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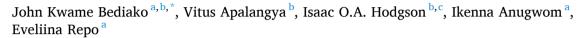
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Adsorbents for water decontamination: A recycling alternative for fiber precursors and textile fiber wastes



^a Department of Separation Science, School of Engineering Science, Lappeenranta-Lahti University of Technology (LUT), FI-53850 Lappeenranta, Finland
^b Department of Food Process Engineering, School of Engineering Sciences, College of Basic and Applied Sciences, University of Ghana, P. O. Box LG 77, Legon, Accra,

^c Council for Scientific and Industrial Research (CSIR)-Water Research Institute, P. O. Box M 32, Accra, Ghana

HIGHLIGHTS

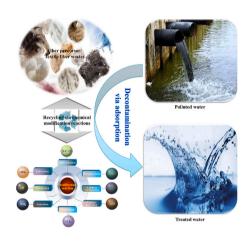
- Critical review of fiber precursor and textile fiber waste recycling into adsorbents.
- Feasibility, environmental impact, and economic considerations are examined.
- Chemical modification markedly improves adsorption performances.
- Cost consideration and post-adsorption handling and treatment are recommended.

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G R A P H I C A L A B S T R A C T



ABSTRACT

The exponential growth in textile fiber production and commensurate release of textile waste-based effluents into the environment has significant impacts on human wellbeing and the long-term planetary health. To abate these negative impacts and promote resource circularity, efforts are being made to recycle these waste materials via conversion into adsorbents for water decontamination. This review critically examines plant- and regenerated cellulose-based fibers for removing water pollutants such as heavy metals, dyes, pharmaceutical and petrochemical wastes. The review reveals that chemical modification reactions such as grafting, sulfonation, carboxymethylation, amination, amidoximation, xanthation, carbon activation, and surface coating are normally employed, and the adsorption mechanisms often involve Van der Waals attraction, electrostatic interaction, complexation, chelation, ion exchange, and precipitation. Furthermore, the adsorption processes and thus the adsorption mechanisms are influenced by factors such as surface properties of adsorbents, pollutant

* Corresponding author at: Department of Separation Science, School of Engineering Science, Lappeenranta-Lahti University of Technology (LUT), FI-53850 Lappeenranta, Finland.

E-mail address: john.bediako@lut.fi (J.K. Bediako).

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characteristics including composition, porosity/pore size distribution, specific surface area, hydrophobicity/ hydrophobicity, and molecular interactions. Besides, feasibility of the approaches in terms of handling and reuse, environmental fate, and economic impact was evaluated, in addition to the performances of the adsorbents, the prospects, and challenges. As current cost analysis is non-exhaustive, it is recommended that researchers focus on extensive cost analysis to fully appreciate the true cost effectiveness of employing these waste materials. In addition, more attention must be paid to potential chemical leaching, post-adsorption handling, and disposal. Based on the review, fiber precursors and textile fiber wastes are viable alternative adsorbents for sustainable water treatment and environmental management, and government entities must leverage on these locally accessible materials to promote recyclability and circularity.

1. Introduction

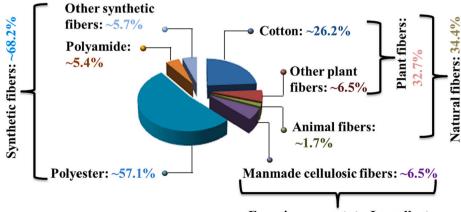
The increasing production and heavy consumption of textile fiber materials inadvertently generates huge wastes that have significant environmental footprints (Bediako et al., 2016c; Lau et al., 2023; Wang, 2010). This phenomenon is due to the increase in population growth, improved economic situations and higher living standards, which have caused substantial expansion of the textile and apparel industry (Sun et al., 2022). Solutions for recycling and reusing fiber precursors and textile fiber wastes are needed to reduce the amount and lower the environmental impacts thereof (Shirvanimoghaddam et al., 2020; Sun et al., 2022). The Textile Exchange 2021 report highlights how textile fiber production has almost doubled in the last 20 years from 58 million tonnes in 2000 to 109 million tonnes in 2020, and it is further expected to increase by another 34 % to 146 million tonnes in 2030 if the industry will build back business as usual (TextileExchange, 2021). Plant-based textile fibers constitute >30 % of the global fiber production in 2020 alone (Fig. 1). The Covid-19 pandemic appeared to have had a very subtle reducing effect on the global textile fiber market, however, the exact effects of the pandemic on fiber production are not yet recognized (TextileExchange, 2021).

The critical points in textile and fashion production have been identified by Niinimäki et al. (Niinimäki et al., 2020). China has the largest textile industry in the world, producing over 36 million metric tons (mmt), constituting approximately 63 % of the global man-made textile fiber production (Dam, 2009). Thus, textile waste generation has witnessed multiple-fold increase, particularly over the last three decades (Juanga-Labayen et al., 2022). In fact, according to 2023 textile waste statistics, the global textile industry generates a staggering 92 million tons of waste each year, with China contributing 20 million tons and the United States 17 million tons, making them the leading culprits in this regard (Arabella, 2023). Currently, textile items constitute a significant 7 % of the total waste found in landfills worldwide. The global clothing production churns out a whopping 80–100 billion new garments annually, however, a startling 87 % of the materials and fibers used to create these clothes ultimately find their way to incinerators or

landfills. Meanwhile, landfilling of textile waste is a predominant option that is deemed unsustainable. Surprisingly, just 20 % of discarded textiles are gathered for recycling, and a mere 1 % of clothing is given a new lease on life through recycling (Arabella, 2023; Juanga-Labayen et al., 2022).

High volumes in textile and fashion production, growing consumption and the underlying logistics increase the environmental impact of this industry. Chemical pollution is greatest in countries where cotton is produced but also in countries where wastewater from the textile industry is not properly treated. Water and energy are exported, as well as clothes, from the countries where they are made to the countries where they are consumed, such as North America and Europe. Wastes are generated both during production and consumption of textile fibers, where they are either disposed of locally or exported to, for example African countries (Ericsson and Brooks, 2016; Niinimäki et al., 2020). The key environmental impacts of textile and fashion supply chains and their geographical distribution is shown in Fig. 2.

The textile industry consumes large amounts of water and produces toxic effluents (Shirvanimoghaddam et al., 2020). Polluted water in general is a global issue, i.e., treatment of municipal, industrial and mining wastewater, and production of potable water. Wastewater streams can be rather complex mixtures, since there are usually many different organic and inorganic substances as suspended solids and dissolved species (Machineni, 2019; Michael-Kordatou et al., 2015; Zhang and Jiang, 2019). Therefore, the treatment requires multiple steps and chemicals. One of the most successful processes applied in water treatment is adsorption, where dissolved species diffuse and adsorb onto the surface of a solid material called adsorbent (Ali, 2012; Bediako et al., 2016a; Futalan et al., 2022; Ge and Li, 2011; Mukhopadhyay et al., 2020). There are different types of adsorbents that are designed for the purpose of water/wastewater treatment. Although the adsorption process is effective, it is much feasible when low-cost adsorbents with high adsorption capacities and potentials for regeneration and application in flow-through systems are available (Ali, 2012; Bediako et al., 2016a; Mukhopadhyay et al., 2020; Wei et al., 2015). Therefore, recent attention has been focused on developing adsorbents



E.g., viscose, acetate, Lyocell, etc.

Fig. 1. Global fiber production in 2020 in million tonnes. A staggering 109 million tonnes of textile fibers was produced in 2020 (TextileExchange, 2021).

using naturally abundant, low-cost, and waste materials, including fiber precursors and textile fiber wastes (Bediako et al., 2015a; Bediako et al., 2016c; Du et al., 2022; Mukhopadhyay et al., 2020). This review article, therefore, provides recent progress with respect to studies undertaken in a bid to recycle plant- and regenerated cellulose-based fiber precursors and textile fiber wastes into sustainable adsorbents for water decontamination, highlighting the most studied cases, the chemical modification methods employed, handling, environmental fate, economic impacts, and suggestions for future research explorations.

1.1. Adsorption versus other water treatment processes

There are different methods for treating water and wastewater. These methods include adsorption, chemical precipitation, coagulation, biological treatment, wet air oxidation, membrane treatment etc. (Bediako et al., 2023a: Machineni, 2019: Michael-Kordatou et al., 2015: Zhang et al., 2022). The selection of any method for water purification may depend on a number of considerations, including the type(s) of pollutants to be treated, cost of treatment, availability of purifying materials, simplicity, economics, environmental sustainability and energy. Adsorption is a simple, low-cost and low-energy requiring technology with many economic and environmental merits (Ali, 2012; Bediako et al., 2016a; Bediako et al., 2023b; Lau et al., 2023; Mukhopadhyay et al., 2020; Wei et al., 2015). It has been proven as one of the most promising water/wastewater treatment technologies, owing to its simplicity and vast availability of adsorbent materials. Fiber precursors and textiles fiber wastes could be recycled as cheap adsorbents due to their wide availability and the presence of lots of cellulosic groups. These groups possess several functional groups that are amenable to post treatment modification or activation, thereby repurposing them as effective adsorbents.

Cost analysis of different water treatment processes compared against effluent volume is summarized in Fig. 3. Incineration and wet air oxidation are the most expensive due to their being energy intensive processes. Ordinarily, coagulation is the cheapest treatment method with high effluent quantities; however, the separation can be more difficult. Adsorption and ion exchange are found between the treatments with a balanced cost and moderate ease of separation, with reference to the effluent volume being treated. Membranes and biological treatment are also part of this category. Not every possible treatment method is shown in this instance, e.g., municipal wastewater treatment methods, and the order probably varies between different applications, since there are many factors that affect the cost. However, the figure provides a general idea of water/wastewater treatment cost analysis for preliminary comparison.

2. Textile fiber production and fiber waste recycling

2.1. Textile fiber production statistics

A textile fiber refers to any material made through weaving, knitting, braiding, felting, and twisting or bonding that may be used in production of further goods. There are natural textiles fibers from plant and animal sources, e.g., cotton, wool, silk, jute, sisal, ramie, hemp, linen, coir, and flax; and man-made textile fibers which are mostly from inorganic, synthetic, or regenerated cellulosic sources (Fig. 4) (Fedorak, 2005). China, USA, India, and Pakistan lead the production frontiers of natural fiber production (Table 1) (Dam, 2009). Given the annual global surge in the production of textile fibers with concomitant increase in textile fiber waste generation, it is unsustainable without efforts to recycle, which would cut down productions from direct sources (Dam, 2009). Recycling could also create new business avenues for alternate income flows for the textile industry.

2.2. Fiber precursor and textile fiber waste recycling

Fiber precursors and textile fiber wastes consisting of natural and synthetic origins can be classified into two types, which are industrial and post-consumer wastes. Industrial waste corresponds to the fraction that is produced along the manufacturing process and contains a

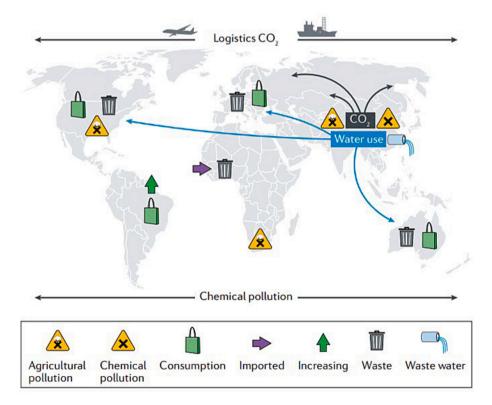


Fig. 2. Critical points in textile and fashion production. Reproduced with permission from (Niinimäki et al., 2020) (copyright (2020) Nature).

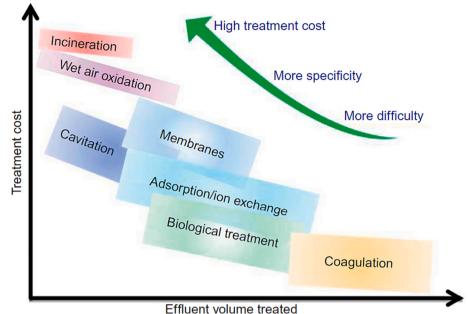


Fig. 3. Treatment processes classified by cost and effluent volume treated. Reproduced with permission from (Ranade and Bhandari, 2014) (copyright (2014) Elsevier).

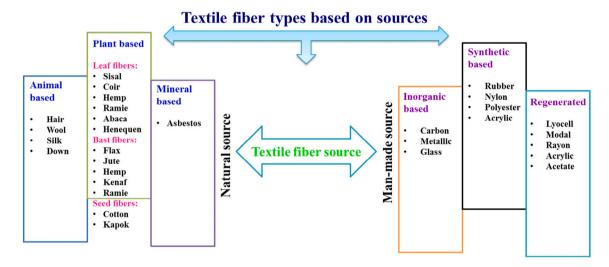


Fig. 4. Types of textile fiber materials based on sources.

| Table 1 |
|---|
| Estimated global natural textile fiber production volumes by leading countries. |

| Fiber | Est. global production (mil. tons) | Leading producing countries |
|----------|------------------------------------|--|
| Cotton | 25 | China, USA, India, Pakistan |
| Jute | 2.5 | India, Bangladesh |
| Wool | 2.2 | Australia, China, New Zealand |
| Flax | 0.50 | China, France, Belgium, Belarus, Ukraine |
| Kenaf | 0.45 | China, India, Thailand |
| Coir | 0.45 | India, Sri Lanka |
| Sisal | 0.30 | Brazil, China, Tanzania, Kenya |
| Ramie | 0.15 | China |
| Silk | 0.10 | China, India |
| Hemp | 0.10 | China (intends to increase production to |
| | | 1.5 mil tons/year) |
| Abaca | 0.10 | Philippines, Ecuador |
| Kapok | 0.03 | Indonesia |
| Henequen | 0.03 | Mexico |

significant amount of unused raw materials that can be reintroduced into the production chain. Post-consumer waste accounts for fiber-based goods that are discarded at the end of their life cycle derived from household or textile industries (Shirvanimoghaddam et al., 2020). Fiber and textile fiber waste recycling is defined as the method of reusing or reprocessing used textile residues into useful products (Cunliffe, 1996; Gulich, 2006). The recycling is a valuable approach to making the textile production chain more sustainable. Besides, it helps in making new and high-quality products from existing materials, while reducing waste (Cunliffe, 1996; Gulich, 2006). There are also many green advantages associated with recycling, which includes carbon footprint reduction, clean air preservation, reduced energy consumption, water conservation, woodland conservation, and reduction of the need for landfills (Gulich, 2006; Sun et al., 2022). Based on the above, the most recent studies conducted in the recycling of fiber precursors and textile fiber wastes into sustainable adsorbents for water decontamination are reviewed. Some relevant results are presented in Table 2, and include the specific applications for water treatment, depending on the type of

Table 2

Adsorbent types, modification methods, target adsorbates, adsorption capacities, fitted models and thermodynamics of fiber precursor and textile fiber waste-based adsorbents.

| Adsorbent | Modification method | Adsorbate | Adsorption condition | Fitted model | Uptake | Thermodynamics | Ref. |
|---|---|---|--|---|--------------------------------------|---|---|
| Schiff base cotton fiber | Chemical modification with ε-caprolactone as monomer and oxydianiline as Schiff base forming agent via V ₂ O ₅ catalyst in DMSO in air at 0.10 MPa/80 °C for 24 h | Cr(VI), rhodamine 6G (R6G) | 1×10^{-5} M, pH 7.2, 2 h, 293–323 K | LM, PSO | 404.02, 696.47 mg/g | Spontaneous, endothermic | (Agathian et al. 2018) |
| Amphiprotic cotton fiber | Modification with cationic (3-chloro-2- hydroxypropyl trimethyl ammo-nium chloride) and anionic (2-acrylamide-2- methyl propane sulfonic acid) | Congo red, methylene blue, Cu (II), Pb(II) | 25–500 mg/L, pH 8.8 (CR), pH 6.2 (MB), pH 5.5, (Cu(II), Pb(II)), 720 min | LM, PSO | 142.8, 88.2, 75, 62.9 mg/ g | N/A | (Xiong et al., 2014) |
| Aodified kenaf fiber | Chemical modification with iminodiacetic acid (IDA) | Cu(II) | 50–1000 mg/L, pH 2–6, 50–75 °C, 0.5–18 h | PSO, LM | 91.74 mg/g | Spontaneous, endothermic | (Razak et al., 2018) |
| Palm tree waste fibers biosorbent | Washed, dried, ground, and sieved | Pb(II) | 100–400 mg/L, pH 2–8, 1–60 min, 25–55 °C | PSO, LM, FM | 61.55 mg/g | Spontaneous, random in nature, exothermic | (Alhogbi et al., 2019) |
| Freated cotton cellulose | Sulfuric acid treatment | Au(III) | 0.5–16 mM, pH ~ 1, 150 h, 293–323 K | LM, PFO | 6.21 mmol/g | Spontaneous, favorable, endothermic | (Pangeni et al., 2012) |
| freated cotton stalk | Sulfuric acid (SCS)/phosphoric acid (PCS) treatment | Methylene blue | 800 mg/L, pH 3–11, 3 h, 308 K | PSO, FM for SCS, LM for PCS | 147, 556, 222 mg/g | N/A | (Deng et al., 2011) |
| Sulfonated cotton linter | Sulfonation using sulfur trioxide pyridine complex | Pb(II) | 0–240 mg/L, pH 6, 30 min, 20–60 °C | TM, PSO | 14 mg/g | Non-spontaneous, endothermic | (Dong et al., 2013) |
| Poly-GMA grafted cotton fabric | Modification of poly-GMA with sulfonic acid group | Acid red, Co(II) | 0–500, pH 3–9, 3 days, 25 °C | N/A | 14, 18 mg/g | N/A | (Sokker et al., 2009) |
| oly-GMA grafted cotton fabric | Modification of poly-GMA with trimethylamine | Cr(VI) | 0–500, pH 3–9, 3 days, 25 °C | N/A | 3 mg/g | N/A | (Sokker et al., 2009) |
| coated cotton fibers | Coating with chitosan via Schiff-base bond/C–N single bond | Hg(II) | 0–0.002 mmol/ L, pH 1–6, 20 h, 278–308 K | PSO at lower temp., PFO at higher temp., LM, FM | 0.32, 0.28 mmol/g | Endothermic, increasing randomness | (Qu et al., 2009 |
| Aodified jute fiber | Integration of silica via sol-gel method and onward modification with octadecyltrichlorosilane | Diesel oil | 5-30 g/L, 1–90 min, 293–323 K | PFO, FM | 8.48 | Spontaneous, favorable, exothermic | (Lv et al., 2018 |
| Modified jute fibers | Loading with C.I. Reactive Orange 13 | Cu(II), Ni(II), Zn(II) | 38.2–483.6 mg/ L, pH 1.5–6.5, 120 min, 35 °C | LM | 8.4, 5.3, 6.0 mg/g | N/A | (Shukla and Pa 2005) |
| Aodified jute fibers | Oxidizing with hydrogen peroxide | Cu(II), Ni(II), Zn(II) | 38.2–483.6 mg/ L, pH 1.5–6.5, 120 min, 35 °C | LM | 7.7, 5.6, 8.0 mg/g | N/A | (Shukla and Pa 2005) |
| ristine jute fibers | Cleaned and dried | Cu(II), Ni(II), Zn(II) | 38.2–483.6 mg/ L, pH 1.5–6.5, 120 min, 35 °C | LM | 4.2, 3.4, 3.6 mg/g | N/A | (Shukla and Pa 2005) |
| Carbonized flax shive Carbonized | Carbonization and activation using phosphoric acid or steam Carbon activation using phosphoric acid | Trichloroethylene (vapor phase) Trichloroethylene | 25 or 35 mg/L, 2 h, 22–24 °C 25 or 35 mg/L, 2 | FM FM | 64 mg/g 80 mg/g | N/A N/A | (Klasson et al., 2009) (Klasson et al., |
| flax shive Coconut bunch | or steam Washing and oven drying at 70 °C | (liquid phase) Methylene blue | h, 22–24 °C 50–500 mg/L, | PSO, LM | 70.92 | N/A | 2009) (Hameed et al., |
| waste Coconut coir dust | Washing and oven drying at 60 $^\circ\mathrm{C}$ | Methylene blue | pH 6.5–7.5, 5.25 h, 30 °C 10–50 mg/L, pH 2–10, 30 min, | PSO, LM, FM, TM | mg/g 29.5 mg/ g | Endothermic, spontaneous | 2008) (Etim et al., 2016) |
| Coir pith | Washing and air drying | Ni(II) | 30–60 °C 145–1250 mg/L, pH 2–7, 2 h, | LM, FM | 9.5 mg/g | N/A | (Ewecharoen et al., 2008) |
| Aodified coir pith | Treatment with NaOH | Ni(II) | 30 °C 145–1250 mg/L, pH 2–7, 2 h, 30 °C | LM, FM | 38.9 mg/ g | N/A | (Ewecharoen et al., 2008) |
| Coir carbon | Carbonization at 700 $^\circ\mathrm{C/1}$ h | Methylene blue | 30 °C 10–40 mg/L, pH 2–11, 40–60 min, 35–60 °C | PFO, PSO, BM, IPD, TM | 5.9 | Endothermic, spontaneous | (Kavitha and Namasivayam, 2007) |

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Table 2 (continued)

| Adsorbent | Modification method | Adsorbate | Adsorption condition | Fitted model | Uptake | Thermodynamics | Ref. |
|---|---|--|--|----------------------------|---------------------------|---|--|
| Coir pith carbon | Carbonization at 700 °C/1 h | 2-chlorophenol | 10–40 mg/L, pH 2–11, 0–120, 35–60 °C | PSO, FM | ~10 mg/ g | Endothermic, spontaneous, increased randomness | (Namasivayam and Kavitha, 2003) |
| Surface modified coir pith | Modification with $Fe(NO_3)_3 \cdot 9H_2O$ | PO ₄ ³⁻ | 20–200 mg/L, pH 2–10, 12 h, 30 °C | PSO, LM | 70.9 mg/ g | N/A | (Krishnan and Haridas, 2008) |
| Coir pith carbon | Carbonization at 700 $^\circ\mathrm{C}/1$ h | Rhodamine-B, Acid violet | 0–40 mg/L, pH 2–11, 0–80 min, 32 °C | PFO, LM, FM | 2.6, 8.1 mg/g | N/A | (Namasivayam et al., 2001) |
| Activated waste cotton fiber carbon | ZnCl ₂ activation at room temperature, followed by heating at 500 °C in a furnace at 10 °C/min under airflow | Reactive Red 14 | 5–50 mg/L, pH 3–11, 0–2 h, 20–50 °C | PSO, IPD | 970.3 mg/g | Exothermic, spontaneous, decrease in disorder | (Behloul et al., 2022) |
| Chemically modified kenaf fiber | Functionalization with phosphoric acid | Cu(II) | 50–1000 mg/L, pH 2–6, 0.5–18 h, 25–75 °C | PSO, LM | 57.14 mg/g | Non-spontaneous, endothermic | (Razak et al., 2020) |
| Surfactant- modified coir pith | Modification with hexadecyltrimethylammonium bromide | SCN ⁻ | 10–50 mg/L, pH 2–11, 0–2.5 h, 32 °C | PSO, LM, FM, DRM | 8.6 mg/g | N/A | (Namasivayam and Sureshkumar, 2007) |
| Surfactant- modified coir pith | Modification with hexadecyltrimethylammonium bromide | Cr(VI) | 20–100 mg/L, pH 2–11, 0–70 min, 32–60 °C | PSO, EM, LM, FM, DRM | 76.3 mg/ g | Endothermic, spontaneous | (Namasivayam and Sureshkumar, 2008) |
| Coir pith | Washing, drying, and grinding | Co(II), Cr(III), Ni(II) | 20–50 mg/L, pH 2–7, 0–2 h, 300 K | PSO, LM | 12.8, 11.6, 16 mg/g | N/A | (Parab et al., 2006) |
| Esterified coir pith | Chemical modification with succinic anhydride followed by activation with NaHCO ₃ | Co(II) | 50–80 mg/L, 2 h, 300 K | PSO, LM, FM | 34.1 mg/ g | N/A | (Parab et al., 2008) |
| Jnmodified coir pith | Washing, drying, and grinding | Co(II) | 50–80 mg/L, 2 h, 300 K | PSO, LM, FM | 12.8 mg/ g | N/A | (Parab et al., 2008) |
| Coir pith | Washing, drying, and grinding | Uranium | 200–800 mg/L, pH 1–7, 2 h, 305–336 K | PSO, LM, FM | 8 243.9 | No effect | (Parab et al., 2005) |
| Activated coir pith | Activation using $\rm ZnCl_2$ | SCN | 20–80 mg/L, pH 2–11, 0–40 min, 35–60 °C | PSO, LM, FM | 16.2 mg/ g | Exothermic, decreased randomness | (Namasivayam and Sangeetha, 2005) |
| Compressed block coir | Grinding, washing, and drying | Pb(II), Cu(II) | 20–500 mg/L, pH 2–5.5, 1 h, 25 °C | PSO, LM, FM | 48.8, 19.3 mg/ g | N/A | (Quek et al., 1998) |
| Modified coir fiber | Chemical modification with hydrogen peroxide | Ni(II), Zn(II), Fe(II) | 38.2–444.8 mg∕ L, pH 1–6.5, 2 h, 35 °C | LM | 4.3, 7.9, 7.5 mg/g | N/A | (Shukla et al., 2006) |
| Surfactant- modified coir pith | Modification with hexadecyltrimethylammonium bromide | Direct Red 12B, Rhodamine B | 20–100 mg/L, pH 2–11, 0–100 min, 32–60 °C | PSO, LM, FM, DRM | 76.3, 14.9 mg/ g | Spontaneous, endothermic, increased randomness | (Sureshkumar and Namasivayam, 2008) |
| Coir pith | Washing and drying at 60 $^\circ\text{C}$ | Acid Yellow 99 | 50–6000 mg/L, pH 1–10, 0–450 min, 20–50 °C | PSO, LFM | 442.1 mg/g | N/A | (Khan et al., 2011) |
| Engineered coir pith | Modification with nickel hexacyanoferrate (NiHCF) | Cesium | 100–900 mg/L, pH 5, 2 h, 300 K | PSO, LM, FM, RPM | 93.3 mg/ g | N/A | (Parab and Sudersanan, 2010) |
| Chemically modified coir pith | Grafting with acrylic acid | Cr(VI) | 0–1171 mg/L, pH 2, 22 h, 30–50 °C | LM | 310.6 | Endothermic, spontaneous and randomness | (Suksabye and Thiravetyan, 2012) |
| Coir pith carbon | Activation using ZnCl ₂ | Molybdate | 10-40 mg/L, pH 2–11, 25 min, 35–60 °C | PSO, FM | 18.9 mg/ g | Endothermic | (Namasivayam and Sangeetha, 2006) |
| Palm kernel fiber | Washing, acid treatment and drying | Methylene blue | 200–500 mg/ dm3, pH 3–10, 1 h, 297 K | PSO | 671.8 mg/g | N/A | (Ofomaja, 2007) |
| amboo-based activated carbon | Carbonization and phosphoric acid activation | COD/color | Color: 486.87 Pt/Co, COD: 251.65 mg/L, pH 2–12, 28 h, 27–30 °C | FM | 75 %/91 % | N/A | (Ahmad and Hameed, 2009) |
| AO-PAN fiber | Amidoximation reaction with hydroxylamine hydrochloride and sodium hydroxide | a reaction with V Uranyl ions pH 8, 24 h, 25 °C N/A 2.4 mg/g N/A | | N/A | (Zhao et al., 2015) | | |
| Bamboo waste activated carbon | Carbonization and phosphoric acid activation | COD/color | Color: 486.87 Pt/Co, COD: 251.65 mg/L, 30 °C | N/A | 74 %/93 % | N/A | (Ahmad and Hameed, 2010) |

(continued on next page)

Table 2 (continued)

| Adsorbent | Modification method | Adsorbate | Adsorption condition | Fitted model | Uptake | Thermodynamics | Ref. |
|---------------------------------------|---|-------------------------|---|-----------------|------------------------------|-----------------------------|------------------------|
| PAN-oxime fiber | Amidoximation reaction with hydroxylamine hydrochloride and sodium carbonate | Pt(IV), Pd(II) | 0–1200 mg/L, pH 1, 24 h, 25 °C | PFO, PSO, LM | 175.6, 244.1 mg/g | N/A | (Lim et al., 2016) |
| Kapok-DTPA | Modification with diethylenetriamine pentaacetic acid | Pb(II), Cd(II), Cu(II) | 50–750 mg/L, pH 2–6.5, 24 h, 25 °C | PSO, LM | 310.6, 163.7, 101 mg/g | N/A | (Duan et al., 2013) |
| PEI-coated PAN fiber | Surface modification with polyethyleneimine | Pt(IV) | 20–1000 mg/L, pH 1, 24 h, 25 °C | PFO, PSO, LM | 155.8 mg/g | N/A | (Yoon et al., 2016) |
| Sulfonated cellulose fiber | Modification with sulfur trioxide pyridine complex | Fe(III), Pb(II), Cu(II) | 25–200 mg/L, pH 1–6, 2–20 min, 25–65 °C | N/A | 99 %, 48 %, 83 % | Endothermic | (Dong et al., 2016) |
| PAN _{MW} -AO fiber | Microwave-assisted amidoximation using hydroxylamine hydrochloride and sodium carbonate | Cr(VI) | 20–320 mg/L, pH 1–10, 3 h, 293–303 K | PSO, LM | 250.7 mg/g | Spontaneous and endothermic | (Deng et al., 2016) |
| Treated kapok fiber | Treatment with sodium chlorite | Methylene blue | 300 mg/L, pH 2–10, 1 h, 30 °C | PSO | 110.3 mg/g | N/A | (Liu et al., 2012) |
| Oil palm shell activated carbon | Activation using HCl | Methylene blue | 50–500 mg/L, pH 6.5, 26 h, 30–50 °C | PSO, LM | 303 mg/g | Endothermic | (Tan et al., 2008) |

Legend: Pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich model (EM), Intra-particle diffusion model (IPD), Langmuir model (LM), Freundlich model (FM), Langmuir-Freundlich model (LFM), Temkin model (TM), Dubinin–Radushkevich model (DRM), Bangham model (BM), Redlich- Peterson model (RPM).

textile fiber waste, chemical modification method, target contaminant of concern, adsorption condition, and thermodynamics.

3. Fiber precursors and textile fiber wastes as adsorbents for water decontamination

3.1. Plant-based fiber precursor and textile fiber waste adsorbents

Due to the high costs of the conventional methods of recycling fiber precursors and textile fibers and need for alternative options, attempts have been made to transform these waste resources into adsorbents for water treatment. This is seen to provide and promote fiber recycling simultaneously with remediation of toxic contaminants in water (Bediako et al., 2015a; Bediako et al., 2015b). In this quest, some investigators have used the raw forms of fiber precursors and textile fibers (woven and unwoven) (Chiu and Ng, 2014; Deng et al., 2011; dos Santos et al., 2011; Etim et al., 2016; Rezić, 2013; Tofan et al., 2013; Tunç et al., 2009; Wang et al., 2014; Yang et al., 2011). Some other researchers adopted chemical modification reactions or graft copolymerization with supplementary materials to form useful adsorbents that exhibit improved adsorptive properties (Gupta et al., 2013a; Gupta et al., 2013b; Huang et al., 2012; Kavaklı et al., 2014; Liu et al., 2010; Ofomaja et al., 2012; Qiu et al., 2014; Suksabye and Thiravetyan, 2012; Zeng et al., 2013). These adsorbents were used to remove dyes (Banerjee and Dastidar, 2005; Deng et al., 2011; Gupta et al., 2013a; Tan et al., 2008; Thangamani et al., 2007; Tunc et al., 2009), heavy metals (Dong et al., 2013; Gupta et al., 2013a; Gupta et al., 2013b; Hajeeth et al., 2013; Kumar et al., 2008; Monier and Abdel-Latif, 2013a; Pejic et al., 2009; Qu et al., 2009; Qu et al., 2012; Rezić, 2013; Sekine et al., 2010; Wang et al., 2012; Zeng et al., 2013), water/oil separation (Jieying et al., 2014; Zhang et al., 2013), solid-phase extraction of organic solvents and gas adsorption (Chiu and Ng, 2014; Dias et al., 2013; Dong et al., 2014; Klasson et al., 2009; Vukcevic et al., 2012; Wang et al., 2014).

Coir for instance, had been extensively used as a precursor in preparing carbon materials for various adsorption applications (Anirudhan et al., 2008; Etim et al., 2016; Kavitha and Namasivayam, 2007; Khan et al., 2011; Krishnan and Haridas, 2008; Parab et al., 2005; Suksabye and Thiravetyan, 2012). Cotton, sisal, jute and Lyocell had been used both in their pristine and modified forms mostly for dyes and heavy metals removal (Banerjee and Dastidar, 2005; Bediako et al., 2015a; Bediako et al., 2015b; Deng et al., 2011; Dong et al., 2013; dos Santos et al., 2011; Hajeeth et al., 2013; Jieying et al., 2014). Acrylic polymers were usually grafted onto other substrates and used for several purposes (Gupta et al., 2013a; Gupta et al., 2013b; Liu et al., 2010). Waste hemps were also used as heavy metal and pesticide adsorbents owing to their good adsorption properties (Pejic et al., 2009). Both carbonized and activated hemps were successfully used as adsorbents for purification of water polluted with pesticides and heavy metals (Kostic et al., 2014). Native textile cellulose was functionalized through surface modification with poly(*N*,*N*-dimethyl aminoethyl methacrylate) to generate anionic and cationic adsorbents which exhibited high efficiency in removing fluoride and arsenic compounds from aqueous solutions even at very dilute concentrations (Tian et al., 2011b). Fig. 5 depicts a graphical illustration of the most prominent studies published regarding the use of plant- and regenerated cellulose-based fiber wastes as adsorbents, which emphasizes the type of fiber wastes and the target contaminants of concern. Further breakdown of these fiber waste adsorbents is discussed in the section that follows, and some important results are summarized in Table 2.

It can be deduced that the common target adsorbates mainly include (heavy) metals, e.g., As, Pb, Cu, Hg, Au, Pt, etc. and dyes, e.g., methylene blue, acid red, rhodamine B, acid violet, etc.; however, some studies have also focused on (emerging) micropollutants, e.g., 2-chlorophenol and trichloroethylene. As discussed later Section 4, various modification reactions have been employed in improving the chemical functionalities of the pristine fibers in most studies. The kinetic data from experimental runs were often examined by the pseudo-first-order (PFO) and pseudo-second-order models (PSO). The data had mostly been better described by the PSO with higher coefficient of correlation, R^2 values, and suggesting that the adsorption processes had mostly be driven by chemisorption (Behloul et al., 2022; Futalan et al., 2022; Tan et al., 2008). In instances where both the PFO and PSO closely fitted the kinetic data, the adsorption processes had been described as a possible blend of physisorption and chemisorption mechanisms (Bediako et al., 2015a; Bediako et al., 2016b). Conversely, the adsorption isotherm data were fitted through several but predominantly the Langmuir and Freundlich models and their derivatives, such as the Langmuir-Freundlich, Redlich-Peterson and Sips models. Not many studies had evaluated the thermodynamics of adsorption; however, the few that did always result in the conclusions that the processes were spontaneous and endothermic in nature with increasing levels of randomness at the solid/ liquid interfaces during the adsorption processes (Razak et al., 2020; Suksabye and Thiravetyan, 2012; Tan et al., 2008) (Table 2).

3.1.1. Cotton

Being one of the most widely used textile materials, spent cotton is

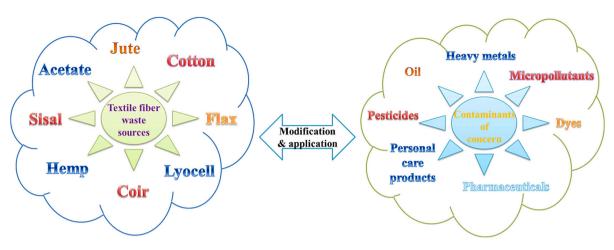


Fig. 5. Illustration of the state of research regarding plant-based textile fiber wastes for water decontamination.

one of the many fiber precursor and textile fiber wastes that have been extensively studied for water treatment applications. Yang et al. produced cellulose acetyl derivatives by esterification of acetic acid with cotton linters and examined them for the selective recovery of Au(III) from acid chloride solution containing Au(III), Pt(IV) and Pd(II) (Yang et al., 2014). The prepared adsorbents exhibited rapid adsorption kinetics, such that equilibria were reached within an hour and Au(III) was readily recovered by incinerating the gold-loaded adsorbent. In another study, the potential use of activated cotton as a low-cost and eco-friendly adsorbent for the recovery of organic solvent vapor was investigated (Chiu and Ng, 2014). Factors including the adsorption speed, saturated adsorption volume and desorption process of the solvent vapor were evaluated. By comparison, the activated cottons adsorbed more solvent vapor than other activated carbons owing to their high micro-porosities. Furthermore, cotton stalk was treated separately with sulfuric acid and phosphoric acid and the adsorbents thereof, were found to possess more functional groups and less specific surface areas, which made them applicable for removing methylene blue from polluted solutions (Deng et al., 2011).

In the study by Dong and others (Dong et al., 2013), heavy metal adsorbents were prepared by acid treatment of cotton linters and subsequent incorporation of sulfonate groups through modification with sulfur trioxide pyridine complex. The adsorbents demonstrated strong adsorption propensity for Pb(II), such that >85 % of Pb(II) was removed at lower concentrations (<20 mg/L). In addition, Sokker and co-workers described radiation-induced grafting of glycidyl methacrylate onto cotton fabric waste and its subsequent modification with sodium sulfite/ H₂SO₄ and triethylamine (Sokker et al., 2009). In the end, ion exchange adsorbents carrying sulfonic acid and amine functional groups were synthesized and used for the treatment of hazardous wastes, such as acidic dye, cobalt, dichromate, and phenols from their aqueous solutions. Similarly, a one-pot procedure was described for the surface functionalization of cotton with glycidyl methacrylate in the presence of Fenton-type reagent and the prepared adsorbent was tested for removing aromatic pollutants, such as phenol, 4-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol and 2-naphtol from contaminated wastewaters (Vismara et al., 2009). Thus, cotton-based adsorbents have the potential to be an effective and sustainable solution for removing pollutants from water. However, the effectiveness of these adsorbents is dependent on the specific application and type of pollutants present in the water.

3.1.2. Jute

Jute is said to be one of the most affordable natural textile materials and is second to cotton in terms of production amount and variety of uses, including its use as vegetable fiber. Jute waste is generated in the field during cultivation and retting, and also during processing of jute

fibers in industries. Hence, efforts to find effective management strategy for jute fiber wastes has led to exploring its use as adsorbent in water purification (Banerjee and Dastidar, 2005). Jute-processing waste (JPW) was first used to treat dye and other organic wastewaters, and the performance was compared with commercial powdered and granular activated carbon adsorbents (PAC and GAC, respectively) (Banerjee and Dastidar, 2005). A maximum removal of 81.7 % was obtained with methylene blue using the JPW, as against the PAC (61 %) and GAC (40 %) under similar adsorption conditions. In a separate study, short chain polyaniline (PANI) was synthesized onto the surface of jute fibers to produce PANI-jute which was used to remove hexavalent chromium from contaminated water (Kumar et al., 2008). Several factors, including the amount of jute fiber on PANI, chain length of PANI, solution pH, initial concentration of Cr(VI), PANI-jute dose, and temperature were varied during the adsorption studies. A maximum monolayer adsorption capacity of 62.9 mg/g was obtained at pH 3 and 20 °C, and 83 % desorption efficiency was achieved with a 2 M NaOH.

In another report, carboxyl modified lignocellulose-biomass jute fiber (CMJF_{MH}) was synthetized using microwave-assisted approach, and high adsorption capacities reaching 157.21, 88.98 and 43.98 mg/g were obtained for Pb(II), Cd(II) and Cu(II), respectively (Du et al., 2016). In this report, the isotherm and kinetics data correlated well with the Langmuir and pseudo second-order models, respectively, and the heavy metal-loaded adsorbent was regenerated at least four times using EDTA-2Na. It was concluded that the cheap and abundant nature of jute, rapid and facile preparation of the adsorbent, fast and efficient adsorption capacity, and high regeneration ability could make the prepared CMJF_{MH} a preferred adsorbent for heavy metal removal from polluted water. Summarily, jute fiber wastes have great potential for use as adsorbents in water decontamination, and further research and development in this area could lead to the advancement of new and innovative technologies for water purification and environmental protection.

3.1.3. Hemp

Hemp is a cellulosic material, which is collected from the Cannabis plant (Tofan et al., 2013). It is a natural, renewable, and biodegradable material that can be sustainably produced, making it an eco-friendly choice for water treatment (Tofan et al., 2020). The use of hemp cuts across a wide range of application areas, and the waste residues generated after processing/use need proper handling and treatment. Hemp wastes have mostly been used as carbonaceous materials or chemically modified adsorbents in water treatment. Hemp-based adsorbents have shown great potential for removing pollutants in water due to their unique properties (Tofan et al., 2020). Owing to their good adsorption affinities towards contaminants, carbonized and activated hemps were successfully used as adsorbents for the purification of water polluted with pesticides, dyes and heavy metal ions. For example, activated carbons were prepared from hemp bast by phosphoric acid activation at 400–600 °C (Yang et al., 2011). The pyrolysis process, textural, and chemical properties were investigated through TG/DTA, SEM, cryogenic N₂ adsorption, FTIR and XPS analyses. The chemical modification prior to carbonization improved the BET surface area, uniform pore size and morphology of the carbonized hemps, which significantly improved their dye adsorption capacities. Moreover, carbonized hemp were successfully applied as solid-phase extractants for analysis of pesticides in water samples (Vukcevic et al., 2012). To improve their adsorption properties, the carbonized hemps were activated with potassium hydroxide which increased the amount of surface oxygen groups and specific surface area up to $2192 \text{ m}^2/\text{g}$ (Vukcevic et al., 2012).

Furthermore, the specific structure of hemp, coupled with its heterogeneous chemical compositions offered a solid property that was exploited to effectively reduce the concentrations of Pb(II), Cd(II) and Zn(II) in wastewater samples (Pejic et al., 2009; Pejic et al., 2011). Kyzas et al. investigated the alternative use of hemp-based adsorbents in the form of hemp fiber (HF) or hemp shive (HS) for the removal of Ni(II) from aqueous solutions (Kyzas et al., 2015). The hemp adsorbents were used either in their pristine forms or chemically modified with NaOH and citric acid to remove likely impurities and improve the adsorption capacities. In the study by Vukcevic and co-workers (Vukčević et al., 2014), heavy metal adsorbents were prepared by carbonization of pristine and chemically modified waste hemp fibers, which presented good adsorption capacities for Pb(II). A mathematical model was developed to describe the structure and phenomenon of metal ions transportation through the porous fiber matrices. A good correlation was observed between the model and experimental parameters, indicating that the proposed mathematical model could be reliably used to optimize the adsorption process by the hemp fibers. In conclusion, the use of hemp-derived adsorbents for removing pollutants in water shows great potential due to their eco-friendliness, high surface area, and ability to remove a wide range of pollutants.

3.1.4. Sisal

Sisal is another plant-based natural fiber obtained from the leaves of the Agave sisalana plant and is known for its high mechanical strength, high surface area, and high porosity (Naveen et al., 2019; Sahu and Gupta, 2017). Sisal is one of the world's most important natural textile materials, it is used in making various products, including ropes, twines, paper, cloth, wall coverings, carpets, and dartboards (FAO, n.d.). In a study, sisal was applied as an adsorbent for removing Pb(II) and Cd(II) from natural waters (dos Santos et al., 2011). The measured BET surface area was 0.0233 m²/g and the O–H and C–O functional groups were observed to be the main groups involved in the adsorption. The maximum monolayer adsorption capacity was 1.85 mg/g for Cd (II) and 1.34 mg/g for Pb (II) at pH 7 and 296 K. In another study, sisal fiber was employed as a cost-effective alternative adsorbent for methylene blue (MB) and reactive black 5 (RB5) dyes, and the adsorption capacities were 553.4 and 310.2 mg/g for MB and RB5, respectively (Vargas et al., 2019). The adsorption was spontaneous, favorable, and involved chemisorption and physisorption for MB and RB5, respectively. The kinetics was explained by the homogeneous surface diffusion model for cylindrical geometry with diffusion coefficients of 3.45 cm²/s for MB and 1.94 \times 10⁻¹⁴ cm²/s for RB5 (Vargas et al., 2019). Furthermore, activated carbons were prepared from sisal waste via chemical activation with K₂CO₃ and used to study the kinetics of paracetamol and ibuprofen scavenging from aqueous solution (Mestre et al., 2011). The severity of the treatment, i.e., increase in K₂CO₃ concentration or activation temperature led to development of super-micropores, and the micropore size distribution changed from mono to bimodal. Consequently, activated carbons with apparent surface area of $1038 \text{ m}^2/\text{g}$ and pore volume of $0.49 \text{ cm}^3/\text{g}$ were obtained at optimum conditions. At last, the efficiencies of wastes removal were >65 % each for paracetamol and ibuprofen. Thus, adsorbents based on sisal are favorable for preconcentration and scavenging of pollutants owing to their good

mechanical properties, high adsorption capacity, low cost, and environmental sustainability.

3.1.5. Coir

Coir-based adsorbents are a type of natural adsorbent materials made from the fibers of coconut husks. These adsorbents have been found to be effective in removing various pollutants from water, including heavy metals, organic micropollutants, and dyes. Adsorbents from coir can be prepared in various forms, including fibers (James and Yadav, 2021; Stelte et al., 2022), granules (James and Yadav, 2021), and powder (Adebayo et al., 2022). For example, activated carbon fiber can be prepared from coconut husk for oil spill clean-up and a composite of coconut husk, raw clay, and Fe can be formulated for pollutants removal (Adebayo et al., 2022). The adsorbents from coir can be used as a standalone treatment method or in combination with other treatment technologies, such as membrane filtration and biological treatment (James and Yaday, 2021; Stelte et al., 2022). To apply coir as metal adsorbent, coir pith (CP) samples were chemically modified by grafting with acrylic acid (AA) and used for the removal of Cr(VI) from electroplating wastewater (Suksabye and Thiravetyan, 2012). The presence of acrylic acid on the CP surface was verified by SEM/EDX and FTIR, and TGA was used to study the thermal degradation. The carboxyl content increased on the CP surface and the stability was much improved after grafting with the AA. At pH 2 and initial concentration of 1171 mg/L, the maximum Cr(VI) removal efficiency was obtained with 1.3 % (w/v) adsorbent dosage and contact time of 22 h at 30 °C. Compared to the pristine CP, which showed maximum Cr(VI) removal of 165 mg/g, the increase uptake by the AA-g-CP was attributed to the enhancement of the carboxyl groups on the surface, which were involved in electrostatic interaction with the main chromium species of HCrO₄⁻. Finally, X-ray absorption near edged structure (XANES) and desorption studies suggested that most of the Cr(III) present on the AA-g-CP were due to the Cr (VI) being reduced to Cr(III) on the surface.

In another study, Parab and Sudersanan described a novel method of engineering CP by incorporation of nickel hexacyanoferrate (NiHCF) inside its porous matrix, and application for adsorption of cesium from radioactive wastewater (Parab and Sudersanan, 2010). Structural characterization confirmed that the CP-NiHCF was successfully synthesized. In batch equilibrium studies, the cesium adsorption capacity of the CP was evaluated before and after modification with NiHCF. By comparison, a nearly double increase in uptake was observed after modification with NiHCF and was concluded that simple surface modification of CP could lead to the development of high-capacity adsorbents for removing radioactive pollutants from aqueous environments. Furthermore, the interaction of Acid Yellow 99 (AY 99) with CP was investigated (Khan et al., 2011). The aim was to understand the mechanism of adsorption and exploration of the potential use of pristine CP for controlling pollution resulting from textile dye wastewaters. SEM characterization demonstrated that the CP developed uneven and irregular surface upon the dye adsorption. EDX indicated that the dye was incorporated into the micropores and macropores of the adsorbent and hence, enhanced its crystallinity. Finally, FTIR revealed that the binding of AY 99 onto the CP occurred through electrostatic and complexation reactions. The adsorption process was found to be a function of pH and the optimum pH value was identified to be pH 2. Consequently, it was established that 1 g of the CP adsorbent could remove 442.13 mg of the AY 99 dye, which was a remarkable performance exhibited by the pristine CP.

3.1.6. Flax

Flax (*Linum usitatissimum*) is a member of the genus *Linum* in the family *Linaceae*. The textiles made from flax are known as linen, and traditionally used for bed sheets, underclothes, and table linen (Zeghioud et al., 2022). Like other plant-based fibers, flax has been proposed as a potential adsorbent for water decontamination owing to its high adsorption capacity, low cost, and ready availability (Karoyo

et al., 2020). In most of such applications, the flax shive (FS) is usually used (Cox et al., 2005). To facilitate the removal of C.I. Reactive Red 228 dye from aqueous media, the cellulose from FS was modified with quaternary ammonium groups (Wang and Li, 2013). The adsorption performance was investigated at various temperatures, adsorbent doses, initial dye concentrations and pH conditions. The maximum uptake was 190 mg/g at pH 3, at adsorbent dose of 0.4 g/L and initial concentration of 80 mg/L. Besides, activated carbon was prepared from FS and applied as adsorbent for removing the chlorinated hydrocarbon, trichloroethylene (TCE) (Klasson et al., 2009). The activation method employed had a little effect on the TCE adsorption in the gas or vapor phase; however, in liquid phase, steam activation was substantially better than phosphoric acid activation. The results showed that the FS-activated carbon performed better than selected commercial activated carbons, especially at higher TCE concentrations. Preliminary cost estimation suggested that the production costs of the activated carbons were \$1.50 to \$8.90 per kg, depending on the activation method and precursor material used; however, steam activation was significantly less expensive than phosphoric acid activation.

Furthermore, the adsorption of Au, Ag, Pd and Pt chlorides onto carbonaceous FS prepared by treatment with hot sulfuric acid was investigated (Cox et al., 2005). The calculated monolayer adsorption capacities were in the order of $Au(III) > Pd(II) > Ag(I) > Pt(II) \approx Pt(IV)$. It was observed that except Pt(IV), the metal ions got reduced on the surface of the adsorbent once they had been adsorbed. Conversely, the adsorbent became oxidized, thereby generating further ion exchange sites for adsorption of the precious metal ions. This was alleged to have allowed the possibility of recycling the adsorbent until significant amounts of the metals had been accumulated, thus simplifying the recovery of the metals by combustion of the residual adsorbent. Moreover, the suitability of FS and beech wood feedstocks for producing biochar as environmentally friendly adsorbents was assessed and the ability to adsorb methylene blue (MB) was tested, along with a series of carbamazepine adsorption tests (Zeghioud et al., 2022). Citric acid posttreatment and surface oxidation through heating at 250 °C in a muffle oven, were performed to improve the adsorption capacities of both FS biochar (FSBC) and beech biochar (BBC). The thermally-treated biochars, BBC and FSBC displayed unique surface areas of 388 and $272 \text{ m}^2/$ g, while the untreated biochars had 368 and 142 m^2/g , respectively. Thus, treating the biochars with citric acid resulted in an increase in the levels of oxygenated surface functional groups, which boosted the adsorption capacities. It was concluded that the biochars were promising as potential adsorbents for removing pollutants, with optimal performance achievable through a mild, low-cost, and environmentally friendly activation treatment.

3.1.7. Lyocell

Lyocell is a form of rayon produced from cellulose by direct dissolution of wood pulp in N-methyl morpholin-N-oxidemonohydrate (NMMO.H₂O) at concentrations ranging between 10 and 16 wt% and then spin-extrusion into high-strength fibers with excellent tenacities in the wet state (Ingildeev et al., 2013). Until recently, all attempts of Lyocell recycling were focused on regeneration or compositing with other matrices to enhance their mechanical strengths owing to its good tensile characteristics (Gindl-Altmutter et al., 2012; Graupner et al., 2013). In an alternative exploration, a number of studies were conducted via the chemical modification of Lyocell into heavy metal adsorbents (Bediako et al., 2016a; Bediako et al., 2015a; Bediako et al.; Bediako et al., 2016b; Bediako et al., 2016c; Bediako et al., 2015b). Foremost among these is synthesis of xanthate adsorbent for treating heavy metal ions, such as Pb(II), Cd(II) and Cu(II) (Bediako et al., 2015a). The metal binding mechanisms were studied via SEM, EDX, FTIR and XRD. The maximum single metal uptakes were recorded as 531.29 ± 0.28 mg/g, 505.64 ± 0.21 mg/g, and 123.08 ± 0.26 mg/g for Pb(II), Cd(II) and Cu(II), respectively. It was observed that the xanthate adsorbent exhibited Cu(II) selectivity in ternary metal system, owing to

its stronger complex formation with Cu(II) than with Pb(II) and Cd(II). It was thus concluded that by its nature, the cellulose xanthate adsorbent could be very effective in treating large volumes of wastewater with the contact of very little amount of the adsorbent.

Furthermore, fabric and strand forms of Lyocell were chemically converted into heavy metal adsorbents by carboxymethylation and crosslinking reactions (Bediako et al., 2016b). Using Cd(II) as a model target metal, the adsorption performance of the developed CMC-LS and CMC-LF adsorbents were compared with a commercial resin, Dowex Mac-3 (DM-3). It was shown that for the same packed column volume, CMC-LS reached \sim 70 % of its total capacity, while DM-3 reached \sim 57 %. The loaded Cd(II) were effectively eluted using 0.1 M EDTA or HCl and regeneration efficiency was relatively high. In addition, the adsorptive treatment of Pb(II)-contaminated wastewater was studied using tripolyphosphate-modified Lyocell fibers (Bediako et al., 2017). Full saturation was reached with initial Pb(II) concentrations ranging from 0 mg/L up to 300 mg/L, and the adsorption capacity was significantly high even at lower pH regimes. The metal binding mechanisms were described as mono, bi and tridentate, owing to the strong chelation properties of the triphosphate molecules. The adsorbent was regenerable in four adsorption-desorption cycles; however, a small amount of P was observed to leach out. The authors therefore suggested further improvement on the stability of the adsorbent for large-scale future application.

3.1.8. Cellulose acetate

Acetate fiber is defined by the Federal Trade Commission as a manufactured fiber in which the fiber forming substance is cellulose acetate (CA). The fibers find uses in apparel as linings, blouses, dresses, wedding and party attire, home furnishings, draperies, upholstery, diapers and slip covers. CA as an adsorbent possesses many advantages, which includes the ability to be easily produced in large quantities. CA fibers (CAFs) were examined as selective adsorbents for recovery of Au (III) from acidic chloride solutions (Yang et al., 2014). The CAFs were effective in separating Au(III) from other metals, including Pt(IV) and Pd (II). The amount of Au(III) adsorbed increased with increase in HCl concentration, but decreased with increase in the ionic strength of the solution. The maximum uptake reached 110 mg/g at 2 M HCl, and the loaded Au(III) was readily recovered by incineration. In addition, nonwoven membrane was prepared from CA and used for the removal of heavy metals (Tian et al., 2011a). The membrane was prepared by electrospinning and surface modification of CA with poly(methacrylic acid) (PMAA). This membrane was used to treat Cu(II), Hg(II) and Cd(II) by varying the initial pH, and high selectivity of Hg(II) was observed. Saturated EDTA was found to easily desorb the metal ions from the loaded membrane, making the membrane reusable in several cycles. In other studies, composites of CA/zeolite (Ji et al., 2012) and CA/polyaniline (Li et al., n.d.) were fabricated and used for treating toxic Cr(IV), Hg(II), Cu(II) and Ni(II), with high efficiencies. Conductive composite membrane of phytic acid (PA)-doped polyaniline (PANI)/CA was prepared by blending aniline with CA/PA solution and polymerizing prior to phase conversion (Li et al., 2014). After characterization and electric resistance measurements, the resultant composite membranes were used to adsorb Hg(II) and Cr(VI) with the maximum uptakes reaching 280.11 and 94.34 mg/g, respectively. CA-based adsorbents thus offer propelling opportunities as adsorbents for water decontamination, and ongoing research is further exploring ways to optimize their performances for specific water treatment applications.

3.2. Mechanisms of pollutants removal

The removal mechanisms of pollutants from contaminated water using fiber precursor and textile fiber waste-based adsorbents are not very different from the mechanisms that play out when other types of adsorbents are applied. This is because the adsorption mechanisms are not based on the solid matrices only, but also the chemical functional groups anchored on the materials or present on the surface of the adsorbents and other important factors. In fact, the adsorption process and thus the adsorption mechanism is influenced by various factors, including the surface properties, characteristics of the pollutants, porosity or pore size distribution, specific surface area, hydrophobicity/ hydrophobicity, the water/wastewater composition, and molecular interactions (Zeghioud et al., 2022). Generally, a variety of binding mechanisms such as Van der Waals attraction, electrostatic interaction, complexation, chelation, ion exchange, and precipitation are involved (Abdolali et al., 2014; Zeghioud et al., 2022). The elucidation of these mechanisms is either derived from experiments or instrumental characterization such as SEM, EDX, FTIR, XPS, and XRD. The experimental techniques include titration, chemical blocking of functional groups, and ion exchange or proton displacement reactions (Abdolali et al., 2014).

Aside estimating the equilibrium adsorption rates, the kinetic data fitted through the pseudo-first-order (PFO), pseudo-second-order (PSO) or intraparticle diffusion (IPD) models, can predict whether the adsorption process occurs through physical or chemical means, or determine the stages of adsorption and what the rate-limiting steps are (Adebayo et al., 2022; Behloul et al., 2022; Futalan et al., 2022; Tan et al., 2008). When both the PFO and PSO models fairly represent the kinetic data, then a combination of physisorption and chemisorption mechanisms are said to be involved (Bediako et al., 2015a; Bediako et al., 2016b). Physical adsorption occurs through the influence of week Van der Waals forces of attraction, while chemisorption arises from comparatively stronger chemical bonds between the adsorbates and functional groups on the surface of the adsorbents, particularly those modified chemically (Abdolali et al., 2014). IPD is usually accompanied by two or three adsorption stages, that is, initial linear adsorption phase characterized by external mass transfer leading to fast kinetics, and a second linear adsorption stage where there is slow diffusion of the adsorbates through the pores of the adsorbents (Adebayo et al., 2022; Akkoz and Coskun, 2023). If the IPD plot passes through the origin, then it becomes the sole rate-limiting step, otherwise, there may be other levels of boundary layers that control the adsorption rate (Adebayo et al., 2022; Khan et al., 2011). In addition, other physical mechanisms such as monolayer and multilayer adsorption are predicted through isotherm models like the Langmuir and Freundlich models or their combined forms (Deng et al., 2016).

Electrostatic interaction is the attraction between a negatively charged adsorption site and a positively charged adsorbate or vice versa. Ion exchange on the other hand, is a specific type of electrostatic interaction involving the exchange of ions between the adsorbent surface and the liquid medium bearing charged adsorbates (Abdolali et al., 2014). In ion exchange, ions of the same charge are replaced or exchanged between the solid adsorbent and liquid phase. This mechanism is more prevalent in the adsorption of inorganic metal ions. In the carboxymethylated reaction of LF using sodium chloroacetate, the adsorption mechanism of Cd was described to be ion exchange between Na(I) and Cd(II), confirmed through EDX and FTIR analysis (Bediako et al., 2016a). Moreover, a shift from higher to lower wave number of O—H groups and the disappearance of C=O stretching band for a coir pitch adsorbent were tipped to be indications of chemical interactions involving hydroxyl and carboxyl groups on the adsorbent and Acid Yellow 99 dye, as well as C=C stretching modes of benzene ring of lignin (Khan et al., 2011). The benzene rings in activated carbons synthesized from fiber precursors and textile fiber wastes also undergo pi-pi interactions with organic molecules such as dyes and pharmaceuticals (Naushad et al., 2019).

In the study by Deng and co-workers, PAN_{MW}-AO fibers exhibited very high adsorptive affinity towards Cr(IV), aided by surface complexation mechanism with amidoxime group present on the fibers, elucidated via FTIR, SEM/EDX and XPS characterization (Deng et al., 2016). In addition, the adsorption of Pb(II) using tripolyphosphate-modified LF was described to involve mono, bi and tridentate binding

due to the compelling chelation properties of the triphosphate molecule (Bediako et al., 2017). Furthermore, the adsorption of Cr(IV) and rhodamine 6G by modified cotton fiber was described to be largely contributed by the inherent surface area and that offered by nanosized V_2O_5 , as well as hydrophobic interactions, nanoparticles formed within interface regions, gel-like structure with micro voids, and complexation championed by the presence of C=N in the structure of the adsorbent (Agathian et al., 2018).

4. Chemical reactions employed in the modification of fiber precursors and textile fiber wastes into adsorbents

Chemical modification of fiber precursors and textile fiber wastes takes different forms, depending on the source of the fiber precursor or textile fiber material and original functional groups. Animal-based textile materials are usually from protein sources and contain amino acid groups, while plant-based textile materials are usually lignocellulosic in nature, i.e., they contain cellulose, hemicellulose and lignin as major components (Abdolali et al., 2014; Hokkanen et al., 2016). In certain instances, the fiber precursors and textile fiber wastes are applied either in their pristine forms after physical cleaning and simple acid/base treatments or functionalized through various chemical modification reactions (Fig. 6). The often-adopted chemical modification reactions include sulfonation, amination, carboxymethylation, xanthation, amidoximation, grafting, coating and carbon activation. These reactions are either carried out independently or as stepwise combination of several reactions to arrive at the final adsorbents with the desired characteristics. Through these chemical reactions viable functional groups, such as carboxyl (COO-), amine (-NH₂), sulfonate $(-SO_3^-)$ sulfate $(-SO_4^{3-})$, phosphate $(-PO_4^{3-})$, thiol (-SH) and hydroxyl (-OH), are incorporated into/onto the fibers (Min et al., 2004; Nada and Hassan, 2006; Nguyen et al., 2014).

Owing to the introduction of active functional groups onto the fibers, the chemically modified fibers often exhibit remarkable improvements in the adsorption performances towards pollutants. For example, raw cotton fiber showed R6G and Cr(VI) uptakes of 481.54 and 290.71 mg/ g; however, after series of modifications, the final adsorbent recorded improved uptakes of 2121.75 and 777.23 mg/g, respectively (Agathian et al., 2018). Furthermore, the adsorption study conducted using carboxymethylated LF with Cd(II) as a model heavy metal pollutant revealed about 17 folds higher uptake compared to the pristine LF (Bediako et al., 2016c). This massive increase in adsorption capacity was enabled by the effective introduction of active carboxyl (-COO⁻) group as against the inactive hydroxyl group (-OH) present on the pristine fiber. In addition, evidence of increased Ni(II) adsorption were observed for mercerized and citric acid-modified hemp fiber (HF) and hemp shive (HS) (Kyzas et al., 2015). The raw HF and HS showed Ni(II) uptakes of 158 and 145 mg/g, while their modified forms displayed significant increase to 184 and 175 mg/g, respectively. It must be noted, however, that some modifications may be rather detrimental to the performance of the adsorbents as evident from the case of modifying cotton fiber with ε-caprolactone monomer (Agathian et al., 2018).

4.1. Carboxymethylation

Generally, carboxymethylation reaction introduces carboxyl groups onto adsorbents. This reaction is often employed in the chemical modification of fiber precursor and textile fiber wastes, as largely applied to Lyocell using NaOH/sodium chloroacetate (Bediako et al., 2016a; Bediako et al., 2016b; Bediako et al., 2016c), and to bamboo as in carboxylated bamboo fibers using citric acid/sodium hypophosphite (Wang et al., 2013). Carboxymethylation using sodium chloroacetate is probably the commonest way of preparing fiber precursor and textile fiber waste-based adsorbents with high degrees of substitutions; however, the hydrophobicity of the materials is changed to hydrophilicity after the reaction (Fig. 7). Therefore, the carboxymethylated adsorbents

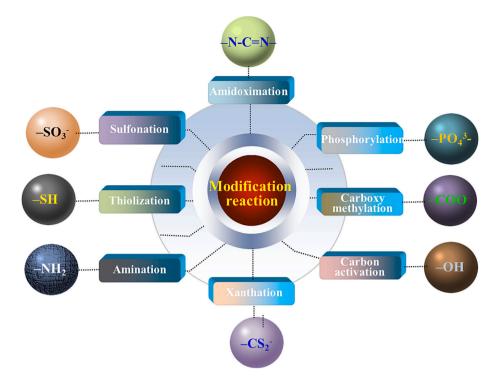


Fig. 6. Common modification reactions employed in converting fiber precursor and textile fiber wastes in adsorbents.

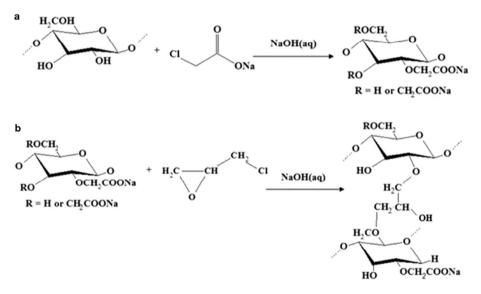


Fig. 7. Reaction schemes of (a) carboxymethylation and (b) crosslinking (Bediako et al., 2016c).

usually require crosslinking reactions to provide the needed stability in aqueous solution. Epichlorohydrin (ECH) is the most utilized crosslinking reagent for this purpose, owing to its high success and low environmental impact. Crosslinked carboxymethylated fiber waste adsorbents have shown some of the most outstanding adsorption performances (Bediako et al., 2016a; Bediako et al., 2016b). An eco-friendly approach which adopts microwave-assistance was used to fabricate fast recyclable carboxymethylated jute fibers with remarkably high adsorption capacity of 157.21, 88.98 and 43.98 mg/g for Pb(II), Cd(II) and Cu(II), respectively, predicted by the Langmuir isotherm model (Du et al., 2016). The adsorbent could be easily regenerated using aqueous EDTA-2Na for up to at least 4 cycles with equivalent high adsorption capacity.

4.2. Sulfonation

Sulfonation involves the introduction of sulfonate or sulfate groups into the matrices of the fiber precursors or textile fiber wastes to improve their adsorption affinities. Sulfuric acid, sodium sulfite and sulfur trioxide pyridine complex are prevalent among several reagents used for this modification reaction (Dong et al., 2016; Dong et al., 2013; Pangeni et al., 2012; Shin and Rowell, 2005). Sulfonation was used to modify Juniper (*Juniperus monosperma*) fiber chips in order to improve their heavy metal adsorption capacities (Shin and Rowell, 2005). The sulfonation of cotton linters and their successful application as adsorbents for high-efficiency removal of Pb(II) was also reported (Fig. 8). The authors used a systematic approach of sulfuric acid treatment followed by sulfur trioxide pyridine complex in *N*,*N*-dimethylformamide solvent (Dong

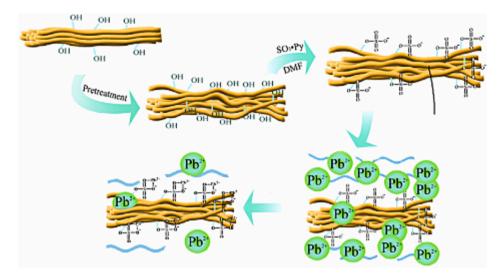


Fig. 8. Graphical illustration of the sulfonated modification of cotton linters and subsequent adsorption of Pb(II). Reproduced with permission from (Dong et al., 2013) (copyright (2013) Elsevier).

et al., 2013). Compared to the original material, >85 % of Pb(II) was removed at <20 mg/L, and equilibrium was attained within 8 min. The kinetics was best fitted by the pseudo-second-order model, while the isotherm was described by the Temkin model and suggested chemisorption. The above approach was similarly used to produce sulfonated cellulose adsorbent for adsorption of Fe(III), Cu(II) and Pb(II) (Dong et al., 2016). The adsorbents were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Fourier-transform infrared spectrometry (FTIR), revealing reduction in the crystallinity and thermostability of the pristine cellulose post-modification. The adsorbent showed good performances with 100 % removal efficiency of Cu(II) at 25 mg/L initial contraction. In addition, adsorption equilibrium was reached within 2 min and the adsorbent was regenerated using 0.1 M of EDTA, HCl or HNO₃.

4.3. Xanthation and amidoximation

Xanthation and amidoximation are other chemical methods used to modify fiber precursors and textile fiber wastes into useful adsorbents. Xanthation is achieved by the chemical reaction of organic hydroxylcontaining substrates with carbon disulfide under alkaline conditions (Fig. 9a, c) (Bailey et al., 1999; Bediako et al., 2015a). Earlier studies have applied this method to convert commercial cellulose (Kim and Lee, 1999), orange peels (Liang et al., 2009), and banana peels (Pillai et al., 2013) into potent heavy metal scavengers. In a recent study, this process was adopted to fabricate high-capacity adsorbent from Lyocell fibers to remove Pb(II), Cu(II) and Cd(II) from single and ternary metal solutions (Bediako et al., 2015a). Adsorption equilibrium was reached within 5 min for all the metals, and the maximum single metal adsorption capacities were estimated to be 531.29 ± 0.28 mg/g, 505.64 ± 0.21 mg/g, and 123.08 ± 0.26 mg/g for Pb(II), Cd(II) and Cu(II), respectively, with Cu(II) selectivity being observed in a ternary mixture. On the other

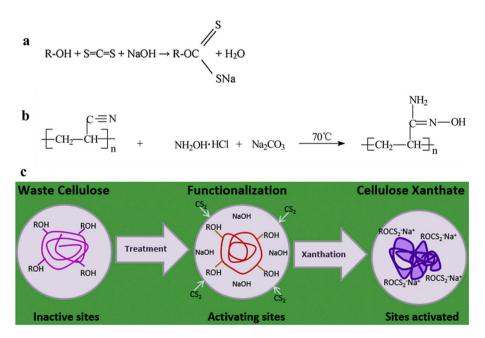


Fig. 9. (a) Xanthation (Bediako et al., 2015a) and (b) amidoximation (Huang et al., 2013; Lim et al., 2016) reactions. (c) Conversion of hydroxyl group in Lyocell fiber into sulfur-containing group via xanthation. Reproduced with permission from (Bediako et al., 2015a) (copyright (2015) Elsevier).

hand, amidoximation is a form of grafting process that converts nitrile groups into hydroxylamine groups (Fig. 9b) (Huang et al., 2013; Yu et al., 2002). This process has been much successful in modifying PAN fiber wastes into both cationic and anionic water decontaminants (Lim et al., 2016; Zhao et al., 2015). Lim et al. reported the application of amidoximated waste PAN fibers for recovery of Pd(II) and Pt(IV) from aqueous phases (Lim et al., 2016). The waste PAN fibers were first dissolved in dimethyl sulfoxide and span into water, followed by the amidoximation reaction to generate the necessary binding sites for adsorption. The raw PAN exhibited no affinity towards the metal ions; however, the amidoximated PAN showed maximum equilibrium uptakes of 244.06 \pm 10.68 and 175.64 \pm 6.62 mg/g for Pd(II) and Pt(IV) respectively, according to the Langmuir isotherm model. In comparison to commercial AmberjetTM 4200 resin, the PAN-oxime adsorbent displayed much faster kinetics and better metal selectivity.

4.4. Grafting/graft polymerization

Grafting or graft polymerization has been one of the most commonly used methods of chemical modification. This process involves the incorporation of different functional materials or polymers onto others for the purpose of improving their adsorption efficiencies. For example, poly(hydroxyethylmethacrylate) was grafted onto coir pith using potassium peroxydisulphate as an initiator and in the presence of N,N methylenebisacrylamide as a crosslinking agent (Anirudhan et al., 2008). The product yielded about 99 % Hg(II) removal, as against the pristine coir fiber. Besides, poly(N,N-dimethyl aminoethyl methacrylate) was grafted onto native cellulose fibers and used as effective adsorbents for removing F^- , AsO₂⁻ and AsO₄³⁻ from aqueous solutions (Tian et al., 2011b). In addition, Fe(III)-loaded iminodiacetic acid modified GMA grafted nonwoven fabric was fabricated for anion adsorption (Kavaklı et al., 2014). Furthermore, Hafrén and Córdova grafted ɛ-caprolatone (E-CL) from cotton through organic acid-catalyzed ring-opening polymerization (Hafrén and Córdova, 2005). In a study by Ma et al., a double network hydrogel (DNH) based on waste cotton fabrics and polyacrylamide (Cellulose/PAM DNHs) was synthesized for heavy metal remediation (Fig. 10) (Ma et al., 2018). The reusable DNH adsorbent demonstrated outstanding adsorption capabilities with extremely rapid kinetics, attaining adsorption equilibrium within 5 min, championed by the porous and sheet-like laminar structures. Using tandem columns packed with cellulose/PAM adsorbent, the system efficiently processed both simulated and real wastewater, with negligible adsorption discrepancy within 3 cycles. The treatment volumes for simulated wastewater were 172.5 BV (7935 mL), 195 BV (8970 mL), and 292.5 BV (13,455 mL) for Cd(II), Cu(II), and Pb(II), respectively. Additionally, actual industrial wastewater treatment volumes were 42 BV (1932 mL) for Cd(II), 63 BV (2898 mL) for Cu(II), and 87 BV (4002 mL) for Zn(II),

Pb(II), and Fe. The study was tipped to present a novel approach to combining repurposing of waste cotton fabrics with heavy metal removal, thereby contributing significantly to the call for resource sustainability and an environmentally friendly society. Other studies include electrospinning and graft modification of cellulose acetate with poly(methacrylic acid) (PMAA) (Tian et al., 2011a), chitin grafted poly (acrylic acid) (chi-g-PAA) (Huang et al., 2012), and acrylic acid grafted *Ficus carica* using ceric ammonium nitrate (CAN) as initiator (Gupta et al., 2013b; Gupta et al., 2013c).

4.5. Carbon activation

Another method that appears common for deriving adsorbents from fiber precursors and textile fiber wastes is carbon activation either via physical or chemical routes (Nguyen et al., 2014). The carbon activation process takes three forms, which are thermal, chemical and steam activations. Thermal activation (also known as calcination) is done at high temperatures in furnaces; chemical activation is carried out using chemical reagents usually before or after thermal treatment in quest to add active binding sites and increase the porosity and surface area of the carbonized material; and steam activation is normally conducted at high temperatures and pressures in the presence of air at low temperature/ steam, and CO₂/blue gas at high temperature (Nguyen et al., 2014). In some cases, there is also hydrothermal treatment pre-step before carbonization, usually in an autoclave at moderate temperatures (Jain et al., 2016). All the activation methods help to create micro, meso and macro pores within the precursor fibers, which lead to improved adsorption by pore diffusion and chemisorption (Nguyen et al., 2014). Carbon activation had been extensively used to convert high mechanical fiber precursors, such as coir and hemp into adsorbents for various contaminants removal (Anirudhan et al., 2008; Etim et al., 2016; Kavitha and Namasivayam, 2007; Khan et al., 2011; Kostic et al., 2014; Krishnan and Haridas, 2008; Parab et al., 2005; Suksabye and Thiravetyan, 2012; Vukcevic et al., 2012; Vukčević et al., 2014). Activated carbons are sometimes further modified, such as in the case of postoxidized treatment of activated cotton (gin) with HNO3, H2O2 and air, leading to improved solvent vapor adsorption (Chiu and Ng, 2014), as well as activated FS for chlorinated hydrocarbon trichloroethylene adsorption (Klasson et al., 2009). It has been shown that the surface of activated carbon bears many functional groups that could be further modified to enhance the removal of organic pollutants in water (Fig. 11) (Naushad et al., 2019).

4.6. Other modification methods

Other modification methods include surface coating, as in the cases of PEI-coated PAN fibers, which were used for Pt(IV) recovery from

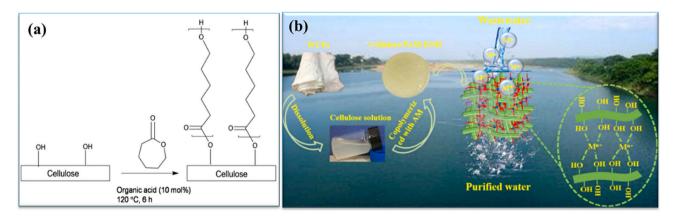


Fig. 10. Schemes showing grafting of cotton with (a) poly(e-caprolactone) and (b) polyacrylamide. Reproduced with permission from (a) (Carlmark et al., 2012) (copyright (2012) Elsevier) and (b) (Ma et al., 2018) (copyright (2017) Elsevier).

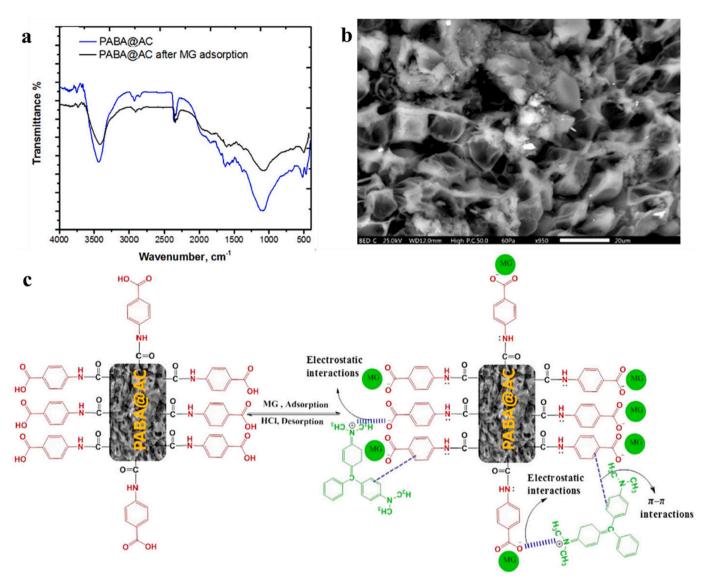


Fig. 11. (a) FTIR functional groups spectra and (b) SEM surface morphology of para-aminobenzoic acid functionalized activated carbon (PABA@AC). (c) Mechanism of malachite green dye adsorption and desorption PABA@AC. Reproduced with permission from (Naushad et al., 2019) (copyright (2018) Elsevier).

acidic media (Yoon et al., 2016), PEI-modified bamboo hydrochar for Cr (VI) scavenging (Chen et al., 2023), and carboxymethyl cellulose coated-Lvocell fibers for Cd(II) removal from contaminated water (Bediako et al., 2015b). Like grafting, coating can introduce different kinds of functional groups, depending on which chemical is coated. MOF/g-C₃N₄ nanospheres were successfully incorporated onto smart textile cotton and used for rapid detection and detoxification of chemical warfare agents (Giannakoudakis et al., 2017). In addition, the loading of metals, such as Zr, Fe, Ca, Zn, La and Ce complexes, quaternization using ammonium salts, surface activation using steam or high temperature furnaces, surface coating using a variety of biodegradable organic and ionic polymers, or simply acid/base treatments, were also studied for cotton, flax, jute, coir and other fiber precursor and textile fiber wastes (Abdolali et al., 2014; Anirudhan et al., 2008; Zhang et al., 2008). Functionalization through periodate oxidation using acidified sodium chlorite is another approach, as in the case of treated kapok fiber for methylene blue removal (Liu et al., 2012), and oxidized cellulose which showed adsorption capacity of 184 mg/g for Ni(II) and 236 mg/g for Cu (II) (O'Connell et al., 2008). Furthermore, plasma treatment such as reactive microwave-assisted cold plasma using mixtures of Ar and CO2 can be alternative treatments to traditional chemical methods (Fig. 12). For example, da Silva et al. examined the influence of surface plasma

treatment on the properties of sisal fibers and subsequent effect on methylene blue adsorption through kinetics and isotherms studies (da Silva et al., 2020). The plasma treatment did not induce loss of the original properties of the fibers and was found to have played a crucial role in increasing the adsorption capacity. The surface modification promoted greater removal of the methylene blue molecules to reach 96 % removal efficiency. Through kinetics and isotherm studies, the adsorption process was observed to be favorable and likely occurred at heterogeneous sites for both the pristine and plasma-treated fibers.

5. Prospects and challenges of fiber precursor and textile fiber waste-based adsorbents

5.1. Handling, regeneration, and reuse

Handling and ease of separation from the aqueous phase after adsorption are among several characteristics expected of ideal adsorbents (Bediako et al., 2016c; Reddy and Yun, 2016). This requirement is very necessary to ensure efficient recovery and reuse of the adsorbents. Unlike other types of adsorbents, most adsorbents prepared from fiber precursor and textile fiber wastes are easy to handle and separate after use. Owing to the relatively longer lengths and thinner sizes of these

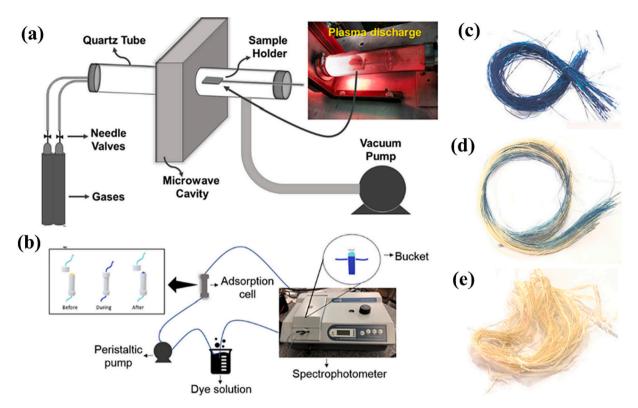


Fig. 12. Illustration of the reactive plasma system used (a), the fixed bed scheme used in the adsorption study which is attached to a spectrophotometer (b), dyeadsorbed fibers (c), pristine (d) and plasma-treated fibers (e) fibers after immersion in 25 g/L aqueous solution of NaClO. Reproduced with permission from (da Silva et al., 2020) (copyright (2020) Elsevier).

Table 3

| Regeneration of fiber | precursor and | textile fiber | waste-based | adsorbents. |
|-----------------------|---------------|---------------|-------------|-------------|
|-----------------------|---------------|---------------|-------------|-------------|

| Adsorbent | No. of cycles | Adsorbate | Uptake (mg/g) | Desorption eff. (%) | Desorbing agent(s) | Ref. |
|------------------------------|------------------|------------------------------------|------------------------|------------------------|--|--------------------------|
| CMC-coated fibers | 4 | Cd(II) | 90 | 100 | 1 M HNO ₃ | (Bediako et al., 2015b) |
| Kapok fiber | 5 | Methylene blue | 110.1 | 92 | 0.1 M HCl | (Liu et al., 2012) |
| CMC-LS | 3 | Cd(II) | 100 | 100 | 1 M HNO ₃ | (Bediako et al., 2016b) |
| TEPA-(GMA-gHF) | 5 | RBBR, RR120, RY160 | 91.74, 76.34, 83.33 | 80, 82, 85 | 1 M NaOH | (Akkoz and Coskun, 2023) |
| Carboxymethylated Lyocell | 4 | Pb(II) | 99 | 94 | 1 M HCl | (Bediako et al., 2016a) |
| Hg-C-TU | 5 | Hg(II) | 91 | - | 0.1 M HNO3 | (Monier et al., 2014) |
| Cu-ABZ | 5 | Cu(II) | - | 95 | 0.1 M HCl | (Monier et al., 2015) |
| WJN-1 | 5 | Cu(II), Ni(II) | 114.5, 102.1 | 90.5, 91.7 | 1 M HCl | (Wang et al., 2012) |
| | | Cu(II), Ni(II) | 129.6, 109.6 | 93.5, 94.1 | 0.1 M EDTA | |
| Schiff base cotton fiber | 3 | Cr(VI), R6G | 404.02, 696.47 | - | Heating at 65 °C in an alkaline medium | (Agathian et al., 2018) |
| PET-TSC | 5 | Hg(II), Cu(II), Co | _ | 85.2, 84.2, 85.6 | 1 M HCl | (Monier and Abdel-Latif, |
| | | (II) Hg(II), Cu(II), Co (II) | | 89.3, 90.5, 89.7 | 0.1 M EDTA | 2013b) |
| PMAA-modified CA | 3 | Cu(II), Cd(II), Hg (II) | 2.8, 2.6, 5 | 90, 90, 100 | Saturated EDTA | (Tian et al., 2011a) |
| PPTA-Sal | 1 | Pb(II0, Cu(II), Ni(II) | _ | 98.5, 99.6, 98.8 | 0.5 M HNO3 | (Qu et al., 2012) |
| Fe(III)-loaded IDA fabric | 1 | PO_{3}^{2-} | 28.4 | ~100 | 0.5 M NaOH | (Kavaklı et al., 2014) |
| PANI | 1 | Cr(VI) | 62.9 | 83 | 2 M NaOH | (Kumar et al., 2008) |
| CMJF _{MH} | 4 | Pb(II), Cd(II), Cu(II) | 157.2, 89.0, 44.0 | 88, 89, 86 | EDTA-2Na | (Du et al., 2016) |
| PANI-CA/PA | 3 | Hg(II), Cr(VI) | 280.1, 94.3 | 50, 32 | acid and alkali solution of varying pH | (Li et al., 2014) |
| Sulfonated cellulose | 4 | Pb(II) | 90 | 100 | 0.1 M EDTA | (Dong et al., 2016) |
| Kapok-DTPA | 8 | Pb(II), Cu(II) | 310.6, 101 | > 90 | 1 M HCl | (Duan et al., 2013) |
| PAN _{MW} -AO fibers | 5 | Cr(VI) | 205 | 80 | 0.1 M H2SO4 | (Deng et al., 2016) |
| PGCP-COOH) | 4 | Hg(II) | - | 91.4 | 0.2 M HCl | (Anirudhan et al., 2008) |
| Modified jute waste | 5 | MB | 2000 | ~80 | Distilled water at pH 2–8 | (Manna et al., 2017) |
| Multilayered coir fiber | 2 | Reactive green 19 | 18.4 | ~90 | 0.1 M NaOH | (Mathew et al., 2019) |

fibers, they are easy to separate from the aqueous phase and can be effectively regenerated through adsorption-desorption cycles (Bediako et al., 2016b). This has been proven in several studies (Bediako et al., 2016a; Bediako et al., 2016b; Bediako et al., 2016c; Bediako et al., 2015b; Monier and Abdel-Latif, 2013b; Wang et al., 2012; Wang et al., 2013). From the literature, most fiber precursor and textile fiber wastebased adsorbents are easily regenerated using simple acid and base solutions, e.g., HCl, EDTA, HNO3, NaOH, NH4OH etc. (Table 3). At lower pH, most anion-functionalized adsorbents (or cationic adsorbents) are better degenerated by acid eluents as a result of the strong competition from hydrogen ions, leading to protonation of the binding sites and release of the metal ions into the desorbing solutions (Bediako et al., 2016c; Repo et al., 2013). More often, the adsorption capacity experiences significant decrease due to inevitable loses; however, desorption efficiency is usually fairly maintained over the adsorption cycles. Bediako et al., described a five-cycle adsorption/regeneration process of Cd(II) using carboxymethylated Lyocell fabric by controlling the pH of distilled water to pH 1 (Bediako et al., 2016c). About 95 % of the adsorbed metal ions were leached out (desorbed) at the end of each cycle. Furthermore, HCl and EDTA were separately used to desorb heavy metals including Hg(II), Cu(II), Ni(II) and Co(II) from loaded PET-TSC (Monier and Abdel-Latif, 2013b) and WJN-1 fibers (Wang et al., 2012) up to 5 cycles. The average desorption efficiencies were 85-90 % and 90- 100 % for HCl and EDTA, respectively. On the average, EDTA appeared a slightly better eluent than HCl, considering the slightly higher desorption efficiencies. This is probably due to the chelating property of EDTA which is significantly stronger than the ionic shielding effect of HCl. In the case where the fibers are converted into particulate materials with smaller sizes, such as activated carbon, biochar, etc., they may face problems of separation and subsequent losses of the adsorbents over the cycles. This could however be solved via immobilization, composite formation with long chain polymers, or magnetization.

5.2. Continuous flow-through applications

Another important required characteristic of adsorbents in general is their convenient application in continuous flow-through systems such as columns and membranes (Bediako et al., 2016a). In flow-through columns for example, the adsorbents are continuously in contact with a fresh solution and the rate of adsorption depends on the concentration of solute in the solution being treated. As a result, the concentration in the solution in contact with a given layer of adsorbent in a column is relatively constant (Ahmaruzzaman, 2011; Chen et al., 2019). For batch operation, the concentration of solute in contact with a specific quantity of adsorbent gradually decreases as adsorption proceeds towards equilibrium, thereby decreasing the effectiveness of the adsorbent in removing the solute (pollutant). The size and shape of the adsorbents play crucial roles in realizing their effective application in the flowthrough systems. When the sizes of the adsorbents are extremely small (e.g., nano sizes), they tend to block the column tubes and cause clogging problems. On the other hand, when the sizes are too big (lump adsorbents), they show slow adsorption kinetics (Bediako et al., 2016b; Park et al., 2018). In membrane operations, nanoadsorbents tend to pass through the filters, thereby re-polluting the clean filtrates. By their nature, it is expected of fiber precursor and textile fiber waste-based adsorbents to be applicable in columns and membranes without problems of column clogging or membrane penetration.

Yoon et al. (Yoon et al., 2016) described the application of PEIcoated waste PAN (PWPAN) fibers in a column for the recovery of Pt (IV). The chromatography column (006SCC-10-10-FF, Omnifit, Danbury, CT, USA) was packed with 0.7854 mL of the PWPAN fibers. A model Pt(IV) solution was run upwards with the aid of a peristaltic pump at the rate of 3 mL/min for 7 h. Aside demonstrating rapid kinetics and significantly high Pt(IV) uptake in the column, the PWPAN fibers also showed extremely low residence time of 0.2618 min, which was described as better than previously reported cases (i.e., \sim 3.81 to 25 min). For industrial application, this achievement was considered laudable because the residence time is a major factor that affects the packing volume (scale) and volumetric flow rate (Yoon et al., 2016). The authors compared the performance of the PWPAN fibers with a commercial resin, M500. It was observed that the Pt(IV) concentration of the outlet was >50 mg/L after 5 min in the case of the M500 resin, whereas the outlet concentration was <5 mg/L in 36 min (W.V. 137.5) when the PWPAN fibers were applied. By calculation, it was estimated that just 1 mL of the PWPAN fibers could recover 137.5 mL of 250 mg/L Pt(IV).

It is not only those fiber precursors and textile fiber waste adsorbents available in fibrous forms that are applicable in columns and membranes. A double network hydrogel (Cellulose/PAM-3) made from waste cotton fibers via copolymerization with polyacrylamide demonstrated effective treatment of simulated and real wastewater containing heavy metal ions, such that discrepancies emanating from the results of three adsorption-desorption cycles were negligible (Fig. 13) (Ma et al., 2018). In addition, Asberry et al. (Asberry et al., 2014) described the successful application of bamboo particles in a flow-through column. At the flow rate of 1 mL/min and feed metal ion concentration of 10 mg/L, the breakthrough curves for Ni(II) and Fe(III) occurred at a short column bed of 1.1 mL volume. The utilization percentage of the binding sites of the adsorbents was effectively raised by the column process. That is, in comparison to the batch adsorption capacities, the continuous flow capacities obtained at the breakthrough points were 2 and 3 folds higher for Fe(III) and Ni(II), respectively. Furthermore, the column study of Cr (VI) adsorption from electroplating industry was carried out using coir pith (Suksabye et al., 2008). Parameters such as bed depth (40-60 cm) and flowrate (10-30 mL/min) were varied to study their effects on the column performance. The adsorption capacity estimated from the BDST model was reduced with increasing flowrate, which was 16.40 mg/cm³ or 137.91 mg/g for the flow rate of 10 mL/min and 14.05 mg/cm³ or 118.20 mg/g for the flow rate of 30 mL/min. At the highest bed depth of 60 cm and lowest flow rate of 10 mL/min, the maximum adsorption capacity reached 201.47 mg/g according to the Thomas model. Finally, about 67-70 % desorption efficiency was obtained in a 3-cycle column regeneration study using 2 M HNO₃.

It must be noted, however, that the ease of application of fiber precursors and textile fiber waste adsorbents in column is not always a sure guarantee. This is evident from the work of Bediako et al. (Bediako et al., 2016b) in which mat (woven) and strand type Lyocell fibers were chemically modified through carboxymethylation reaction and applied to Cd(II) adsorption. In a column separately packed with the prepared adsorbents, clogging was observed in the case of the mat type adsorbent but not the strand type. Consequently, the adsorption performance of the strand type adsorbent was compared with that of Dowex Mac-3 resin. For the same volume of packed column, the Lyocell adsorbent reached \sim 70 % of its total capacity at the breakthrough time of 100 min, while the resin reached \sim 57 % at the breakthrough time of 400 min. It was thus concluded that the successful application of textile fiber wastebased adsorbents in flow-through column depends on the oriental forms of the materials before and after chemical modification.

5.3. Environmental fate

One important factor to consider when developing adsorbents for water decontamination is the effect of the adsorbents on the environment. Inasmuch as adsorbents are developed for treating water contaminants, care must be taken not to introduce secondary pollutants. During the conversion of fiber precursors and textile fiber wastes into adsorbents, several chemical reagents are used for the modification reactions. Most of these chemicals may not be very friendly to the environment (flora and fauna). As a matter of fact, every chemical, including the so-called "green chemicals" have traceable negative effects on the environment to some extent; however, efforts must be made to avoid the use of extremely toxic ones. For example, the adsorbents produced using carbon disulfide and *N*,*N*-dimethylformamide may pose serious threats

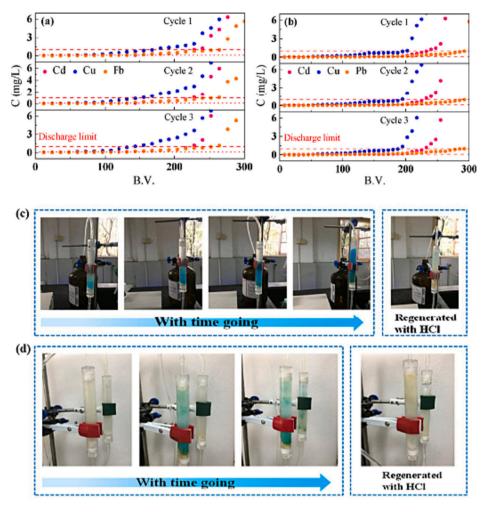


Fig. 13. Simultaneous adsorption of Cd(II)/Cu(II)/Pb(II) using fixed-bed columns packed with Cellulose/PAM-3. The concentrations of Cd(II)/Cu(II)/Pb(II) in the effluent during three regeneration cycles were measured as a function of bed volume for both (a) a single column and (b) a tandem of two columns. Photos were taken during the adsorption process to show the appearance of both (c) a single column and (d) a tandem of two columns. The pH was kept constant at 5.00 ± 0.01 and one bed volume was equal to 23 mL for a single column and 46 mL for the tandem of two columns. Reproduced with permission from (Ma et al., 2018) (copyright (2017) Elsevier).

to users and aquatic species. This is because these chemicals have long history of severe health problems on the environment and its inhabitants (Davidson and Feinleib, 1972; Kim and Kim, 2011). Thus, appropriate methods that require less or non-toxic and less harsh chemicals must be adopted in order to meet the goals for which the adsorbents are developed.

Another important consideration that is lacking in most of the studies undertaken is the absence of account on the stability of the adsorbents during the adsorption/regeneration cycles. It must be encouraged that researchers report both the performance and environmental shortcomings of the developed adsorbents. The issue of leaching of chemicals into the aqueous solutions during adsorption is an important factor to always consider. Given that a significant amount of phosphorus was observed to have leached out during the adsorption and desorption of Pb(II) using tripolyphosphate-modified Lyocell fibers (Bediako et al., 2017), it calls for attention to be paid to this all important issue. Furthermore, postadsorption treatment and disposal of the spent adsorbents is another important factor that must be looked at. Researchers normally do not give account on how they treat their spent adsorbents or suggestions on the possible post-adsorption applications of the exhausted adsorbents. It is most likely that the exhausted or metal-laden adsorbents are disposed of just like any other laboratory wastes; however special disposal protocols must be designed for these types of wastes. This is an important issue that must be critically examined to avoid secondary pollution in

the open environment. Another area that should be considered in making adsorbents from fiber precursors and textile fiber wastes should be their potential environmental persistence. Since this is not only a value addition but also a waste management strategy, the comparative environmental cost of each treated fiber by each treatment technology and pristine fiber wastes should be evaluated using life cycle assessment analysis. This will not generate an immediate cost valuation but the long-term environmental cost of each technology.

6. Economic perspective and analysis

Cost evaluation is an important issue to consider when undertaking water treatment activity, particularly on a commercial scale, since the total cost is influenced by the cost of the adsorbent (Futalan et al., 2022; Singh et al., 2017). In fact, lack of sufficient cost records can make the best available treatment technology less appreciable (Donkadokula et al., 2020). Quite unfortunately, few studies have evaluated treatment costs associated with the use of fiber precursor and textile fiber waste adsorbents but did not consider all processing aspects of the treatment technologies. According to an initial cost analysis conducted by Klasson et al. (Klasson et al., 2009), the production expenses of the activated carbons obtained from FS and cotton gin wastes varied between \$1.50 to \$8.90 per kg, depending on the precursor material utilized and the activation technique adopted. Nonetheless, it was observed that the cost

of steam activation was considerably lower than that of phosphoric acid activation. Furthermore, Ma and co-workers noted that by broad consideration, the cost of chemicals and operating equipment are the most prominent cost determinants for utilizing fiber precursor and textile fiber waste adsorbents. Extracting pricing information from the official website of Alibaba, these researchers conducted a cost analysis in their work involving adsorption of heavy metal ions by waste cotton fabrics-based double network hydrogels (Ma et al., 2018). The materials/chemicals used, and their corresponding costs (in bracket) are waste cotton fabrics ($(0.8 \times 10^3/t)$, acrylamide ($(2.1 \times 10^3/t)$, NaOH $($0.3 \times 10^3/t)$, urea $($0.4 \times 10^3/t)$, potassium persulfate $($1.2 \times 10^3/t)$, *N*, *N*-methylenebisacrylamide ($(1.8 \times 10^4/t)$, epichlorohydrin ($(1.3 \times 10^4/t)$) 10^{3} /t), and HCl (\$3.5 × 10^{3} /t). The power of the peristaltic pump used for running the flow-through column experiment was 22 W. The cost of electricity was calculated as \$0.2/kW-h. However, labor and machine maintenance costs were not considered in the cost analysis. Based on the synthesis ratio, the cost of producing dried cellulose/PAM-3 adsorbent was estimated at 8.7×10^3 /t. The input and operating costs for the single column and tandem of two columns for treating 345 BV of simulated wastewater were approx. \$0.182 and \$0.171, respectively. When the treatment volume was increased to 600 BV, the input and operating costs for the single column and tandem of two columns were estimated at \$0.307 and \$0.262, respectively. The cost analysis showed that the cost savings achieved by using columns in series increased with the increase in effluent processing capacity. It was remarked that for such a small column, the cost savings are reasonably significant. Based on the above, fiber precursor and textile fiber waste adsorbents could potentially help to solve some of the demerits of commercial adsorbents, while still maintaining effective adsorption characteristics at relatively lower costs.

7. Recommendations and outlook

It is evident from the review that fiber precursors and textile fiber wastes are a good alternative as adsorbents for water decontamination; however, certain deficiencies ought to be addressed. The literature regarding plant- and regenerated cellulose-based fiber wastes in water treatment is limited to few, such as cotton, flax, hemp, coir, sisal, kenaf, etc., hence, more work need to be done to cover others, such as abaca, silk, and henequen. For better efficiency, improved methods using less toxic chemicals must be adopted, and leaching tests of prepared adsorbents must be performed. Furthermore, post-adsorption valorization of the adsorbents must be exploited. These may include, but not limited to feed additive, catalysis, sensing, antioxidant, and fertilizer applications of the spent adsorbents (Fig. 14). In fact, suggestions have been made regarding the post-adsorption application of adsorbents in the areas of catalysis (Harikishore Kumar Reddy et al., 2017; Ma et al., 2014), antioxidants (Ge et al., 2014), medical and sensing fields (Dodson et al., 2015). These suggestions must be adopted and applied to fiber precursors and textile fiber waste-based adsorbents for complete realization of the course being championed. Noticeably, dyes and heavy metals are observed to be the most studied pollutants. It is therefore recommended that more studies on the other contaminants, including emerging micropollutants, e.g., pharmaceutical and personal care products be explored as well.

For most studies, it appeared that saturation of the regeneration cycles (adsorption-desorption) were not fully attained. This is because the studies were often limited to fewer cycles of regeneration, usually 3–5 cycles (Table 3). Therefore, more cycles are required to ascertain when the adsorbents become fully exhausted, especially those that record higher efficiencies of regeneration. Finally, evaluation of the prepared adsorbents in real industrial effluents may be useful in assessing their practical applications. Presently, only few studies were extended to cover actual wastewater effluents, which is inadequate. With the above considerations, the idea of recycling or repurposing fiber precursors and textile fiber wastes into adsorbents for water purification can be well



Fig. 14. Potential post-adsorption application exploits for spent textile fiber waste-based adsorbents.

achieved. This will not only reduce their indiscriminate presence in the open environment but also add to the vast range of low-cost adsorbents available for water decontamination.

8. Conclusion

The indiscriminate disposal of fiber precursors and textile fiber wastes into the environment can lead to severe pollution. Landfilling and incineration are the conventional disposal methods; however, these methods have many technical, economic, and environmental limitations that discourage their continuous deployment. Hence, recycling through conversion into adsorbents for water decontamination is a good way forward. This strategy has been useful in developing several adsorbents for removing various water contaminants; the common ones being metals ions, dyes, and other organic products. Chemical modification reactions, such as grafting, carbon activation, sulfonation, amination, carboxymethylation, amidoximation, xanthation, and surface coating with functional materials or chemicals are often applied. The modified fibers generally show enhanced adsorption capacities inspired by Van der Waals attraction, electrostatic interaction, complexation, chelation, ion exchange, and precipitation. The adsorption mechanisms are also influenced by factors such as the surface properties, characteristics of the pollutants, porosity or pore size distribution, specific surface area, hydrophobicity or hydrophobicity, composition of water/wastewater, and molecular interactions.

Cost evaluation has been analyzed in relation to the use of low-cost adsorbents; however, there is limited data showing detailed cost reports. Hence, researchers are encouraged to focus on cost analysis of the produced adsorbents and operational/treatment costs in the coming future. The environmental issues identified in this review are the types of chemicals used in the modification reactions, likely leaching problems associated with the prepared adsorbents, post-adsorption handling, treatment and disposal of the adsorbents, and the overall impacts on human health and aquatic lives. For example, the post-recovery of spent adsorbents may require some modification and the chemicals needed for the modification could be toxic and expensive. Moreover, some of the post-recovery processes could be time- and labor-intensive. Although many target contaminants have been studied, most of the studies were focused on metal ions and dyes to the neglect of other micro and emerging contaminants. Adsorption and desorption studies were captured in some reports; however, the cycles were unexhausted. Therefore, further research should be done on the regeneration efficiency of each adsorbent to increase the number of adsorption cycles for their usability on larger scales, so as to decrease the operational costs incurred to adsorbent regeneration. Furthermore, government entities should invest more on the development of these novel technologies since they can leverage on locally accessible materials to exploit valuable waste resources and promote the recyclability and circularity of solid waste for toxic pollutants treatment.

CRediT authorship contribution statement

John Kwame Bediako: Writing – original draft, Software, Methodology, Funding acquisition, Conceptualization. Vitus Apalangya: Writing – review & editing, Data curation. Isaac O.A. Hodgson: Writing – review & editing. Ikenna Anugwom: Writing – review & editing. Eveliina Repo: Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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