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REVIEW PAPER

# Utilisation of natural cellulose fibres in wastewater treatment

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**Abstract** Water safety and security are global problems. Indeed, researchers have taken this matter seriously and have begun to find alternative ways of treating wastewater. The conventional method for treating wastewater has been found to be uneconomical, and the polymeric materials used were not environmentally friendly. Biosorption techniques and mechanisms have been shown to be an effective alternative to replace conventional technologies. As agricultural waste is abundantly available, it has been chosen as the best starting material to produce biosorption material. Also, the hydroxyl functional groups in cellulose act as important parts to produce better absorbent materials. This review has explored the role of natural fibres as adsorbents for wastewater treatment while at the same time, for the removal of adsorbates such as oil, dyes, heavy metals, ionic compounds, and others as reported in the literature. Also investigated in this study, were the different modification types used to enhance the fibres and the mechanism of contaminant removal by the absorbents. Lastly, the physical forms of adsorbates and common types of effluents treated using natural fibres were examined and discussed.

**Keywords** Adsorbents · Natural fibres · Cellulose · Wastewater · Effluent · Water treatment · Biosorption

## Introduction

Water is one of the primary necessities to sustain life. As reported by the United Nations, in 2017, the estimated world population of 7.6 billion is placing increasing pressure on the world's limited water resources. However, while more water is being consumed, the quality of water is declining due to the significant amounts of pollutants being discarded into the world's river systems, lakes and oceans each day. Accordingly, there are both point- and non-point sources of pollutants that contain different types of effluent. Therefore, different approaches must be employed for wastewater treatment.

Point source pollution originates from a single, specific site such as municipal or industrial waste. Since it originates from a specific location, it is easily monitored, identified and regulated. Municipal wastewater frequently contains pathogens and oxygen-depleting nutrients, both of which may cause serious health complications. Industrial point sources contribute heavy metals, toxic contaminants, and oils while non-point source pollution may result from

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urban and agricultural run-off and run-off from construction and mining sites. Therefore, since pollutants originate from many different sources, they are often difficult to identify. Contaminants can include sediment, organic matter, nutrients, and other toxic matter.

Wastewater treatment technology was initially designed to treat and clean up wastewater depending on the types and the extent of contamination while at the same time providing low-cost consumption. Over the years, innovation surrounding water treatment systems has intensified, beginning with conventional media filters to high-efficiency centrifuge filters, disk filters, membrane filtration (including micro and ultra-filtration) and non-membrane filtration systems (Karen 2014). However, the traditional materials employed, and conventional wastewater treatments have been unable to meet the environmental standards and hence, have been ineffective in addressing the removal of heavy metals at low concentrations in some instances (Demirbas 2008). This also includes the broad spectrum of toxic chemicals found in wastewater. Moreover, most of the materials used to produce the absorbents were produced from polymeric materials (Ji et al. 2012; Wang et al. 2011) and industrial by-products (Tripathi and Ranjan 2015) which are quite expensive.

Many studies, as a result, are now focusing on cost-effective approaches utilising natural fibres as the main material to produce absorbents. Notably, plant-based materials such as agricultural waste have been considered as promising materials to remove most contaminants from wastewater as they are inexpensive, readily available in large quantities, stable, eco-friendly, and non-toxic (Das 2010; Won et al. 2014). The benefits of using natural fibres include; high porosity, superior adsorption ability (Gaballah et al. 1997; Nakajima and Sakaguchi 1990; Tripathi and Ranjan 2015), low specific gravity (Dharmarathne et al. 2013) and regenerability (Sud et al. 2008).

This review focuses on the use and advantages of natural fibres as starting materials in wastewater treatment. Most natural fibres originate from agriculturally-based materials such as cotton, kenaf fibre, wheat straw, banana trunks and oil palm empty fruit bunches (Wang et al. 2012a). Accordingly, this paper is structured into four main sections; an overview of natural fibres, fibre treatments, physical forms of absorbent materials and the types of effluents treated using natural fibres.

## Overview of natural fibres

The interest in using natural fibres as raw materials has been growing rapidly due to the increasing awareness towards sustainability of the environment (Chandramohan and Marimuthu 2011). Recently, over the last few years, bio-based materials have secured high demand in the market and industries (Faruk et al. 2012). The common natural fibres produced worldwide are listed in Table 1.

Natural fibres are defined as materials derived from plants and animals source (Ticoalu et al. 2010). Further, they are hydrophilic because lignocellulose contains strongly polarised hydroxyl groups. Therefore, these fibres are inherently incompatible with the hydrophobic polymer matrices. Before starting any treatments or modifications, it is important to understand the chemistry of natural fibres. Natural fibre is composed of cellulose, hemicelluloses, lignin, extractives, and inorganics.

Many studies have concentrated more on cellulose as it possesses unique properties such as its hydrophilic capabilities, processability, is insoluble in many solvents due to the hydrogen bonds and crystallinity, and is non-toxic (Suhas et al. 2016). Notwithstanding, cellulose is commonly made up of glucose units

**Table 1** World production of natural fibres (reproduced with permission from Faruk et al. 2012)

| Natural fibres | World production ($10^3$ t) |
|---|---|
| Palm oil | 186,400 |
| Bamboo | 30,000 |
| Sugarcane bagasse | 75,000 |
| Jute | 2300 |
| Kenaf | 970 |
| Flax | 830 |
| Grass | 700 |
| Sisal | 375 |
| Hemp | 214 |
| Coir | 100 |
| Ramie | 100 |
| Abaca | 70 |

(French 2017) that bind together by many glycosidic linkages (see Fig. 1). Linking just two of these sugar units produces a disaccharide called cellobiose (Kalia et al. 2011).

The hydroxyl groups (−OH) in these glucose units are important in fibre modifications since they are the most reactive. Therefore, detecting the reactive hydroxyl groups is very important for optimising the modification process of natural fibres (He et al. 2012). Table 2 displays the chemical compositions of some common natural fibres.

## Fibre treatments

To enhance and manipulate natural fibres as adsorbents, some modifications are required, usually by physical and chemical means.

### Physical treatments

Physical adsorption is one of the most convenient methods of attaching compounds to fibre surfaces. The fundamental objectives of physical treatment are to remove surface contamination or impurities on the fibre and simultaneously, to provide better contact between the fibre surface (Mukhopadhyay and Fangueiro 2009). Physical approaches have been claimed as clean, fast and environmentally friendly (Cho et al. 2013). The process may involve size reduction by cutting or grinding, or via heat treatment. Usually, by physical treatment, the surface of the fibre will be roughened to enhance the contact area and provide mechanical interlocking between the fibre surface (Mukhopadhyay and Fangueiro 2009). Due to this reason, the surface area and porosity of the fibres would be increased while at the same time removing any impurities. Thus, the surface functional groups not accessible previously to the adsorbate could be exposed (Loganathan et al. 2013a). However, these types of treatments do not alter the chemical composition of the fibres (Adekunle 2015; Adekunle et al. 2010) and are not widely used due to their low effectiveness (Nguyen et al. 2013).

#### Physical adsorption

Physical adsorption typically occurs with the presence of weak van der Waals forces of attraction and occurs at low temperature with the formation of a multilayer of adsorbate on the adsorbent which decreases with increasing temperature. One of the most common techniques via electrostatic adsorption is applied to fibre that has undergone carbonisation under certain conditions. In this case, during carbonisation, the fibre is exposed to the selected gas at a certain temperature, which causes the fibre to loosen its crystal packaging and may lead to the formation of pores (Rombaldo et al. 2014). However, since fibre is negatively charged due to the carboxylic group on the fibre surface, it is possible for the cationic ion to be adsorbed onto the surface. Also, the adsorption is not selective, and the mechanism involves outer sphere surface complexation (Loganathan et al. 2013b) which means that it involves ion migration and does not involve electron

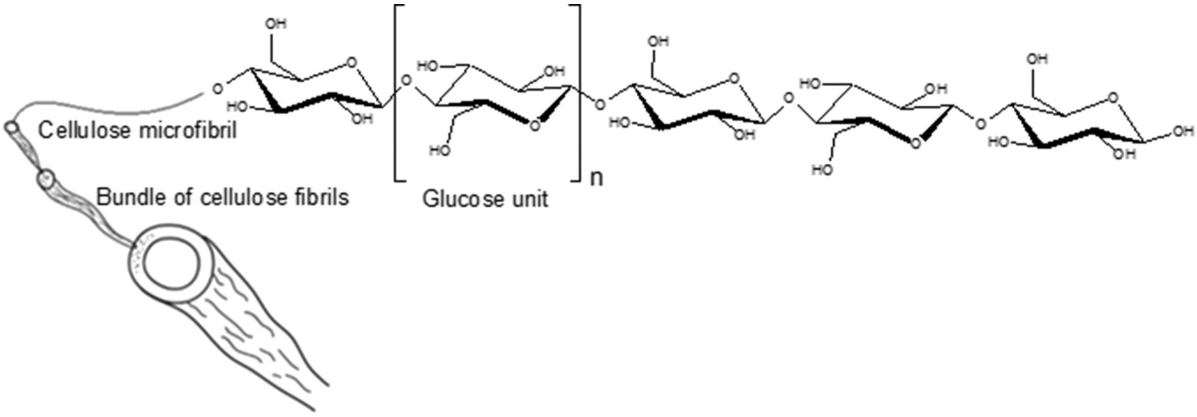



**Fig. 1** The chemical structure of the fibre

**Table 2** The chemical composition and structural parameters for some common natural fibres

| Types of fibres | Cellulose (wt%) | Lignin (wt%) | Hemicellulose (wt%) | References |
|---|---|---|---|---|
| Jute | 61–71.5 | 12–13 | 13.6–20.4 | Bledzki et al. (1996), David (1992), Kucharyov (1993) |
| Flax | 71 | 2.2 | 18.6–20.6 | Bledzki et al. (1996), David (1992), Kucharyov (1993) |
| Hemp | 70.2–74.4 | 3.7–5.7 | 17.9–22.4 | Bledzki et al. (1996), David (1992) |
| Ramie | 68.6–76.2 | 0.6–0.7 | 13.1–16.7 | Bledzki et al. (1996), David (1992), Kucharyov (1993) |
| Kenaf | 31–39 | 15–19 | 21.5 | David (1992), Rowell et al. (1992) |
| Sisal | 67–78 | 8.0–11.0 | 10.0–14.2 | Bledzki et al. (1996), David (1992), Ugbolue (1990) |
| Pineapple leaf | 70–82 | 5–12 | – | Asim et al. (2015) |
| Cotton | 82.7 | – | 5.7 | Bledzki and Gassan (1997) |
| Coir | 36–43 | 41–45 | 0.15–0.25 | Ugbolue (1990) |
| Banana stem | 39.12–59.3 | 8.88–17.5 | 10.2–12.5 | Jayaprabha et al. (2011) |
| Oil palm trunk | 41.02 | 24.51 | 32.04 | Abdul Khalil et al. (2008) |
| Oil palm frond | 56.03 | 20.48 | 27.51 | Abdul Khalil et al. (2008) |
| Empty fruit bunch (EFB) | 50.49 | 17.84 | 29.6 | Abdul Khalil et al. (2008) |

transfer in a redox reaction (Ru et al. 2011; Song et al. 2016; Welgemoed 2005). Thus, the adsorption is not effective.

Due to this reason, the researcher invented activated carbon which is more effective in capturing effluent especially dye and heavy metals. In this case, the carbon was converted into activated carbon by a heating process without the presence of air. As a result, fine pores were created in the carbon particles (O'Connell et al. 2008) with the extended surface area, high adsorption capacity, more micro-pore structures and a higher degree of surface reactivity (Bharathi and Ramesh 2013).

The mechanism of adsorption occurs in several stages (see Fig. 2) and involves the transportation of adsorbates to the external surface of the absorbent. The adsorbates will then be transported within the pores of the adsorbent, and finally, some of the adsorbates will be adsorbed on the interior surface of the adsorption either by monolayer or multilayer adsorption (Bharathi and Ramesh 2013; Sivakumar and Palanisamy 2010).

A number of natural fibres such as oil palm fibre (Hameed and El-Khaiary 2008), coir pith (Namasivayam and Sureshkumar 2008; Parab et al. 2009), sugarcane fibre (Parab et al. 2009), rice husk (Malik 2003), and banana peel (Annadurai et al. 2002) have been used to study the removal of different dyes from aqueous solutions at different conditions (Bharathi and Ramesh 2013). Inyang et al. (2012), found the removal efficiency of heavy metal using biochar made from sugar beet root. The results indicated that the sorption capacity of activated carbon made from natural fibres is comparable to those that are commercially available.

## Modifications using ionic liquids

Ionic liquids are known as environmentally friendly solvents. Their unique properties such as low toxicity, non-volatile, high ionic conductivity and non-flammable have received intense scrutiny as green media in various chemistry processes (Mallakpour and Rafiee 2011). A study by Wendler et al. (2009) found that direct dissolution of cellulose and dry, wet shaping in ionic liquid provided regenerated fibres with high tenacity with the versatile application.

According to Takada and Kadokawa (2015), during the dissolution of cellulose in the ionic liquid, the crystalline structure of cellulose was loosened, and the

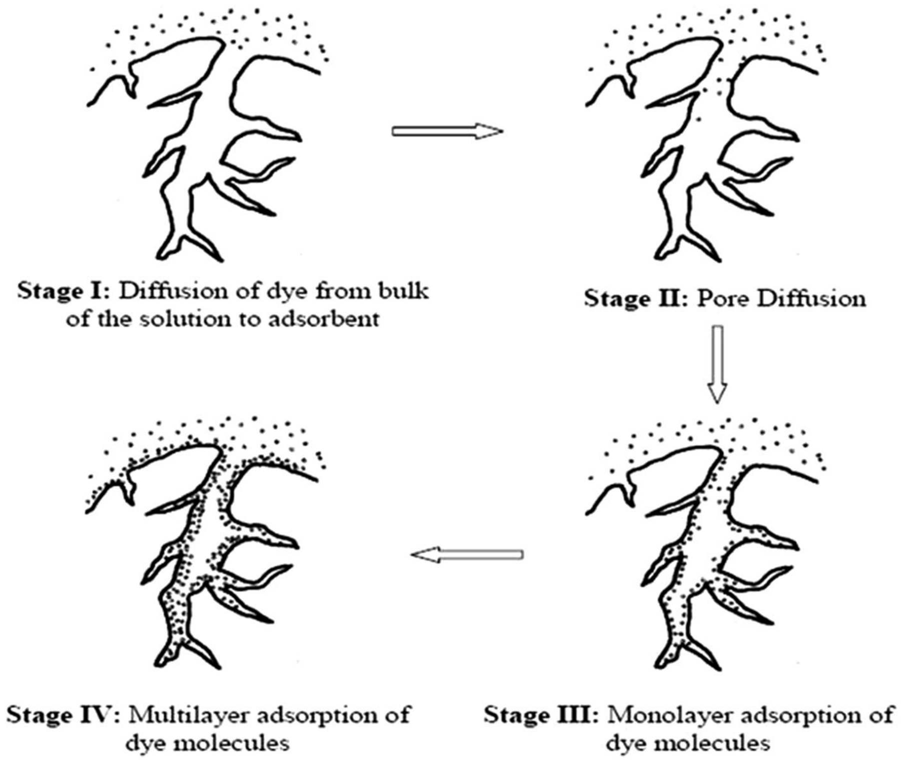



**Fig. 2** Mechanism of dye absorption (reproduced with permission from Sivakumar and Palanisamy 2010)

excess water surrounding the cellulose was absorbed into the ionic solution. The cellulose crystalline parts then started to aggregate and possibly acted as a crosslinking point for the formation of ion gel (Fig. 3).

In a separate study by Sun et al. (2009) they used ionic liquid to form cellulose and chitin composite biosorbents for heavy metal adsorption. However, there are some drawbacks using ionic liquid modification. For instance, the high cost of ionic liquid prompted the researchers to reconsider using it as a media for cellulose dissolution. Moreover, the recovery and recycling process of the ionic liquid was entirely new to the researchers, and some of the ionic liquid may have been lost during the recycling process.

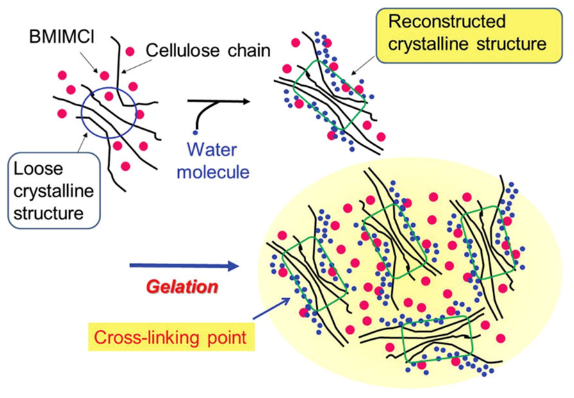



**Fig. 3** The mechanism of the formation of cellulose ionic gel (reproduced with permission from Takada and Kadokawa 2015)

## Plasma treatment

Plasma treatment has also been considered as an option for water treatment which involves electrical gas discharges and free radicals (Mukhopadhyay and Fangueiro 2009; Wang et al. 2012b). There are two types of plasma treatments available; vacuum plasma treatment and atmospheric treatment. The differences are explained further by Mukhopadhyay and Fangueiro (2009)in their review that follows.

Theoretically, this treatment was believed to bring physical modification on the surface of the fibre. Further, it may help to promote surface cleaning (Cho et al. 2004; Han et al. 2014; Mukhopadhyay and Fangueiro 2009), an etching effect, grafting and a functionalisation effect (Yang et al. 2015; Fig. 4). Basically, for surface cleaning and etching, it may

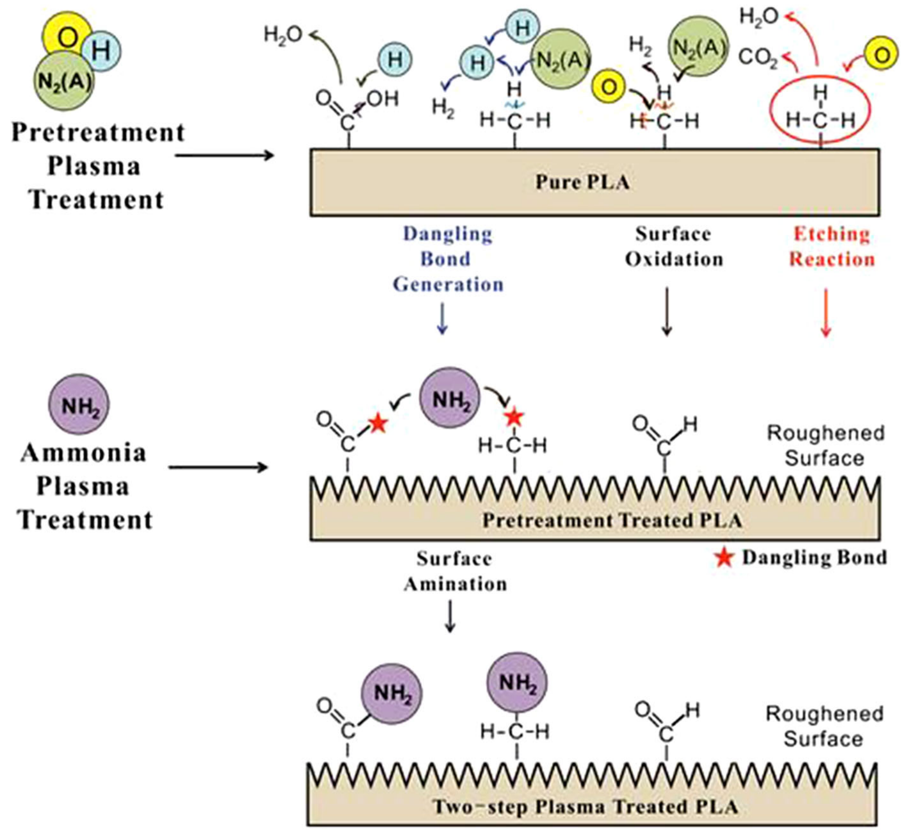



**Fig. 4** Steps of atmospheric pressure plasma treatment (reproduced with permission from Yang et al. 2015)

result in promoting physical adhesion on the fibre surface whereas for grafting or crosslinking, it may help to strengthen the surface. On the other hand, for a functionalisation effect, it helps to modify the surface chemical structures and at the same time introduces free radicals (Mukhopadhyay and Fangueiro 2009).

In wastewater treatment, this treatment was applied for the degradation of dyes (Jin et al. 2012; Kozáková et al. 2010; Yan et al. 2012), benzene derivatives (Kareem and Kaliani 2012), phenolic compound (Liu et al. 2010; Liimatainen et al. 2012), algae (Liu et al. 2015) and other ionic material (Ran et al. 2014).

In another study by Kim et al. (2017) they used a green and simple approach to synthesise hierarchical nanoporous $MnO_2$ by applying plasma in a liquid precursor using three types of sugar as an inducer. Based on the findings, they found that more than 99% for an initial dye concentration of 10 mg $L^{-1}$ was removed within 2 min. Therefore, this demonstrates that the technique could be effective in treating wastewater.

Accordingly, plasma treatments have their own advantages such as being reliable, reproducible and can be monitored accurately using a plasma diagnostic device (Mukhopadhyay and Fangueiro 2009). Moreover, plasma treatments may help in altering the variety of surface characteristics as needed depending on their application. However, the disadvantages of these treatments are that only one side of the material, directly facing the plasma jet, can be altered (Mukhopadhyay and Fangueiro 2009; Qiu et al. 2002).

## Chemical treatments

Chemical modifications improve the adsorption capacity and stability of biosorbents (Demirbas 2008). As reported previously by Hokkanen et al. (2016), cellulose cannot be effectively used as absorbent first, without undergoing modification. The modification can be carried out by functionalising the cellulose functional groups according to the preferences either by esterification, oxidation, alkaline treatment, silylation, grafting or by other processes.

## Esterification

Cellulose modification, especially esterification, has attracted widespread attention among researchers especially in homogeneous conditions (El Hamdaoui et al. 2016). During esterification, the ester functional groups (O–C=O group) are attached to hydroxyl groups of cellulose via precursor condensation (Missoum et al. 2013). Notably, cellulose modification by esterification can affect the fibres depending on the reagents used. The chemical route to form ester bonds with the hydroxyl of cellulose can be performed by either using carboxylic acid, alkydes, alketonedimers or acid chloride as described by Hubbe et al. (2015). Ma et al. (2014), also used betaine hydrochloride as a cationic agent to modify the cellulose to produce cationic adsorbent. In this case, the cationic cellulose absorbent acts to adsorb the anionic dyes due to the electrostatic attraction between the modified cellulose and the dyes. Esterification has also been found to increase the hydrophobicity nature of cellulose surface (Ashori et al. 2014; Bourbonnais and Marchessault 2010; Hubbe et al. 2015; Lackinger et al. 2012; Li et al. 2011; Pan et al. 2013) which may assist towards improving oil absorbency. Asadpour et al. (2016) reported that viscosity of oil has an important role in sorption. In this case, low viscosity oil penetrates the acetylated oil palm empty fruit bunch (OPEFB) fibres faster than the high viscosity oil. Asadpour et al. (2016) also reported that the oil concentration equilibrium fitted the Langmuir, isotherm model. However, in some cases, several disadvantages have been observed as the cellulosic surface may need to be oxidised before the esterification, in order to achieve a satisfactory degree of substitution (Hubbe et al. 2015).

## Oxidation of cellulose

Oxidation of cellulose can be referred to as a condition where the functional groups of cellulose are attacked by the oxidising media. Usually, before oxidation occurs, the natural fibres are generally bleached to expose more hydroxyl functional groups. Notwithstanding, this could help to create further opportunities for functionalisation by the oxidising materials (Collinson and Thielemans 2010). The two main oxidants customarily used are superoxide anion ($O_2^{-}$) and hydrogen peroxide ($H_2O_2$).

During oxidation, the hydroxyl groups of cellulose can be converted to dialdehyde groups using sodium periodate ($NaIO_4$; Kim et al. 2000). Those aldehyde groups, later on, can be further oxidised to carboxyl groups by sodium chlorite ($NaClO_2$) under heterogeneous conditions (Kim et al. 2000; Liimatainen et al. 2012). In contrast, some researchers have preferred to use a catalyst such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and azide modification to carboxylate the cellulose (Okita et al. 2010; Takaichi and Isogai 2013).

Zhu et al. (2015) successfully produced excellent coagulation-flocculation of the kaolin suspension with a turbidity removal of 99.5% using bamboo pulp via $NaIO_4$ oxidation, urea grafting, and NaOH hydrolysis. In this case, the high anhydroglucosepyranose units' oxidative cleavage of dicarboxyl cellulose led to excellent coagulation–flocculation by the mechanism of interaction between ionic polymer and mineral pigments via neutralisation or adsorption/bridging coagulation of metals salts. This was followed by the formation of large floc by a flocculation process. However, this method was claimed to be too complicated, expensive, and restricting the mass production of carboxylated cellulose.

## Alkaline treatment

Alkaline treatment has been considered as one of the low cost and most effective surface treatments (Mohanty et al. 2001) which helps in removing the wax and lignin covering the surface of the fibre. Moreover, it creates greater potential of crystallisation, promotes interfacial bonding, and simultaneously increases the compatibility of the fibres. Therefore, it helps to enhance the mechanical properties of the fibres. According to Li et al. (2015), the mechanical properties of the alkaline treated bamboo fibre composites increased by more than 50% as compared to the untreated bamboo fibres.

Sodium hydroxide (NaOH) has also been used as an activating agent in the production of activated carbon. Coconut shell (Cazetta et al. 2011), olive husk (Michailof et al. 2008), and bamboo (Hameed et al. 2007) are among the fibres that have been used for the activation process.

According to Cazetta et al. (2011), NaOH helped to increase the micropores and diameter of the cavities. The presence of the capillaries with a large diameter increased the adsorption capacities especially for treating water effluent with large diameter molecules such as dyes, heavy metals, and pesticides.

Silylation

Silylation is another popular method in fibre modification involving the substitution of silyl groups to the fibres. Silane coupling agents have been used as they are bifunctional. Furthermore, there are many types of silane coupling agents with different functionalities. The most common types of silanes frequently used for natural fibres are gamma-aminopropyl trimethoxy silane (APS), gamma-diethylenetriaminopropyl trimethoxy silane (TAS), and gamma-Methacryloxypropyl trimethoxy silane (MPS; Abdelmouleh et al. 2002). Abdelmauleh et al. (2002) investigated the interaction between cellulose and silane coupling agent. In their study, they claimed that by heating up to 100 °C the covalent bond between the substrate, silane was formed via condensation reaction. Regarding the application as an adsorbent, Gebald et al. (2011) formed an amine-based absorbent using nano fibre cellulose for $CO_2$ captured from air. Based on the result, following 12 h of exposure in normal air, 506 ppm of $CO_2$ was successfully removed (Gebald et al. 2011). Indeed, a similar concept of the absorbency may also be applied in wastewater treatment.

Grafting

Graft polymerisation has attracted immense interest and attention as it has helped to alter the properties of cellulose and increase its functionality (Kang et al. 2007). Graft polymerisation allows for the combination of two or more polymers in one physical unit (Roy et al. 2009). The graft polymerisation of cellulose can be accomplished using various techniques, namely; ring-opening polymerisation (Hafren and Córdova 2005), free radical polymerisation (Srivastava et al. 2006), reversible addition fragmentation chain transfer (RAFT; Roy et al. 2005), nitroxide mediated polymerisation (NMP; Karaj-Abad et al. 2016), and atom transfer radical polymerisation (ATRP; Çankaya 2015).

In the application of wastewater treatment, Maimaiti et al. (2014) grafted cotton pulp cellulose with buthylmethacrylate via the homogeneous ATRP method. From the saturated adsorption rates using different oils, they found that the grafted cotton cellulose pulp adsorbent adsorbed three to six times better as compared to commercial polypropylene sorbate. Also, it was reported to have higher buoyancy recovery during oil clean-up over water (Maimaiti et al. 2014).

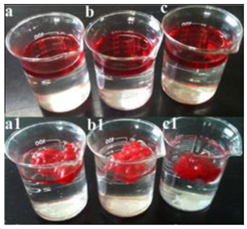
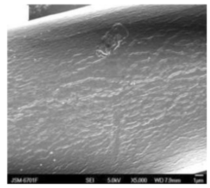
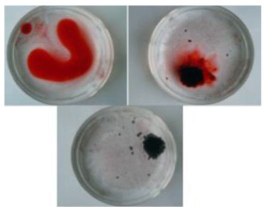
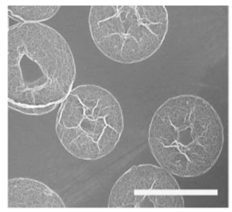
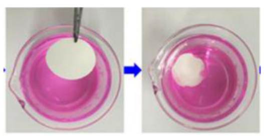
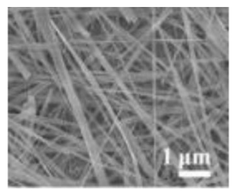
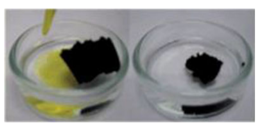
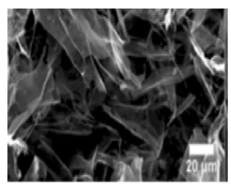
## Types of physical forms of adsorbent materials

In general, the physical form of adsorbent material plays an important role in removing contaminants in wastewater. For adsorbent using natural fibres as starting materials, the types of physical form can be divided into four main categories (Table 3), namely; fibre form, powder or granule form, film or membrane form and hydrogel.

In fibre form, the fibre would typically be fabricated for easy handling following treatment. To develop renewable and sustainable adsorbent with high sorption capacity and selectivity, the fibre needs to undergo a modification process to modify the hydroxyl groups of the cellulose (Wang et al. 2016). Moreover, the fibre could also be processed and converted into a composite form. Wang et al. (2013b) synthesised polybutylmethacrylate/kapok fibre (PBMA/KF) composites to enhance the oil sorption capacities. The results indicated that the performance of the PBMA/KF with 8% kapok fibre loading exhibited higher oil sorption capacity compared to PBMA. Also, PBMA/KF composite had better oil retention capabilities and reusability (Wang et al. 2013b).

Activated carbon has continued to attract interest among researchers regarding its powder form. In this case, the process of producing activated carbon involves two steps; carbonisation followed by either physical (water steam or carbon dioxide) or chemical (acid or bases) activation (Rodríguez Correa et al. 2017). The mechanism of decomposition and char formation involves the release of hydrogen and an oxygen compound as well as a condensable volatile formed due to the cleavage weak inner bonds such as the C–O bond and β–O–4 structure (Britt et al. 1995; Rodríguez Correa et al. 2017; Shen et al. 2017) which leads to the formation of single and multi-phenolic

**Table 3** Types of physical forms of adsorbent

| Types of physical form | Example of testing | Image under scanning electron microscope (SEM) | References |
|---|---|---|---|
| Fibre form |   |  | Wang et al. (2013a, b) |
| Powder form |  |  | Tian et al. (2013) |
| Film or membrane form |  |   | Wen et al. (2016) |
| Hydrogel |  |   | Wang et al. (2014) |

compound (Faravelli et al. 2010; Rodríguez Correa et al. 2017). According to Dorrestijn et al. (2000), the secondary phase of reaction contributed to the formation of char. At this phase, the solid phase structure started to rearrange through the crosslinking of C–C bonds. Also, at a temperatures higher than 500 °C, the aromatic structures started to grow and rearrange into turbostratic graphene sheet (Kercher and Nagle 2003; Williams and Besler 1996).

Different treatment may produce different size and absorption effects. Granulated activated carbon (GAC) and powdered activated carbon (PAC) have been the most common types of activated carbon used to remove low molecular weight compounds (Phan et al. 2006). However, PAC was preferred since it provided higher and faster adsorption velocities (Van Oss 1990). This was due to the increase of porosity and higher surface area caused by the activation condition, such as temperature, time, and gas used during the preparation process (Oshida et al. 1995). According to Ashby et al. (2009), the relationship among porosity and pore size was the most important factor in producing adsorbent. However, commercial activated carbon is very expensive as far as the consumption cost and regeneration process are concerned (Bharathi and Ramesh 2013). Therefore, agricultural wastes have become popular raw materials for producing activated carbon.

The most common fibres used for making activated carbon are cotton (Liu et al. 2007), jute (Phan et al. 2006; Rombaldo et al. 2014), kenaf (Phan et al. 2006), rice husk (Chen et al. 2013) and oil palm shell (Ahmad et al. 2011). These adsorbents exhibit excellent adsorption capacities typically for pollutants such as phenol (Phan et al. 2006), dyes (Tan et al. 2008), and pesticides (Memon et al. 2008). Kulkarni et al. (2015), studied the efficiency of rice husk as cadmium sorbent and found that the adsorbency can reach up to 69% based on its original weight.

Adsorbents are also be used in membrane form. Membrane form filtration such as microfiltration, nanofiltration, ultrafiltration, and reverse osmosis have been considered as being highly effective in removing pollutants in wastewater treatment (Ahmad et al. 2004; Gebru and Das 2017a, b, 2018; Qin et al. 2007; Strathmann 2001; Van der Bruggen and Vandecasteele 2002; Walha et al. 2007). According to Owen et al. (1995), the membrane technique could be a better alternative in wastewater treatment compared to the traditional method due to more cost-effective and of higher efficiency. Moreover, the membrane technique is not capable of removing solid particles, and other inorganic contaminants such as heavy metals and ions. Juang and Shiau (2000) studied the removal of metal ions such as Cu (II) and Zn (II) from synthetic wastewater using chitosan enhanced membrane filtration.

In this case, the process of membrane synthesis involved the use of commercial membrane solution such as cellulose triacetate (Villalobos-Rodríguez et al. 2012) and cellulose nitrate (Soylak and Cay 2007). In order to make it porous, calcium carbonate was reacted with hydrochloric acid to form bubbles (Kellenberger et al. 2012). As illustrated in Fig. 5, the presence of calcium carbonate acted as a pore template to fabricate the polymeric membrane with tunable pore sizes (Kellenberger et al. 2012; Kaiser et al. 2017). The membrane also appeared to have a fine mesopore and micropore after heating the membrane in a hot water bath which helped in the rejection of the salt produced from the reaction of acid and calcium carbonate.

To remove the smallest component or charged solute, nanofiltration was used by reducing the pores

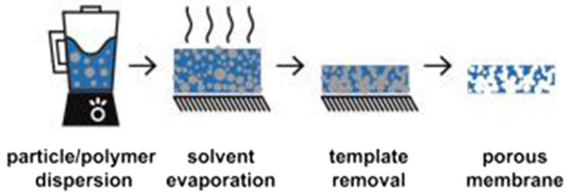



**Fig. 5** The production of the porous polymeric membrane using calcium carbonate as pore template (reproduced with permission from Kaiser et al. 2017)

on the membrane, and the membrane surface was modified by either ionic or cationic surface. Accordingly, this involved the adsorption process such as physical, chemical and ionic adsorption (Barakat 2011).

The most advanced form of adsorbent from amongst all the various types is a hydrogel which is produced from polysaccharide-based materials. Usually, the preparation of hydrogel involves crosslinking with other functional groups or coupling agents to form a water-insoluble crosslinked network. The nano-cellulose material may act as an additive, binder, or reinforcing agent (Carpenter et al. 2015). The high surface area to volume ratio allows for easier incorporation of chemical moieties, thus increasing the binding efficiency of the pollutants to the adsorbent. Wang et al. (2014) studied the effect of ultralight nanocomposite aerogel with graphite oxide that could absorb organic liquids such as cyclohexane and dimethylformamide (DMF). In separation technology, the transmission rate of solute is usually determined by the membrane pores and the relative size of solute (Liu et al. 2010). Liu and team also claimed that by increasing the concentration of regenerated cellulose made from cotton fibre in LiOH/urea/water solution, the membrane produced became denser with decreased pore structure.

## Natural fibres for effluent treatment

Different types of agricultural waste can be treated using different approaches. Since the main components of agricultural waste and natural fibre are cellulose, hemicellulose and lignin with the hydroxyl functional group, they have a potential sorption capacity for various pollutants (Bhatnagar and Sillanpää 2010; Bhatnagar et al. 2015; De Gisi et al. 2016). However, the approach in removing the solute is different according to the effluent types either by removing physically, chemically or by adopting the ionic approach.

Oil-based effluent is categorised into two distinct types; free oil and emulsified oil. Free oil is easy to remove because it can be separated by gravitation and skimming off. However, for emulsified oil, it is more difficult to remove since it is more stable in the aqueous phase (Ibrahim et al. 2010; Nag 1995). As a solution, the functional groups on the surface of

**Table 4** The types of fibres used as an adsorbent to treat different types of adsorbates

| Adsorbates | Types of fibres used as an adsorbent | Percentage of effluent removal (%) | References |
|---|---|---|---|
| Oil | Wool | 88–93 | Radetić et al. (2003) |
| | Bark | 95 | Haussard et al. (2003) |
| | Rice husk | 78–94 | Bazargan et al. (2014) |
| | Banana | 85 | Teli and Valia (2013) |
| | Kapok | 75 | Wang et al. (2013a) |
| | Oil palm leaves | 90 | Sidik et al. (2012) |
| | Sugarcane bagasse | 99 | Brandão et al. (2010) |
| Heavy metal | Sugarcane bagasse | 86 | Kong et al. (2014) |
| | Rice husk | 75–95 | Wong et al. (2003) |
| | Soybean hulls | 65–75 | Marshall et al. (1999) |
| | Orange peels | 34 | Gönen and Serin (2012), Telkapalliwar and Shivankar (2016) |
| | Maize cob and husk | ± 66 | Igwe and Abia (2007) |
| Dye | Oil palm biomass | 90.0 | Ahmad et al. (2011) |
| | Coconut coir | 99 | Etim et al. (2016) |
| | Kapok fibre | 99 | Zhang et al. (2016) |
| | Jute | 80 | Mondal and Islam (2014) |
| Ionic ($NO_3^-$, $NO_2^-$, $PO_4^-$, $NH_3^+$) | Wheat straw | 70–75 | Xu et al. (2010) |
| | Almond shell | 64–80 | Rezaee et al. (2008) |
| | Oak wood | 25–99 | Wang et al. (2015) |
| | Coconut coir pith | ± 99 | Anirudhan and Unnithan (2007) |

natural fibres are attached with a cationic surfactant such as hexadecylpyridinium chloride monohydrate (CPC, $C_{21}H_{88}NCl$) for oil adsorption (Ibrahim et al. 2010). As a result, a positive charge is formed on the fibre surface forcing the adsorption on the opposite surface charge to form a hydrophobic layer. This allows oil droplet partition into the surface layer (Ibrahim et al. 2010; Rawajfih and Nsour 2006).

Heavy metals are the most hazardous contaminants found among the chemical-intensive industries. Since they are highly soluble in the marine environment, these heavy metals can be easily absorbed by living organisms (Barakat 2011). Usually, the surface of natural fibres must be modified in order to function as an adsorbent. The charging effect on the heavy metal makes it easy to remove either by ion exchange, chemical precipitation, electrostatic removal or adsorption process. However, the capability to remove heavy metal depends on the pre-treatment method and the pH condition during the treatment process (Babel and Kurniawan 2003; Barakat 2011). For ionic effluent, a similar removal method for heavy metals is employed.

In dye removal, a different condition is observed as the dye characteristics, and the particle size are much larger as compared to heavy metal and other ions. Typically, the interaction between the absorbent and the dye particles are categorised under physisorption involving van der Waals attraction. Activated carbon is the most popular adsorbent that is used for the removal of dyes (Ahmad et al. 2011; Etim et al. 2016; Mondal and Islam 2014; Zhang et al. 2016).

Table 4 lists the various types of agricultural wastes used as adsorbents. The adsorbates are categorised according to their types. However, the percentage of effluent removal depends on the fibre treatments and physical forms of the adsorbents.

## Conclusion

Many researchers continue working towards producing effective adsorbents having low cost and low energy consumption. The use of natural fibres as the adsorbent is an emerging trend in wastewater treatment technology as the fibres are abundant, readily available and are more environmentally friendly as compared to polymeric based materials. Many types of natural fibres, especially agricultural wastes have the potential to be utilised as absorbents.

To determine the best modification methods, the basic chemical properties of fibres need to be thoroughly understood. Cellulose possesses many desirable properties and is easily modified since it contains hydroxyl functional groups, thereby creating many active sites for adsorption. Based on the review, many researchers have preferred chemical modifications since they offered the greatest potential in adsorbing adsorbates. Furthermore, by chemical modifications, the hydroxyl functional groups can be modified according to the types of solutes and adsorbates to be removed.

However, after thorough observation, it was observed that almost none of these modified fibres could remove more than one type of contaminant at a time, as far as industrial and domestic relevant pollutants are concerned. Most researchers only focussed on removing one type of adsorbate each time, and only selective adsorbates could be removed. Therefore, further research is required on the practicality and durability of the adsorbents made from natural fibres.

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