



Research article

Application of modified water treatment residuals in water and wastewater treatment: A review

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ABSTRACT

Large quantities of sludge known as water treatment residuals (WTRs) are generated from water treatment facilities across the world. Various attempts have been made to reuse these residuals. Among the different applications of WTRs, their reuse in water and wastewater treatment has received more attention. However, direct application of raw WTRs is associated with some limitations. In the last decade, in order to improve their characteristics, numerous investigators have modified WTRs by different methods. This paper reviews the different methods applied to WTRs to enhance their characteristics. The effects of these modifications on their characteristics are explained. The applications of modified WTRs as a filtration/adsorption medium for treating textile/dye wastewater, groundwater containing different anionic and cationic pollutants, storm water runoff, and as a substrate in constructed wetlands are presented in detail. Future research needs are highlighted. The review clearly indicates the potential of different modification methods to improve the removal of a variety of pollutants by WTRs from water and wastewater.

1. Introduction

With rapid increase in population, urbanization and standard of living, the demand for safe drinking water is increasing worldwide [1,2]. Coagulation/flocculation is the most common process used for producing drinking water from surface water sources. This process removes colloidal impurities, microorganisms, natural organic matter, and metals along with other pollutants from water. Aluminum and iron-based compounds are generally used as coagulants, and treatment plants produce large amounts of waste called water treatment residuals (WTRs) or water treatment sludge (WTS) [3]. Management of water treatment residuals has emerged as a major issue in recent years due to its large quantity and disposal constraints. At present, most of these residuals are disposed of in landfills or discharged into water bodies [4,5], which is least desired in waste management hierarchy [6]. However, with the realization of the negative impacts of their carefree disposal, policymakers are planning stricter control on their disposal [7,8]. This has resulted in greater interest in the reuse of these materials.

Among the different applications of WTRs, their use in the water and wastewater industries has received more attention. Different types of reuses have been suggested in water treatment, which include (a) recovering coagulants from WTRs and using them as coagulants in wastewater treatment, and (b) direct reuse of WTRs as adsorption/filtration medium in wastewater treatment [9–13]. While some of these are already applied on a field/pilot scale, some are still at the laboratory scale investigations. WTRs have been used as an adsorbent or coagulant for the removal of different classes of pollutants such as heavy metals, nutrients, dyes, organic

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matter, and trace organic compounds. Recent studies have shown strong adsorption capacities, high reactivity, and coagulation power for these residuals [14]. However, utilization of raw WTRs is associated with some limitations such as poor efficiency in certain applications due to excessive amounts of organic matter in the WTRs, difficulty in separating the WTRs after treatment, and inability to regenerate the used WTRs [15]. This has resulted in a large number of studies using modified WTRs in the last decade. The modifications of WTRs are undertaken with an aim to increase the specific surface area to achieve high adsorption capacity. Another approach to modification is to combine WTR with other materials to obtain a stable material that can be easily separated after its application in pollution control.

WTRs have been modified in a number of ways such as thermal modification and calcination [16–18], chemical modification with acid [19–22], surface modification with metals [23–26], and synthesis of composite sorbents made by amendment with waste products such as rice husk, wood mulches, scrap tire chips, fly-ash and shell materials [27–33]. These modifications result in favorable characteristics such as enhanced specific surface area and easy regeneration capacity. These modified WTRs have been used for the removal of a variety of pollutants such as fluoride [34], nitrogen and phosphorus [35], turbidity [19], molybdenum (VI) [20], chromium [36] and dyes [26,31,37], among others.

Recently, a number of papers reviewed the application of WTRs/WTS in water and wastewater treatment [38–47]. However, no review paper is available in the literature on the application of modified WTRs in pollution control. In this paper, the different modification methods applied to WTRs to enhance their characteristics are first discussed. The effects of these modifications on their characteristics are then explained. The applications of modified WTRs for treating textile/dye wastewater, groundwater containing different anionic and cationic pollutants, wastewater containing nutrients and stormwater runoff along with their use as a substrate in constructed wetlands are then presented in detail.

2. Modification methods

Water treatment residuals (WTRs) are subjected to a variety of modifications to make them a viable material. These methods include thermal treatment, chemical treatment with acid, chemical surface modification by metal addition, physical surface modification by surface coating to wood mulches and tire chips, amendment, or compositing with waste such as rice husk, activation of iron to synthesize nanoparticles or magnetic/nano particles, and granulation via different methods. A summary of these methods is presented in Fig. 1, and a discussion on these methods is presented here.

2.1. Thermal treatment

Water treatment residuals (WTRs) are reported to have comparable adsorption capacity to that of commercially available adsorbents [17]. However, these residuals have natural organic matter, which inhibits the adsorption process by occupying the active adsorption sites, thus forming a diffusion limiting layer on their surface [17,48]. Therefore, to further enhance the adsorption capacity of WTRs, thermal treatment is an easy method of modification which eliminates organic matter present in WTRs that would otherwise occupy the active sites of the adsorbent [20]. Different processes, such as drying, pyrolysis, calcination, and thermal roasting, have

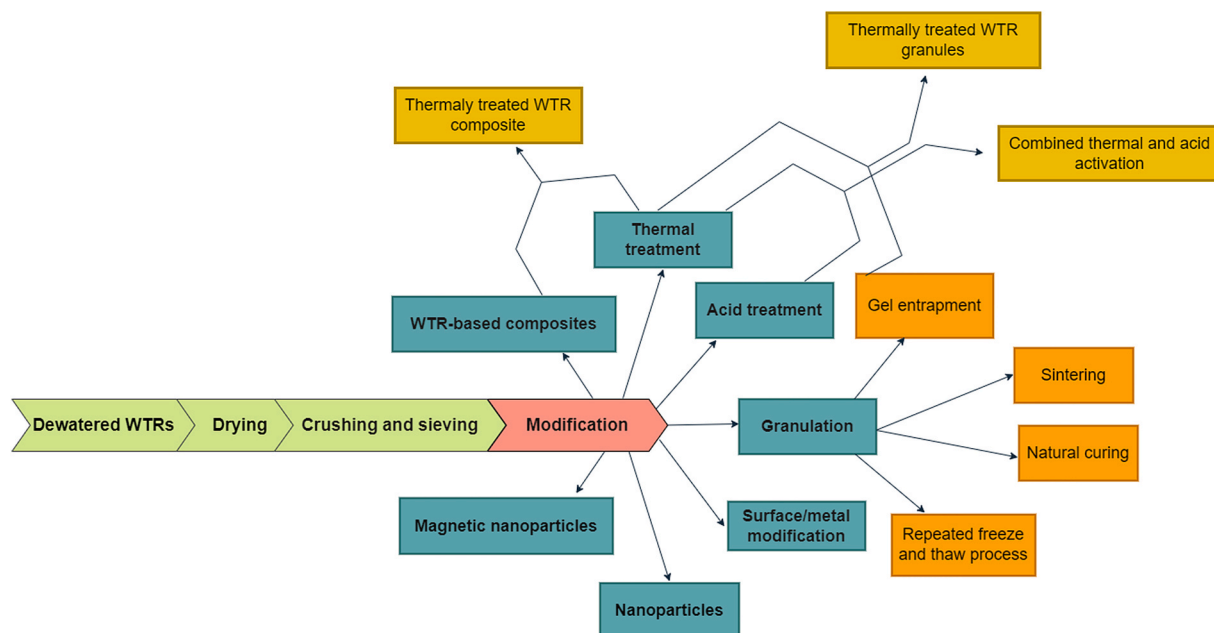


Fig. 1. Summary of various modification methods for WTRs.

been used as thermal treatments to modify WTRs. However, thermal treatment of WTRs which remove organic matter sometimes affects the adsorption ability of WTRs as the organic matter present in WTRs also contributes to the adsorption of hydrophobic organic pollutants [49]. Also, the raw and dried WTRs are amorphous in nature, and at high temperatures, they are transformed to crystalline form, which reduces their adsorption capacity. Hence, to resolve these problems and to strike a balance between crystallization and decomposition of organic matter, optimum temperature is a crucial factor in heat treatment [17].

Wang et al. [18] reported that the high temperature roasting volatilizes the organic matter in the form of CO₂, and the hydroxyl groups are transformed into water vapor at high temperatures, with the formation of pores. This results in increased specific surface area, average pore size and pore volume of the WTRs based ceramsite. A number of studies found that the optimal temperature range for thermal activation is up to 600 °C, after which crystalline transformation of amorphous Al/Fe WTRs into mineral crystals starts taking place [20]. Some of the researchers attempted to reuse WTRs by modifying it to a more reliable porous material, such as biochar via pyrolysis, an oxygen-limited thermal treatment, and hydrochar via hydrothermal carbonization [50,51]. This enhances its adsorption potential for various organic and inorganic pollutants by increasing adsorption sites related to Al and Fe [52]. Furthermore, various studies reported the effect of pyrolysis in enhancing the adsorption potential of powdered WTRs [52–55].

Recently, due to poor source water quality, activated carbon is being added in many water treatment facilities. This discarded activated carbon present in WTRs can be regenerated via thermal treatment in pyrolytic conditions at 200–700 °C for a definite time [56]. This enhances the specific surface area of WTRs. Also, at high temperature (>600 °C), this approach increases the multiple adsorption potential due to the increase in the basicity of the carbon surface as well as regenerated pores. Leaching of heavy metals such as Cu, Ni, As and Pb compared to total heavy metal present in the material was found to be very low while leaching of phenolic compounds occurred at low pyrolytic temperatures [56].

2.2. Acid/alkali treatment

One of the conventional methods to treat residuals is acid treatment where raw water treatment residuals (WTRs) are water-washed and soaked in acid. The residuals are taken out and washed with water after the supernatant is filtered off [22,34] or the residues are dried without filtering supernatant [20]. Acid activation is reported to enhance the surface morphology of WTRs [22]. The acid activation of WTRs enhances the pollutant removal efficiency and the adsorption is improved with the increase in acid concentration [20,34]. The high acid content can intensively volatilize the organic matter thus reducing the carbon content and increasing the ash content. In acid treatment, due to protonation of WTRs surface, positive surface charges are developed, which helps in the adsorption of anionic species [57,58]. Moreover, some studies applied ultrasonic assisted acid activation, which aids in disintegrating the floc size of WTRs which increases the active adsorption sites on the surface of WTRs [19,59]. This is achieved by the reduction of particle size by breakdown of organic matter, metal oxides and other components of WTRs [60]. Also, reduction of floc size of WTRs results in the release of the soluble organic matter from WTRs which increases the soluble COD.

Alkali modification of WTRs, on the other hand, introduces oxygen-containing functional groups, which increase the negative charge on exchange sites on the surface of alkali modified WTRs. Alkalinization augments the surface area and negative charge of alkalinized WTRs, resulting in the deprotonation of accessible sites and the attraction of positively charged contaminants [61].

2.3. Composites with water treatment residuals

A few authors modified the surface of water treatment residuals (WTRs) by coating it with materials such as metals while some applied WTR coating to materials such as wood mulches. For example, Soleimanifar et al. [27] examined a novel low-cost approach that incorporated physical alteration of wood mulches as a supporting material via coating it with powdered Al-WTRs. Here, crushed and sieved WTRs are coated to wood mulches or other solid media. This enhances the permeability of mulches thereby increasing the adsorption ability of WTRs [27]. Sidhu et al. [33] investigated both Al-WTR and Fe-WTR coated wood mulches for effective sorption of storm water pollutants. In another study, WTR-coated tire rubber scrap was also found to improve the permeability of the filter media. Tire rubber contains about 31% of carbon black which had good pollutant adsorption properties similar to activated carbon [29].

TiO₂ to WTR is used as a photocatalyst for the degradation of toxic organic contaminants such as dyes. TiO₂ is economical but has high agglomeration and low-adsorption capability [62]. Also, the regeneration and recycling of TiO₂ is difficult. However, good chemical stability and synergetic properties allows its addition in WTRs to form composites [26]. Al-WTRs are reported to have mixed with TiO₂ colloids to create a novel composite sorbent. TiO₂ can be easily regenerated when mixed with WTRs and it enhances the adsorption capability of the Al-WTRs to adsorb contaminants in water solution [63].

Further, various problems such as colloidal suspension, difficulty in separation, lower adsorption capacity in using powdered WTRs are documented in literature. To overcome these difficulties, granulation and pelletization of WTRs is introduced to enlarge the size of WTRs. Various inorganic and organic binders have been used to form composites with WTRs. Inorganic binders after balling and drying require roasting at optimum temperature followed by cooling. However, high temperature roasting is not required in composites made with organic binder [64]. Kang et al. [54] reported use of molasses as binder for pelletization of WTRs. To enhance the size and adsorption potential, pellets were further treated thermally in air, N₂ or CO₂ reaction mediums. In another study, bentonite in different proportions were used as binder for the pelletization of WTRs [65]. These pellets are further treated thermally to increase their adsorption potential. This addition of bentonite increased the amount of silica which enhanced the strength of the pelleted WTRs. However, the increased amount of bentonite resulted in the reduction in strength [65]. In another study, mussel shells which are rich in calcium carbonate was incorporated in WTRs [66]. Addition of mussel shells enhances the physical properties of WTRs. It helps maintain neutral pH, lowers the porosity of composite and increases the adsorption capacity by increase in surface area [66].

Wang et al. [67] also combined thermal and granulation method, consisting WTR as the skeleton, bentonite as a binder and corncob as a structure regulator. On comparison with high temperature sintering (≥ 1000 °C) process, Wang et al. [67] found that, combining granulation and applying the low temperature treatment (300–700 °C) requires lower energy and produces material with increased adsorption capacity.

2.4. Granulation method

The majority of studies reported in the literature used dewatered and dried water treatment residuals (WTRs) in cake form or in crushed or powdered form for adsorption of contaminants. However, when used as filtration/adsorption media, some difficulties such as channeling in the bed, obstruction of the homogeneous water flow by blocking the pores of adsorption bed media were observed. Also, the micro particles of WTRs can pass through the filter bed along with effluent making it harder to separate the WTRs after the filtration/adsorption process. Due to these reasons periodic back-washing and additional post-treatment are required [17,68]. These shortcomings made WTRs less appealing as an adsorbent and limited their application in wastewater treatment [4,69,70]. In order to overcome this problem, the granulation approach was proposed to modify powdered WTRs to granulated, pelleted or beads forms, which worked well in overcoming the aforementioned issues and also provided better beneficial reuse of WTRs in pollutant removal with high bulk density, better handling and bulk flow properties [35,57]. Granulation involves shaping and stabilization of WTRs by agglomeration of fine/coarse/powdered WTRs [70,71]. With an aim to improve hydraulic conditions, this modification technique of size enlargement increases the hydraulic conductivity and compressive strength of WTRs in filter media [67]. Further, the granulated WTRs are easy to transport and can be easily separated and recovered from water after adsorption, making them more appropriate for use in wastewater treatment facilities as columns, beds and filters [18,72]. The literature documented various granulation techniques such as sintering, gel entrapment, natural curing and repeated freeze and thaw process [73].

2.4.1. Sintering method

Sintering is a thermal treatment, and it removes the organic matter to obtain a stable structure and makes surface of water treatment residual (WTR) porous and rough, thereby improving the adsorption capacity by increasing the adsorption sites [73]. Sintering of WTRs is the first reported and widely employed granulation technology for modification of raw powdered WTRs in to a ceramsite [74]. The pelleted form of ceramsite was made with sintering the mixture of WTRs and wastewater treatment plant residuals [74,75]. According to Wang et al. [76], the composition of WTRs is almost the same as that of clay, so it can be used as a substitute for clay as a new source of raw materials in the preparation of ceramsite. Some sintered materials expand inside the system under high temperature conditions [74]. The WTRs based ceramsite recently gained attention with its property in improving the adsorption capability and controlling water pollution. The WTR based ceramsite can be made by using two ways namely sintering and non-sintering methods [46]. Sintered ceramsite is granulated and thermally treated whereas, non-sintered ceramsite is made by granulation and solidification [46].

Ceramsite is used as media in bioretention columns or biofilters [75] and constructed wetlands [72,76]. The production of ceramsite or ceramic materials under high temperature improves the strength, stability, and micropores for good adsorption capacity, and removes pathogens and organic contaminants from WTR [32,77,78]. Nowadays, due to the blockage, post treatment issue and short operating cycle of traditional wetland media matrix, composite substrates with long service life, high adsorption potential and improved hydraulic conditions are gaining importance. Various studies documented the use of ceramsite substrate in constructed wetlands made from WTRs. Other waste products such as coal fly ash and oyster shell have been reused as raw materials combinedly with WTRs in preparing ceramsite by solidification at high calcination temperature which increases the maximum adsorption capacity up to 40 times relative to the traditional substrate made of only sand and gravel [18,32]. On the other hand, a low-cost ceramic membrane prepared from WTRs was introduced by applying dry pressing and sintering [79]. The mixture of WTRs, clay and starch homogenized in mortar and uniaxially pressed using hydraulic press. This pressed membrane was then thermally treated at 480 °C to decompose organic matter and sintered at 950–1000 °C. After sintering, the membrane is cooled down [79].

2.4.2. Gel entrapment method

Various organic and inorganic binders such as sodium alginate, polyvinyl alcohol, water glass, agar, AlCl_3 , carboxymethylcellulose, NaOH, methyl cellulose, and molasses have been used for granulation and pelletization to aggregate particles [73]. Sodium and calcium alginate are widely used for encapsulation of WTRs [80,81]. Jung et al. [16] firstly reported a gel entrapment of WTRs by mixing thermally pretreated WTRs with sodium alginate followed by dropwise addition of this mixture to chemical agents like calcium chloride [16,35,81] or ferric chloride [70]. This dropwise addition is required for shaping the WTRs through crosslinking. Zeng et al. [82] utilized chitosan to granulate WTRs. The utilization of WTR granules might provide an alternative to activated carbon or other commercial adsorbent materials.

2.4.3. Natural curing method

This granulation technique is an advancement over the conventional high pollution, low recoverability and high energy consuming sintering method [70]. Wang et al. [76] introduced a novel non-combustible sustainable filler substrate involving preheating of WTRs with aluminum slag in oven at 105 °C. Later, WTRs and aluminum slag are combined with gypsum, silica and mafian stone in different proportions, and thereafter, NaOH is added to obtain spherical granules. These pellets are then dried. The addition of different raw materials increases the Fe, Ca and Al contents which improves the adsorption potential of modified WTR substrate. This filler substrate is dried and ventilated naturally and undergo three stages of curing process: (a) material hardening stage when evaporation with no

cracking due to the preliminary strength of filler occurs (b) oven drying stage which removes free moisture and space between particles by drying at constant temperature in oven (c) natural drying stage where natural dehydration increases the hydration products improving filler hardness and compressive strength. As time passes, more and more hydration products are formed, and the strength increases more rapidly. Hence, the non-combustible WTR based substrate can replace high energy consuming thermal treatment [76].

2.4.4. Repeated freeze and thaw method

Granulation by sintering and gel entrapment is a two-step process involving first shaping of powdered water treatment residuals (WTRs) and then stabilizing pellets or granules by sintering at high temperature or by chemical crosslinking. The repeated freeze and thaw granulation technique attempts to granulate WTRs by shaping and stabilizing them in a single step. This stabilizing involves physical crosslinking with chemical binders such as poly vinyl acetate (PVA). Here, WTRs are mixed in PVA solution, and the mixture is mixed thoroughly. This mix is frozen (-20°C for 12 h) and thawed repeatedly at room temperature for 4 h. Thereafter, the product is washed and air dried [4]. This method produces WTR granules of controlled size (by adjusting mold dimensions) with good water permeability and mechanical stability [4]. Moreover, repeated freeze and thaw aids in reducing leaching of metals within WTRs [73]. However, this method is time and energy consuming with several freeze and thaw cycles.

2.5. Surface modification with metals

Another method reported to modify water treatment residuals (WTRs) is by its surface modification which mainly involves the addition/loading of different metals such as Fe, Cu, Pt, Ag and La. This metal loading reportedly enhances the surface properties of WTRs by increasing surface area and pore volume up to an optimum loading of metals which helps in better adsorption of pollutants [23,24]. Lanthanum loading to WTRs increased the initial adsorption capacity of WTRs [24]. In addition, these metals also work as antibacterial agents causing inactivation of bacterial pollutants by increasing the bacterial removal efficiency [23]. Moreover, little leaching of metals is found from these modified WTRs during their use [23].

2.6. Nanoparticles from water treatment residuals

Recently, nanoparticles have been synthesized from water treatment residuals (WTRs). This approach can replace expensive commercially available nano-adsorbents with low-cost easily available WTR based nano-adsorbents (nWTRs). These nano-adsorbents have high surface area and increased number of active sites, with unique reactivity toward contaminants in environmental media [83].

Elkhatib et al. [84] developed a cost-effective method for preparing water treatment residual nanoparticles using precision milling. In this method, dried WTRs are ground in a grinding bowl with stainless steel grinding balls thereby reducing micro-WTRs particles to sizes below 100 nm by breaking of WTRs by high impact forces generated by ball-ball and ball-wall collisions [84]. Developing stable nWTRs from bulk WTRs results in very promising and practical solution to remediate various environmental contaminants by increasing surface area and pore volume by 2–3 times [85]. Thus, nWTRs due to their smaller size have more active sites resulting in increased sorption capacity up to 30 times compared to powdered raw WTRs [84,86,87].

2.7. Magnetic and nano-magnetic particles from water treatment residuals

Another route widely reported to modify water treatment residuals (WTRs) is to synthesize magnetic particles and nano-magnetic particles from iron-WTRs. Fe-WTRs from water treatment plants consist of abundant amounts of metal ions such as iron and aluminum, however they do not exhibit magnetic properties. Separation of magnetic adsorbents from solution is easier due to their strong magnetic properties. Magnetic nanomaterials due to their directional movement in the magnetic field, can be easily separated from a

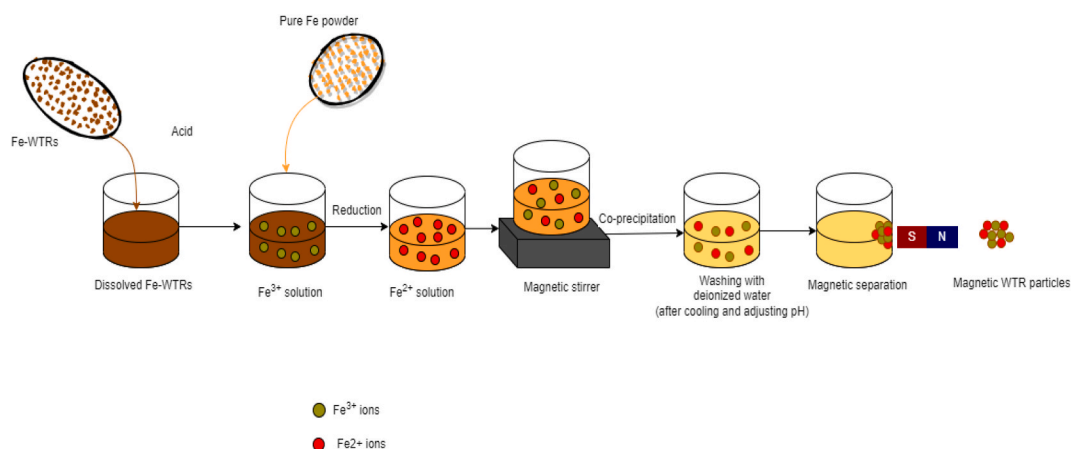


Fig. 2. Synthesis of magnetic particles from iron-water treatment residuals.

solution after adsorption via a simple magnet. Particularly, superparamagnetic nanomaterials can be rapidly magnetized under a magnetic field and rapidly demagnetized when the external magnetic field is removed, exhibiting zero remanence and zero coercivity [88].

Fig. 2 presents the method of synthesis of magnetic particles from iron-WTRs. Fe^{3+} ions from WTR are first dissolved in an acid. Fe^{3+} ions are reduced to Fe^{2+} by adding pure iron powder. This prepared $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution is mixed and heated on a magnetic stirrer up to a certain temperature, and pH of the solution is adjusted to alkaline range. After cooling, the precipitate is washed with deionized water and collected with the help of simple magnet and is vacuum dried [88]. In another study, Zhu et al. [89] used solvothermal process to synthesis of Fe_3O_4 magnetic particles from Fe-WTRs by dissolving WTRs in a solvent and a reducing agent. This suspension was magnetically stirred and calcined in a drying oven. After cooling at room temperature, black precipitate was collected and washed ultrasonically. Zeng et al. [90] suggested synthesizing iron as $\text{Fe}_3\text{O}_4@\text{C}$, a core-shell structure prepared with crystalline iron oxide core and amorphous carbon shell, which is a surface modification technique to enhance stability and functionality of the WTR based adsorbent [90].

In another study, Fe-WTRs were transformed to magnetic particles by calcinating at different temperatures of 105 °C, 300 °C 500 °C and 700 °C. Magnetic particles calcined at 500 and 700 °C showed high saturation magnetization compared to those at low temperature because of the formation of Fe_3O_4 which allowed easy separation in magnetic field [36].

2.8. Combination of different techniques

Several reported studies used combination of two or more methods to modify the WTRs. Siswoyo et al. [22] performed acid treatment followed by encapsulation with agar and alginate and compared the results with unmodified WTRs. Nayeri and Mousavi [19] used calcination of WTRs followed by ultrasonically activated acid treatment. Vinitnantharat et al. [57] utilized pelleted and acid treated WTRs while Lian et al. [20] used thermal and acid activation.

3. Characteristics of water treatment residuals

Characteristics of residuals from water treatment plants vary with the quality of source water, treatment operation used, and dose and type of chemical coagulant used. Thus, composition of residuals generally measured in terms of solid content, metals and inorganic and organic contents varies from plant to plant [91,92]. Water treatment residuals (WTRs) are composed of amorphous mass of metal oxides/hydroxides along with sediments, humic substances, minerals, and metals removed from the raw water. WTRs are generally less polluted with toxic chemicals as the drinking water supply sources are protected from potential pollutants. However, the source water characteristics vary widely worldwide. Further, since the early 2000s, there is a marked increase in the concentration of heavy metals in surface and groundwater sources due to anthropogenic pollution [40].

Alum flocs are generally gelatinous and settle readily but have higher resistance to decanting due to electrovalent character of Al ions [93]. Scanning electron microscopy and X-ray diffraction observations show that dewatered sludge has an amorphous structure, rough surface and are poorly ordered [94–96]. The amorphous nature of alum sludge is due to the presence of non-crystalline $\text{Al}(\text{OH})_3$ which also increases the specific surface area of the material.

Apart from silica, Al_2O_3 or Fe_2O_3 is the main component of the WTR depending on the coagulant used. Other components including MgO , CaO , Na_2O , K_2O , P_2O_5 and TiO_2 are found in smaller percentages [79]. Table 1 presents the mean values of chemical and elemental composition of Al and Fe-WTRs reported from different parts of the world. As can be seen, average Al and Fe contents of 6.7

Table 1
Chemical and elemental composition of aluminum and iron-based water treatment residuals.

Parameter	Unit	Al-WTRs	Fe-WTRs
SiO_2	(%)	39.02 ± 17.65	23.07 ± 11.66
Al_2O_3	(%)	34.84 ± 19.99	6.98 ± 10.16
Fe_2O_3	(%)	4.76 ± 2.61	31.31 ± 28.21
CaO	(%)	4.64 ± 6.38	12.73 ± 15.73
MgO	(%)	1.30 ± 1.20	0.91 ± 0.68
Na_2O	(%)	0.54 ± 0.50	0.93 ± 0.59
K_2O	(%)	1.37 ± 0.97	0.64 ± 0.27
P_2O_5	(%)	0.59 ± 0.45	5.14 ± 4.12
TiO_2	(%)	0.62 ± 0.42	0.55 ± 0.71
pH		6.60 ± 0.74	7.00 ± 1.3
Al	mg/g	66.77 ± 38.94	34.54 ± 10.01
Fe	mg/g	30.11 ± 28.611	189.38 ± 37.97
Mn	mg/kg	2401.46 ± 1640	2954 ± 2638
Zn	mg/kg	95.90 ± 95.36	88 ± 73.54
Cu	mg/kg	165.66 ± 259.01	58 ± 16.97
Ni	mg/kg	18.14 ± 11.05	47 ± 24.04
Pb	mg/kg	31.02 ± 42.44	118.50 ± 101.12
Cr	mg/kg	55.88 ± 84.22	19 ± 26.87
Total solids	g/L	2.5–52.345	2.132–5.074

[7,73,98–110].

and 18.9%, respectively were observed in Al-WTR and Fe-WTR. It is clear that heavy metal such as Zn, Cu, Cr, Pb and Cd are found at relatively low concentrations depending on the raw water quality. Tie et al. [36] reported a high Fe content of 78.62% in WTRs. This high Fe content is due to the Fe based coagulants used in the water treatment process [36]. Likus et al. [97] also reported high Fe content (32–56%) in groundwater treatment residuals.

3.1. Effect of modifications on the characteristics of water treatment residuals

The modification practices greatly influence the physical and chemical properties of water treatment residuals (WTRs) by changing their morphological and physiochemical characteristics. Removal of different pollutants is influenced by different morphological,

Table 2
Comparison of the characteristics of raw and modified Water Treatment Residuals.

Material	Specific surface area SBET (m ² /g)	Pore volume (cm ³ /g)	Aperture size (nm)	References
Raw WTR	6.50	0.0024	15.05	[56]
Thermally treated WTR at 500 °C	131.80	0.1950	0.20	
Dried WTR	7.0	0.0195	11.17	[17]
Thermally treated WTR at 300 °C	181.3	0.2153	4.75	
Thermally treated WTR at 500 °C	98.2	0.2191	8.93	
Acid activated WTR	50.97	0.0218	17.14	[26]
TiO ₂ and acid activated WTR composite	82.46	0.0341	16.55	
Raw WTR	86.37	0.20	9.47	[23]
Fe-surface modified WTR	177.50	0.37	4.13	
Cu-surface modified WTR	193.85	0.38	3.90	
Raw-WTR	364.55	0.067	1.84	[65]
0.5% bentonite and WTR based composite	227.81	0.049	1.78	
1% bentonite and WTR based composite	113.95	0.026	1.76	
Raw WTR	35.99	0.0270	3.939	[35]
Thermally treated WTR	34.71	0.1104	3.939	
Thermally treated and sodium alginate WTR	25.31	0.0700	3.937	
Raw WTR	31.56	0.096	9.89	[64]
Powdered WTR	28.79	0.083	11.56	
Granulated WTR	23.12	0.073	13.20	
Raw-WTR	78.83	0.07	3.59	[114]
Thermal and acid activated WTR	21.72	0.02	3.61	
Raw WTR	62.94	0.0511	1.84	[30]
Thermally treated rice husk (RH) WTR composite	341.2 @ 5% RH	0.0271	3.20	
	182.2 @10% RH	0.1320	2.80	
	94.25 @ 15% RH	0.0679	2.10	
Sodium alginate WTR granules	225	0.291	–	[81]
Raw WTR	6.85	0.0007	8.88	[34]
Acid activated-WTR	53.59	0.0064	3.23	
Raw WTR	15.58	0.061	15.10	[117]
Thermally treated WTR at 300 °C	40.87	0.108	11.24	
Fe-WTR	106.12	0.1120	5.34	
Thermally treated WTR at 550 °C (T-WTR)	100.30	0.271	10.81	[37]
(T-WTR) + Acid activated	582	0.439	3.02	
Raw-WTR ceramsite	6.07	1.310	6.22	[18]
Thermally treated WTR ceramsite	8.15	1.880	8.53	
Raw WTRs	19.66	0.07	15.67	[20]
Thermal (600 °C) and acid treated WTRs	36.73	0.06	7.83	
Raw WTRs	29.39	0.091	7.77	[51]
WTRs based biochar at 400 °C	34.22	0.127	10.50	
Raw WTRs	40.93	0.062	6.01	[118]
Rice husk WTR composite	62.29	0.065	4.17	
Rice husk biochar WTR composite	68.22	0.068	3.96	
Raw WTRs	53.10			[86]
nWTRs (nanoparticles)	129			
Thermally treated WTR at 550 °C (T-WTR)	38.45	0.110	11.65	[6]
T-WTR +0.5 M H ₂ SO ₄	45.24	0.143	12.65	
T-WTR + 1 M H ₂ SO ₄	59.84	0.175	11.72	
T-WTR + 3 M H ₂ SO ₄	80.75	0.175	8.65	
T-WTR + 6 M H ₂ SO ₄	93.89	0.185	7.86	
Raw-WTR	115.34	0.281	9.75	[36]
Polymer-magnetic WTR composite	19.73	0.095	19.21	
Raw-WTR	34.19	0.120	10.06	[3]
Fe WTR composite	50.29	0.090	11.19	
Raw WTR	13.91	0.060	5.89	[61]
Alkali modified WTR	23.33	0.128	12.75	

surface and physio-chemical characteristics of WTR [42]. The characteristics change with the modification techniques, used and modification generally enhances the adsorption potential of WTRs.

The physical characteristics of WTRs vary with the modification technique applied. Colour is an easily observable physical characteristic of WTRs before and after modification. Generally, Al-WTRs are black in colour and exhibit visible colour changes from black to dark brown to light brown following thermal modification [110]. These visible colour changes could be caused by the burning and subsequent removal of organic matter present in WTRs [106,111]. Organic matter volatilization results in the formation of pores on the surface of WTRs, which is advantageous for the adsorption process [112]. A study by Mouratib et al. [79] found that WTR-based membrane produced by sintering showed colour change from dark brown to yellow at high temperatures between 950 and 1150 °C. The resulting membrane had a homogeneous surface and was free of defects and cracks. During the synthesis of magnetic particles from Fe-WTRs, the yellowish-brown colour of raw Fe-WTRs was changed to black.

Mass loss in WTRs is associated with the temperature of thermal treatment [89]. For example, Barbooti and Zahraw [113] observed a mass loss of 16.56% during thermal treatment of the Al-WTR due to the thermal decomposition of the organic content and the possible decomposition of some carbonates. This mass loss is attributed to the conversion of organic matter to inorganic carbon so as to increase Al content for better adsorption and coagulation [6,101]. Spade et al. [111] used pre-wetting of WTRs prior to thermal treatment which resulted in a mass loss of more than 25% and a significant volume gain due to the expansion of micropores caused by moisture evaporation. The destruction of the diffuse double layer during thermal treatment causes WTRs' hydraulic conductivity to increase [106]. As a result, the baking of WTR may change its crystallinity and thus its sorption potential [114,115].

Lee et al. [116] reported that water treatment residuals from a facility with large amounts of algal blooms exhibited high volatile content and less ash content after thermal treatment. This will increase the loss of mass during thermal treatment. On the other hand, WTRs with low organic matter will inhibit the volatilization of organic matter resulting WTRs with high yield value [116]. Further, thermal treatment considerably increases the amorphous Al and Fe contents but increasing the temperature above optimal temperature (typically >500 °C) results in major reduction in amorphous Al and Fe content suggesting ageing of Al and Fe induced by thermal treatment and crystallization starts taking place [48].

Structural changes also occur during different modifications. Literature reported that smooth surface of raw WTRs converts to rough after modification methods. During thermal modification, majority of studies reported that homogeneous surface of raw WTRs was transformed to heterogeneous, rougher and more porous due to heat effect [54]. Geng et al. [63] described the sheet-like structure of thermally modified WTRs after 2 h of calcination at 600 °C and the presence of irregular particles on the modified WTRs' surface. In another study, Fu et al. [35] found that raw WTRs had compact sheet like structure with fewer voids which became thinner, rough and loose after encapsulation with sodium alginate and thermal roasting. A significant increase in pore diameter and specific surface area was observed because of the replacement of the larger cations in raw WTRs with sodium ions and collapse in pore walls after high temperature firing [35]. After alkali modification of WTRs, Jiang et al. [61] reported a dense laminar structure of WTRs with looser and larger pores. The flat surface of WTRs becomes covered in small particle bumps, hence increasing their surface area [61]. Vinitnantharat et al. [57] found that acid activated WTRs have more smooth and wide pores than raw WTRs indicating leaching of cations from the adsorbent surface on acid activation. In contrast, no structural deviations were observed in combined thermal and acid modified WTRs.

Powdered raw WTRs have good adsorption potential but clogging of pores is its main drawback. To enhance its usage, Soleimanifar et al. [27] coated powdered WTR to wood chips. The grinding of WTR could crash clumping of WTRs thus making the WTR particle size small and uniform. Sidhu et al. [33] reported that when small-sized chips are used, higher adsorption rates and better pollutant adsorption are expected because of the availability of larger specific surface area. Similar results were observed by Soleimanifar et al. [27], Soleimanifar et al. [28] and Sidhu et al. [33] with mulches. Mulches have relatively smooth surfaces and have fibrous structure while the modified WTR coated mulches had rough and porous surface and had more active sites for adsorbing the pollutants in water [33].

It is known that morphological properties such as specific surface area (SSA), pore volume, and pore size play a significant role in the adsorption process, and during modification these properties change [33]. The changes in morphological characteristics before and after different modifications are summarized in Table 2. Thermal treatment of raw WTRs produced no change in aperture size but it showed a decline in thermally treated and sodium alginate entrapped WTRs. Specific surface area of raw WTRs was decreased by 29 and 3.5% in thermally treated and thermally treated sodium alginate WTR composite, respectively [35]. This may be due to the volatilization of carbon during thermal process and indicated a lesser adsorption capability of thermally treated sodium alginate WTRs [35]. In another study, SSA of thermally modified WTRs gradually increased from 6.5 to 131.8 m²/g when temperature was increased up to 500 °C indicating the volatilization of organic matter, but a decline in SSA was observed beyond 500 °C indicating collapsed pores [56]. After pyrolytic conversion and rice husk combustion, Shalaby et al. [30] and Lee et al. [56] also made similar observations of narrower pore size, and decreasing pore volume due to the settling of decomposed elements in pores, as well as decreasing surface area. Additionally, when the temperature was increased slightly, crystallization transformed the amorphous Fe into magnetite Fe₃O₄. The majority of investigations indicated the mesoporous structure of WTRs [89]. In contrast, Poormand et al. [81] reported that sodium alginate WTRs had a nonporous and uneven shape, indicating a smooth surface with distributed cavities and bumps. The formation of bumps enhances the adsorption potential of the modified WTRs. However, it was noted that when activated carbon is used in the water treatment process, the amount of carbon volatilized during thermal treatment of WTRs releases more pores. Hence, a large surface area of 225 m²/g was observed in the modified WTR bead [81].

Lee et al. [56] described the pyrolytic valorization of WTRs, which gave powdered activated carbon-based WTRs different adsorbent characteristics. As the pyrolysis temperature increased, powdered activated carbon's purity increased, pores were regenerated, and SSA increased from 6.5 m²/g to 131.8 m²/g. According to Kang et al. [68], the calcination increased the surface area of

Table 3
Effect of modification on elemental composition of water treatment residuals.

Adsorbent	Al	Si	Fe	Ca	Mg	K	Na	N	O	C	H	S	P	Ti	Mn	Cl	References
Raw-WTR	13.2	14.4	8.7			2.4						3.3	8.9				[120]
Pelleted WTR	13.1	14.6	9.2			2.5						3.4	8.6				
Thermally treated SAW	15.1	15.3	8.6			2.4						2	8.1				
Dried WTR	22.49	7.66	0.54		0.22				48.19	13.31	3.95	0		0			[17]
Thermally treated at 300 °C	31.8	10	0.9		0.3				49.34	4.29	2.32	0		0			
Thermally treated at 500 °C	24.95	10.02	0.8		0.39				55.4	0	1.53	0		0.03			
Thermally treated WTR at 400 °C	8.52	10.87	0.94	0.6			0.46			31.5		2.05					[121]
Raw-WTR	25.67	17.31	3.78	1	0.23	0.7	0.05						0.41	0.26	0.68	0.46	[122]
Thermally treated at 300 °C	26.25	17.44	3.32	0.87	0.26	0.65	0.05	1.69	15.01	19.78	3.18	0.44	0.4	0.22	0.56	0.45	
Thermally treated at 400 °C	26.63	17.45	3.23	0.88	0.26	0.63	0.06	1.48	12.23	18.34	2.65	0.41	0.4	0.22	0.54	0.42	
Thermally treated at 500 °C	27.22	17.52	3.1	0.84	0.27	0.62	0.05	1.12	8.53	14.59	1.82		0.38	0.2	0.53	0.36	
Raw-WTR	8.55	29.03	6.32	6.03					41.66	14.45							[25]
Thermally treated at 300 °C	9.61	19.37	22.52	1.13					34.06	8.27							
Thermally treated at 400 °C	9.73	20.42	22.81	1.37					33.52	5.65							
Thermally treated at 500 °C	8.92	19.09	23.06	6.28					30.72	5.15							
Raw-WTR	6.45	5.54	1.98	0.25	0.55	0.58			52.39	31.8							[35]
Thermally treated WTR	7.71	8.16	2.39	–		1.04	0.99		54.11	25.19							
Thermally treated sodium alginated WTR	7.85	9.48	3.09	3.19	0.1	1.08	1.03		47.93	25.81							
Raw								0.09	19.91	0.74	0.42						[22]
Acid activated WTR								0.06	17.07	0.57	0.32						
Raw-WTR	7.58	12.35	4.2	6.37	3.02	1.4	0.36		52.83	11.47		0.09	0.09	0.33			[123]
Composite Sorbent (acidified)	6.26	12.74		3.47	3.19	1.03	0.83		52.29	14.24		0.09	0.32	0.19			

WTR beads 36–100 times compared to powdered WTRs, resulting in rough surface and a more porous structure. Jeon et al. [17] showed a 25-fold increase in surface area at 300 °C compared to dried WTRs, indicating that the modified WTRs have increased adsorption capability. However, at 500 °C, the surface area was reduced significantly, indicating the transformation of amorphous to crystalline structure after thermal treatment. Everaert et al. [15] reported that the SSA of modified WTRs increased by 11 times after calcination at 400 °C. At elevated temperatures, crystallization starts taking place and specific surface area decreases. Lian et al. [20] also found two-fold increase in the average SSA and pore size of thermal and acid treated WTRs compared to raw WTRs with approximately similar pore volume. In addition, thermal treatment converted the amorphous WTR structure to crystalline form which again transformed to amorphous form by acid treatment [20]. Kang et al. [68] observed the decomposition of the organic matter in WTRs at the temperature range of 250–600 °C. However, at temperatures above 500 °C, the amorphous aluminum oxides' transformation to the crystalline structure was observed, which could influence the pollutant adsorption.

Jung et al. [16] reported an increase in the BET surface area of WTRs in calcium-alginate beads due to the opening of previously hidden pores after pre-thermal modification [82]. prepared amorphous mesoporous WTR-based spherical beads using chitosan as a binder. They obtained brownish-red colour adsorbent due to iron loadings with size ranging from 1.6 to 1.8 mm with a specific surface area of 110.3 m²/g. Furthermore, when 0.5% bentonite was utilized for the granulation of WTRs, the BET surface area fell by 60% compared to the raw WTR based adsorbent [65]. The adsorption capacity of pellets made of 0.5% bentonite was greater than that with 1% bentonite. Also, excess bentonite reduced surface area and pore size thereby reducing adsorption efficacy. On the other hand, the addition of bentonite improved compressive strength and helped the pellets maintain their shape during the adsorption process [65].

Laib et al. [25] identified a more homogeneous distribution of particles with a relatively high surface area (106.12 m²/g) when iron nitrate was additionally doped to WTRs, as compared to raw WTRs (15.58 m²/g), and thermally treated (300 °C) WTRs (40.87 m²/g). In another study, Fe (III) ions were loaded to raw WTRs and this modification enhanced the SSA of raw WTRs from 34.19 m²/g to 50.29 m²/g after iron modification [3]. Li et al. [34] found that the SSA and aperture size of HCl-modified WTRs were 6.82 and 7.93 times higher than the raw WTRs respectively. They also found that modified WTRs had a high adsorption potential despite the small pore size. Using phosphoric acid to modify WTRs, the surface area and pore volume were increased, thereby increasing the adsorption potential of modified WTRs [22]. Recently, using a new approach, Filho et al. [119] and Filho et al. [37] aimed to improve the physical structure of WTRs and developed a mesoporous structure with relatively high surface area-activated carbon from WTRs by acid and thermal activation with a total pore volume of 0.439 cm³/g and SSA of 582.0 m²/g. This modification of WTRs by acid treatment removed the inorganic material present in WTRs by the hydrolyzation of inorganics and pyrolytic operation removed volatile compounds from the pores thereby increasing the porosity and functional groups on the surface of adsorbents. In another study, WTRs were alkalinized with NaOH to modify WTRs. The Na⁺ ions exchanged the Fe³⁺, Ca²⁺ and Mg²⁺ ions on modified WTRs surface. This increased the modified WTRs' aperture size by 116.43% and surface area by 67.67% compared to raw WTRs [61].

Additionally, compared to the flaky raw ceramsite, the thermally roasted WTR-based ceramsite was mesoporous, which enhanced bio-capacity of ceramsite due to increment in pores [18]. The transformation of hydroxyl groups into water vapor and volatilization of organic matter in the form of CO₂ at high temperatures caused pore formation mostly concentrated at 0–20 nm. The SSA, average pore size, and pore volume increased significantly by 34.27, 37.14, and 43.51%, respectively [18]. Surface modification of WTRs by metal addition of Fe and Cu increased the BET surface area by more than two times compared to unmodified WTRs [23]. Also, this modified the surface by enlargement of inner pores showing an increase in total pore volume, but the total pore width was reduced after modification which may be due to the pore blockage caused by the accumulated coating groups [23].

Modification of WTRs affects its elemental composition. Table 3 compares the elemental composition of WTRs before and after different modifications. During different thermal treatments significant reduction in organic content occurs while proportion of other active elements in WTRs such as Al and Fe is increased. Moreover, the calcium content in WTRs modified by sodium alginate due to the effect of calcium chloride in cross linking increases the carbon content [35]. In water treatment plants, where activated carbon is used in treatment operation, the content of carbon in WTRs is found high which after the thermal treatment is reduced. In a study, Lee et al. [56] found above 19% carbon content in one such plant in raw WTRs which was reduced to 15% and content of other elements such as H, S, N, and O were also reduced after thermal modification at 500 °C. Lee et al. [56] also reported that when temperature is above 500 °C partial volatilization of activated carbon introduces char residues in modified WTRs which increases the carbon content in modified WTRs [56]. Jeon et al. [17] studied the effect of temperature during thermal treatment of WTRs and found total carbon was reduced to 4.3% at 300 °C from an initial value of 13.3%. At 500 °C, negligible carbon content was found indicating effectiveness of calcination in removing carbon content from WTRs.

From Table 3 and it is clear that majority of studies reported a significant increase in Al, Fe and Si content during modification. In a study by Wang et al. [115], Al and Fe increased by 50% and 44% respectively after combined thermal and acid activation of WTRs indicating potential increase in adsorption capacity compared to raw WTRs. Jung et al. [16] reported C and N content of raw WTRs as 23.6 and 2.9% which considerably reduced to 4.4 and 0.5% respectively after thermal pre-treatment. Also, Al content increased from 30.7 to 48.5% after thermal treatment. Jeon et al. [17] compared dried WTRs at 105 °C with thermally modified WTRs at 300 °C and found an increase in Al content by 9.3% and a decrease in the carbon content by 9.0%, which indicated that the overall aluminum content of thermally modified WTRs at 300 °C was not altered by the calcination process. Moreover, at 500 °C, the oxygen and silica content were increased by approximately 7.2% and 2.4%.

pH_{pzc} is one of the important parameters affecting adsorption process in aqueous phase [53,82]. It is the pH at which net surface charge on the surface become neutral and the numbers of positive and negative charges of the adsorbent are equal [6]. The pH_{pzc} value aids in interpretation of the adsorption potential of modified WTRs under different pH values [1,51]. When the solution pH exceeds pH_{pzc}, the surface of adsorbents is negatively charged showing strong potential to attract positively charged pollutants such as methylene blue, Pb²⁺ and Cu²⁺. In contrast, if the solution pH < pH_{pzc}, the surface become positively charged and is beneficial for

Table 4
Summary of the studies on dye and textile wastewater.

Adsorbent	Dyes studied	Adsorption capacity (mg/g)/Removal efficiency (%)	Test conditions	Isotherm model	Kinetics	References
Thermally activated WTRs at 550 °C (T-WTR)	Methylene Blue (MB)	2.60 mg/g	Initial concentration = 50 mg/L	Freundlich	Pseudo-second order	[6]
T-WTR + 0.5 M H ₂ SO ₄		3.65 mg/g	Dose = 1–40 g/L	Langmuir	Pseudo-second order	
T-WTR + 1 M H ₂ SO ₄		5.29 mg/g		Freundlich	Pseudo-second order	
T-WTR + 3 M H ₂ SO ₄		6.00 mg/g		Langmuir	Pseudo-second order	
T-WTR + 6 M H ₂ SO ₄		10.85 mg/g		Langmuir	Pseudo-second order	
Thermally treated WTRs at 400 °C	Real textile dyeing wastewater	6.5 mg/g	pH = 7, Temp = 25 °C, Contact time = 1 h Initial concentration = 11.8 mg/L, Dose = 2 g/L	Langmuir	Pseudo-second order	[121]
Thermally treated WTRs at 400 °C	Congo red	116.4 mg/g	pH = 7, Contact time = 12 h Temperature = 10–50 °C, Dose = 2 g/L	Langmuir	Pseudo-second order	[51]
Raw WTRs	MB	8.57 mg/g	pH = 7	Freundlich	Pseudo-second order	[118]
WTR-rice husk (WRH) composite		13.96 mg/g	Initial concentration = 100 mg/L	Langmuir	Pseudo-second order	
WTR-rice husk-biochar composite (WRHB)		16.94 mg/g	Temperature = 25 ± 0.5 °C Dose = 0.1–4 g/L	Langmuir	Pseudo-second order	
Thermally treated WTR membrane	Textile wastewater	Removal efficiency Turbidity = 98.6%, COD = 67.9%				[79]
Magnetic nanoparticles-WTR	MB	99.4 mg/g	pH = 6.8, Initial concentration = 50 mg/L	Langmuir		[89]
WTR/TiO ₂ composite	Rodamine B (RB)	Removal efficiency = 96.85% using UV irradiation, and 99.85% using UV/H ₂ O ₂	pH = 7, Irradiation time = 4 h Initial concentration = 50 mg/L, Dose = 2.5 g/L	Langmuir	Pseudo-first order	[26]
WTR/TiO ₂ composite	MB	26 mg/g	pH = 11, Contact time = 1 h, Dose 1.25 g/L	Freundlich	Pseudo-second order	[63]
Thermal (700 °C) and acid activated (0.25 M HNO ₃) WTR	MB	Al-WTRs = 70.4 mg/g, Sedimented mud WTRs = 65.79 mg/g	Initial concentration = 100 mg/L, Contact time = 1 h Temperature = 25 C, pH = 7, Dose = 2.5 g/L	Langmuir	Pseudo-second order	[126]
Sodium alginate WTR	MB	909.1 mg/g Removal efficiency = 88.5%	pH = 8, Contact time = 1 h Dose = 0.3 g/L	Langmuir	Pseudo-second order	[81]
Thermally treated rice husk (5%)-WTR composite	Remazol red	Removal efficiency = 81.2%	pH = 3, Initial concentration = 30 mg/L, Dose = 1 g/L, pH = 5, Contact time = 30 min	Freundlich	–	[31]
nWTRs	Indigo Carmine	172.4 mg/g Removal efficiency = 95%	Concentration = 100 mg/L, Dose = 2.5 g/L	Langmuir	First order	[86]
Fe synthesized magnetic WTRs	MB	16.33 at 25 C and 19.13 mg/g at 35 C	Initial concentration = 8 mg/L, Dose = 1 g/L	Freundlich	Intraparticle diffusion	[90]
Thermally treated WTRs	MB	6.78 mg/g	Dose = 20 g/L	Freundlich		[56]
Thermal (550 °C) and chemical activation (ZnCl ₂)	MB	9.29 mg/g Removal efficiency = 95%	pH = 7, Contact time = 13.2 min, Dose = 6.59 g/L	–	–	[37]
Thermally treated WTRs at 550 °C	MB	8.86 mg/g Removal efficiency = 99%	Contact time = 30 min, Temperature = 25 C, Dose = 40 g/L	Sips model	Elovich	[119]
Iron doped WTRs	RB 19 MB	40.65 mg/g for RB19, and 46.73 mg/g for MB	pH _{RB19} = 3, pH _{MB} = 6.5, Contact time = 0–30 min, Initial concentration = 50 mg/L, Temperature = 25	Langmuir	pseudo-second order	[117]

(continued on next page)

Table 4 (continued)

Adsorbent	Dyes studied	Adsorption capacity (mg/g)/Removal efficiency (%)	Test conditions	Isotherm model	Kinetics	References
			C Dose = 1.5 g/L (MB), Dose = 2 g/L (RB19)			

adsorbing anionic pollutants such as PO_4^{3-}P and Congo red (anionic dye) [124].

Modifications employed on WTRs affects its pH_{pzc} value. For example, pH_{pzc} of raw powdered WTRs was 6.34 which increased to 7.43 for thermally treated (450 °C) and sodium alginate WTRs [16]. Jeon et al. [17] reported pH_{pzc} value of the thermally treatment WTRs at different temperatures and the pH_{pzc} value of 7.5 at 300 °C was reduced to 5.8 at 500 °C. Another study reported thermal modification of pelleted WTRs (molasses used as binder) under different reaction mediums (air, N_2 and CO_2) and the reaction medium had insignificant effect on pH_{pzc} value. The pelleted WTRs under dry air, N_2 medium and CO_2 medium had pH_{pzc} value of 7.3, 7.7 and 7.4, respectively. This suggests that molasses significantly affected the surface areas but no significant change in charge [54]. pH_{pzc} of 7.6 for raw WTRs was changed to 6.0 and 5.0 respectively during thermal treatment and combined thermal and acid treatment respectively. This reduction of pH_{pzc} was due to insertion of H^+ ions to the surface of acid activated WTRs [6].

4. Application of modified water treatment residuals in water and wastewater treatment

Water treatment residuals (WTRs) modified by different methods have been used for the removal of a variety of contaminants from aqueous solutions. This section summarizes their applications in treating different types of waste streams.

4.1. Dye and textile wastewater

Due to the complex mixture of many polluting substances ranging from residual dyestuffs to heavy metals associated with the dyeing and printing processes, wastewater from the textile/dye industry has always been a potential source of pollution to aquatic life [30]. Dyes are toxic and non-biodegradable in nature and prevent penetration of sunlight in water bodies causing anoxic conditions [125]. Various studies in the literature documented the potential of reusing modified WTRs for uptake of dyes from textile and dyeing wastewater, and Table 4 summarizes some of these studies.

Chantaramanee et al. [6] reported the use of thermal and acid activated WTRs for the removal of methylene blue (MB). Results showed 90% MB removal at 40 g/L of thermally activated WTRs dosage. Increased removal up to 99.5% was achieved with a smaller dose of 20 g/L when thermally treated WTRs were acid activated at different acid concentrations. This enhancement in removal efficiency clearly showed the superiority of thermal and acid activated WTRs compared to thermally treated WTRs. Acid activation produced high surface area at higher acid concentrations resulting in both physical and chemical adsorption. Column tests conducted with thermally treated WTRs also showed the potential of the medium for MB removal and the adsorption capacity observed in batch and column tests were similar [6].

In another study, raw WTRs were compared with WTR-rice husk composite (WRH) and WTR-rice husk-biochar composite (WRHB) on their performance for MB removal. The adsorption capacity of raw WTRs increased two-fold from 8.5 mg/g to 16.9 mg/g when WTRs were composited with biochar (WRHB) [118]. It is also reported that WRHB showed higher removal of MB (1.7–2.0 times) than WTR-rice husk composite due to removal of organic matter from WRHB and the resulting increase in the surface area up to 1.67 times [118]. Ceramic membrane synthesized from WTRs by dry pressing technique was used as a microfiltration membrane and complete de-colourization of real textile wastewater was achieved along with 68% COD reduction [79]. Lee et al. [56] found MB removal exceeded 95% from textile wastewater using thermally treated WTRs. They observed that temperature of the pyrolysis affected the decomposition of carboxylic and phenolic groups, and also the basicity of the carbon surface. At higher pyrolysis temperature, the removal of MB by the WTRs was higher [56].

Filho et al. [119] investigated the use of thermally treated and ZnCl_2 modified WTRs for methylene blue removal. The adsorption capacity of this material was found to be affected by the presence of phenolic and carboxylic compounds present on the surface of adsorbent. Filho et al. [37] optimized the process parameters such as adsorbent dose, contact time and pH and an adsorption capacity of 18.86 mg/g was observed with a removal efficiency of 99%. Tony [121] applied thermally treated WTRs on real textile wastewater and reported that increasing initial dye concentration (7.7–27.8 mg/L) increased the maximum adsorption capacity from 2.9 to 6.5 mg/g.

Magnetic particles synthesized from WTRs (MP-WTR) also have shown promising results with maximum adsorption capacity of 99.4 mg/g for MB removal [89]. Separation of MP-WTR was much easier as compared to powdered activated carbon. Further, it was found that MPs exhibited higher MB adsorption capacity even with low pore volumes than the commercially available powdered and granular activated carbon [89]. In another study, iron doped WTR was reported to have high adsorption potential for Reactive blue 19 (40.65 mg/g) and methylene blue (46.73 mg/g) [117].

Zeng et al. [90] synthesized magnetic particles from groundwater treatment residuals ($\text{Fe}_3\text{O}_4@\text{C}$) without addition of any iron reagents by one step hydrothermal reaction. They observed an adsorption capacity of 19.13 mg/g for MB at 35 °C. This material was effective in a wide pH range of 5–12 for MB removal. Also, $\text{Fe}_3\text{O}_4@\text{C}$ exhibited good reusability, stability and recyclability with removal efficiency of 72.1% for MB even after five regeneration cycles [90]. El-Kammah et al. [86] used WTR-based nanoparticles for

adsorption of indigo carmine and found that due to the larger availability of active sites, maximum adsorption capacity of nWTRs (172.4 mg/g) was 5.6 times higher than that of the raw WTRs (30.86 mg/g).

Poormand et al. [81] modified WTRs using sodium alginate and used it for the removal of methylene blue. They reported a maximum removal of 88.5% under the optimum parameters of pH 8, initial concentration 50 mg/L, reaction time 60 min, and adsorbent dosage 0.3 g/L. A high sorption capacity of 909.1 mg/g was achieved at optimum conditions. The nitric acid activated and thermally treated WTR showed an adsorption capacity of 70.4 mg/g at optimum conditions of 100 mg/L initial MB concentration, 1 h contact time, 7 pH and 0.25 g/L adsorbent dosage. Hamzah et al. [31] used rice husk-WTR composite for the removal of Remazol red. The composite showed high adsorption capacity, and a high removal of 81% was achieved with 1 g/L adsorbent dosage at pH 3 with an initial dye concentration of 30 mg/L. TiO₂ loaded WTR composite showed 95% MB dye removal efficiency under photocatalytic degradation at optimum conditions (pH 7, WTR composite dose 2.5 g/L) at an initial dye concentration of 50 mg/L [125].

pH is one of the most important factors that affects the adsorption process. Cationic dyes such as methylene blue form positively charged ions when dissolved in aqueous solutions and show low adsorption in acidic solutions. When solution pH increases the surface of modified WTRs becomes negatively charged. Rashed et al. [126] found that for thermal and acid activated WTRs the removal efficiency of MB increased when solution pH rises from 3 to 7 but further increase in pH resulted in the decline of removal efficiency. Most studies reported similar observations. When the pH of the solution is below pH_{pzc} , high density of H⁺ are developed on the surface

Table 5

Summary of the studies on storm water runoff.

Modification method	Target pollutants	Batch/column	Test conditions	Adsorbent dose/bed depth	Max. adsorption capacity (mg/g)/ Removal Efficiency (%)	References
Eucalyptus wandoo-WTR mixture	NH ₃ ⁻ -N, NO ₂ ⁻ -N, PO ₄ ³⁻ -P, NO ₃ ⁻ -N	Batch	Initial concentration = 0.5–5.0 mg/L pH = 4–9 Contact time = up to 24 h	Biochar: WTRs = 8:2	Removal efficiency NH ₃ N = 98.2% NO ₂ N = 99.4% PO ₄ P = 99.8%	[52]
Metal modified WTR (Fe, Cu, Pt and Ag)	<i>E. coli</i>	Batch	Initial <i>E. coli</i> concentration = 1–3 × 10 ⁶ CFU/100 mL, Time = 4 h, Temperature = 25 °C	0.1 g/L	Average log removal of <i>E. coli</i> = 0.11 ± 0.010, Fe-WTRs = 0.73 ± 0.028 Cu-WTRs = 1.20 ± 0.022 Pt-WTRs = 0.48 ± 0.007 Ag-WTRs = 1.24 ± 0.047	[23]
Al-WTR coated wood mulches	P Cu Zn Pb	Column (Intermittent flow)	Initial concentration (<i>E. coli</i>) = 1–3 × 10 ⁶ CFU/100 mL, Temperature = 25 °C Time = 18 weeks pH = 7, Temperature = 22 °C Filtration rate = 8 mL/min Initial concentration: Cu = 100 µg/L, Zn = 800 µg/L, Pb = 100 µg/L, and TP = 2.30 mg/L	10.2 cm	<i>E. coli</i> removal efficiency Fe-WTRs = 89.3% Cu-WTRs = 96.2% Removal efficiency P = 58% Cu = 74% Zn = 40% Pb = 91%	[28]
Al-WTR coated wood mulches	P Cu Zn Pb	Batch	pH = 7, Temperature = 25 °C Contact time = 120 min Initial concentration: Cu = 100 µg/L, Zn = 800 µg/L, Pb = 100 µg/L, and Total phosphorus = 2.30 mg/L	10 g/L	Removal efficiency P = 97% Cu = 81% Zn = 76% Pb = 97%	[27]
Fe-WTR coated wood mulches	P Cu Zn Pb	Column	pH = 7 Temperature = 25 °C Filtration rate = 10.9 cm/h Run time = 98 h	10.2 cm	P = 25% Cu = 88% Zn = 34% Pb = 92%	[33]
Thermally treated bentonite-corn cob-WTR granules	Cu Pb Cd PO ₄ ³⁻ -P	Column	Time = 54 days		Cu = 94.82% Pb = 97.50% Cd = 93.50% PO ₄ ³⁻ -P = 86.40%	[67]
		Batch	Initial concentration PO ₄ ³⁻ -P = 80 mg/L, Pb = 100 mg/L Time = 24 h	2 g/L	Adsorption capacity PO ₄ ³⁻ -P = 8.63 ± 0.24 mg/g, Pb = 18.47 ± 0.56 mg/g	

of adsorbent. This results in competition between H^+ and methylene blue or other cations for adsorption sites and thereby removal efficiency is lowered. When solution pH goes above pH_{pzc} , the negatively charged surface of the adsorbent elevates the adsorption of MB [81].

Adsorbent dose also plays a significant role in the adsorption process. With increase in modified WTRs dosage, adsorption efficiency of dyes considerably increases. However, at higher adsorbent dosages, adsorptive capacity of the sorbent decreases due to availability of excess adsorption sites compared to the dye concentration. Modified WTRs generally show a higher adsorption potential due to increased specific surface area in them. For example, Poormand et al. [81] reported negligible effect on removal efficiency for doses higher than 0.3 g/L while removing MB using sodium alginate WTRs and similar results were reported by Rashed et al. [126] while using thermal and acid treated WTRs at 0.25 g/L. Table 4 shows varying adsorption capacity for sorbents prepared by different modification methods.

Several studies reported kinetics of dye removal by modified WTRs. The dye removal process generally follows pseudo-second order kinetics (Table 4). Langmuir or Freundlich model are found to be the best fitted isotherm model to describe the adsorption equilibria for dye removal depending upon the monolayer or multilayer adsorption of dye molecules on the surface of modified WTRs.

Various mechanisms are responsible for the adsorption of dyes by modified WTRs. It is reported that dye adsorption on modified WTRs is mainly attributed to electrostatic attraction, π - π interactions, van der Waals forces and, hydrogen bonding. El-Kammah et al. [86] proposed that adsorption of anionic dye, Indigo carmine (IC) to WTR nanoparticles (nWTRs) was governed by three mechanism (a) Electrostatic attractions: Surface hydroxides on nWTRs will become protonated in acidic medium ($pH > pH_{pzc}$) and will attract negatively charged IC molecules, (b) Hydrogen bonding: IC molecules contain O and is a strong H donor which releases H. These H interacts with OH on the nWTRs surface and form hydrogen bond, (c) Formation of Al/Fe and IC complexes: Bonding of Al and Fe on nWTRs with nitrogen atoms on IC. Nuanhchamnon et al. [118] studied the interaction of positively charged MB molecules with negatively charged -OH and C-O functional groups on rice husk-biochar WTR composite. They suggested that both physio-sorption and chemical sorption including surface precipitation, electrostatic attraction, ion exchange and pore diffusion mechanisms are responsible for adsorption of MB on modified WTRs. In another study, He et al. [51] reported that electrostatic attraction, π - π conjugation and hydrogen bonding governs the adsorption mechanism of Congo red dye on the surface of thermally treated WTR biochar. According to Chantaramanee et al. [6], adsorption of MB molecules to surface of thermal and acid activated WTRs hold for both physio and chemisorption mechanisms. Tony [121] reported the adsorption of real textile dye, Procion blue followed physical adsorption. Zhu et al. [89] reported that adsorption mechanism of MB on to magnetic nanoparticle WTR involves both physical and chemical forces. According to Geng et al. [63] adsorption of MB molecules on TiO_2 -WTR composite was based on chemical adsorption.

4.2. Treatment of storm water runoff

Urban storm water runoff, a non-point source of pollution, typically contains toxic heavy metals such as Pb, Cu and Zn, nutrients such as P and N, pathogens, and sediments [34]. A number of studies have been reported on the reuse of raw powdered (WTR) for treating storm water runoff [27,106,127]. However, direct use of raw WTR as an adsorbent media is not a viable option since the powdered or cake form WTRs generates poor hydraulic conditions and blocks pores when wet, reduces permeability, and inhibits water infiltration [34]. As a result, various attempts to integrate modified WTRs into stormwater management strategies have been attempted. The efficacy of modified WTRs' adsorptive behavior to remove these pollutants from storm water runoff has been extensively investigated [29,128,127]. Table 5 presents the summary of a few recent studies on the application of modified WTRs for stormwater treatment.

Komlos et al. [106] compared the performance of raw and thermally treated (1000 °C) WTRs for removing phosphorus from stormwater runoff. The modified WTRs showed a lower adsorption capacity compared to raw WTRs in removing phosphorous. However, re-suspension of Fe and colloidal Mn was found in the case of raw WTRs while no such re-suspension was observed for thermally treated WTRs due to the crystalline and stable nature of the modified material as well as the fact that colloidal Mn oxides disappeared at elevated temperatures [106].

Deng et al. [29] developed an adsorbent using waste tire rubber chips integrated in to WTRs for metal adsorption. WTRs-amended rubber chips enhanced the hydraulic conductivity of filter media as well as inhibited the re-suspension of Zn from rubber chips which was observed in absence of WTRs. Also, significant release of other metals such as Pb and Cu occurred only in the presence of a strong chelating agent [29]. In another study, O'Neill and Davis [127] immobilized P from storm water by incorporating Al-WTR into bio retention soil media amended with hardwood mulches. This increased P adsorption under batch conditions and in column tests. However, use of this media was found to increase Al and Fe content in soil, increasing their toxicity in soil. Moreover, in intermittent flow conditions, hardwood mulches retained moisture preventing crystallization caused by drying which aids adsorption.

Simultaneous removal of heavy metals and phosphorus from stormwater was achieved using coating powdered Al-WTRs on to wood mulches [27]. In a batch study, the removal efficiencies of 97, 76, 81 and 97%, respectively were observed for Pb, Zn, Cu, and P in 120 min with adsorption capacity of 9.74 $\mu\text{g/g}$, 61.07 $\mu\text{g/g}$, 8.14 $\mu\text{g/g}$, and 0.22 mg/g. Ion exchange plays a major role in adsorption of metals on Al hydroxides in WTRs by replacing bound protons while ligand exchange plays principal role in P adsorption by replacing single hydroxyls [27]. In another study, Soleimanifar et al. [28] investigated the same media for removal of multiple pollutants in urban runoff using column tests. Higher removal was observed with deeper columns. When short depth of WTR-coated mulches bed was used, non-uniform flow caused the variation in removal of pollutants due to the heterogeneous shape and size of mulches leading to poor pollutant removal efficiency [28].

Also, P adsorption decreased with increasing pH (6–8) but Cu and Pb removal increased. This study demonstrated the significance of ionic strength, indicating that the formation of a phosphate surface complex plays a crucial role in phosphate adsorption. Recently,

Sidhu et al. [33] employed the Fe-WTR-mulch composite. They found promising results with complete removal of targeted metals with partial removal of phosphorus from runoff medium. Further, this media showed good adsorption potential compared to raw mulches due to its high reactive nature, specifically for single pollutant. This study also highlighted the significance of bed depth and the need of optimum contact time. Moreover, these studies suggest that leaching is not an issue when WTRs are coated on wood mulches with the released contaminants falling under different criteria of runoff and landfilling conditions.

In another study, surface of WTRs was modified with metals such as Fe, Cu, Pt, and Ag as antibacterial agents and was tested for bacterial removal from stormwater runoff [23]. Cu and Ag-modified WTR showed >1.2 log removal of *E. coli* which was significantly greater than unmodified WTRs. Application of Pt and Ag modification might not be economical due to the expensive reagents necessary for synthesizing. Modified WTRs were found to be a stable medium with promising *E. coli* removal efficiency, high cost-effectiveness, and no leaching. The removal mechanism is based on biosorption, and the antibacterial effect of metal coatings led to the *E. coli* inactivation at solid liquid interface [23]. In addition, the Cu and Fe-modified WTRs media produced consistent results for 18 weeks under intermittent flow conditions for both synthetic and natural stormwater runoff [23]. Incorporation of WTRs on to *Eucalyptus wandoo* biochar, resulted in 98% removal of nutrients in batch tests from synthetic storm water [52].

Wang et al. [67] with a view to enhancing the hydraulic conductivity of stormwater filtration systems, synthesized bentonite-corn-cob-WTR granules by thermal treatment. The resulting medium had a high cation exchange capacity. The thermal treatment significantly improved the Pb^{2+} and PO_4^{3-} -P adsorption capacity of the mixture but about 15% reduction in adsorption capacity was observed after granulating this mixture due to the reduction in surface area of modified medium. However, the medium showed good permeability and stable hydraulic conductivity over a 54-day rainfall period and gave 86% reduction in phosphate under column study [67].

4.3. Pollutants from groundwater

Groundwater is one of the major sources for drinking water in many parts of the world. Many groundwater sources contain different anionic and cationic pollutants such as arsenic, fluoride, iron, and manganese. Several studies recently reported the use of modified water treatment residuals (WTRs) for removal of these contaminants. These studies are summarized in Table 6.

4.3.1. Arsenic removal

Arsenic is one of the most toxic and carcinogenic naturally occurring pollutants found in to-be-treated drinking water [84,129]. Powdered raw WTRs show excellent adsorption capacity for As, but the channeling in the adsorption bed and its release from the bed

Table 6
Summary of studies on the removal of various pollutants groundwater.

Modification method	pollutant	Test conditions	Adsorbent dose	Adsorption capacity (mg/g)/ Removal Efficiency (%)	References
Nano WTRs	As	Time = 24 h	5 g/L	Raw WTR = 3.33 mg/g nWTR = 50 mg/g	[87]
Calcium alginate WTRs	As(III)	pH = 4.5	10 g/L	As (III) = 3.40 mg/g	[129]
Thermally treated WTRs	As(V)	Time = 24 h	3.3 g/L	As(V) = 2.86 mg/g	[17]
	As(V)	Initial concentration 100 mg/L		Adsorption capacity	
		500 mg/L		at 105 °C = 6.07 mg/g	
		100 mg/L		at 300 °C = 62.92 mg/g	
		pH = 6		at 500 °C = 10.39 mg/g	
Sodium alginate WTRs	As(V)	Time interval = 10–960 min	3.3 g/L	As(V) = 26.39 mg/g	[68]
		Initial concentration = 150 mg/L			
Molasses-WTR composite	As(V)	–	15 g/L	CO ₂ medium = 22.50 mg/g Air medium = 28.90 mg/g	[54]
Magnetic WTR nanoparticles	As(V)	pH = 6.6 Temperature = 25 °C Time = 60 min.	0.20 g/L	Adsorption capacity = 12.74 mg/g	[88]
Chitosan-WTR composite	As(V)	pH = 6.5, Temperature = 25 °C,	1 g/L	As (V) = 14.95 mg/g	[130]
Bentonite-WTR composite	As	Time = 24 h	15 g/L	22.19 mg/g	[65]
HCl treated WTRs	F	pH = 6.12	14.10 g/L	Max removal efficiency = 81.15%	[34]
Magnetic WTRs	F	pH = 7 Temperature = 25 °C	3 g/L	Max. removal efficiency = 85%	[131]
Thermal and acid activated WTRs	F	Initial concentration = 10 mg/L Temperature = 25 °C	40 g/L	Max. removal efficiency = 98.90%	[57]
Calcium alginate WTRs	F	Temperature = 30 °C Time = 12 h pH = 6	10 g/L	39.59 mg/g	[16]
WTRs-geopolymer	F	Concentration = 100 mg/L, Time = 24 h pH = 8.3	10 g/L	Removal efficiency = 100%	[132]
Fe WTR composite	F	pH = 6.5, Time = 1.5 h Initial concentration = 50 mg/L	10 g/L	16.09 mg/g	[3]
Alkali modified WTR	Mn	Time = 12 h	100 g/L	26.39 mg/g	[61]

lowered the overall performance of the adsorbent [17,54]. This has resulted in various modifications of WTRs. Granulation and pelletization have been applied to enlarge the size of powdered WTRs, and the process requires binders to enlarge the size [54,68]. Several researchers explored thermal modification and reported that the adsorption capacity of dried WTRs was enhanced by thermal treatment. Jeon et al. [17] found 5.4 to 8.7 times higher As adsorption capacity for thermally treated WTRs at 300 C compared to raw WTR. Ociński et al. [129] reported that at higher temperatures considerable reduction in removal of arsenic occurred due to irreversible structural modifications by the removal of surface bound hydroxyl groups in WTRs. The adsorption of As on WTRs is reported to be affected by chemisorption and film diffusion mechanisms due to the presence of natural organic matter which releases protons and becomes negatively charged and competes with the adsorption As(V) ions on Al-WTRs. Therefore, the organic matter removed by calcination resists the electrostatic repulsion and pore blocking [17].

Ociński et al. [129], attempted the entrapment of chemically and thermally pretreated WTR into calcium alginate composite beads. However, due to its low surface area, the composite showed poor adsorption capacity for As as compared to unmodified WTRs. The maximum sorption capacities of 132.13 mg As(III)/g and 76.73 mg As(V)/g were observed for unmodified WTRs while for composites these adsorption capacities were only 3.4 mg/g for As(III) and 2.9 mg/g for As(V). The adsorption of arsenic was affected by the presence of negatively charged carboxylic groups on alginate. The intraparticle diffusion played a key role in inhibiting the arsenate removal whereas two step granulating processes influenced the As (III) adsorption [129]. Another study reported modification of powdered WTRs to granule type WTRs by calcination with sodium alginate and polyvinyl alcohol. The adsorption rate of calcined granulated WTRs was enhanced by 3–21 times but a slight reduction was observed in the adsorption capacity compared to that of un-calcined granulated WTRs [68].

The pore structure of pelleted WTRs gets changed through shrinking under thermal drying because of the removal of moisture present in WTRs resulting in lesser pores at higher temperatures. To enhance the strength of pellet and to make a porous structure Kang et al. [68] performed thermal treatment under different reaction mediums of air, N₂ and CO₂. Air medium oxidizes the organic matter whereas non-oxygen media such as N₂ and CO₂ carbonizes the organic matter. Thermal treatment under CO₂ medium enhanced the removal rate for arsenic. Kang et al. [54] used molasses as a binder to create more pores and to increase the surface area. It was found that molasses greatly improved the strength of pellet, however at higher molasses content reduction in the adsorption of As occurred as the char material of molasses blocked the adsorption sites. Zeng et al. [82] used chitosan as a binder to make a novel granular composite adsorbent and found a maximum adsorption capacity of 14.955 mg/g in removing As from water because of the high specific surface area and high iron content but the adsorption capacity was less than that of raw and powdered WTRs. The As removal was also affected by the pH of solution, adsorbent dosage and the background ions. The adsorption-desorption test indicated the reusability of granular adsorbent [82]. The adsorption was hindered by the strong competition caused by co-existing anions such as H₂PO₄⁻ and SiO₃²⁻. Also, presence of coexisting background cations showed the positive effect on As removal [82].

In order to improve the strength of the adsorbent, bentonite was added to WTRs [68]. The bentonite addition was found promising in increasing the compressive strength and stability of pelleted WTRs but it led to reduction in porosity and adsorption ability caused by blocking of pores on the surface of adsorption sites by bentonite [63]. In the batch test, the maximum adsorption capacity of pelletized adsorbent was 22.2 mg As/g, which was about 40% of powdered WTR. In column tests, the pellet adsorbents showed adsorption capability similar to that of powdered WTR and commercially available adsorbents [65]. Moreover, the presence of anions such as Cl⁻, SO₄²⁻, NO₃⁻, HCO₃⁻, SiO₃²⁻ and PO₄³⁻. In groundwater reduced the adsorption of As on to the pelleted WTRs [65].

In another study, the magnetic nanoparticles of WTRs (nWTRs) worked efficiently for adsorbing Arsenic [82]. Due to their large surface area, 16 times more adsorption capacity (50 mg/g) than raw WTRs (3.33 mg/g) was achieved. Rapid adsorption was reported in the first 15 min with 89% of As adsorbed on active sites of nWTRs and after that it continued at slower adsorption rate [87]. The removal was pH dependent with lower removal at pH greater than 5. The presence of Hg and Cr reduced the As removal efficiency [87]. Zeng et al. [133] synthesized magnetic adsorbent using solvothermal process and a maximum As(V) adsorption capacity up to 13.4 mg/g was achieved. The presence of anions like PO₄³⁻ and SiO₃²⁻ significantly inhibited adsorption of As(V). Magnetic nanoparticles synthesized from WTRs showed an adsorption capacity of 12.74 mg/g for As. These adsorbents are easily separable from water with a simple hand-held magnet in 2 min. More than 90% of arsenic was removed within 60 min with an adsorbent dose of 0.2 g/L at pH 6.6 [88].

4.3.2. Fluoride removal

Fluoride is beneficial for the human body when it is present in appropriate concentrations (0.5–1.5 mg/L) in drinking water [109]. Elevated levels of fluoride are found in many groundwaters.

Various studies reported the use of modified WTRs for fluoride removal. Vinitnantharat et al. [57] prepared pelleted water treatment residuals (WTRs) by extrusion which on activation with acetic acid enhanced the fluoride adsorption capacity with the fluoride concentration reducing from 10 mg/L to 0.11 mg/L with a WTR dose of 40 g/L. The adsorption faced competition from ions present in groundwater typically containing high concentrations of Na⁺, Ca²⁺ and Cl⁻ in the range of 200–1200 mg/L and low concentrations of CO₃²⁻, SO₄²⁻, Fe²⁺ and NO₃⁻ in the range of 2–10 mg/L. The fluoride removal efficiency reduced to below 90% in the presence of nitrate and carbonate ions. In contrast, low concentration of Fe²⁺ increased the adsorption of fluoride [57]. Jung et al. [16] synthesized WTR-calcium alginate beads which showed high fluoride removal from real industrial wastewater compared to raw WTRs. In fixed bed column tests, this medium gave up to 93% removal efficiency for fluoride from real industrial wastewater which was 98% for synthetic wastewater. This difference was due to the competition for adsorption sites by co-existing ions in the real wastewater [16]. Recently, Jing et al. [131] prepared a magnetic composite adsorbent from WTRs and this material gave up to 85% fluoride removal efficiency.

Li et al. [34] compared the fluoride removal efficiency of different acid treated thermally treated WTRs. HCl acidified WTRs showed

higher efficiency with an optimum removal efficiency of 81% with a dose of 14.10 g/L at pH 6.12. They observed negative effect of the competing ions such as SO_4^{2-} , PO_4^{3-} , SiO_4^{4-} , and NO_3^- on fluoride removal [34]. Ning et al. [3] reported that the fluoride removal efficiency of raw WTRs (6.09 mg/g) was increased by 1.6 times after loading with iron (16.09 mg/g). Among co-existing anions, HCO_3^- strongly affected the fluoride adsorption.

4.3.3. Iron and manganese removal

A porous water treatment residuals WTRs based geopolymer was synthesized from WTRs with aluminum and silica content and was used for the removal of Fe/Mn [133]. This WTR-based geopolymer was calcined at 400 °C and 600 °C to obtain a strong geopolymer matrix. Geopolymer with a calcination temperature of 400 °C showed complete Fe removal after 24 h of immersion. Hydroxide ions are released from the geopolymer and form an $\text{Fe}(\text{OH})_3$ precipitate and it is coprecipitated with the $\text{Mn}(\text{OH})_2$ in the Fe/Mn solution leading to a significant reduction of Mn from the solution [132]. The approach showed good Mn removal of Mn in solution when combined Fe/Mn removal was performed as compared to the only Mn removal. Final pH of the solution played a significant role in the removal. In another study, Jiang et al. [61] reported application of alkali modified WTRs for Mn(II) removal which showed adsorption capacity of 26.39 mg/g.

4.4. Removal of nutrients

Excess nutrients (nitrogen and phosphorus) in wastewater promote eutrophication in receiving water bodies [35,134]. Water treatment residuals (WTRs) have been used to remove nutrients due to their high sorption capacity [135]. However, direct use of raw WTR on a large scale is difficult due to its fine nature. This has resulted in the use of modified WTRs for nutrient removal and a summary of recent studies is presented in Table 7.

Truong and Kim [53] compared raw and thermally treated WTRs. They reported 2 to 3 times increase in phosphate adsorption capacity (35.02 mg/g) compared to that of raw WTRs (16.91 mg/g). The organic matter removal from WTRs increased the surface area and the adsorption potential of thermally modified WTRs. Also, the positively charged aluminum oxide electrostatically attracts the negatively charged phosphates. Nanoparticles adsorbent developed from WTRs using precision milling showed 30 times higher P sorption capacity compared to raw WTRs [68]. Higher adsorption was observed in acidic conditions and a drastic reduction (from about 40 to 9 mg/g) in P adsorption was observed when pH was increased from 3 to 11 due to electrostatic repulsion between the negatively charged WTRs nanoparticles and the phosphate ions at higher pH values [68].

Wu et al. [64] reported the use of granular WTRs prepared with organic/inorganic binder. The resultant pellets, dried and sintered at 500 °C for 2 h showed P adsorption capacity of 0.9 mg/g when treating real printing and dyeing wastewater. Wet WTR beads microencapsulated with sodium alginate and Ca^{2+} as gelling agents gave better results with maximum adsorption capacity of 19.42 mg/g when compared with raw powdered WTR for P removal [136]. WTRs modified with similar technique showed remarkable increase in removal efficiency of both nitrogen and phosphorus with maximum adsorption capacities of 2.52 mg/g and 6.45 mg/g, respectively [35]. Smaller bead size, higher WTR concentrations and acidic pH conditions resulted in greater P adsorption rates and adsorption capacity. However, the maximum P adsorption capacity of granulated and calcined WTRs was found less (7.27 mg/g) as compared to raw WTRs due to reduction in surface area by granulation [15]. Ceramsite prepared by mixing WTRs with Kaolin clay and

Table 7
Summary of studies on nutrient removal by modified water treatment residuals.

Modified WTRs adsorbents	pollutant	Batch/ Column	Test conditions	Adsorbent dose/bed depth	Adsorption capacity (mg/g)/ Removal Efficiency (%)	References
WTR nanoparticles	P	Batch	pH = 3-11 Initial concentration = 150 mg/L	5 g/L	50 mg/g	[84]
WTRs-clay pellets (6:4)	P	Batch	pH = 7 Temperature = 25 °C Contact time = 24 h	10 g/L	10.2 mg/g	[80]
Thermally treated WTRs	P	–	pH = 6, Time = 48 h, Temperature = 15 °C Dose = 2 g/L		35.02 mg/g 32.99 mg/g	[53]
Sodium alginate WTRs	$\text{NH}_3\text{-N}$	Batch	Temp = 15 °C Time = 24 h pH = 5	10 g/L	2.52 mg/g Removal efficiency = 95.14%	[35]
	P		Time = 24 h pH = 5 Temp = 35 °C	10 g/L	6.45 mg/g Removal efficiency = 98.31%	
Granulated and calcinated WTRs (550 °C)	P	Batch	pH = 7 Time = 60 min	50 g/L	7.27 mg/g	[15]
		Column	Flowrate = 200 L/h	32.5 kg	Removal efficiency = >86%	
Ceramsite from WTRs	TP	Column	Time = 21 days Flow rate = 1.5 L/h	60 cm	TP = 98.6%	[72]
	TN				TN = 91.0%, COD = 85.8%	

water at different ratios gave good phosphorus removal efficiency. Adding 40% of kaolin clay and heating at 650 °C resulted in maximum P adsorption capacity of 10.2 mg/g [80]. Chen et al. [72] observed that the biofilm on WTRs based ceramsite was more stable and high removals of total phosphorus (98.6%), total nitrogen (90.1%) and COD (85.81%) were achieved. Lanthanum loaded WTR was used for adsorbing P from aqueous solutions [24,137]. The modified material could rapidly immobilize P with adsorption capacity up to 18.1 mg/g/day with 5% loading. Rapid immobilization was achieved for P removal. Lanthanum loading did not show any toxic effect on the snail *Bellamya aeruginosa* [138].

4.5. Substrate in constructed wetlands

Constructed wetlands (CW) is recognized as a green approach for treating wastewater especially from economically underdeveloped areas [139]. Selection of proper substrate is important in the construction of CWs [32]. Several studies reported the direct application of raw water treatment residuals (WTRs) in past and found poor percolation and other related problems obstructing the adsorption and reducing the removal efficiency.

Various treatments have been attempted to improve the characteristics of WTRs for their use in CWs. Wang et al. [138] synthesized heat expanded balls from WTRs and COD removal efficiency exceeding 90% was obtained along with TP, $\text{NH}_4^+\text{-N}$, TN removals of 97, 23.3 and 86.1% respectively when domestic wastewater was treated continuously for one and half years [138]. This system was found least impacted by variations in pH, temperature, hydraulic and contaminant loading rates. In another study, ceramsite substrate derived from WTRs, fly ash and additive oyster shell showed lower pollutants removal efficiency compared to haydites with COD removal up to 70% along with TP and $\text{NH}_3\text{-N}$ removals of 79 and 60% [32]. Chen et al. [72] used WTRs derived sintered ceramsite on synthetic wastewater. The ceramsite gave removal efficiency of 98.6, 91, and 85.8%, respectively for total phosphorus, total nitrogen and COD, which was significantly higher than commercial ceramsite. Zhao et al. [140], prepared ball shaped WTR-based sintered ceramsite and used as floating bed for water purification using wetlands. This study operated in four stages (each for over 40 days) and was found as an advancement over the traditional floating beds with TP, TN, COD, $\text{NH}_4^+\text{-N}$ removal efficiency of 53.2, 46.7, 78.2 and 58.1% respectively. In another study, Wang et al. [18] prepared WTR ceramsite and used it as a matrix to treat sewage in constructed wetlands. The removal efficiency obtained for total phosphorus, COD and $\text{NH}_3\text{-N}$ were 79, 70 and 60% respectively.

The previously mentioned preheated or calcined substrates used in constructed wetlands are found highly energy consuming demanding with high cost and poor recoverability. Wang et al. [76] developed a non-combustion method of developing an artificial WTR based filler substrate derived from gypsum, silica, aluminum slag and mafian stone. The combined application of gypsum and silica condensed each other in alkaline environment forming an unfired filler similar to cement showing great P removal efficiency of 95% [76]. In another study, Gao et al. [141] prepared a WTR-composite substrate using bentonite, cement, zeolite and fly ash as additives. The optimum proportions of each additive and WTRs were determined with maximum P adsorption capacity of 40 mg/g. The substrate showed best phosphorus removal in acidic medium (pH 3) [141].

Zhao et al. [142] prepared WTR coated zeolite granules, which is an advancement over the traditionally used powdered WTRs as well as high energy consuming fired substrates in constructed wetlands. The proportions of zeolite and WTRs were optimized for phosphorus adsorption. The presence of humic acid and low pH was found conducive for better phosphorus adsorption. However, CO_3^{2-} inhibited the phosphorus removal efficiency due to competitive effect [142]. Moreover, in the past few years intensive research has been done on integrating WTR based constructed wetland system with microbial fuel cell (MFC) for pollutant removal from wastewater along with electricity generation [49,143–146]. However, this field is still under developing stage and requires extensive research to obtain reliable results. Recently, Al-WTRs and pyrochite were utilized as substrate in a novel two tiered CW-MFC system which was operated for 477 days [147]. This approach simultaneously generated electricity along with COD removal up to 85% and N and P removals up to 79% and 97% respectively [147].

5. Regeneration and reuse of modified adsorbents

A good adsorbent should possess a high adsorption capacity, and easy regeneration of spent sorbent is also important for successful application of this technique [20]. To evaluate the regeneration potential of modified water treatment residuals (WTRs) in the adsorption process, a few researchers repetitively performed the adsorption-desorption process several times to restore the adsorbent back to its initial properties and to recover the adsorbent or adsorbate for effective reuse as well as to reduce the overall cost. Adsorption-desorption cycles can also be used to evaluate a material's compatibility and stability for adsorption applications. The regeneration process would result in the loss of some materials. The practical application of some adsorbent materials is constrained by this shortcoming.

Zeng et al. [82] studied the recycling of chitosan-bound WTRs in removal of As(V). Though each regeneration cycle reduced the removal rate significantly, the removal remained above 60% even after four cycles [82]. The decline in As(V) adsorption was due to the inability to desorb As completely from the sorbent as only 80% of the adsorbed As(V) could be desorbed in each cycle. No crushing or weight loss by the granular adsorbent was seen, indicating the adsorbent had good mechanical stability [82]. In a different study, WTR-based magnetic particles demonstrated excellent regeneration capacity using 1% NaOH as the regenerating agent and gave 86% of the initial As(V) adsorption capacity after four reuse cycles [133]. WTR-based magnetic particles also showed good regeneration capability by removing more than 95% As(V) throughout five regeneration cycles using 0.5% NaOH as the desorbing medium [130].

Fu et al. [35] observed reduction in removal of P and $\text{NH}_4^+\text{-N}$ with thermally treated sodium alginate WTR with each regeneration cycle. P removal was reduced from 94% to 85% in four cycles whereas $\text{NH}_4^+\text{-N}$ removal was reduced from 91 to 81% in three cycles [35]. Each regeneration cycle resulted in gradual mass and quality loss of the adsorbent [35,70]. In another study, the phosphorus

removal efficiency gradually reduced to 70% after three cycles using sodium alginate WTR [70]. Using calcium alginate WTRs, fluoride removal efficiency significantly reduced by 54% of the initial removal efficiency (98.6%) after five regeneration cycles [17]. Magnetic nano-WTR sorbent showed less than 2% release of adsorbed arsenic after four desorption cycles suggesting the stability of As-nWTR surface complexes [87]. El-Kammah et al. [86] found excellent results with 88% removal efficiency for indigo carmine dye even after 5 regeneration cycles of nWTRs using deionized water as the desorbing agent.

In another study, Jing et al. [131] found that the Fe/Al composited acid treated carbonized WTRs showed in high adsorption efficiency for meeting the standards for safe drinking water even after 6 regeneration cycles. This effective regeneration was possible by the use of methanol as regenerating agent, which can be reused for a long period of time [131]. For thermal and acid treated WTRs, five consecutive adsorption/desorption cycles were successfully carried out and the removal rate for Mo(VI) was still higher than 84%, and the desorption rate was stabilized at 88% [20].

The reduction in adsorption capacity observed with adsorbents is mainly because of the incomplete desorption of pollutant from

Table 8
Comparison of different modification methods.

S. No	Modification method	Advantages	Drawbacks	References
1.	Thermal treatment	<ul style="list-style-type: none"> Improves the stability and strength of pelleted WTRs. Enhances the adsorptive power of the materials and improves the porosity and surface area by inter layer spaces collations. Upto 100 times more surface area increase compared to powdered dried WTRs. Improves the adsorption kinetics. Removes organic matter from WTRs. 	<ul style="list-style-type: none"> Introduces irreversible changes in structure. Transforms amorphous structure to crystalline at high temperatures. Results in surface-bound hydroxyl removal High energy cost Melting and crystallization behavior of Al/Fe particles, as well as the reduction of active adsorption sites and SSA, reduces adsorption in sintering. Releases accumulated gases generated from the decomposition of organic/inorganic matter 	[53,54,68,73,129,148]
2.	Granulation	<ul style="list-style-type: none"> Increases the size of adsorbent, leading to convenient transportation, storage, and utilization. Can be used in fixed beds, filter media and column tests. Can be easily separated and recovered from aqueous medium after adsorption. Regeneration of spent sorbent can be easily done. Flexibility in adjusting the size. Reduces bio-accessibility of heavy metals 	<ul style="list-style-type: none"> A lower adsorption capacity compared to powdered raw WTRs. Requires binders to aggregate particles. Reduces the adsorption rate, and it is essential to find optimal fixed-bed parameters 	[54,68,82,136]
3.	Magnetic particles	<ul style="list-style-type: none"> Reduces hydraulic retention times, improve volumetric loading rates, thus reduces the reactor size requirements. Simple and easy operation Better stability and high magnetic strength Easy separation from water by placing an external magnetic field 	<ul style="list-style-type: none"> Higher cost 	[89,131]
4.	Acid treatment	<ul style="list-style-type: none"> Development of a positive surface charge due its protonation which in consequence is favorable for anionic species adsorption. Leaching of cations increases the porosity and increase in surface area Enhances the activity of oxygenated aggregates and increases porosity of the adsorbent 		[6,20,148]
5.	Nano particles	<ul style="list-style-type: none"> Does not require additional purification steps, but instead directly creates small, clean, and active nanoparticles. Increases adsorption capacity up to 30 times as compared to raw WTRs 		[84]
6.	Composites	<ul style="list-style-type: none"> Low-cost process with use of locally available waste materials Easy to prepare 	<ul style="list-style-type: none"> Release of sorbed pollutants under anoxic conditions 	[28]
7.	Surface modification	<ul style="list-style-type: none"> High efficiency in removing targeted pollutants. Cost-effectiveness, local availability 	<ul style="list-style-type: none"> Leaching of metals may occur. High cost of energy and chemical reagents 	[23]

the WTRs. The adsorption sites of modified adsorbent become saturated, and it cannot continue to effectively adsorb the pollutant. However, according to Wang et al. [115], the regeneration or recycling of thermal and acid activated WTRs is difficult when used for the removal of phosphorus. TiO₂ composited WTRs regenerated with UV light showed reduction in methylene blue removal efficiency from 85% to 70% after four cycles. This reduction was more significant when the composite was unregenerated [63]. In another study, using acid activated TiO₂-WTR composite, Rhodamine-B degradation efficiency was reduced to 85.65% from its initial value 96.85% after five cycles [26].

6. Comparison of different modification methods

As discussed in Section 2, several different methods have been used for modifying water treatment residuals (WTRs). Each method has its own advantages and drawbacks, and these are summarized in Table 8. Thermal treatment, in general, enhances the adsorption capacity of WTRs and is an easy method. However, at high temperatures, the amorphous WTR is converted to crystalline form which reduces the adsorption capacity. Hence, to strike a balance between crystallization and decomposition of organic matter, optimum temperature is a crucial factor in heat treatment [17]. Ociński et al. [129] observed reduction in removal of arsenic due to some irreversible changes in the structure of amorphous WTRs at temperature ≥ 200 °C and crystalline formation started taking place which explicitly led to decrease in arsenic removal.

The strength of an adsorbent is inversely proportional to its pore size [65]. Larger particles with pore structure require longer time for pollutants to be transported into the deep pores from the surface [65]. In some studies, increasing the size of adsorbents led to reduction in adsorption capacity compared to the small sized adsorbents. The slower adsorption kinetics demands longer contact time to achieve adsorption [65]. Similarly, Fu et al. [35] observed that modification with sodium alginate significantly increased the adsorption potential of WTRs. The removal efficiency of NH₄⁺-N and PO₄³⁻-P increased to 96.42% and 98.17% respectively for thermally treated WTRs from 22.34 to 77.13% with raw WTRs [35]. The removal efficiency further reduced significantly when thermally treated sodium alginate WTR was used.

The sintering leads to continuous weight loss until the removal of free and adsorbed water and oxidation of organic matter are complete [79]. Hence, high temperature sintering is found to be a high energy and time-consuming process. It transforms the amorphous WTRs to crystalline form at very high temperatures leading to reduction in adsorption capacity. Sintering at high temperature (1000 °C) also causes significant impact on shrinkage due to high weight loss and the densification of ceramic matrix [79].

Different types of granulation methods have been used for modifying WTRs. This method increases the size of the adsorbent, leading to convenience in transportation and storage. Also, the granular form of WTRs can be conveniently used in fixed bed filter medium. Further, they can be easily separated and regenerated after use. However, this technique leads to reduction in surface area which potentially reduces the adsorption capacity.

Gel entrapment and natural curing methods are tested as alternatives to the high energy consuming sintering process. The natural curing method requires further research on the metal leaching and bio-accessibility issues [76]. The repeated freeze–thaw process also needs significant energy and a chemical binder to form the pellets. Energy and time requirements (almost similar to sintering method) are still the big concerns. Two types of granulation techniques, namely wet granulation with liquid and dry granulation without liquid are used for modifying WTRs [149]. Majority of the literature documented wet granulation whereas a few studies used dry granulation [54]. The dry granulation is a superior method in which no additional water is required and inherent moisture is sufficient to make pelleted WTRs. In contrast, in wet granulation method, WTRs are firstly dried in oven, crushed and mixed with binders, and require more water and energy.

Wood mulches coated with Al and Fe-WTRs serve as effective sorbent exhibiting significantly better removals for metals and phosphates than uncoated mulches or WTRs alone from stormwater runoff. However, for Fe-WTRs, Fe (III) (hydr)oxides were reduced to more soluble Fe(II), which leads to the release of sorbed contaminants back to the solution under anoxic conditions which was not seen in the application of Al-WTRs.

7. Summary and future research needs

While a large number of studies have been reported on the use of water treatment residuals (WTRs) for removal of different contaminants from water/wastewater, their commercial and large-scale application is limited due to their low adsorption capacity and due to the difficulty to separate out the powdered adsorbent from the treated effluent. This has led to different modifications of WTRs in the last decade. Modified WTRs has shown improved adsorption capacity over raw WTR in the removal of different pollutants from aqueous environment. The modifications have led to improved material characteristics resulting in increased adsorption capacity as well as easy regeneration of spent adsorbent. As discussed in this paper, different classes of pollutants such as dyes, nutrients, and pollutants in storm water and groundwater have been successfully treated by modified WTRs. While a number of methods for modification of WTRs have been reported, each method has its own advantages and drawbacks which are discussed in the paper.

More studies should be carried out on the characteristics of WTRs. The characteristics of WTRs vary widely from treatment plant to treatment plant and also seasonally due to the changes in the source water quality and the treatment processes used. The characteristics of WTRs play an important role in determining their applications and modification methods. Most countries do not have regulations regarding disposal and reuse of WTRs. Proper regulations should be framed so as to encourage the reuse of WTRs in different forms.

It is found that while some modifications improved adsorption capacity of WTRs, some other methods reduced their capacity to remove different pollutants due to among other reasons, reduction in surface area. For example, while granulation is advantageous with respect to easy separation of spent medium, this method gave poorer adsorption capacity compared to that of raw WTRs.

Modifications methods with all desirable properties should be identified and developed. Most of the investigators used laboratory scale batch tests using synthetic water/wastewater and very few studies utilized long-term column tests to evaluate the potential of modified WTRs. The true potential of a medium can be identified only with long-term studies employing real wastewater. Further, pilot-scale and field-scale studies are lacking in literature. More tests to determine the optimum operating conditions are also needed.

Various modification methods have their own advantages and drawbacks. A comparative evaluation of these methods should be conducted in terms of cost-benefit analysis for a particular application which will identify the best modification method for this application. The field-scale use of a medium depends on its recyclability. More studies are needed for identifying the method for regeneration.

Not many studies have been reported on the effectiveness of microbial removal by modified WTRs. Similarly, though many studies have been reported on the use of raw WTRs for heavy metal removal, only few studies have been reported on the use of modified WTRs for their removal. Leaching of metals and other components during the use of modified WTRs has been reported in the literature. Methods should be identified to reduce this. Most of the studies reported in the literature used aluminium-based WTRs presumably due to their abundance. More studies should be carried out on the use of iron-based WTRs. Further research on methods for disposal of used WTRs is also needed.

Several innovative applications of modified WTRs have been suggested recently. For example, Laib et al. [25] and Grassi et al. [150] recently developed low-cost photo-Fenton catalysts from WTRs and used for removal of dyes. Nguyen et al. [151] used WTRs as a catalyst for the treatment of real dyeing wastewater by electro-Fenton process. Zhu et al. [152] synthesized a novel bimetallic catalyst from Fe-WTRs which exhibited superior catalytic performance in the degradation of ciprofloxacin. More studies on such applications should be conducted.

Author contribution statement

Shubhani Sharma: conceived; analysed and interpreted the data; contributed analysis tools and data; wrote the paper.

M Mansoor Ahammed: conceived; analysed and interpreted the data; contributed analysis tools and data; wrote the paper.

Data availability statement

Data included in article/supp. material/referenced in article.

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.

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