply with the Freundlich isotherm.

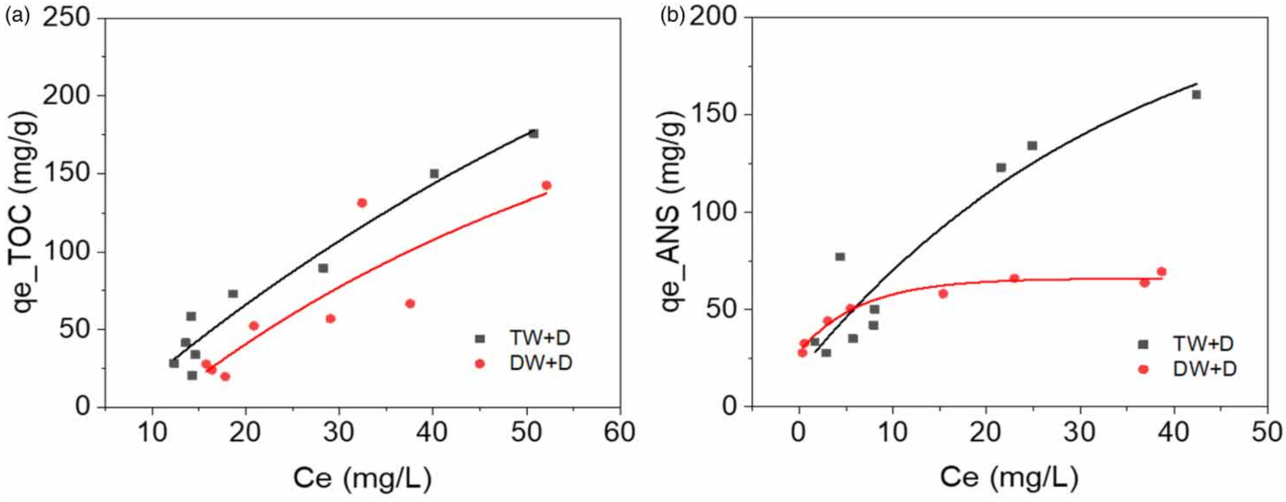


Figure 7 | (a) TOC and (b) surfactant tap water effect of the PAC surfactant adsorption capacity.

Table 4 | Parameters of Langmuir and Freundlich isotherm models obtained from adsorption isotherm experimental results based on TOC data

Isotherm For TOC	**Langmuir** q_{max}	K_L	R^2	**Freundlich** K_F	**1/*n***	R^2
TW + D	154	0.026	0.21	2.475	0.966	0.93
TW + D-0.1 μm	238	0.009	0.33	2.901	0.840	0.94
TW + D + SG	625	0.010	0.39	8.130	0.845	0.92
TW + D + SG-0.1 μm	196	0.024	0.77	6.081	0.776	0.95
TW + SG	313	0.049	0.68	18.076	0.750	0.98
TW + SG-0.1 μm	2.5	1.039	0.72	14.312	0.989	0.94
DW + D	111	0.039	0.98	7.315	0.611	0.91

Table 5 | Parameters of Langmuir and Freundlich isotherm models obtained from adsorption isotherm experimental results based on ANS data

Isotherm For ANS	**Langmuir** q_{max}	K_L	R^2	**Freundlich** K_F	**1/*n***	R^2
TW + D	179	0.077	0.92	30.346	0.4301	0.68
TW + D-0.1 μm	103	2.553	0.99	27.090	0.4696	0.79
TW + D + SG	500	0.018	0.33	12.109	0.7971	0.94
TW + D + SG-0.1 μm	152	0.579	0.93	46.420	0.3817	0.83
DW + D	74	0.523	0.99	34.706	0.2093	0.91

In the isotherm models to ANS, TW + D + SG water fit the Freundlich isotherm, while TW + D water filtered through 0.1 μm, TW + D + SG water filtered through 0.1 μm and DW + D water fit the Langmuir isotherm.

In the Freundlich isotherm, 1/*n* is the surface heterogeneity and the value approaches zero as the heterogeneity increases; when 1/*n* is less than 1, it is understood that adsorption is feasible (Aksu & Yener 2001; Okuş 2018; Oz *et al.* 2019).

In the adsorption study of sodium dodecyl sulfate (SDS), the isotherm was found to fit the Langmuir isotherm describing adsorption on a monolayer surface (Shami *et al.* 2020). In the study conducted with distilled water and detergent, compliance with the Langmuir isotherm was found for both TOC and surfactant data.

When the adsorption of microplastics was studied, it was observed that the isotherm model was more suitable for Freundlich and the correlation coefficients were close to 1 in the microplastic adsorption–desorption study on heavy metal (Sharma & Krupadam 2022). In studies for the adsorption of microplastics on persistent organic pollutants, it is stated that the isotherm fits Freundlich, Freundlich assumes that adsorption occurs on a heterogeneous surface (Zhu *et al.* 2021). In the Lin *et al.* (2020) study, microplastic adsorption to another organic pollutant was studied and it was stated that the isotherm in this study fits Langmuir better.

When the isotherms are examined in terms of TOC, it is seen that all waters except detergent with distilled water fit the Freundlich isotherm; for ANS, except TW + D + SG water, all types of water match Langmuir isotherm. In other words, the isotherms of the waters in the systems vary between Langmuir and Freundlich. As seen in the literature, both isotherms are applicable. According to Zhang *et al.* (2021)'s study, Langmuir is applicable when the surface of microplastics is considered uniform and Freundlich is applicable when it cannot be considered uniform.

4. CONCLUSION

This study aimed to investigate the treatment of domestic laundry wastewater, specifically focusing on the removal of microfibers/nanofibers and detergents that are present due to the washing of synthetic clothing. We performed a systematic analysis of the utilization of PAC for the removal process in various scenarios. The scenarios encompassed wastewater containing detergent alone, microfibers/nanofibers alone, and a combination of both.

In order to achieve these goals, kinetic and isotherm analyses were conducted to explore the interactions between PAC and various constituents present in laundry effluent. The influence of detergent on the adsorption capacity of PAC for microfibers/nanofibers was observed, indicating potential uses in the treatment of effluent. The kinetics of all the types of laundry waters follow a pseudo-second-order reaction kinetics and the isotherms vary between Freundlich and Langmuir, indicating monolayer and layered adsorption possible with different laundry water contents.

Comparing the adsorption of 0.1 μm filtered laundry wastewater with the unfiltered version yielded important findings regarding the differential affinity of PAC for nanofibers and microfibers. These findings emphasize the intricate relationship between different elements of wastewater and PAC. The adsorption capacity of PAC was found to be higher for NPs/nanofibers compared to microplastics/microfibers. Ions in the water play a role in enhancing adsorption capacity. Activated carbon, microfibers/nanofibers, and surfactants are synergistic in increasing organic pollutant removal. However, this is a preliminary study and further studies are required to explain the relationships of this complex structure.

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DATA AVAILABILITY STATEMENT

The authors declare that all data analyzed during this study are included in the article.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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