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Review Article

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Hydrochar for Industrial Wastewater Treatment: An Overview on its Advantages and Applications

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Abstract

Water pollution is one of the environmental challenges facing the world society. Consequently, the pollutants both domestic and industrial wastewater are identified as an environmental threat. Hydrochar (HC) appears as a cost-effective and eco-friendly solution to this environmental threat. HC is the solid produced from the wet pyrolysis process for biomass that is rich in carbon in a sub-critical liquid phase, called the Hydro-Thermal Carbonization Process (HTC). This review aims to address the possibility of using HC as the most effective solution to the industrial wastewater. HTC has proven a greater yield than dry pyrolysis (30%-60% wt). To date, HC is listed as a promising lower-cost alternate adsorbent for removing wastewater pollutants. In Egypt for example, only few studies have been published investigating the properties of HC and its environmental applications. In this review, we will shed light on the preparation, characterization, and previous studies on the development and recent applications of HC. In addition, we will discuss the challenges to produce HC at a commercial scale. To the best of our knowledge, there is only few research studies addressing the HC production in the Middle East countries. Therefore, the door is still opened for more research on developing production techniques on HC from different biomass, and implementation in various environmental applications.

Keywords: Hydrochar • HTC • Industrial pollution • Wastewater • Eco-friendly • Adsorption • Different approach

Introduction

Water pollution is a crucial environmental challenge facing all societies. Thus, pollutants from sewage and/or industrial wastewater are a real threat to the environment [1]. Many wastewater sources contain significant levels of organic and inorganic pollutants. Physicochemical, and biological characteristics of raw water and treated water are essential to guarantee their disposal safety, whether in the aquatic or in the desert [2]. Among several contaminant removal techniques, liquid-solid adsorption emerged as the best efficient method in terms of removing several types of pollutants [3].

Leaching pollutants into groundwater from sewage or industrial water cause serious health problems to biological systems. It is worth mentioning that heavy metals, such as aluminum, arsenic, cadmium, iron, manganese, lead, and zinc, cause serious health effects if found in drinking water at levels higher than permitted [4].

The climate change mitigation approach is recommended by the Intergovernmental Panel on Climate Change (IPCC) by planning to decrease anthropogenic emissions by switching to eco-friendly processes. One of the great examples of the eco-friendly processes is carbon production using HTC [5].

As recommended by the Intergovernmental Panel on Climate Change (IPCC), it is a highly demanded task to scientists finding safe and eco-friendly pathways based on ideas from green chemistry. In the same line applying the recommendations of IPCC, bio-sorbents HC is an outstanding tool to achieve the goal [6]. No doubt, this will have a positive impact on ecosystem protection in terms of using an eco-friendly process for removing water pollutants.

The origin of the biomass used for the elimination of pollutants is the key factor that needs to be considered when designing the techniques, which based on green chemistry. If the biomass contains an agriculture/industry waste or a simply cultivated microorganism, green chemistry works to minimize both the environment and economy. Additionally, adsorption could generate water of high quality, as well as it is an economically viable and technologically straightforward process. Consequently, adsorption processes are essential in the purification of water, wastewater disinfecting, and numerous different regions of separation and recovery applications [7]. While traditional pollutant reduction adsorbents are favored for such commercial products, their widespread industrial use is limited by their considerable cost [8]. Unlike commercial products, biosorbents provide a costly-effective platform due to their natural sources and highly competence in removing metal ions from polluted water. These biosorbents contain agricultural and biological products, so that they are known as HC [9].

HC is the solid produced from the wet pyrolysis process for biomass that is rich in carbon in a sub-critical liquid phase, called the hydrothermal carbonization (HTC). The HTC process commonly employs relatively low temperatures (150-350°C), and it can be operating directly to wet feedstocks, such as wet animal composts, biomass, and algae [10,11]. HTC has been reported to be more dynamic and more efficient than dry pyrolysis [12]. Also, it has stronger sympathies for polar and nonpolar organic pollutants than the biochar produced by thermal processes [13]. HTC is an environmentally friendly process in which no harmful chemical waste or by-products are generated [11]. Those properties make HC a potential choice as an inexpensive adsorbent for pollutants removal from wastewater [14]. Han et al. has reported that HC made by HTC of all fruit peels, contain polar functional groups, as of -OH, $-NH_2$, and -COOH found on the surface [6]. Few research tested the adsorption properties of aqueous pollutants on HC [13].

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For all the previous, the main objective of this review is to highlight the industrial wastewater treatment in Egypt using adsorption techniques with a focus on HC as a green adsorbent.

Literature Review

Hydrochar research history

The HC related publications in environmental science are shown in Figure 1. It depicts the significant increase in the number of publications that started in 2014 and went exponentially until 2018. We also screened the HC publications ratio in different research fields, as illustrated in Figure 2.

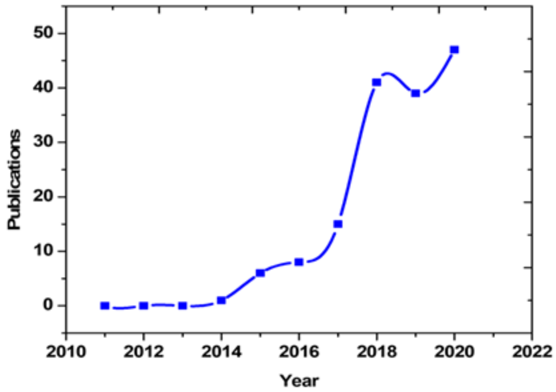

Figure 1. Publications on hydrochar in environmental science from 2011 to 2020.

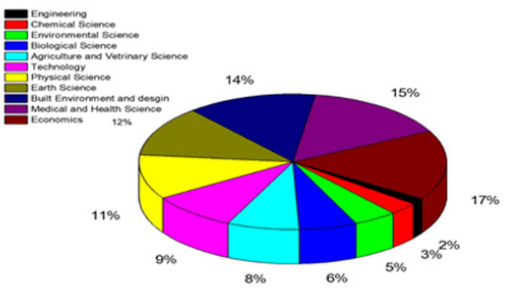

Figure 2. Publication ratios of hydrochar in many different research fields.

In 2010, AVA-CO_2 company made the first step in an industrial application of HTC by starting up the world's first commercial production scale HTC demonstration plant in Karlsruhe, Germany [5]. Likewise, the Middle East countries recently started to follow the German model in this field. In Egypt for example, HC adsorbents with highly functionalized surface active sites were developed from cellulose and lignin that made of rice straw *via* HTC at 180° C for 20 hours, followed by carbonization process at 500°C for 2 hours [15].

Water pollution overview

World Health Organization (WHO) has revealed that accidental occupational poisoning by heavy metals and pesticides are severely influencing many health problems. Both are ranked at the most massive hazard scale to natural environmental safety. The primary sources of heavy metals to our water are included mining, fertilizer, sewage, irrigation, sludge reuse, and smelting. Mining and smelting are the main sources of heavy metal contaminations that leach out the soil through waste transportation, wastewater irrigation, sludge reuse applications, and atmospheric deposition [16]. "Sewage irrigation" describes the utilization of sewerage discharge for irrigation uses without any treatment methods or with only solids removal, ordinarily including toxic substances. In Egypt, the untreated sewage outflow is taken from small towns to irrigate farm fields directly without any pretreatment. As a result, areas that are receiving sewage irrigation will be at a very high level of contamination by heavy metals, as mercury (Hg), lead (Pb), and cadmium (Cd) [17]. The accumulation of heavy metals into surface water and underground water not only has a serious effect on food safety but also shows a negative impact on health and society [18].

Pollutant types and removal techniques

Pollutants can be classified into three main categories: biological, inorganic, and organic pollutants, according to their nature and origin, as shown in Figure 3.

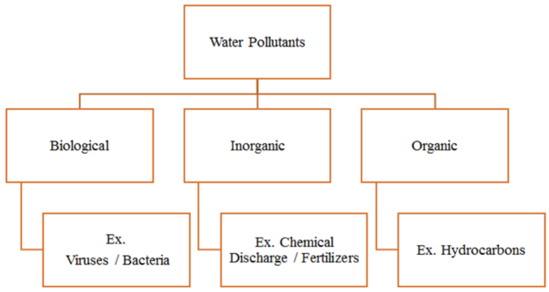

Figure 3. Schematic diagram illustrates the different types of water pollutants.

Currently, we are in the Pollutants removal age and not surprising that it has been a widespread effort to reduce pollutant discharges. Several techniques are presently available to treat domestic and industrial wastewater, containing biological, chemical, and physical processes. In many cases, these methods reduce pollutants significantly; however, with recalcitrant compounds, the discharge criteria obligatory requirements cannot be achieved. Discharge of inadequately treated effluents will cause severe ecological pollution and harm our environment [19].

Many techniques have been developed to remove pollutants from wastewater, such as:

- Adsorption [20].
- Coagulation/Flocculation [21].
- Chemical precipitation [22].
- Electrolysis [23].
- Ion exchange [24].

All these techniques have been used to remove different pollutants from water and wastewater. However, all of them do not have the advantages of HC. In this paper, we will focus only on the adsorption technique for industrial wastewater treatment as a platform for HC.

Adsorption: Adsorption is when substances in gaseous and/or liquid phases are trapped on a solid substrate known as adsorbent. Water treatment adsorbents have two main types of adsorbents: natural origin or a manufactured process. There are many adsorbents, such as biopolymers, clay minerals, oxides, or zeolites. We can group these adsorbents into carbonaceous adsorbents, oxidic adsorbents, polymeric adsorbents, and zeolite molecular sieves. Carbonaceous adsorbents are the most widely used adsorbents in water treatment. Polymeric adsorbents made by copolymerization of nonpolar or weakly polar monomers showed approximately the same adsorption properties as activated carbons. At the same time, oxides and zeolites are mostly used as stronger hydrophilic surface adsorbents [25].

Choosing the right adsorbent depends on the type of water that needs to be treated and the suitable technique that might be applicable. For example, activated carbon is the most suitable adsorbent in the swimming pool, drinking water, wastewater, industrial wastewater, and groundwater. In contrast, aluminum oxide and some polymers are the most common adsorbents in wastewater and industrial wastewater [25].

To date, adsorption is the most accredited method that has been accepted globally as an eco-friendly technique for wastewater treatment. Undoubtedly, choosing the appropriate adsorbent is the crucial point in wastewater treatment using the adsorption technique not only to ensure the highest efficacy of waste removal but also to select the cost-effectively and eco-friendly adsorbent. HC has proven to be the best-selected adsorbent in terms of its effectiveness in large-scale adsorption [26].

Types of biomass adsorbents

The significant barrier in wastewater and industrial wastewater treatment is the synchronized presence of many different forms of pollutants, such as phenols, dyes, pesticides, heavy metals, and pharmaceuticals. Adsorption is the most promising method for wastewater treatment. For economic considerations, researchers should turn their attention to low-cost adsorbents, which is called green adsorption. These low-cost adsorbents derived from:

• Agricultural sources (fruits, vegetables, and foods).

• Agricultural residues and wastes.

• Low-cost sources (activated carbons after dry or wet pyrolysis of feedstocks).

Fruit peels and raw leaves: For many years, various fruit peels have been utilized as an adsorbent platform for pollutants removal from domestic and industrial wastewater. Leaf adsorbents are among the most investigated biosorbents for metal ions removal because they are: available, low-priced, eco-friendly, and have high sorption capacity. However, it has been often ignored because it possesses low mechanical strength [6]. Even though many natural materials can bind heavy metals, only those with sufficiently high metal-binding capacity and high selectivity are the most favorable in a full-scale biosorption process.

Activated carbon: Activated carbon (AC) is produced from coal, coconut shell, peat, and wood; AC has a wide surface area and a high porosity, usually in the range 600-1200 m^2/g. AC in all forms "powdered activated carbon (PAC) and granular activated carbon (GAC)" are commonly used in drinking water and waste water removal for many decades. Adsorption by AC, GAC or PAC, is known to be the best technique possible. They are generally used to remove traces of organic pollutants from surface water. Interestingly, Microcystins (MCs) are successfully captured by AC with a removal level of up to 99% [27].

In Egypt as an example, AC is successfully used for Fe (III) and Mn(II) ions elimination at El-Umum drain water, Alexandria coast. Extensive studies have been made during the last ten years to develop low-cost with high adsorption capacity for metal ions removal from wastewater [28].

Hydrochar: Hydrothermal Carbonization is an innovative thermal conversion method, under a quite low temperature (180°-350℃), of waste streams to valuable products known as HC. During this method, energy is preserved within a solid product (HC) to take full advantage of the added value of regaining products. Cellulose is the most abundant natural raw material and one of the elementary ingredients of lignocellulosic materials, which can produce HC [29].

A significant increase in HTC carbon yield has been noticed with a longer time. It can be described by polymerization of soluble fragments in the liquid phase that leads to precipitation of insoluble solids [30].

The conventional and microwave methods vary in terms of the amount of transferred heat. For the conventional way, the heating for biomass occurs in a sealed container under pressure from 60 to 100 bars in the presence or absence of a catalyst. However, the conventional preparation method has a range of disadvantages, like heat or energy loss, unregulated process conditions, unwanted side reactions leading to lower yields, superficial, nonselective heating, and more extended residential periods. Microwave heating was recommended as an alternative method to traditional heating to address those deficiencies. In a microwave, the material is heated through the molecular interaction with the waves of electromagnetic [31]. Microwave heating is less expensive, quicker, and a more vitality proficient strategy for setting up various substances, such as HC. It also offers regular heating, which results in a considerable reduction in reaction time comparing to the previously heated method due to the direct dealings of the electromagnetic field with biomass [32].

Hydrochar as an environmentally friendly pathway

HTC is the replacement process of the pre-drying feedstock. Therefore, non-conventional biomasses should be at the forefront of HC production. Animal litters, food wastes, and other high moisture content feedstocks are more favorable to be used in HTC instead of long-established dry thermal pre-treatments, such as pyrolysis [33].

The HTC method introduces a range of advantages over traditional dry heat treatments like slow pyrolysis, enhancing process efficiency, and economic performance, particularly processing wet feedstocks without pre-drying. The temperature is 150 to 350 °C and using water as a solvent in the reaction medium with self-pressure. The char produced from both processes exhibits significantly different physicochemical properties that influence their potential applications, including carbon sequestration, soil improvement, bioenergy production, and wastewater pollution treatment. Compared to char produced by pyrolysis characteristics, the HC produced from the HTC process has favorite properties. It contains plenty of oxygen-rich functional groups, weak acidity, low carbonization levels, and porosity. As then, great attention was given to preparing HC to improve its characteristics for environmental advantages and activate environmental remediation [34].

Difference between hydrochar and biochar: The hydrothermal carbonization process of biomass is the way to produce HC. In this process, the biomass is treated by hot compressed water instead of drying conditions. HTC process has several advantages rather than the traditional dry-thermal pre-treatments that supplied the biochar. The yielded char from both processes shows significantly dissimilar physiochemical properties that affect their common applications, as for example, bioenergy production, soil enhancement, and wastewater pollutants removal. The reaction mechanisms of the HTC processes proved that HC (HTC char) is a valued supply; it is better than biochar. This is because it holds alkaline earth content and reduced alkali metals. However, its effective usage would require additional research and investigations in terms of the biomass feeding against pressure; properties and relationships between feedstock structures, HC features, and method conditions; development in the manufacture technique(s) for improvement in the physicochemical performance of HC; and the advance of a numerous range of processing choices to produce HC [35].

Hydrothermally treated biomass could not just be utilized as a fuel or a fertilizer but also can be converted into valuable items such as activated carbons [36]. The HTC biomass and the activated carbons were categorized and characterized, utilizing a few techniques. The biomass was carbonized to a different degree during the aqueous treatment, which relied upon the unique natures of the biomass. The HTC biomass and the activated carbons were categorized and characterized using numerous methods. The HTC biomass was activated into PACs by both physical methods, using CO_2, and by chemical methods, using H_3PO_4. Activated carbons with embedded iron oxide nanoparticles were synthesized through HTC, followed by CO_2 activation. These composites have high surface areas and represent a strong magnetism; besides its ashes can be separated from the solution by applying a magnetic field [37].

Chemical structure of hydrochar: Successful hydrolysis and dehydration process of biomass converts it to HC with wealthy oxygenated functional groups (C-O, COO-, C=O, etc.). This HC can be used as an adsorbent for heavy metals removal from wastewater. The content of oxygenated functional groups mostly depends on the process conditions and the types of feedstock. The HTC of saccharides as glucose, starch, sucrose, and dehydrated banana peels can lead to the formation of HC with rich oxygenated functional groups [29,38].

Hydrochar preparation: Biomass application has received more attention for high-density solid fuels production. Using cost-effective and accessible precursors *via* an eco-friendly method is a crucial track. Pyrolysis and hydrothermal carbonization (HTC) are well-recognized technological routes suitable for manufacturing solid biofuel using conventional or microwave techniques. Microwave heating is an easier and more effective heating technique than conventional heating [32]. Hydrothermal processing using microwave has been applied to modify two bismuth oxides: $MgBi_2O_6$, $ZnBi_2O_6$ with the uncommon oxidation state of Bi5+ be prepared under restricted hydrothermal conditions. The study proved that microwave hydrothermal processing for dissolution-precipitation reactions and soft-chemical method has many advantages more than conventional hydrothermal processing in terms of the reaction kinetics [39].

Microwave-induced hydrochar as an efficient production method: Green waste (GW) is an excellent source of cellulose and hemicellulose. Developing an alternative and a sustainable method to recycle GW is of high interest for various industrial applications. Microwave hydrothermal carbonization (MHTC) parameters, temperature-time-liquid-to-solid percentage can be optimized to achieve the best surface properties of HC. The calorific value has usually evaluated the HC properties. The results showed that HC with the best properties could be obtained at 190°C for one h and 8:1 as a liquid-to-solid ratio. These findings of the best GW-HC open the door for further research applications, as a fuel source and as a low-cost adsorbent [40].

Different methods of microwave used for cellulose hydrothermal carbonization have been studied, and their first-order kinetics model based on carbon contents were established. Chemical analysis revealed that HC with the microwave technique could be produced at 5-10 lower times than other methods. Besides, the kinetics study showed that the major mechanism of the reaction depends on the difference in the reaction rates. Finally, the improvement effects of microwave heating will be doubled under both solid and soluble pathways; therefore, microwave-assisted hydrothermal carbonization is the most e interesting technique for carbon-enriched HC production [29].

The methodology parameters of microwave-supported hydrothermal carbonization (MIHTC) assume a critical role in the HC yield. The reaction temperature, reaction time, particle size, and biomass to water proportion can influence the HC yield. Further, the optimum conditions for produce HC from rice straw have been portrayed and was observed to be the temperature 180°C, the reaction time 20 min, the biomass to water p

roportion to be 1:15 (w/v) and a 3 mm particle size, yielding 57.9% of HC [41] (Figure 4).

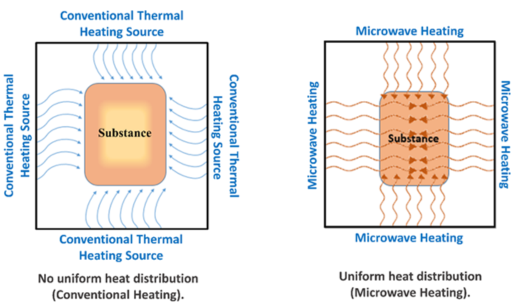

Figure 4. Difference between conventional and microwave heating.

Generally, the HTC product chemical structure is more like natural coal than dry pyrolysis products. Among numerous applications of HTC products, the main research flows in water treatment have been assumed to heavy metals removal. It was notified that HTC could remove heavy metal ions from water without an extra activation process, which is a critical requirement for conventional dry pyrolysis products. HTC formed resources with great functional surface area *via* the integration of small minimal quantities of carboxylic groups holding organic monomers in the carbon structure. HTC adsorbent supplied higher capacities than normal synthetic ion exchange resins and other types of sorption materials [30].

The diameter of the significant pathogenic virus in waterborne diseases ranges from 20-100 nm (WHO, 2008). Concerning this size, HTC materials can offer (mesopore 2~50 nm/microporous>50 nm) adsorption sites for viruses' removal from water that can be simply implemented by advanced technology with low cost [30].

Conventional method for hydrochar production

Traditional hydrothermal carbonization takes place in a conventional oven. The preparation may be carried using the feedstock like Prosopis Africana shell or banana peels as biomass into a Teflon-sealed autoclave mixed with deionized water. The autoclave was adjusted at 200°C for 2-4 hr. After the HTC process, the autoclave was cooled down to room temperature. The expected HC was filtered out with filter paper, washed several times with deionized water until a neutral pH was achieved. Then it was dried at 80°C for approximately 16 h and stored in the desiccator for further use [42].

It was found that the ratio of C/O content and C/H content increase as HTC temperature increases above 200°C; besides, deoxygenating reactions enhance the carbon content [34].

Characterization and surface modification of hydrochar

It is essential to characterize the HC once prepared to confirm the expected properties. An elemental analyzer can measure elemental compositions of carbon, hydrogen, nitrogen, oxygen, and sulfur. Mass yield and higher heating value can be calculated besides the estimation of ash content. Currently, C13 CP/MAS solid-state NMR technique has been reported for the comparative analysis of the produced HC and the original micro-crystalline cellulose. Additionally, the presence of furfural is confirmed by Scanning Electron Microscopy (SEM). The most common techniques in HC characterization are Transmission Electron Microscopy (TEM) and SEM [43]. It is worth mentioning that the composition of HC consists of carbon-microspheres in the core-shell as shown by the morphological techniques [34].

FTIR analysis is utilized to study the functional groups of the HC surface. The FTIR spectra in the range of 4000-550 cm-1 for both feedstocks, old-fashion HC, and modified HC can confirm any chemical interaction or any functional group changing. Moreover, it can be used to confirm the successful preparation of HC [43]. Additionally, XRD analysis of HC and modified HC show the crystalline and amorphous phases present in the samples.

In the last decade, many studies have been made to investigate the possibility of using the HC as an eco-friendly adsorbent agent, as summarized in Tables 1 and 2.

The main objective of the surface modification process is to improve the biosorption efficacy. The most effective and widely used method of biomass surface modification is chemical modification [44]. Recently, surface modification of HC is of paramount importance in environmental applications. The common methods of HC's surface modification are chemical activation or physical surface modification. The chemical activation can be occurred by adding chemicals directly into the reactor when hydrothermally carbonizing the feedstock or by soaking the HC in an activation solution after the HTC process. For chemically soaked HC, it may be used as-is after washing with DI water, or it may be extra activated by heat in an inert environment. Chemicals that commonly used for this process include H_3PO_4, $ZnCl_2$, and KOH. The compounds that they formed with the char are dehydrated, caused deposits inside the matrix of the char that is porous. The chemicals used for this activation are dehydrating agents, which resulted in water leaving the matrix structure. This leads to the formation of the mesoporous and micro-porous nature of the HC [11,45]. As shown in Table 1, the surface enactment of HC with potassium hydroxide and its applications were listed. HC with less aromatic structure and thermal recalcitrance, low surface area, and poor porosity will be unfavorable HC for environmental applications and energy storage.

Feedstock	Activation method	Surface area $m^2 . g^{-1}$	Specific performance
Potato starch, cellulose, and eucalyptus sawdust	KOH	1260-2850	CO_2 capture 2.9-4.8 mmol g^{-1}
Lignocellulosic	KOH	1080- 2510	Adsorbent for 1-butyl-3-methyl imidazolium chloride, 0.171 mmol g^{-1}
Cellulose		20	Adsorbent for 1-butyl-3-methyl imidazolium chloride, 0.171 mmol g^{-1}
Lignin waste	KOH	1157- 1924	H_2 uptake (3.2 - 4.7 wt. %)

Table 1. Hydrochar surface modifications and their impacts on performance.

In contrast, HC with high aromaticity, high surface area, good porosity is the most favorable for adsorption applications. Likewise, surface modifications of HC can be optimized to yield the best quality of the favorable HC. Therefore, HC can be turned into a promising material for ecological remediation and energy storage. Recently, researchers have reported that H_2O_2 modification can enhance the oxygen-containing functional groups, mainly carboxyl groups, on the HC surfaces. This leads to an enhanced sorption ability more than 20 times of untreated HC [46].

While in physical activation, the biomass is carbonized in an inert atmosphere then activated with a slightly oxidizing gas such as CO_2 or steam at temperatures higher than 800°C. However, the physical techniques for activation require more energy than chemical activation. It is expected to produce HC with higher surface area and pore volume in most circumstances. For example, the synthesized activated HC (from hickory and peanut hull feedstock) under CO_2 gas, the surface areas increased from 7, 380 m^2/g to 1300 m^2/g after activation. The improvement of activated HC properties will considerably be depending on the operating temperature [11].

Advantages, limitations, and potential applications of hydrochar

Different advantages can trigger the production of HC based on several aspects. In Egypt for example, the availability of raw biomass from agriculture waste, such as fruit peels, is the first one on the list among these advantages. The annual production of fruits is 12 million tons, according to Egyptian agriculture ministry data [47]. Weather in Egypt is a positive point that adds another advantage to HC production, in which solar power can be used to provide the required heat to produce the HC or using direct sunlight in the summer season to dry the feedstock. Besides that, the availability of alkalis and acids in Egypt can reduce the cost of the activation process.

Feedstock	HTC temp.ºC	Modification	Characterization	pollutant	Removal efficacy
Peanut hull	300°C for 5 h at a pressure of about 1000 psi	10% H_2O_2 solution for 2 h at room temperature	XPS, FTIR, pH, Bulk density, surface area	Pb^{2+}	22.82 mg/g
Peanut hull	300°C for 5 h at a pressure of about 1000 psi	10% H_2O_2 solution for 2 h at room temperature	XPS, FTIR, pH, Bulk density, surface area	Cd^{2+}, Cu^{2+} , Ni^{2+}, Pb^{2+}	0.21, 1.22, 0.07 and 16.45 mg/g respectively
Peanut hull	300°C for 5 h at a pressure of about 1000 psi	Without modification	XPS, FTIR, pH, Bulk density, surface area	Pb^{2+}	0.88 mg/g
Rice straw	573 K and maintained at this temperature for 30 min, then washed with ethyl acetate and distilled water, and finally dried for 4 h at 373 K.	chemical activation by K_2CO_3 followed by hydrothermal co-precipitation reaction to produces magnetic hydrochar	Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD), X-ray photoelectron spectroscopy analysis (XPS), Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), and transmission electron microscopy (TEM).	Triclosan (antimicrobial agent)	303 mg/g.
Salix psammophila	300°C. washed with distilled water and ethyl acetate and dried at 100°C for 2 hours	Chemical activation with (K_2CO_3) for 24 h under continuous agitation (200 rpm). Then dried at 100ºC for 4 h	the pH of Zero Point Charges, N_2 adsorption-desorption isotherms,	malachite green	476 mg/g.
Peanut hull	300°C for 6 h, washed, then 70 °C for 24 h	Without modification	Elemental Analysis, Surface area, pH, Zeta potential, thermal stability	Pb^{2+}	7.46 mg/g
Peanut hull	300°C for 6 h, washed, then 70°C for 24 h	Without modification	Elemental Analysis, Surface area, pH, Zeta potential and Thermogravimetric analysis (TGA)	Methylene blue	38.55 mg/g.

Hickory	200°C for 6 h, washed, then 70°C for 24 h	Without modification	Elemental Analysis, Surface area, pH, Zeta potential and Thermogravimetric analysis (TGA)	Methylene blue	35.04 mg/g.
Sawdust		$ZnCl_2$ and iron salts	Elemental composition, BET surface area, XRD, FTIR, XPS, SEM,	organic pollutants (roxarsone)	Max. 416.7 mg/g.
Coffee waste	HTC at t 200°C for 6 h. For hydrochar loaded iron nanoparticles: 5 mL 5 M HCl, 40 mL water, and 5 mL ethanol were mixed in a 100 mL flask. Then, 13.32 g $FeCl_3.6H_2O$ and 19.88 g $FeCl_2.4H_2O$ were added to the above solution and heated at 40°C to complete the dissolution of the salts. Then, 1 g hydrochar was added to 30 mL of the prepared solution and stirred for 2 h at room temperature.	Fe_3O_4-loaded coffee waste hydrochar (Fe_3O_4-CHC)	Point of zero charges, SEM, TEM, EDX, XRD, surface area (BET), and FTIR.	Acid Red 17 dye	16.3 mg/g.
Pinewood sawdust	200°C for 1 h under 1.8 MPa. Followed by vacuum filtration and dried in an oven at 105°C for 12 h. Then	A total of 20 g of the hydrochar was impregnated with 100 ml of iron nitrate solution followed by vacuum filtration and dried at 105°C for 24 h.	ICP for iron content determination, FE-SEM, HR-TEM, XRD, surface area (SBET)		
Sawdust	HTC at 250°C for 2 h. then drying at 120°C for 4 h	KOH, 800°C, then soaked in $FeCl_3$	X-ray photoelectron spectroscopy (XPS), FTIR, Surface area and porosity - nitrogen adsorption-desorption isotherms,	tetracycline	423.7 mg/g
Rice straw	Sawdust	Chemical treatment by 1.66 N of NaOH solution (2 g in 30 mL distilled water) and stirred for 30 min before HTC. Then, the mixture was changed into a 100 mL Teflon-lined autoclave tube inside a stainless-steel reactor then heated in an electrical muffle at 180°C for 20 hr. It was followed by heated in a vertical stainless tube at 500°C for 2 hr without the flow of any external gases.	SEM, TEM, FTIR, Boehm's titration and adsorption of N_2 ga	MB	100 mg/g.
Beech Wood, Straw, Cauliflower, Garden Garlic, Carrots/Potatoes, Lignin, Cellulose	180-250°C	Some of the studied materials are thermally post-treated (490 ◦C and 700◦C)	Thermogravimetric (TGA) and FTIR	--	--
Male oil palm flower	180ºC for 8 h in an air atmosphere. Characterization, then, washed several times with DI water. Afterward, the solid, hydrochar, was dried in an oven for 24 h t	Without modification	FTIR, surface area BET, SEM, point of zero charges, and the elemental composition.	Methylene blue	42.92 mg/g.

Table 2. Recent studies on hydrochar in terms of environmental applications.

Egypt can produce commercial furnaces in both public and private sector factories with high control technology, which opens the door to produce HC locally.

On the other hand, water consumption for the HTC process may be a challenge for HC production in Egypt due to water shortage, which exceeds 30 BCM/year [15,48]. However, it can be a national demand to use secondary or tertiary treated wastewater in HC production, given that about 4.15-8.30 billion cubic meters are generated annually in Egypt [49]. Paradoxically, there are only a few research studies on HC production and application in Egypt, using the liquid phase to produce biofuels.

Discussion and Conclusion

HC production from HTC and its application in wastewater treatment is still at an early stage of its development; therefore, many points require further research and investigation. The lack of research studies in Egypt makes the HC a promising technology for wastewater treatment. With the availability of biomass feedstock from different sources, HC production can be produced at a large scale and low-cost. This paper reviewed the chemical compositions, morphological features, and surficial functionalities of HC, as well as their significant impact on the feedstock as highly versatile benchmarks in industry and environmental applications. HC surface modification has a major influence on its adsorption capacity. Therefore, it is suggested to maintain a continuous research on the HC surface characterization and its applications for different purposes in wastewater treatment, such as dyes exclusion, heavy metals removal, disinfection by-products deletion, and other organic pollutants elimination. Moreover, reusing the secondary or tertiary treated wastewater in HC production as a hydrolysis agent is an auspicious point to save our freshwater and produce HC with cost efficiency.

Declarations

On behalf of all authors, the corresponding author states that there is no conflict of interest

Author’s Contributions

AH and YA participated equally on writing the first draft of the paper. SE and HJ designed all tables and figures. S.M, HK and GK suggested the research topic and drew the general outline for the paper; they also edited and proofread the final manuscript. All authors have read and approved the current manuscript for submission.

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References

1. Gavrilescu, Maria, Katerina Demnerov, Aamand Jens, and Spiros N Agathos, et al. “Emerging Pollutants in the Environment: Present and Future Challenges in Biomonitoring, Ecological Risks and Bioremediation.” *New Biotechnology* 32 (2015): 147-156.

2. Perman, Roger, Yue Ma, Michael Common, and James McGilvray. *Natural Resource and Environmental Economics*. (2011).

3. Gupta, Himanshu, and Bina Gupta. “Adsorption of Polycyclic Aromatic Hydrocarbons on Banana Peel Activated Carbon.” *Desalination and Water Treat* 57 (2016): 9498-9509.

4. Wongsasuluk, Pokkate, Srilert Chotpantarat, Wattasit Siriwong, and Mark Robson. “Heavy Metal Contamination and Human Health Risk Assessment in Drinking Water from Shallow Groundwater Wells in an Agricultural Area in Ubon Ratchathani province, Thailand.” *Environ Geochemistry Health* 36 (2014): 169-182.

5. Clementi, Andreas. Elemental and Structural Analysis with SEM-EDX of Hydrochars Obtained from Hydrothermal Carbonisation of Different Organic Materials. (2015).

6. Kyzas, George Z, and Margaritis Kostoglou. "Green Adsorbents for Wastewaters: A Critical Review." *Materials* 7(2014): 333-364.

7. Brunner, Paul H, and Helmut Rechberger. Handbook of Material Flow Analysis. For Environmental, Resource, and Waste Engineers. Routledge, (2017).

8. Burakov, Alexander E, Evgeny V Galunin, Irina Vladimirovna Burakova, and Anastassia E. Kucherova. "Adsorption of Heavy Metals on Conventional and Nanostructured Materials for Wastewater Treatment Purposes: A Review." *Ecotoxicol Environ Saf* 148 (2017):702-712.

9. Ngo, Huu Hao, Wenshan Guo, Thi An Hang Nguyen, and Rao Y Surampalli, et al. 2016. Agricultural By-Products for Phosphorous Removal and Recovery from Water and Wastewater: A Green Technology, (2016).

10. Fang, June, Bin Gao, Jianjun Chen, and Andrew R. Zimmerman. “Hydrochars Derived from Plant Biomass Under Various Conditions : Characterization and Potential Applications and Impacts.” *Chem Eng J* 267 (2015): 253-259.

11. Fang, June, Lu Zhan, Yong Sik, and Bin Gao. “Mini-review of Potential Applications of Hydrochar Derived from Hydrothermal Carbonization of Biomass.” *J Ind Eng Chem* 57(2018): 15-21.

12. Miliotti, Edoardo, David Casini, and Matteo Prussi, Giulia Lotti, et al. “Lab-Scale Pyrolysis and Hydrothermal Carbonization of Biomass Digestate : Characterization of Solid Products”. *ECI Digital Archives*. (2017).

13. Han, Lanfang, Kyoung S Ro, Ke Sun, and Haoran Sun, et al. 2016. “New Evidence for High Sorption Capacity of Hydrochar for Hydrophobic Organic Pollutants.” *Environ Sci Technol* 50 (2016): 13274-13282.

14. Oliveira, Ivo, Dennis Blhse, and Hans Gnter Ramke. “Hydrothermal Carbonization of Agricultural Residues”. *Bioresource Technology*, (2013).

15. Mohamed, Ghada M., Ola I. El-Shafey, and Nady A. Fathy. “Preparation of Carbonaceous Hydrochar Adsorbents from Cellulose and Lignin Derived from Rice Straw.” *Egypt J Chemistry* 60 (2017): 793-804.

16. Khalid, Sana, Muhammad Shahid, Natasha, and Irshad Bibi, et al.2018. "A Review of Environmental Contamination and Health Risk Assessment of Wastewater use for Crop Irrigation With a Focus on Low and High-Income Countries." *Int J Environ Res Public Health* 15 (2018): 895.

17. Ali, Hazrat, Khan Ezzat, and Ilahi Ikram. "Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation." *J Chem* (2019): 1-14.

18. Yonglong, Lu, Shuai Song, Wang Ruoshi, and Liu Zhaoyang, et al. "Impacts of Soil and water Pollution on Food Safety and Health Risks in China." *Environ Int* 77 (2015): 5-15.

19. Vitale, Paula, Ramos Pamela Belén, Colasurdo Viviana, and Fernandez María Belén, et al. "Treatment of Real Wastewater from the Graphic Industry Using Advanced Oxidation Technologies: Degradation Models and Feasibility Analysis." *J Clean Prod* 206 (2019): 1041-1050.

20. Nechita, Petronela. Applications of Chitosan in Wastewater Treatment. Biological activities and application of marine polysaccharides, Croatia, (2017).

21. Bratby, John. Coagulation and Flocculation in Water and Wastewater Treatment. *IWA publishing*, London, UK, (2016).

22. Ibigbami, Tope Babatunde, Dawodu Folasegun Anthony, and Akinyeye Olayinka John. "Removal of Heavy Metals from Pharmaceutical Industrial Wastewater Effluent by Combination of Adsorption and Chemical Precipitation Methods." *Am J Appl Chem* 4 (2016): 24-32.

23. Singh, Santosh Bahadur, Gupta Mahesh Kumar, Shukla Neelam, and Chaurasia Girdhari Lal, et al. "Water Purification: A Brief Review on Tools and Techniques used in Analysis, Monitoring and Assessment of Water Quality." *Green Chem Technol Lett* 2 (2016):1-8.

24. Zheng, Guikun, Ye Hui, Zhang Yuzhong, and Hong Li, et al. "Removal of Heavy Metal in Drinking Water Resource with Cation-Exchange Resins (Type 110-H) Mixed PES Membrane Adsorbents." *J Hazard Toxic Radioact Waste* 19 (2015): 04014026.

25. Worch, Eckhard. Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling. *De Gruyter, Germany*, (2012).

26. Moreno-Pirajn, Juan Carlos and Giraldo Liliana. “Heavy Metal Ions Adsorption from Wastewater Using Activated Carbon from Orange Peel.” *E-J Chem* 9(2012): 926-937.

27. Bui, Xuan-Thanh, Chiemchaisri Chart, Fujioka Takahiro, and Sunita Varjani, et al. Water and Wastewater Treatment Technologies. Singapore, (2019).

28. bin Ahmad Nazria, Mohd Ariff, and binti Ghazali Nurul Liyana. "The Effectiveness EM Mudball and Banana Peels for Textile Wastewater Treatment." *MATEC Web Conf* 87(2017): 01009.

29. Junting, Zhang, Ying An, Aiduan Borrion, and Wenzhi He, et al. "Process Characteristics for Microwave Assisted Hydrothermal Carbonization of Cellulose." *Bioresour Technol* 259 (2018): 91-98.

30. Jae Wook, Chung. Pathogen Removal using Saturated sand Colums Supplemented with Hydrochar. Wageningen University. Promotor (en): Piet Lens, co-promotor (en): JW Foppen-Leiden: CRC Press/Balkema, (2015).

31. Madhuchhanda, Bhattacharya, and Tanmay Basak. "A Review on The Susceptor Assisted Microwave Processing of Materials." *Energy* 97 (2016): 306-338.

32. Nizamuddin, Sabzoi, Baloch Humair Ahmed, Siddiqui MTH, and Mubarak NM, et al. "An Overview of Microwave Hydrothermal Carbonization and Microwave Pyrolysis of Biomass." *Rev Environ Sci Biotechnol* 17(2018): 813-837.

33. Kambo, Harpreet Singh and Dutta Animesh. “A Comparative Review of Biochar and Hydrochar in terms of Production, Physico-Chemical Properties and Applications.” *Renew Sust Energ Rev* 45(2015): 359-378.

34. Sharma, Ronit, Jasrotia Karishma, Singh Nicy, and Ghosh Priyanka, et al. "A Comprehensive Review on Hydrothermal Carbonization of Biomass and its Applications." *Chemistry Africa* 3(2020): 1-19.

35. Marija, Mihajlović, Jelena Petrović, Mirjana Stojanović, and Jelena Milojković, et al. "Hydrochars, Perspective Adsorbents of Heavy Metals: A Review of the Current State of Studies." *Zaštita materijala* 57(2016): 488-495.

36. Fu, Ming Ming, Mo Ce Hui, Li Hui and Zhang Ya Nan, et al. “Comparison of Physicochemical Properties of Biochars and Hydrochars Produced from Food Wastes.” *J Clean Prod* 236(2019): 117637.

37. Hao, Wenming. "Refining of Hydrochars/Hydrothermally Carbonized Biomass into Activated Carbons and their Applications." PhD Diss., Stockholm University, (2014).

38. Zhang, Shicheng, Zhu Xiangdong, Zhou Shaojie, and Shang Hua, et al. Hydrothermal Carbonization for Hydrochar Production and its Application. In Biochar from Biomass and Waste, China, (2019).

39. Horikoshi, S and Serpone N. “In-liquid Plasma: A Novel Tool in the Fabrication of Nanomaterials and in the Treatment of Wastewaters.” *RSC Adv* 7(2017): 47196-47218.

40. Shao, Yuchao, Long Yuyang, Wang Hengyi and Liu Dongyun, et al. “Hydrochar Derived from Green Waste by Microwave Hydrothermal Carbonization.” *Renew Energy* (2018).

41. Li, Yin, Tsend Nyamkhand, Li Ti Kai and Liu Heyang, et al. “Microwave Assisted Hydrothermal Preparation of Rice Straw Hydrochars for Adsorption of Organics and Heavy Metals.” *Bioresour Technol* 273(2019): 136-143.

42. Elaigwu, Sunday E, and Gillian M. Greenway. “Microwave-Assisted and Conventional Hydrothermal Carbonization of Lignocellulosic Waste Material: Comparison of the Chemical and Structural Properties of the Hydrochars.” *J Anal Appl Pyrolysis* 118(2016): 1-8.

43. Elaigwu, Sunday E, and Greenway Gillian M. “Characterization of Energy-Rich Hydrochars from Microwave-Assisted Hydrothermal Carbonization of Coconut Shell.” *Waste Biomass Valori* 10(2019): 1979-1987.

44. Bao, Yan, Zhang Yuanxia, Guo Jiajia and Ma Jianzhong, et al. “Application of Green Cationic Silicon-Based Gemini Surfactants to Improve Antifungal Properties, Fiber Dispersion and Dye Absorption of Sheepskin.” *J Clean Prod* 206(2019): 430-437.

45. Gai, Chao, Zhang Fang, Lang Qianqian and Liu Tingting, et al. “Facile One-Pot Synthesis of Iron Nanoparticles Immobilized into the Porous Hydrochar for Catalytic Decomposition of Phenol.” *Appl Catal B* 204(2017): 566-576.

46. Xue, Yingwen, Gao Bin, Yao Ying and Inyang Mandu, et al. “Hydrogen Peroxide Modification Enhances the Ability of Biochar (hydrochar) Produced from Hydrothermal Carbonization of Peanut Hull to Remove Aqueous Heavy Metals: Batch and Column Tests.” *Chem Eng J* 200 (2012): 673-680.

47. Fao. “FAOSTAT: Food Balance Sheets”. (2018).

48. Mohamed, Nader Noureldeen. “Egyptian Food Insecurity under Water Shortage and its Socioeconomic Impacts.” *Springer* (2019): 245-273.

49. Batisha, Ayman F. “Greywater in Egypt: The Sustainable Future of Non-Conventional Water Resources.” *Environ Sci Pollut R* 27 (2020): 35428-35438.

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