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Textile Waste as a Resource: Investigating Dyed and Undyed Cotton for Heavy Metal Adsorption from Contaminated Water

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ABSTRACT
The escalating demand for textile fibers has led to an equally rapid rise in textile waste (Dyed and undyed cotton), creating significant environmental and health challenges. Novel approaches are being investigated to lessen these negative consequences and encourage sustainability, such as turning textile waste into adsorbents for water filtration. Reduction of water pollution and effective handling of waste management are the pivotal concerns for environmental sustainability in our country. Heavy metal removal from the contaminated water is one of the key factors to be followed in water purification. The prospect of textile waste-cotton in particular-as an efficient adsorbent for removing heavy metals from contaminated water sources is explored in this article. The principal aims of this study are to appraise the capabilities of adsorbents obtained from textile waste, scrutinize the efficacy of diverse chemical changes, and appraise the regenerability and reusability of such materials. This review article investigates the synthesis and application of chemically modified cotton fibers in water treatment processes. The effects of significant chemical modification processes on adsorption efficiency such as carboxymethylation, sulfonation, and carbon activation are discussed. Moreover, this study focuses on the adsorption methods that increase cottons ability to bind heavy metals, such as ionic liquid CBA exchange and chitosan cotton base adsorbents (CBA). The findings reveal that textile waste that has undergone chemical modification demonstrates noteworthy adsorption abilities for different heavy metals like lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As). Certain alterations result show the improvements of up to 90% removal efficiency. More research is needed to address issues including long-term stability across several regeneration cycles, environmental concerns from chemically modified adsorbents, and economical scalability to commercial uses. Future research could focus on sustainable strategies like enzymatic regeneration and green chemical changes.

Keywords: Textile fiber, Chemical modification, Heavy metal, Adsorption, Biosorption mechanism

1. Introduction

The manufacturing of textile fibers is growing exponentially, and this is releasing textile waste-based effluents into the environment at a rate that is negatively affecting both human health and the overall health of the planet [1] . The majority of this trash, which is mostly made up of natural fibers like cotton, polyester, and other blends, is disposed of in landfills, which adds to pollution and the depletion of resources. The world's top cotton-producing nations—India, China, the United States, Brazil, Pakistan, Australia, Turkey, Uzbekistan, Turkmenistan, and Burkina Faso—produced about 23.6 million tonnes of cotton in 2017–2018; the textile and apparel industries used the majority of these natural fibers [2] . The textile business produces a significant amount of cotton waste, such as industrial scraps and post-consumer clothing, which frequently wind up in landfills and worsen the environment. To minimize the quantity and lessen the environmental effects of textile fiber wastes, solutions for recycling and reusing fiber precursors are required. In addition to addressing the problem of textile waste, using this waste for water treatment offers an affordable and sustainable adsorbent material for eliminating heavy metals from wastewater.

Pollution in water is poses such serious health hazards, has emerged as a major environmental concern. The majority of these pollutants include petroleum products, dyes, medicines, pesticides, heavy metals (HMs), and other organic and inorganic substances that dissolve in water [3], [4], [5] .HMs are the most common pollutant present in environmental waters in different parts of the world [6] . The primary means by which they enter the environment are industrial processes related to the metallurgical, nuclear, battery, leather, fertilizer, pesticide, petroleum, and textile industries [7], [8] . Common heavy metals are lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As). HMs are a group of metals and metalloids with an atomic density of more than 4000 kg/m^3, atomic weights between 63.5 and 200.6 and gravity is greater than 5.0 [11]. Heavy metals are not biodegradable and accumulate in living creatures, causing significant dangers to ecosystems. Contaminated drinking water and agricultural runoff can affect aquatic life and reach the food chain. Lead (Pb) exposure, particularly in children, can result in kidney failure, anemia, neurological problems, and developmental delays [9-10]. Cadmium (Cd) is associated with kidney impairment, bone demineralization, respiratory difficulties, and cancer. Mercury (Hg), particularly methylmercury from fish, is neurotoxic and impairs memory and development. Arsenic (As) in drinking water increases the risk of cancer and cardiovascular disease. Thus, effective heavy metal removal from wastewater is required.

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Heavy metals are usually extracted from contaminated water through a number of standard techniques, such as flotation, ion exchange, electrochemical treatment, precipitation, solvent exchange, sedimentation, filtration, coagulation, ozonation, flocculation, evaporation and adsorption, etc. [9], [10], [11] . Depending on the application, adsorption presents specific benefits and drawbacks in comparison to alternative treatment techniques [12] . Chemical precipitation is frequently used to remove heavy metals, although it produces a considerable volume of sludge, complicating disposal. Membrane filtration and ion exchange are effective, although they can be costly due to specialized equipment and regeneration chemicals. Coagulation-flocculation is also prevalent, however it results in secondary waste. Reverse osmosis and nanofiltration use semi-permeable membranes to effectively filter and remove pollutants from water [13] . However, because of membrane fouling, membrane processes need frequent maintenance, are expensive to operate, and consume a lot of energy. Among these techniques, adsorption has drawn a lot of interest due to its ease of use, high efficiency, and ability to use inexpensive materials [14], [15] . Many adsorbents, such as activated carbon, remain costly and energy-intensive to generate. Adsorption is unique because of its adaptability, affordability, and simplicity of use, particularly when low-cost, renewable resources like textile waste cotton are used. As a result, research is always being done to find sustainable and reasonably priced adsorbents for the removal of heavy metals, especially from wastewater.

Textile waste, especially cotton waste, has become a viable substitute for heavy metal removal because of its special qualities and quantity. In this paper, we focus specifically on the use of both dyed and undyed cotton textile waste for the adsorption of heavy metals. Dyed cotton contains additional chemical groups, such as azo, anthraquinone, or reactive dyes, which introduce functional groups like amines (-NH2), hydroxyl (-OH), or sulfonates (-SO3H) [1]. Because of electrostatic interactions, functional compounds such as amines and sulfonates from dyes can improve lead (Pb) adsorption in dyed cotton [2]. Undyed cotton, on the other hand, depends on organic hydroxyl groups to bind metal . Apart from that, cotton also has the advantage of wide availability in many different parts of the world, it is applied extensively in textile industries and has different parts that can be harnessed [17] . Dyes may compete for adsorption sites with metals such as nickel (Ni) or cadmium (Cd), decreasing their efficacy[2]. Optimizing adsorption in testing requires distinguishing between dyed and undyed cotton, and future studies should examine the effects of various dyes on metal adsorption.

Cotton-based adsorbents have potential, but issues including regeneration costs, adsorbent stability across several cycles, and the effects of chemical changes on the environment need to be addressed. In order to reduce environmental concerns, future research could concentrate on enhancing the adsorbents' endurance, scaling up to industrial applications, and employing more environmentally friendly chemical modification techniques.

Textile fiber production and waste recycling details are described in Section 2. Section 3 explains the cotton-base absorbents. Opportunities and challenges of using textile waste absorbents are illustrated on Section 4. Discussions are concluded in Section 5.

2. Textile Fiber Production and Waste Recycling

Any material created by weaving, knitting, braiding, felting, twisting, or bonding that may be used to create other things is referred to as a textile fiber. The waste produced by the textile industry is enormous. The growing amount of textile fiber materials produced and consumed unintentionally results in massive wastes with detrimental effects on the environment [3]. Most textile waste ends up as landfill or is burned, which releases toxic chemicals and greenhouse gases into the atmosphere. According to the Textile Exchange 2021 report, the production of textile fiber has nearly doubled over the past 20 years, from 58 million tonnes in 2000 to 109 million tonnes in 2020. If business as usual continues, this growth is predicted to continue, with an additional 34% to 146 million tonnes in 2030 [4]. China is the world's largest producer of textiles, accounting for around 36 million metric tons (mmt) or over 63% of the world's total production of man-made textile fibers [5]. At the moment, textile products account for a sizeable 7% of all garbage that is dumped in landfills globally [5]. As per the textile waste statistics of 2023, the textile industry worldwide produces an astounding 92 million tons of garbage year. China and the United States are the primary contributors to this waste, accounting for 20 million tons and 17 million tons, respectively [5]. The process of turning used textile remnants into useable goods is known as textile fiber waste recycling. Recycling also has a lot of positive environmental effects, including as lowering carbon emissions, maintaining clean air, using less energy, conserving water, protecting forests, and reducing the need for landfills. The most recent research on repurposing textile fiber waste and fiber precursors to create long-lasting adsorbents for water purification is examined. Table 1 displays a few pertinent findings.

Table 1 Adsorption of heavy metals onto cotton-based adsorbents

Adsorbent	**Modification method**	***Adsorbate***	***Uptake***	**Ref.**
Sulfonatedcotton linter	Sulfonation using sulfur trioxide pyridine complex	Pb(II)	14 mg/g	[1]
Chitosancoated cotton fibers	Coating with chitosan via Schiff-base bond/C–N single bond	Hg(II)	0.32, 0.28 mmol/g	[6]
Cotton stalk activated carbon (CSAC)	carbonizing cotton stalks at high temperatures	Cu(II)	3.1mg/L	[7]
Citric acid treated cotton fibre (CACF)	soaking cotton fibers in a citric acid solution	Cd(II)	0.1 mmol/L	[2]
Fe(III)-coated cotton (CCFe)	Immersing cotton fibers in a solution of ferric chloride ($FeCl_3$)	As(V)	32.8mg/g	[8]

3. Cotton-base Adsorbents

Cotton-based adsorbents (CBAs) have been widely studied and found to be effective for HM decontamination by many researchers [9], [10]. Using scrap cotton from abandoned garments or textile industry leftovers is a cost-effective way to prevent water pollution. Cotton cellulose's hydroxyl (-OH) groups facilitate metal ion binding via ion exchange, complexation, and electrostatic interactions. Its large surface area and porosity promote heavy metal adsorption, making it perfect for wastewater treatment. Chemical changes, such as acid, alkali, or chelating agent treatments, can boost adsorption capacity by adding new functional groups and increasing surface area [11]. For example, Acid-treated cotton, which contains more carboxyl groups, improves lead adsorption by generating stable compounds with lead ions. Using leftover cotton encourages recycling and sustainability while tackling rising textile waste. Cotton is a biodegradable alternative to typical adsorbents such as activated carbon or synthetic resins, decreasing environmental damage from discarded adsorbents. It is also inexpensive and abundant. Cotton is an effective and environmentally safe option for removing heavy metals from wastewater.

3.1. Heavy metal biosorption mechanism into cotton-base absorption

The common mechanisms involved in the biosorption process are ion exchange, chelation, complexation, precipitation, reduction, electrostatic interaction and adsorption [28] . Several crucial stages lead to an understanding of the biosorption mechanism. The hydroxyl (-OH) and carboxyl (-COOH) functional groups found in cotton fibers, which are mostly made of cellulose, are essential to the adsorption process. While carboxyl groups can take part in ion exchange and complexation events, hydroxyl groups can establish hydrogen bonds with metal ions [13] . Cotton's affinity for heavy metals makes it possible for it to extract and hold onto metal ions from aqueous solutions. Ion exchange is one of the main processes of heavy metal biosorption [29] . During this process, cations (such sodium or calcium) attached to the functional groups on the cotton fibers are displaced by metal ions in the solution, such as lead (Pb^{2+}), cadmium (Cd^{2+}), or copper (Cu^{2+}) [29] . Heavy metals are more concentrated in the cotton matrix as a result of this exchange process, which makes it easier to remove them from water. Furthermore, cotton's many functional groups enable the development of stable complexes between the adsorbent and heavy metal ions. The oxygen atoms in hydroxyl and carboxyl groups can create coordination bonds with metal ions, strengthening the metals' adhesion to the cotton fibers [29], [30]. The complexation increases cotton's ability to bind several heavy metals. The entire biosorption system also benefits from physical adsorption, or physisorption. Van der Waals forces and electrostatic interactions between metal ions and the cotton surface are involved in this process [31]. With 90% removal using sulfonated cotton, lead (Pb) had the highest adsorption efficiency. Carbon-activated cotton demonstrated a 78% removal effectiveness for cadmium (Cd) [2] . Sulfonation, which added sulfonic acid groups (-SO3H) to the cotton structure and improved its capacity to bind heavy metals, was the most successful modification technique[1].
Certain pressures, albeit weaker than chemical bonds, have a major influence on early metal ion uptake. The concentration gradient of metal ions on cotton fibers versus in solution drives the biosorption process. Contact time, temperature, and starting metal concentration all have an effect on adsorption rates as ions diffuse toward the cotton surface. Adsorption effectiveness was assessed in a range of settings, such as metal ion concentrations between 50 and 200 mg/L and pH values between 3 and 7. With an 85% removal efficiency at 100 mg/L, the ideal pH for lead (Pb) elimination was determined to be 5. The greatest removal of cadmium (Cd) was 78% efficient at pH 6. These results emphasize how crucial it is to regulate pH and metal ion concentration in order to maximize the adsorption process.

3.2 Technology adopted for modification of textile fiber waste into adsorbents

Any surface modification of cotton-based material carried out in an attempt to boost HM uptake could simultaneously raise processing costs, complicate the process, and possibly release secondary contaminants into the environment, even though it would make CBAs even more effective as decontaminants [12]. There is little quantitative information on dyed cotton, despite the fact that undyed cotton's adsorption capability after several chemical changes has been thoroughly investigated. Additional functional groups like hydroxyl groups, amines, and sulfonates are added by dyes and can either compete with or improve metal ion binding sites. To quantitatively assess the adsorption efficiency of colored and undyed cotton after chemical changes, more research is therefore required.When compared to other contaminants, the affinity between a certain metal and the adsorbent must be strong for the metal to be absorbed. Thus, more investigation into the adsorption of multicomponent HM systems onto unaltered CBAs is necessary [13].

3.2.1 Carboxymethylation

Adsorbents typically get carboxyl groups added to them through the carboxymethylation process. This reaction is frequently used to chemically modify fiber precursors and textile fiber trash, primarily utilizing sodium chloroacetate and NaOH in Lyocell [14], [15], [16]. The most popular method for producing fiber precursor and waste textile fiber-based adsorbents with high substitution rates is likely carboxymethylation with sodium chloroacetate; however, the materials' hydrophobicity is converted to hydrophilicity during the reaction [5]. Waste adsorbents made on crosslinked carboxymethylated fiber have demonstrated some of the best adsorption results [14], [15] . Carboxymethylation-modified undyed cotton fibers have been found to have greater adsorption capabilities based on the Langmuir isotherm model, including 294.12 mg/g for Pb(II) and 137.59 mg/g for Cd(II). Because dye molecules may compete with or obstruct adsorption sites, dyed cotton, especially that treated with reactive dyes, may interfere with the carboxyl group binding process. This lowers the overall uptake of metal ions, particularly for lead and cadmium [5].

3.2.2 Sulfonation

Sulfonic acid groups (-SO_3H) are added to the fiber structure during sulfonation, increasing the hydrophilicity of the fibers and their availability as binding sites for metal ions. Since electrostatic interactions between sulfonate groups and Pb(II) might increase adsorption capacity, sulfonated dye molecules that are already present in dyed cotton may aid in lead adsorption. For Pb(II), sulfonation of undyed cotton has shown strong adsorption capabilities of 14 mg/g. Due to the presence of sulfonate groups, dyed cotton may have somewhat greater efficiency, although more research is necessary [1], [17]. By systematic approach of sulfuric acid treatment followed by sulfur trioxide pyridine complex in N,N-dimethylformamide solvent author found that compared to the original material, >85 % of Pb(II) was removed at <20 mg/L, and equilibrium was attained within 8 min [1]. The above approach was similarly used to produce sulfonated cellulose adsorbent for adsorption of Fe(III), Cu(II) and Pb(II) [17].

3.2.3 Carbon activation

Textile fibers are turned into activated carbon via carbon activation. There are three methods for activating carbon: chemical, steam, and thermal activations. The process of thermal activation, also referred to as calcination, is carried out in furnaces at high temperatures; chemical activation, on the other hand, is typically carried out at high temperatures and pressures with the presence of air at low temperature/steam and CO_2/blue gas at high temperature. Chemical activation is typically performed before or after thermal treatment in an effort to add active binding sites and increase the porosity and surface area of the carbonized material [18]. The high surface area and porosity of textile-derived activated carbon greatly increase its adsorption capability for heavy metals and other pollutants. Remaining dyes may break down as a result of carbon activation of dyed cotton, which could alter the pore structure and lower the adsorption capacity. The adsorption capacities of activated undyed cotton for Pb(II) and Cd(II) are 118.6 mg/g and 92.3 mg/g, respectively. During carbon activation, dyes in dyed cotton can decompose, altering pore structure and surface area, leading to decreased adsorption capacity compared to undyed cotton [19].

3.2.4 Ionic liquid modification

Textile fibers can be altered by ionic liquids, which are room-temperature salts in a liquid state. It has recently been discovered that ionic liquid (IL) modifications of adsorbents are very effective at removing heavy metals (HMs) and other contaminants from water [20], [21]. By adding particular functional groups that increase the fibers' affinity for metal ions, ionic liquids can be used to change the surface characteristics of the materials. According to reports in ambient temperature, ILs are "green" solvents that dissolve cellulose effectively, are compatible with a variety of liquids, and have low vapor pressure [22]. This alteration can increase the adsorbent's stability in a variety of environmental settings and improve its adsorption selectivity for specific heavy metals. Ni(II) and Cu(II) ion adsorption was achieved well by using cellulose cotton functionalized with IL [9]. By employing a ring-opening polymerization method, 1-N-butyl-3-methylimidazolium chloride (IL) was used to create copolymers of polycaprolactone-grafted cellulose cotton (CPL) with different grafting compositions. In contrast to undyed cotton, which permits more consistent surface modification, dyed cotton may undergo competing reactions with ionic liquids, depending on the type of dye, marginally decreasing their effectiveness [9].

3.2.5. Chitosan CBA

Applying chitosan, an abundant natural biopolymer derived from the deacetylation of crustacean shells, to HM adsorption results in a very effective linear polysaccharide. Because chitosan-based adsorbents (CBAs) contain functional groups including hydroxyl (-OH) and amino (-NH_3) groups, which have a strong affinity for interacting with metal ions, they are being utilized more and more to remove heavy metals from water [23]. It is a popular material for many applications, especially in water treatment, due to its outstanding biocompatibility, biodegradability, and non-toxic qualities. Its easy dissolution in acidic solutions is a drawback, though. In order to increase its stability in acid solution and create an effective adsorbent by adding its functionality to the adsorbent substrate, it is often grafted onto an insoluble substrate [24]. Such grafting of chitosan into cotton has been exploited for adsorption of Hg(II) ions. Two types of chitosan-coated cotton adsorbents were created: Schiff-based bonded (SCCH) and C-N single bonded (RCCH). The scientists noted that Hg(II) was preferentially removed by both RCCH and SCCH with significant absorption capability, despite the presence of nine coexisting HMs in solution [25]. 60% removal from a solution containing 200 mg/L of HMs was achieved, demonstrating the adsorbent's effectiveness [13].

4. Opportunities, Challenges, and Future Directions for Textile Fiber Waste-Derived Adsorbents

Among the many qualities anticipated of perfect adsorbents are handling and simplicity in separating from the aqueous phase following adsorption [16]. In contrast to other adsorbent types, the majority of adsorbents made from waste textile fiber and fiber precursors are simple to handle and segregate after usage. These fibers are easily separated from the aqueous phase and may be efficiently regenerated during adsorption-desorption cycles because of their comparatively longer lengths and thinner diameters

Some important elements that are currently ignored in research on adsorbents obtained from textile waste should be addressed in future studies. The absence of assessment of adsorbent stability across several adsorption and regeneration cycles is one significant gap. Researchers ought to pay attention to any possible environmental problems that adsorbents may cause in addition to how well they work. The possible leaching of chemicals like sulfonates into water bodies, which could provide secondary environmental problems, is one issue with employing chemically modified adsorbents, like sulfonated cotton. Because they are less harmful to the environment and have a lower leaching risk, green solvents like ionic liquids (ILs) should be investigated for chemical alteration in order to lessen this.

Additionally, it is crucial to evaluate a greater number of regeneration cycles because many studies only analyze three to five cycles, which leaves room for uncertainty regarding the adsorbents' full exhaustion point. More cycles of thorough testing would yield more accurate information about their long-term reusability. Specific areas for further exploration include: The removal of multiple heavy metal ions in competitive conditions using cotton adsorbents; improving uptake efficiency by using chemical, chitosan, ionic liquid, and nanoparticle treatments; assessing the stability of impregnated nanoparticles; analyzing isotherms, kinetics, thermodynamics, and reusability of the adsorbents to better understand the mechanisms; scaling up the use of these adsorbents for industrial applications; and optimizing the adsorption process using various cutting-edge techniques. Furthermore, in-depth research is required to determine how different dyes in dyed cotton affect competitive binding and adsorption capability in multicomponent heavy metal systems. To fully achieve the potential of textile waste-based adsorbents in wastewater treatment, it will also be essential to extend research to industrial-scale applications and test for a broader variety of contaminants, beyond heavy metals.

5. Conclusion

There are serious environmental problems associated with the incorrect disposal of textile waste and fiber precursors, which results in pollution and resource waste. The substantial potential of using textile waste-especially cotton waste-as a practical and long-term way to remove heavy metals from water has been brought to light by this review. In addition to addressing the environmental problems related to waste disposal, recycling textile waste into adsorbents provides an affordable substitute for traditional water treatment techniques. The adsorption capabilities of textile-derived adsorbents have been improved by a variety of chemical modifications, including carbon activation, sulfonation, and carboxymethylation. These modifications have shown the adsorbents' ability to bind and remove heavy metal ions from contaminated water. Notwithstanding the potential of adsorbents obtained from textile waste, a thorough cost study is still lacking, highlighting the necessity for additional research to assess the costs of both production and operation. Prioritizing environmental issues with chemicals used for modifications and handling wasted adsorbents is also necessary. In order to guarantee the safety and sustainability of adsorbents obtained from textile waste in practical applications, it will be imperative to address these concerns. In order to increase the usefulness of these materials in a variety of water treatment settings, researchers should look into a wider spectrum of pollutants than just metal ions and dyes as the focus on contaminant removal grows.

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