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RECENT ADVANCES IN AGRICULTURAL WASTE-BASED ADSORBENTS FOR THE REMOVAL OF POLLUTANTS IN WATER (2017-2020)

(Kemajuan Terkini dalam Penjerap Berasaskan Sisa Pertanian untuk Penyingkiran Bahan Pencemar dalam Air (2017-2020))

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Abstract

Rapid human activities result in the increasing production of pollutants from both industrial processes and agricultural practices, which negatively impact the environment and human health. Most of chemical pollutants are discharged either intentionally or accidentally via water bodies. Therefore, various pollutants removal techniques have been developed including utilization of agricultural waste as adsorbents. Agricultural waste-based adsorbents are easily prepared, cheap and moderately to highly efficient. A good understanding of agricultural waste-based adsorbents would be beneficial for future research improvements as well as industrial applications. Thus, this review aims at shedding light on recent advancements (from year 2017-2020) in the preparation, characterizations and application of agricultural waste-based adsorbents for removal of different types of chemical pollutants in water and wastewater.

Keywords: agriculture waste, adsorbent, pollutants removal, water, wastewater

Abstrak

Kegiatan manusia yang giat mengakibatkan peningkatan penghasilan bahan pencemar dari kedua-dua proses industri dan amalan pertanian yang memberi kesan negatif terhadap alam sekitar dan kesihatan manusia. Kebanyakan bahan pencemar kimia disingkir secara sengaja atau tidak sengaja melalui takungan air. Oleh itu, pelbagai teknik penyingkiran bahan pencemar telah dikembangkan termasuk penggunaan sisa pertanian sebagai penjerap. Penjerap berasaskan sisa pertanian mudah disediakan, murah dan daripada sederhana hingga sangat cekap. Pemahaman yang baik tentang bahan penjerap berasaskan sisa pertanian akan bermanfaat untuk peningkatan penyelidikan masa hadapan dan juga aplikasi industri. Oleh itu, tinjauan ini bertujuan untuk menjelaskan kemajuan terkini (dari tahun 2017-2020) dalam penyediaan, pencirian dan penggunaan penjerap berasaskan sisa pertanian untuk penyingkiran pelbagai jenis bahan pencemar kimia di dalam air dan air sisa.

Kata kunci: sisa pertanian, penjerap, penyingkiran bahan pencemar, air, air sisa

Introduction

Several of the most relevant categories of environmental pollutants are the one caused by heavy metals, pesticides, herbicides, dyes and phenolic compounds, which are present in large amount in wastewater from various industry activities. The release of these pollutants into water bodies is alarmingly causing severe effects to the environment and human health, whereby the latter happens due to the accumulation since they are non-biodegradable [1]. World Health Organization (WHO) has set a standard of 10 μg/L of arsenic (As) content in drinking water for the public safe consumption worldwide [2]. Human will suffer in skin lesions and skin coloration upon contact, while prolonged consumption of high level as drinking water may cause skin cancer [3]. The maximum allowable level of copper (Cu) and nickel (Ni) in drinking water set by WHO are 2.0 [4] and 0.07 mg/L [5], respectively. Paulino *et al.* [6] reported that high level of ingested Cu may cause vomiting, cramps and even death. Ni accumulated in human body can decrease the level of red blood cells, leading to the dysfunction of immune and cardiovascular systems. Human are at risk to suffer osteoporosis and kidney failure if ingestion of cadmium (Cd) is above 3 μg/L as stated by WHO [7]. Furthermore, lead (Pb) level above permissible level of 10 μg/L also affect in neurological system, kidney function and synthesis of red blood cells [8]. In addition, significant impairment of intellectual ability is reported to be the consequence of even low level of Pb concentration in children's blood [9]. Removal can be done by chemical precipitation and physical treatments (i.e., ion exchange, solvent extraction and reverse osmosis) from water and wastewater. However, these methods provide some disadvantages due to incomplete removal, low selectivity, high costs, and large amount of waste [10]. Among these techniques, adsorption is thought to be the most promising because of its high efficiency, simplicity, relatively low quantities of residue, and ability to isolate a wide variety of chemical compounds. Moreover, this is the most widely used technique for removing organic and inorganic pollutants from aqueous solutions [11].

Dye production industry and other industries (e.g. printing, paper and textile, cosmetics and pharmaceuticals, and food industries) that involve dyes and pigments in their processes generate large amount of waste water [12]. Every year, there are about 10,000 types of dyes and over 7×10^5 tonnes of dyes are produced around the world [13]. Due to this variation, dyes wastewater is difficult to be treated. Dyes are stable and resistant towards heat, light, oxidizing agent and aerobic digestion [14]. They can absorb sunlight and cause intensity of sunlight in water bodies to decrease, thus reducing photosynthesis and concentration of dissolved oxygen. Consequently, level of chemical oxygen demand (COD) increases [14]. Dyes can cause irritation to the skin and respiratory tract [15]. For example, malachite green (MG) and leucomalachite green, that present in tissues of treated fish can cause severe effect to human consuming the fish due to genotoxity and carcinogenicity of dyes. However, cheaper cost, availability and its effectiveness cause the usage of these dyes still continue [16].

Phenolic compounds are another type of pollutants released into water bodies from various industries such as petroleum refineries, coal, production of dye, pharmaceuticals, pesticides and others [17]. Some examples of phenolic compounds are phenol, chlorophenol, catechol and chlorocatechols, nitrophenols, methylphenols, alkylphenols, bisphenols and aminophenols. On top of that, the production and decomposition (e.g., photo-oxidation, leaching, comminution and mineralization) [18] of organic matters (e.g., dead plants and animals) also lead to the formation of phenols in ecosystem [19]. Radical reaction which can damage cell membrane takes place easily with donation of free electrons from phenols. For example, 2,4,6-trichlorophenol (2,4,6-TCP), a yellow colour and sweet smell phenolic pollutant that is listed in Group B2 by Environmental Protection Agency (EPA) [20] is probable to bring carcinogenicity effect to human and animals. Its usage and production are already banned in the United States of America. 2,4,6-TCP is difficult to be removed due to its stable structure. Therefore, removal of phenolic compounds prior discharge to water bodies is pertinent.

Conventional pesticides can be divided into six types which are insecticides, herbicides, rodenticides, bactericides, fungicides and larvicides [21]. Pesticides can be classified by components of active ingredients, for examples organochlorines, carbamates, organophosphorus pyrethrin and pyrethroids [22]. They can be categorized as extremely hazardous, highly hazardous, moderately hazardous, slightly hazardous and acute hazard [23]. Pesticides make a great contribution in production and growing of crops by controlling the pest. However, high toxicity of pesticides brings negative effect to human health. Moreover, pesticides are difficult to be treated using biological treatment due to their non-biodegradable properties and abundancy [24]. Improper usage of pesticides causes residual effect in food chain, pollution and eventually affect the ecosystem. Prolonged exposure of pesticides in environment through ingestion, inhalation and skin contact increase the risk of cancer, severe renal failure, serious effect to immune system, reproductive system, nervous system, endocrine system and behavioural disorder [25]. Therefore, removing them from industrial effluents has become a big environmental concern in recent years. There are some conventional methods being used to remove these pollutants, however they may have come with several significant limitations. For example, coagulation and flocculation which are usually used to treat high concentration of phenol in wastewater have issue with large amount of sludge disposal [26]. Biological treatment is both environmentally friendly and energy saving but it cannot treat phenol effluents with high concentrations. Hence, chemical oxidation can usually be used for most of the time. [27]. In the case of pesticides, ozonation [28], photocatalytic degradation [29], advanced oxidation processes [30], nanofiltration and photo-Fenton oxidation [24] are all commonly used methods. Although some of these methods shown to be effective, some of them suffered some drawbacks and limitations such as using excess amount of chemical solvent, having high operating costs, and producing a lot of sludge, which has serious disposal issue [31].

Adsorbents made from agricultural waste, or usually called as biosorbents are reported able to reduce the disposal amount, avoid on-site burning and save disposal cost. They are low-cost, high-efficient, environmentally friendly and becoming increasingly important in the removal of pollutants mentioned above as an alternative to conventional methods. It manipulates biomass's natural ability to immobilise dissolved elements on its surface. Thus, discovering efficient adsorbents made from waste biomass is of great interest. Waste produced from different agricultural operations may consist constituents of lignin, cellulose, hemicellulose, extractives, lipids, proteins, sugars, water and different functional groups. Carboxyl, amine and hydroxyl group are ionizable functional group that build up potential binding sites for adsorption [32]. Several researchers modified adsorbent materials by functionalizing them with other chemical and substances to enhance their capacity to adsorb pollutants. The adsorption of pollutants by these low-cost adsorbents were usually evaluated under various conditions such as pH, pollutants' concentration, contact time, mixing speed and adsorbent dose through kinetic and/or isotherm studies. The optimum removal condition was also identified for each metal ion. This review paper highlights the recent advancements (from year 2017-2020) in the preparation, characterizations and application of agricultural waste-based adsorbents for removal of different types of chemical pollutants in water and wastewater. Removal characteristics of heavy metals, dyes, pesticide, herbicides and phenolic compounds in water or wastewater using coir pith ash, carnauba straw powder, banana peels, tea and coffee ground waste, coconut shell, rice straw, pine bark powder and etc were reviewed. Where available, information was given about their adsorption capacity, isotherm and/or kinetic model and adsorption mechanism. Table 1 represents all adsorption parameters of different agricultural waste-based adsorbent for the adsorption of different classes of pollutants; pertinent methods are detailed in the next sections.

Table 1. Adsorption parameters of different agriculture waste for the adsorption of different classes of pollutants in water

No.	Agriculture Waste	Pollutant	Contact Time	Adsorbent Dosage	Adsorption Capacity	Isotherm Model and/or Kinetic Model	Ref.
1	Coir pith ash	As	60 min	5 g/L	36.5 mg/g	Langmuir isotherm model	[33]
2	Natural pine sawdust	Cu, Pb	5 min	10 g/L	9.59 mg/g	Freundlich isotherm model	[34]
3	Carnauba straw powder	Cu	5 min	10 g/L	9.5 mg/g	Langmuir isotherm model	[35]
4	Rice husk	Pb, Crystal violet	90 min	0.1 g/20mL	93.5 mg/g	Langmuir isotherm model and Lagergren pseudo-second order kinetic model	[36]
5	Fern plant-cyclosorus interruptus	Pb	12 h	30 mg	133 mg/g	Langmuir isotherm model and pseudo-second order kinetic model	[37]
6	Pulp lignin	Cr(III)	30 min	0.2 g	44.5 mg/g	Langmuir and Dubinin-Radushkevich isotherm models, pseudo-first and second order kinetic models	[38]
7	Tea waste	As, Cr	1 h	NA	21.2-38 mg/g	Langmuir Isotherm model	[39]
8	Coffee ground powder	Rhodamine dyes	3 h	50 mg/50mL	5.26-17.4 mmol/g	Langmuir isotherm model	[40]
9	Wood apple shell	MG dye	3.30 h	0.4 g	80.7 mg/g	Langmuir isotherm model	[41]
10	Coffee waste	MCPA	5 min	0.825 g/L	340 mg/g	Langmuir isotherm model	[42]

Table 1 (cont'd). Adsorption parameters of different agriculture waste for the adsorption of different classes of pollutants in water

No.	Agriculture Waste	Pollutant	Contact Time	Adsorbent Dosage	Adsorption Capacity	Isotherm Model and/or Kinetic Model	Ref.
11	Switchgrass	Phenoxy herbicides	6 h	1 -2 g/L	50-134 mg/g	Freundlich or Redlich-Peterson isotherm model	[43]
12	Pine bark powder	2,4,6-TCP	120 min	0.4 g	88 mg/g	Langmuir isotherm model	[44]
13	Pinecone powder	Phenol, 2-CP, 4-CP	60 min	0.6 g/0.1 L	165 - 220 mg/g	Langmuir isotherm model	[45]
14	Coconut shell	Phenol	120 min	100 g (fluidized-bed reactor)	58.1 -415 mg/g	Langmuir, Freundlich and Redlich Peterson isotherm models	[26, 46]
15	Coconut spathe	Phenol, 2-CP, 4-CP	15 min	100 mg/L	120-275 mg/g	Langmuir isotherm model	[47]
16	Avocado seed	15 phenolic compounds	120 min	1.5 g/L	99.5- 327 mg/g	NA	[31, 48]
17	Tucuma seed	2-nitrophenol	30 min	1.5 g/L	1382 mg/g	Liu isotherm model and general order kinetic model	[49]
18	Rice straw	Phenol	24 h	2.5 g	5.78 mg/g (Langmuir)	Freundlich and Langmuir isotherm models	[50]
19	Rice husk	Cd	60 min	0.5 g/L	139 mg/g	NA	[51]
20	Corn cob	Cr(III) and Cr(VI)	120 min	0.1 g	277 mg/g	Langmuir isotherm model and the pseudo-second order model	[52]
21	Corn	Phosphate and Cd	75 min	0.1 g	57.5 mg/g	Langmuir isotherm model and pseudo-first-order kinetic model	[53]
22	Banana peel	MB dye	150 min	0.05 g	222 mg/g	Pseudo-second kinetic order	[54]

Table 1 (cont'd). Adsorption parameters of different agriculture waste for the adsorption of different classes of pollutants in water

No.	Agriculture Waste	Pollutant	Contact Time	Adsorbent Dosage	Adsorption Capacity	Isotherm Model and/or Kinetic Model	Ref.
23	Indian almond shell, ground nutshell, areca nutshell, tamarind shell, cashew nutshell	Azure A dye	30 min	2.0 g/L	21.9 -834 g/g (based on Langmuir)	Freundlich, Langmuir, Temkin, Redlich–Peterson and Dubinin–Radushkevich isotherm models.	[55]
24	Black and green olive stones	MB dye	24 h	0.05 g	714 and 769 mg/g	Freundlich isotherm model	[56]
25	Barley and wheat	Ni	65 min	0.01 g	303 mg/g	Freundlich isotherm model and pseudo-first-order kinetic model	[57]
26	Alfalfa hays	Tetracycline	1818 min (fixed bed)	1 g	302 mg/g	Elovich and Freundlich isotherm models	[58]
27	Grape stalk	Basic Blue 41 dye	NA	0.5-5.0 g/L	205 mg/g	Pseudo-second order kinetic model	[59]

Abbreviations:

2-CP	2-chlorophenol	MG	Malachite green
4-CP	4-chlorophenol	MPC	Magnetic porous carbonaceous
As	Arsenic	Ni	Nickel
Cd	Cadmium	NPs	Nanoparticles
CGP	Coffee ground waste	NA	Not available
Co	Cobalt	Pb	Lead
CSAC	Coconut shell activated carbon	PBP	Pine bark powder
Cu	Copper	PCP	Pinecone powder
Fe	Iron	Rh6G	Rhodamine 6G
Hg	Mercury	RhB	Rhodamine B
MB	Methylene blue	Zn	Zinc

Advances on the adsorbents for the removal of toxic heavy metals

The adsorption of heavy metals by low-cost agricultural waste materials has attracted much attention since the 1980s [60-64]. Because heavy metals are positively charge in nature, removal studies would require deep investigation of adsorbents' functional groups and physical properties to understand the mechanism for efficient adsorption. It was found that coir pith ash [33], pine sawdust [34], carnauba straw powder [35], rice husk [36], banana peel [65], corn [53] and fern plant[37] were utilized for the past four years. A heat-treated natural coir pith ash (CPA) was prepared by Bahar et al. [33] as biosorbent to remove As ions in contaminated water. As(III) was oxidised to As(V) in order to remove it from water. The characterization of the biosorbent showed the presence of S-H and C=O functional groups in CPA that aid in the adsorption of As(V) onto the surface of the adsorbent for effective removal. The conditions obtained via batch sorption reported that the adsorption of As(V) could be done in a wide pH range (pH 2–12) and the best adsorbent dose was 5 g/L. The data fitted Langmuir isotherm with maximum adsorption capacity As of 36.5 mg/g at 25°C. In addition, the mean free energy obtained from Dubinin–Radushkevich (D–R) isotherm was 8.64 kJ/mol, showing that the adsorption of As(V) was based on ion-exchange mechanism. On top of that, the studies of desorption and recovery of As(V) proved that hydrochloric acid could be used as a solvent to replace toxic As(V) ions from the biosorbent for full recovery of As(V), and sodium hydroxide for the regeneration of CPA. These findings show that the alkaline-in-nature CPA biosorbent has great potential for removing As(V) from contaminated water, particularly acidic wastewater. Semerjian et al. [34] directly utilized natural pine sawdust as a biosorbent to remove Pb and Cu in water. The biosorbent was only sifted, washed and dried, and did not undergo any chemical pre-treatment to maintain its status as green biosorbent. The removal of metal ions was based on the presence of polyphenolic groups of various organic compounds (i.e., lignin, cellulose, and hemicellulose) within the pine sawdust. The factors influencing the metals adsorption were studied through batch sorption experiments to obtain the highest removal efficiency. From the result, optimum pH levels for Cu and Pb removal were 7 and 5, respectively with the adsorbent concentration of 10 g/L and contact times of 5 min for both Cu and Pb using initial concentration of 1 mg/L [34]. The adsorption capacity was 9.59 mg/g. Equilibrium adsorption for Cu fitted with Freundlich isotherm, while Pb data fitted equally both Freundlich and generalized isotherm models. The adsorption kinetics were best described by the pseudo second-order model. They implied that removal involved valance forces through sharing or exchange of electrons between pine sawdust and metals. The author reported that the equilibrium adsorption capacity of sawdust improved at higher temperature (~60 °C) and the adsorption was an endothermic chemical process (as proven by positive values of standard entropy of adsorption ($\Delta S°$)). Similarly, Ferreira *et al.* [35] explored the potential of carnauba straw powder (CSP) as adsorbent to remove Cu in water. CSP possessed lignocellulosic components consisted of functional groups available for adsorption site for Cu. The adsorption of Cu was maximised at pH 6 due to the increase of negatively charged surface of CSP functional groups resulting in better sorption of metal ions via electrostatic attraction of cation and anion binding sites. At optimum conditions (adsorbent dosage of 10 g/L, removal at pH 6 at 50 °C for 1 hour), the efficiency of Cu adsorbed was reported to improve with the decrease of granule size of biosorbent. The smaller the size, the higher the surface area for the sorption of Cu onto the CSP surface. The obtained adsorption capacity was 9.5 mg/g at 50 °C, where it fitted both the pseudo-second order and Langmuir adsorption models [35]. As compared to pine sawdust biosorbent developed by Semerjian [34], the carnauba-based biosorbent was comparable in removing Cu as both adsorption capacity was ~ 10 mg/g. However, both adsorbents were not yet tested with real wastewater, therefore further studies are required.

Masoumi and co-workers [36] developed a nanoparticle adsorbent based on the modification of rice husk and a copolymer to remove Pb from water. The mechanical and physical properties of the adsorbent were improved through the addition of poly-methylmetacrylate and poly-maleic anhydride. On top of that, the interaction between tartaric acid and rice husk enhanced the binding capacity of metal. The removal efficiency of Pb could be as high as 98% when using the modified nanoparticles rice husk as compared to the untreated rice husk and copolymer individually. This might be due to the presence of various chelating sites of carboxylic acid and amine from the backbone of the synthesised polymer resulting in more adsorption mechanism of metal ions on the surface of adsorbent. The maximum sorption capacity of Pb was 93.5 mg/g that fitted the Langmuir isotherm. Based on the kinetic data, the increase of temperature enhanced the adsorption of Pb as the values of ΔG, ΔH and ΔS favoured to be spontaneous, more disorder and endothermic physical adsorption. Mahindrakar et al. [65] explored the potential of banana peels waste for removal of strontium, Sr(II) from water. The presence of anionic groups of hydroxyl, carbonyl and carboxyl in the adsorbent were responsible to bind with the cationic metal of interest. The optimum pH was at pH 7, giving more adsorption sites on the surface of adsorbent for the binding Sr(II). Within 10 min of contact time, the adsorbent achieved 99% removal of Sr(II). The maximum adsorption of Sr(II) was 41.5 mg/g, which fitted with the pseudo-second order model. The authors found out that the adsorbent could be reused up to 5 cycles and still maintained the 90% range removal. In 2020, Faheem et al. [53] developed a corn-based multifunctional biochar adsorbent to remove phosphate and Cd in wastewater in a two-stage adsorption set-up. They successfully grafted and introduced multiple functionalities with both amino and carboxylic functional groups on biochar surface after chemical modification route was applied. The uptake capacity of phosphate was 57.50 mg/g P g in acidic conditions. Then, as-obtained multifunctional biochar loaded with phosphate could adsorb Cd ion up to 61.4 mg/g when it was further applied for second-stage adsorption. Both residual carboxylic group and phosphate loaded on the biochar surface were responsible for Cd^{2+} sorption. The synergistic effects between phosphate and Cd^{2+} ions helped phosphate removal up to 95% in the presence of Cd^{2+}. Both Langmuir and Freundlich models were implemented, however Langmuir isotherm fitted data the best ($R^2 > 0.992$).

Magnetic-based adsorbent was one of the current trendy techniques in removing heavy metal efficiently in aqueous media. Zhou et al. [37] reported a fast removal of Pb in water using magnetic multi-porous biosorbent after modification with amino siloxane. A comparison of this magnetic adsorbent was also reported for its capability to adsorb other metals, i.e. Zn, Ni and cobalt (Co). The adsorbent was prepared from a fern plant-cyclosorus interruptus (CI) which has an abundant amount of porous structure with crinkled morphology and then assimilated with Fe_3O_4 nanoparticles. The uppermost part of activated cyclosorus (ACI) was coated with a layer of 3-aminopropyltriethoxysilane (AS). The highest Pb adsorbed was 133.3 mg/g using AS-ACI-2.0 (2 g of ACI) based on Langmuir isotherm model at 323K which showed a favourable and feasible adsorption process (separation factor, R_L was 0.02-0.10). Furthermore, the Pb adsorption kinetics followed a pseudo-second-order model ($R^2 \geq 0.995$) and Pb was adsorbed onto this bio-based magnetic adsorbent through both chemical (chelation) and physical adsorption (from the multi-porous structure and puckered morphology) (E_a was 23.9 kJ/mol). Pb showed the greatest adsorption capacity as the adsorbent portrayed higher selectivity towards Pb. This might be due to the nitrogen atoms present on the adsorbent that able to bind with Pb in water. Based on Pearson acid-base theory, the interaction of Pb with amine and hydroxyl groups on the adsorbent had precedence over other metals. The adsorbent was reusable up to five cycles, keeping >90% of the original adsorption capacity. In 2019, Dai et al. [38] prepared a magnetic alkaline lignin−dopamine nanoparticle adsorbent. Alkaline lignin was a type of waste from pulping and bio-energy industry. It was functionalized by the conjugation with dopamine molecules and nano-precipitation method to make a candidate adsorbent for removal of Cr(III) from wastewaters. Furthermore, this magnetic adsorbent possessed sensitive magnetic responsiveness up to 24.6 emu/g, which is beneficial for magnetic recovery (>90% recycled within 2 min), and reusability for subsequent adsorption–desorption cycles. The maximum adsorptive capability of the adsorbent was 44.6 mg/g, thanks for the three-dimensional network and catechol structure of lignin and dopamine within the adsorbent. The sorption isotherms suited

Langmuir and Dubinin-Radushkevich models. The initial (<0.5 h) and the following stages (> 0.5 h) of Cr(III) adsorption onto the adsorbent followed pseudo-first ($R^2 = 0.9995$) and second order kinetic model ($R^2 = 0.9996$), respectively.

Advances on the adsorbents for the removal of dyes
Dye pollution is one of the major concerns in environmental problems. Hence, high quality wastewater treatment towards these toxic and carcinogenic dyes is necessary before they are discharged into water bodies. Water quality criteria used to evaluate quality of dye-related effluent are pH 5.5-9.0, BOD level below 50 mg/L and COD level below 100 mg/L [66]. It was found that tea waste [39], coffee waste [40], wood apple waste [41, 67] were utilized as adsorbents for the past four years. Tea production in China produced large amount of tea wastes annually. Thus, tea wastes were usually chosen as raw materials for synthesizing magnetic porous carbonaceous (MPC). Wen et al. [39] synthesized MPC (MPC-300, MPC-400, MPC-500) material using tea waste for the removal of dyes and other contaminants (i.e. arsenic (As), chromium (Cr) and humic acid). Thermal pyrolysis of $FeCl_3$ in treated tea waste caused embedding of nanosized γ-Fe_2O_3 nanoparticles (NPs) into porous structures. Chemical composition in tea waste prevented agglomeration of γ-Fe_2O_3 NPs and promoted the growth of γ-Fe_2O_3. BET surface area for MPC underwent pyrolysis at 300°C was 63 m^2/g, which was higher than MPC pyrolyzed at 400 °C (34 m^2/g) and 500 °C (31 m^2/g). Adsorption capacities of MPC-300 towards methyl orange, methylene blue (MB) and rhodamine B (RhB) were 73.12 mg/g, 45.74 mg/g and 31.94 mg/g, respectively. MPC-300 had better adsorption ability towards MO as compared to MB and RhB because the anionic MO had strong electrostatic attraction towards positive charge of γ-Fe_2O_3 surface.

Coffee ground waste has been used for environmental remediation, adsorption of toxic pollutants from aqueous and gas phase and removal of salt from effluents [68]. World annual coffee manufacture is projected to be 165 million bags (60 kg bag) in 2020 [69]. Thus, wide application and high abundant coffee ground are gaining popularity to be utilized as raw material for adsorbents synthesis. Shen and Ghondal [40] reported that non-modified coffee ground powder (CGP) could remove rhodamine dyes (RhB and Rhodamine 6G (Rh6G)) from wastewater. Acidic condition was more favourable for the adsorption process as compared to alkaline condition [40]. Positive surface charge of CGP existed with any pH <3.5. Thus, pH played an important role on degree of ionization of dye molecule. Rh6G and RhB experienced highest adsorption under acidic condition at pH 2, resulting to adsorption capacity of 25.1 and 7.18 μmol/g, respectively. These two cationic dyes exhibit electrostatic interaction with the negatively charged CGP surface. However, Rh6G showed a higher adsorption capacity compared to RhB. The presence of ester group in Rh6G might be responsible in the uptake on the CGP surface. Meanwhile, RhB comprised carboxylate ion, which could attribute to the repulsion forces between RhB and the negatively charged CGP surface. On the other hand, under alkaline condition of pH 10, Rh 6G and Rh B achieved adsorption capacities of 9.1 and 1.7 μmol/g only. The adsorption process was reversible for both dyes and this was proven through positive value of ΔS^o. Adsorption process for RhB and Rh6G were non-spontaneous and spontaneous, respectively (based on standard Gibbs energy of adsorption (ΔG^o)).

Wood apple (*Feronia acidissima*) commonly found in India, Sri Lanka, and Pakistan contains functional group of alcoholic, carboxylic and ether [67]. Bark, leaves and fruits of wood apple have been reported to be used as medicinal biosource. However, disposal of plenty of shells as agricultural waste may lead to environmental pollution because the decomposition of shell waste can produce various unwanted chemical compounds and microorganism [70]. Sartape et al.[41] prepared adsorbent from wood apple shell to remove MG dye. They reported that adsorbent's surface and MG dye (pKa 10.3) experienced positive charge under acidic condition. Consequently, electrostatic repulsion formed between the surface of wood apple shell and MG dye, thus weakened the adsorption of MG towards wood apple shell. Alternatively, removal conducted under alkaline condition (pH 10-12) resulted in the accumulation of OH- ion at adsorbent surface, forming negative layer. Adsorption capacity was strengthened due to electrostatic attraction between surface and cationic MG [41, 71]. They reported that 98.9% of MG dye removal was achieved with initial dye concentration 100 mg/L at pH 7-9 shaking with 150 rpm for 3.30 h at room temperature. Increasing initial dye concentration from 100 to 700 mg/L led to a better adsorption with the evidence of adsorption capacity increased from 12.35 to 80.645 mg/g. Higher MG concentration provided a driving force of mass transport and hence strengthened the interaction between adsorbates and adsorbent. They reported maximum adsorption capacity of 80.645 mg/g with Langmuir isotherm model.

Advances on the adsorbents for the removal of pesticides/herbicides

The presence of pesticides in water bodies has increased considerably for the past few years, therefore, it was important to develop methods in order to minimize and prevent pollution of water bodies due to leaching of pesticides [72]. There are several techniques developed to remove pesticides in water including adsorption [72], ozonation [73], hydrostatic pressure [74] and ultrasonic treatment [75]. The phenomenon of adsorption was where the molecules of pesticides attracted to the surface of a solid and linked together by physical or chemical bonds. Adsorption used low cost agricultural waste has been explored because of eco-friendly nature, cost effectiveness, easy operation and integration opportunity with the present system of water treatment [76]. From the survey of literatures, coffee waste [42] and switchgrass [43] were utilized as adsorbents for the past four years. Coffee waste-based adsorbent was investigated by Al Zaben et al. [42] to remove 4-chloro-2-methyl phenoxy acetic acid (MCPA) pesticide in aqueous solution. The adsorbent was prepared only by washing and boiling coffee waste to eliminate chemicals adherences like acid and metal ions. The synthesized adsorbent was known to have equal size and shape for the nanoparticles' distribution, which was proved by the dynamic light scattering measurement and transmission electron microscopy. Based on zeta potential analysis, the biosorbent showed negatively charged particles due to the presence of carboxylate and hydroxylate anions. These anions were responsible to provide binding sites for the adsorption of MPCA onto the surface of the biosorbent. The author reported that there was no significant change on the adsorption capacity of MCPA with the change of pH since the coffee waste charge was pH independent.

In addition, kinetic study conducted showed a rapid adsorption in the first few minutes (5 min), then decreased gradually due to the lesser adsorption sites available. The maximum adsorption recorded was 340 mg/g that fits Langmuir isotherm. The authors suggested that the coffee waste biosorbent was a great alternative to remove MCPA in wastewater [42]. Next, an agricultural waste based on switchgrass was prepared by Essandoh et al. [43] by fast pyrolysis to remove phenoxy herbicides in aqueous solutions. They aimed to remove MCPA and 2,4-dichlorophenoxyacetic acid (2,4-D) due to the highest usage and their significant detrimental effect towards environment. Switchgrass possessed 3-D swollen solid structure after heating at high temperature, exposing more adsorption sites throughout the biochar to adsorb MCPA and 2,4-D effectively. In addition, the silica content in switchgrass improved the biochar surface with Si-OH groups, resulting the adsorbent to be hydrophilic in nature. The hydrophilicity of the surface was able to adsorb analytes of interest and ease water diffusion within the solid structure of biochar. Low pH of solution increased electrostatic attraction for the adsorption to occur due to the presence of hydrogen bonding from carboxylic acid group of the biochar. The maximum adsorption for MCPA and 2,4-D were 50 mg/g and 134 mg/g, respectively. Despite the low surface area (1.1 m^2/g) portrayed by the synthesized biochar based on BET analysis, both analytes still adsorb effectively over a wide pH range (pH 2-10) [43].

Advances on the adsorbents for the removal of phenolic compounds

Trend is showing researchers utilizing agricultural wastes to synthesize adsorbents for removal of phenolic contaminants. Examples of wastes used were pine bark powder [44], coconut shell [26, 46], pine cone biomass [45], coconut spathe [47], avocado seed [31], tucuma seed [31] and rice straw [50]. Unmodified adsorbent is the easiest to prepare as not many chemicals are needed. While for activated carbon, chemical, physical activation or pyrolysis are involved. This is reflected by studies by Siva Kumar *et al.* [44, 45]. They utilized both unmodified and chemical modification routes to prepare their adsorbents. Only used distilled water to wash dirt and impurities on pine bark and pine cone, followed by drying process for 48 h. Samples were grounded to obtain fine powder with particle size varied from 55 to 75 µm for pine bark power (PBP) and 53 to 74 µm for pine cone powder (PCP). PCP was placed in desiccator before used while PBP was soaked in 0.1 M NaOH and followed by 0.1 M H_2SO_4 to remove lignin compound. After that, PBP was washed and dried. Siva Kumar et al. [44] synthesized pine bark powder (PBP) to remove 2,4,6-trichlorophenol (2,4,6-TCP) from aqueous media. After washing, drying and grinding to the size of 55 to 75 µm, PBP was soaked in 0.1 M NaOH and followed by 0.1 M H_2SO_4 to remove lignin compound. After that, PBP was washed and dried. The PBP had maximum adsorption of 289.09 mg/g, which was as predicted by using Langmuir isotherm model and could achieve 97% of removal percentage. BET surface area for PBP was only 0.1 m^2/g. Adsorption capacity of 88 mg/g could be achieved at pH 6. 2,4,6-TCP was a weak acid with pKa value of 6.23. Acidic pH favoured for adsorption process as protonated form of chlorophenols were easier to be adsorb. However, electrostatic repulsion existed between negatively charge adsorbent surface and chlorophenolate anions at pH greater than 6. Percentage removal increased from 45% to 97% with increment of adsorbent dosage from 0.05 to 0.40 g but no further increment with higher adsorbent dosage. Biosorption capacity was improved from 50 to 325 mg/g with increased of initial adsorbate concentration from 100 ppm to 400 ppm. Optimum conditions to remove 2,4,6-TCP were pH 6, 0.4 g of PBP, and 120 minutes contact time [44]. Pine cone powder (PCP) produced by the same group [45] was used to remove phenol, 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP). They only used distilled water to wash dirt and impurities on pine cone, followed by drying process for 48 h. Samples were grinded to obtain fine powder with particle size varied from 53 to 74 µm. BET surface area for PCP was 7.1 m^2/g. Phenol, 2-CP and 4-CP had pKa values of 9.9, 8.8, and 9.2, respectively. These compounds existed as phenolate anions under alkaline condition and predominant as molecular form under acidic condition. Biosorption capacities increased at pH < 5 and decreased with further increased in pH. Repulsion force formed between negatively charge PCP surface and phenolate anions at higher pH. At pH 5, maximum adsorption for phenol, 2-CP, and 4-CP were 70.41, 79.12, and 84.84 mg/g, respectively. Increment of adsorbent dosage 0.05 to 0.6 g improved biosorption ability with greater percentage removal but no significant improvement after 0.6 g. Maximum removal percentage for phenol, 2-CP, and 4-CP with 0.6 g adsorbent used were 86%, 93% and 95% respectively. Optimum conditions to remove phenol, 2-CP, and 4-CP were pH 5, only 60 minutes contact time needed and 0.6 g/0.1 L PCP used [45]. The optimum adsorption capacities were 164.51 mg/g, 189.44 mg/g and 220.12 mg/g, respectively. Both adsorption PBP and PCP on phenolic compounds favoured acidic condition. However, PCP with shorter contact time was more applicable in industry as compared to PBP.

Karri et al. [26, 46] and Prashanthakumar et al. [47] both used coconut as raw material for their adsorbents. Karri *et al.* [26, 46] synthesized activated carbon from coconut shell to remove phenol while Prashanthakumar et al. [47] used coconut spathe to remove phenol, 2-CP and 4-CP. Coconut shell activated carbon (CSAC) synthesized by Karri et al. [26, 46] underwent chemical and physical activations. After that, samples were rinsed with 0.5 N HCl and distilled water with pH maintained at pH 6, while last step of synthesis involved drying process at 110 °C. From Karri's study [46], adsorption of phenol increased with increasing of adsorbent dosage and decreasing of initial phenol concentration. Percentage removal up to 96% was achieved with 100 g of adsorbent used. 78% of percentage removal increased to 96% when initial phenol concentration reduced from 100 mg/L to 25 mg/L. Equilibrium was reached after 95 minutes. They reported the chemisorption mechanism since it was observed that pseudo second order model, fits the experimental phenol adsorption data as compared to the pseudo first order model.

Prashanthakumar et al.[47] reported that their pre-carbonized coconut spathe material was treated with potassium hydroxide (KOH) that acted as activating agent to produce KOH-treated activated carbon (KAC).

Hydrochloric acid was added to unclog pores from chemical residues. Through SEM analysis, the KAC showed smooth surface texture and pores could be observed appeared on the top surface. The pore opening provided access into the internal pores. Due to the interaction between phenolic compounds and the functional groups present in the adsorbent, some of the pores became widened. Highest removal of 98% was achieved for phenol by using 100 mg of adsorbent. BET surface area for KAC was a staggering 1705 m^2/g. Percentage removal increased with initial adsorbate concentration from 10 ppm to 100 ppm. Adsorption for phenol, 2-CP and 4-CPat 100 ppm were 120, 262, 275 mg/g respectively. Equilibrium was reached after 30 minutes. Optimum pH to remove adsorbate was pH 7. Adsorption ability was weak at higher pH due to electrostatic repulsion between adsorbent surface and adsorbates. However, adsorption performance at strong acidic condition (<pH 3) decreased as well because proton in solution competed with adsorbates for active site. From pH 3-7, percentage removal increased from 74% to 80% for phenol, 87% to 90% for 2-CP and 94% to 95% for 4-CP. Both Karri et al. [26, 46] and Prashanthakumar et al. [47] used coconut waste as precursor for their adsorbent. KAC could be concluded as a more effective adsorbent for phenol as compared to CSAC due to its shorter contact time, lower adsorbent dosage and highest removal percentage. The adsorption mechanism was reported to be largely dependent on the −OH and −Cl functional groups and their interaction with the adsorbent surface. For removal of phenol, 2-CP and 4-CP, Siva Kumar et al. [45] and Prashanthakumar et al. [47] reported that removal percentage of adsorbates increased with more amount of adsorbent but could not improve adsorption density or amount of adsorbate adsorbed per unit mass. This was due to agglomerations and overlapping of high amount of adsorbent that led to decreasing of surface area. 4-CP and 2-CP had higher adsorption capacities as compared to phenols. This was because driving force for phenols from bulk solution to adsorbent surface decreased when small-sized phenols molecules diffused easily into internal pores [47].

Activated carbon from avocado seed had different synthesis procedure. Leite et al. [31, 48] grinded 100 g of avocado seed to obtain particle size < 250 μm and followed by mixing of water and $ZnCl_2$ as activating agent. The paste was put in furnace for heating under nitrogen flow (150 mL/min). Final heating temperature (500-700 °C) and heating time (30,45,60 min) were determined by using a 2^2 full-factorial design of experiment. Pyrolysis step was done when samples cooled down under nitrogen atmosphere with temperature < 150 °C. Samples were refluxed at 80 °C with concentrated HCl. Adsorption process involved 1.5 g/L of ASAC adsorbent, contact time of 120 min and temperature of 25 °C. Activated carbon had adsorption capacity of 99.5 to 327 mg/g towards 15 phenolic compounds. Specific surface area for adsorbent was a staggering 1584 m^2/g. In the ASAC, they found out the surface contained large amounts–OH, –COO, –O and –NH which exhibit hydrophilic behaviour for adsoprtion. Umpierres et al. [49] synthesized activated carbon from tucuma seed (palm family) to remove 2-nitrophenol from aqueous solution. Tucuma seed was added with water and $ZnCl_2$ that acted as activating agent until a homogeneous paste was formed. Later, the paste was subjected to microwave-assisted pyrolysis. Pyrolyzed materials were then refluxed at 75 °C with concentrated HCl solution. Specific surface area of adsorbent was 1318 m^2/g. Optimum conditions to remove 2-nitrophenol were pH 7, contact time of 30 minutes, adsorbent dosage 1.5 g/L and temperature of 50 °C. Maximum adsorption capacity for adsorbent (TMAC-2.0) based on the most suitable isotherm model (Liu model) was 1382 mg/g at elevated temperature (50°C). Adsorption of 2-nitrophenol onto adsorbent was exothermic and spontaneous.

Both Leite et al. [31, 48] and Umpierres et al. [49] synthesized activated carbon from seed using pyrolysis method with $ZnCl_2$ as activating agent. Adsorption ability of avocado seed activated carbon towards 2-nitrophenol was better than tucuma seed activated carbon due to greater specific surface area and lower operating temperature. However, contact time of 120 minutes was too long to be utilized in industry. Rice straw is lignocellulosic waste after harvesting paddy. Alternative to in-situ burning, piling and dumping, the waste can be converted into other useful environmental friendly products because it is a carbon-neutral renewable resource [77]. Sarker et al. [50] prepared raw rice straw without activation and synthesized 2 activated carbon from rice straw through physical activation and thermal activation methods. For physical activation, rice straw was boiled for 2 h and dried until a constant weight was achieved. While for thermal activation, rice straw was heated in high temperature until ash was formed. Phenol removal efficiency of 84.07 % was achieved using 2.5 g thermally activated rice straw ash having size <1 mm. Adsorbent with smaller particle size (<1 mm) could remove more phenol as compared to 1 mm particles that had percentage removal of 76.67%. Equilibrium was reached after 1 hour of contact. Thermally activated rice straw ash had greater removal efficiency (84.1%) as compared to physically activated and raw rice straw (<30%). This was because organic matrix in rice straw could be destructed by thermal treatment and thus increased the adsorption surface area.

Conclusion

Safe water supply and effective treatment of wastewater remain as one of the worldwide environmental concern. It is found that for the past four years, there has been significant advances in development of adsorbents from agricultural waste for the removal of pollutants in water or wastewater. Removal characteristics of heavy metals, dyes, pesticide, herbicides and phenolic compounds in water or wastewater using various adsorbents (e.g., coir pith ash, carnauba straw powder, banana peels, tea and coffee ground waste, coconut shell, rice straw, pine bark powder etc) were reviewed. The adsorbent preparation and mechanism of adsorption (e.g., ion-exchange, chemisorption, chelation, electrostatic attraction and hydrophilicity) were specifically discussed. The effect of physicochemical factors on the performance of these adsorbents were reviewed. It can be concluded that the surface area and type of functional groups play a big role in removing pollutants. In most of the research, good removal percentages and adsorption capacities were obtained. The adsorption of the pollutants either follow Langmuir, Freundlich or other linearized isotherms. However, most of the research were developed in synthetic aqueous solutions, which contain the pollutants of interest without the real sample matrix interferences. Thus, it is deemed necessary for future works to conduct experiments in real samples as well as in industrial setup. Subsequently, economic analysis to know the overall cost of the process applicable to industrial setup is also predicted to be inevitable.

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