Agricultural biomass-derived magnetic adsorbents: Preparation and application for heavy metals removal

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ABSTRACT

This paper discusses the synthesis of magnetic adsorbents from agricultural waste and their applications in heavy metals removal. The general methods for preparing magnetic adsorbents and the mechanisms of heavy metal sorption are also reviewed in detail. These mechanisms are related to the utilization of magnetic adsorbents, particularly sugarcane bagasse in heavy metals removal, such as nickel, cadmium, lead, and arsenic. Converting sugarcane bagasse into magnetic adsorbents could solve environmental problems, such as agricultural waste and water pollution. A brief summary of the synthesis of magnetic biochar from sugarcane bagasse and its applications in heavy metals removal is also presented. Thus, this study proposes magnetic-based materials as potential candidates for wastewater treatment, and this adds new dimensions to numerous applications of the carbon family.

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1. Introduction

Recent developments in the field of biochar have led to a renewed interest in the production of synthetic biochar with magnetic properties, known as magnetic biochar. Magnetic biochar is a type of charcoal, which is manufactured by combining a type of biomass with various magnetic modifiers. The mixture undergoes pyrolysis at different temperatures, which would result in a biochar that has been imbued with the magnetic modifier. Abundant waste byproducts from industrial and agricultural activities may be potential inexpensive alternatives for various applications, such as carbon dioxide capture [1], fabrication of electrical double layer capacitors (EDLCs) [2], carbon sequestration [3], soil amendments [4–6], removal of dyes [7], and heavy metals [8–16]. In recent years, several agricultural wastes with high adsorptivity have been tested for their heavy metal removal efficiencies, from simulated wastewaters. Activated carbons prepared from agricultural wastes [3,17–20], as well as various industrial wastes, such as fly ash [21,22], and animal manures [23,24], are a few examples of low-cost materials used in the removal of heavy metal ions from wastewater.

Sugarcane bagasse (SCB) is an abundant agricultural residue from sugarcane processing in South Africa [4,5], India [11], and Brazil [10]. Sugarcane bagasse has been converted into activated carbon and used in numerous applications [3,8,9,11,16,25] due to its high surface area, high surface acidity, and microporous structure [5]. Sugarcane bagasse consists of 3 main components, namely, cellulose, hemi-cellulose, and lignin. Each component presents a different value, as shown in Table 1. Based on these data, it was concluded that sugarcane bagasse is rich in cellulose. Therefore, it can lead to the production of higher microporous biochar concentration [26]. Sugarcane bagasse also contains carboxylic and hydroxyl groups, and hence, shows high efficiency for the removal of metals over a wide range of pH. Lignin is also said to be an ideal precursor for activated carbon as it has a high carbon content, and its molecular structure is similar to bituminous coal [27]. Creamer et al. [1] found that all biochar samples in their work were rich in carbon (>69%), oxygen (>11%), and hydrogen (>2%). Parts of the oxygen, hydrogen, and nitrogen elements in the biochar samples were likely to be in functional groups on the carbon surface [1]. In another work, the presence of polysaccharides and polyphenols were confirmed in pine bark powder [28].

Harikishore et al. [29] studied the IR spectra of magnetic biochar composite prepared from pine bark waste. The spectra of

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Cellulose (%)	Hemi-cellulose (%)	Lignin (%)	References
45	28	18	[88]
46	24.5	19.95	[16]
50	29	13	[89]
42.6	6.2	n/a	[90]

pine bark powder sample and magnetic biochar composite were compared. Several peaks had shifted and several new peaks were observed. Their study suggested that the high frequency band at 560 cm^{-1} and the low frequency band at 441 cm^{-1} corresponded to the Fe–O stretching mode of $CoFe_2O_4$. The peaks observed at 3440 cm^{-1} and 1628 cm^{-1} were assigned to OH groups. The band observed at 1631 cm^{-1} was due to carboxyl groups, which represent a hydrophilic nature, and can act as anchoring sites for ferrite particles in the preparation of magnetic biochar composites. It was concluded that the absorption bands were common characteristics for inverse spinel ferrites. FTIR analyses of thermally treated oak barks were conducted by [14].

The main objective of this current study was to utilise agricultural waste into a magnetic material. Additionally, the use of magnetic-based materials as potential candidates for any kind of liquid pollutant removal was discussed in detail in the following section.

2. Preparation of magnetic adsorbent from agricultural biomass

There are two common approaches to produce a magnetic adsorbent, namely, chemical co-precipitation and pyrolysis at dissimilar febricities. A combination of both methods to produce magnetic biochar or magnetic activated carbon is also favoured. The combination of pyrolysis and co-precipitation starts with the co-precipitation of biomass, and followed by chemicals to improve the adsorption capability of the biomass [14,30–34]. Then, the biomass is carbonised at different temperatures (normally below 800 °C), in the absence of oxygen to increase its porosity and surface area. Other methods to synthesize magnetic adsorbents include co-precipitation [14,29–34], thermal decomposition [35], hydrothermal [36,37], polyol process [38], sol–gel [39], and chemical reduction [40].

2.1. Co-precipitation

Co-precipitation is a facile and convenient way to synthesize iron oxides (either Fe_3O_4 or γ-Fe_2O_3) from aqueous Fe^{2+}/Fe^{3+} salt solutions by adding a base under inert atmosphere at room temperature or at an elevated temperature. The size, shape, and composition of the magnetic adsorbents depend on the type of salts used. Fe^{2+}/Fe^{3+} ratio, reaction temperature, pH value, the ionic strength of the media, and the mixing rate with the base solution are some of the factors that promote precipitation. Co-precipitation is the preferred route due to its simplicity. Additionally, the reaction temperature and time are lower compared to in other methods. The solvent is also environmental friendly (water), while producing high and scalable reaction yield. However, controlling the particle size is among the challenges of the co-precipitation method, which often leads to a narrow particle size distribution. Particles prepared via co-precipitation tend to be polydispersed. It is well known that a short burst of nucleation and the subsequent slow and controlled growth is crucial to produce monodispersed particles [41,42]. For example, magnetic biochar was synthesized from pine bark (PB) waste via chemical co-precipitation for the removal of cadmium and lead from an aqueous solution. The pink

bark waste residue was collected and crushed into powder form before being washed and dried. Cobalt nitrate and ferric nitrate were dissolved in ethanol, and then mixed with the powder before undergoing pyrolysis [29]. A mixture of ferrous chloride and ferric chloride solution was added into the resultant dried orange peel powder to produce magnetic biochar [19]. A suspension of activated carbon at room temperature was added into a mixture of ferric sulphate and ferrous sulphate solution, and was slowly stirred for 30 min. After the solution has been thoroughly mixed, its pH was adjusted, using 10 M NaOH, to pH 10–11. This solution was mixed for another 60 min, before being aged at room temperature for 24 h. The suspension was then filtered and repeatedly washed with water and ethanol, followed by subsequent drying at 323 K [43].

On the other hand, Yu et al. (2012) developed magnetic sugarcane bagasse (SCB) by co-precipitating modified SCB with a mixture of $FeCl_3$ and $FeSO_4$ solution [25]. The magnetic sorbent was collected by magnetic separation after 30 min of reaction. First, the collected solid was washed with EDTA solution to remove the absorbed iron ions, and followed by distilled water to neutralise the pH. Magnetic activated carbon was developed by Kakavandi et al. (2013) using chemical co-precipitation method [44]. Activated carbon powder was added into an aqueous solution containing Fe_3O_4 and stirred for 1 h at 80 °C. Then, the sample was filtered and dehydrated in an oven at 105 °C for 1 h to form the AC-Fe_3O_4 magnetic nanoparticles, the filtered suspension was calcined at 750 °C for 3 h under nitrogen gas. Finally, the synthesized adsorbent was washed with deionized water, and dried at 105 °C.

2.2. Thermal decomposition

One of the simplest and most important methods for preparing magnetic adsorbent is via the decomposition of metal precursors, most often of the organometallic complexes. Small sized magnetic nanocrystals can be synthesized through the thermal decomposition of organometallic compounds in high-boiling organic solvents that contain stabilizing surfactants. Thermal decomposition appears to be the best method to control the size and morphology of nanoparticles, as well as to produce high and scalable yields. However, one of the major disadvantages of this method is the production of organic soluble nanoparticles, which limits the extent of application of this method in biological fields. Additionally, surface treatment is required after the synthesis, which usually leads to complicated processes, and relatively high temperatures [41].

Several steps were involved to synthesize magnetic adsorbents for the removal of Pb(II) using thermal decomposition, which included the formation of microemulsion [35]. Then, a mixture of cobalt chloride, ferric sulphate, and $H_2C_2O_4 \cdot 2H_2O$ were added into two identical microemulsions. Then, these two solutions were mixed under vigorous stirring for 1 h. After the reaction, the yellowish-brown precipitate was collected via centrifugation. The collected precipitate was washed several times with distilled water and absolute ethanol, and then, dried in vacuum. A black powder was obtained after calcination, which was collected for further investigation.

2.3. Hydrothermal

Hydrothermal is a method for synthesising magnetic nanoparticles, which can be performed in an aqueous media in reactors, or autoclaves, at pressure of higher than 2000 psi and temperature of higher than 200 °C. Hydrothermal processing is an effective way to grow crystals from different materials. This technique can also be used to grow dislocation-free single-crystal particles, and grains formed in this process could have better crystallinity than those from other processes. Moreover, hydrothermal reactions

can proceed at the same level of conversion efficiency as higher temperature processes [45]. Although the hydrothermal technique is very versatile, one of the main drawbacks of conventional hydrothermal method is the slow reaction kinetics at any given temperature [41]. Hydrothermal method has been used to synthesize magnetic Fe_3O_4 microspheres as potential adsorbents for the removal of trace heavy metal ions (Cu^{2+}) [36]. Ferric chloride was dissolved in ethylene glycol to form a yellow solution at 50 °C. An appropriate amount of basic sodium salt was then added to the mixture. It was vigorously stirred for 30 min until homogenized, and then, transferred to a Teflon-lined stainless steel autoclave. The autoclave was heated at 198 °C for 14 h, and then allowed to cool down to room temperature. The resultant black particles were separated via centrifugation, washed with water and ethanol, and dried at room temperature.

2.4. Polyol

The polyol process is a route for preparing finely divided metal powders of easily reducible metals, or less reducible metals from the reduction of inorganic precursors in liquid polyols. Polyols can either be polyhydric alcohols (also known as a-diols), such as 1,2-ethanediol (ethylene glycol) and 1,2-propanediol (propylene glycol), or ether glycols, namely, diethylene and triethylene glycol. The solid precursor is suspended in the liquid polyol, which may be quite soluble (nitrate, chloride, acetate) or only slightly soluble (oxide, hydroxide). The solution, or suspension is stirred and heated to a given temperature, which can reach the boiling point of the polyol for less reducible metals; conversely, for easily reducible metals, the reaction can be conducted at temperature of as low as 0 °C. Polyols are interesting among non-aqueous solvents because like water and monoalcohols, they are hydrogen-bonded liquids with high values of relative permittivity. Therefore, they are able to dissolve, to some extent, ionic inorganic compounds. Moreover, polyols and monoalcohols are mild reducing agents, but reduction can be conducted in these solvents under atmospheric pressure and at temperature of up to 250 °C if necessary. A series of polysulphone membranes grafted with polyol polymers, for boron removal via complexation of the vicinal diol structure with boric acid, has been synthesized using the polyol method [38]. The as-prepared membranes were washed thoroughly with deionized water and ethanol before being dried under vacuum at 60 °C until a constant weight was obtained.

2.5. Sol–gel

The sol–gel process is a wet-chemical technique that uses either a chemical solution (sol is short for solution) or colloidal particles (sol for nanoscale particles) to produce an integrated network (gel). Sol–gel technology is a well-established colloidal chemistry technology, which offers endless possibilities for producing various materials with novel, predefined properties in a simple process and at relatively low process costs. The sol–gel process consists of the chemical transformation of a liquid (the sol) into a gel state, and with subsequent post-treatment and transition, into a solid oxide material. Metal alkoxides and metal chlorides are typical precursors that would undergo hydrolysis and polycondensation reactions to form a colloid, which is a system of nanoparticles dispersed in a solvent. The sol will evolve into an inorganic, continuous network that contains a liquid phase (gel). The formation of a metal oxide involves connecting the metal centres with oxo (M–O–M) or hydroxo (M–OH–M) bridges to generate metal-oxo, or metal-hydroxo polymers in the solution. The liquid phase is removed from the gel via a drying process. Then, thermal treatment (calcination) may be performed, which favours further polycondensation and enhances the mechanical properties of the gel. The main benefits of the sol–gel process are high purity and uniform nanostructures, which are achievable at low temperatures.

Magnetic mesoporous silica-coated carbon nanotubes were produced from hydrophilic monodispersed magnetic carbon nanotubes (CNTs) using the sol–gel method for the adsorption of methylene blue (MB) [39]. Briefly, the obtained CNTs/Fe_3O_4 nanocomposites and cetyltrimethylammonium bromide (CTAB) were dispersed in a solution containing deionized water, concentrated ammonia solution, and ethanol. The mixture was homogenized to form a uniform dispersion. Then, different amounts of TEOS were added dropwise into the dispersion under vigorous stirring. After an 8 h reaction, the product was collected using a magnet, and washed 3 times with deionized water and ethanol to remove byproducts, and finally dried overnight in a vacuum condition at 60 °C. The surfactants were removed using a fast and efficient ion exchange method to obtain CNTs/Fe_3O_4@mSiO$_2$ core–shell structures.

2.6. Chemical reduction

Chemical reduction of metal salts is the most common method for producing magnetic adsorbents and nanoparticles among the various solution-phase chemistry routes. The key advantage of this method is its simplicity. It can be safely conducted in most laboratories, with simple chemical reagents and at room temperature conditions [41]. Manganese ferrite nanoparticles were synthesized for dye removal by Mahmoodi (2014) [40]. A mixture of manganese nitrate and iron nitrate was added into an aqueous solution of NaOH in distilled water and ethylene diamine (EG). This mixture was heated at 90 °C for 1 h to achieve complete chelation. Calcination at 500 °C for 1 h, with a heating rate of 10 °C/min was performed. Manganese ferrite nanoparticles and (3-aminopropyl)trimethoxysilane were poured into a mixture of water, ethanol, and nonionic surfactant, which were mixed for 24 h at 25 °C. Finally, the precipitate was filtered, washed with deionized water, and dried.

2.7. Microwave-assisted pyrolysis

The main objective for using microwave heating is to reduce the preparation time as well as to improve the adsorption quality of the adsorbent. Normally, biomass will be impregnated with an activation agent, such as phosphoric acid, sulphuric acid, zinc chloride, and potassium hydroxide [15,17,46–51]. Following the impregnation process, the biomass will be placed in a microwave for the activation and carbonization process. To produce magnetic adsorbents, different activation agents must be used. Activation agents for magnetic adsorbents normally consist of metallic particles, such as nitrate, cobalt, chloride, and oxide particles. Oxide particles have been proven to give better magnetic property compared to other metallic particles [52]. Microwave heating is able to heat the target compounds without heating the entire furnace, which consequently saves time and energy. Microwave heating transfers energy instead of heat. Thus, it is able to heat sufficiently small objects throughout their volume, or in other words, produces more uniformed heating.

In this process, the microwave power, impregnation ratio, and radiation time have significant effects on the samples produced [53]. Total pore volume will increase progressively with time at high microwave power due to the formation of new pores. BET surface area will also increase at high microwave power due to the carbon–CO_2 reaction and higher release of volatile matters [54]. Increasing the impregnation ratio will significantly increase the adsorption capacity, but it will decrease beyond the optimum impregnation ratio [55]. This phenomenon could be due to several

reasons, such as the blockage of access activation agents, the widening or burning of pores, and the formation of new pores [53]. Radiation time also has a significant effect on the surface area as well as the total pore volume. Liu et al. (2010) reported that prolonged radiation time may cause micropores to enlarge and consequently, the total pore volume will increase, even though the number of micropores has decreased [56].

2.8. Conventional pyrolysis

Conventional pyrolysis is also commonly used to produce magnetic biochars. This method transfers heat between objects via conduction, radiation, and convection. Thus, the surface of the material is first heated, and followed by the heat moving inward. This means that there is a temperature gradient from the surface to the inside of the material. Instead of using a single-route synthesis, conventional pyrolysis consists of two processes, namely, carbonization and activation. Carbonisation involves the formation of a non-porous char via pyrolysis of the precursor at a temperature that ranges between 600 and 900 °C in an inert atmosphere. The second stage (activation) involves contacting the char with an oxidising gas, such as CO_2 or steam at 600–1200 °C, which would remove the more disorganised carbon, and the formation of a well-developed micropore structure [27].

3. Mechanism of heavy metal sorption by biochars

Magnetic biochars are frequently used as adsorbents to remove toxic metals from wastewater [14,29,31,32,57]. This removal process consists of four main metal sorption mechanisms: (i) ion exchange, (ii) metal complexation, with free functional groups, in addition to physical adsorption, (iii) surface precipitation, and (iv) intra-particle diffusion.

The resultant characteristics of metal sorption are closely related to the source material used for biochar preparation. Agricultural wastes are usually composed of lignin and cellulose as the main constituents. Other components include hemicellulose, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other compounds that contain various functional groups in the binding process. Biochar derived from lignin has poorly developed structure; hence, metals are predominately adsorbed by a combination of ion exchange and metal chelation, mainly with carboxyl functional groups. Due to the porous nature of the bagasse/lignin biochars, an intraparticle diffusion model was applied to describe the sorption kinetics. Sorption is more efficient, and such metal-interactions are extremely strong compared to physical sorption. The functional groups in biomass molecules have the affinity for metal complexation. Some biosorbents are non-selective and would bind to a wide range of heavy metals, with no specific priority, whereas others are specific for certain types of metals, depending on their chemical compositions.

It was observed that metal ion sorption is influenced by pH, temperature, and the various functional groups present on the adsorbents. The pH of the solution is one of the dynamic parameters in an adsorption process, which could affect the solubility of the metal ion, the degree of ionization, and the surface characteristics of the adsorbents. Thus, most metal ions adsorption studies have extensively investigated the pH effect. The types of agricultural-based adsorbents and the target metal ions will determine the optimum pH values for particular conditions. The optimum pH value for the removal of a majority of cationic metal ions was observed to range between pH 5.0 and pH 6.0. In the case of cationic metal ions, it was observed that metal removal was increased at higher pH values. At low pH, most of the functional groups in the adsorbents would be protonated and presented in positively charged forms. Additionally, the large numbers of H^+ and H_3O^+ in the aqueous solution may compete with the metal ions for available adsorption sites on the adsorbents. Thus, electrostatic repulsion will occur between the metal ions and the positively charged adsorbents' surfaces. Therefore, lower adsorption is usually observed at low pH by most of the previous studies. Similar trends were observed for divalent metal cations with various types of adsorbents. In a study of Cd(II), Pb(II), Ni(II), Zn(II), and Cu(II) adsorption on the xanthation of sugarcane, the removal percentages of these metal ions reached maximum values at pH range of 4–6 [16]. Similarly, the adsorption of Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) ions onto marine algal biomass showed that the optimum pH for all studied metal ions was at pH 5.5, except for Pb(II) ions, which was at pH 5 [58]. Meanwhile, the optimum removal percentage for anionic metal ions occurs at low pH. The effect of pH on anion adsorption was observed to be dependent on the type of anions and type of adsorbents. In a study of Cr(VI) adsorption using aluminon-functionalized magnetic nanoparticles, it was reported that the optimum pH 1 was required for Cr(VI) removal [37]. In the case of Cd(II), the adsorption would increase with increasing pH. However, at pH 7.0, the hydrolysis of cadmium ions will occur [11]. The solution's pH can influence the chemical speciation of metal ions. Furthermore, the concentration of hydrogen ions would be high at pH of lower than 6.0, and their high mobility would create a competition with metal ions [11,16]. The surface functional groups on the biomass and the metal chemistry in the solution could affect the metal uptake based on pH. Lesser surface ligands with negative charges at low pH would create a repulsive force among the metal cations and decrease the adsorption [16,58,59].

Knowledge of the kinetics of the adsorption process is required for a practical application of agricultural-based adsorbents for pollutant removal. Thus, kinetic models have been developed to analyse the experimental data, to determine the adsorption mechanism. Batch adsorption reactions of more than one parameter are usually conducted for kinetic studies. Linear and/or non-linear regression equations are then used to determine the best-fitting kinetic rate equation. Several kinetic models have been established to understand the adsorption kinetic models. However, the three most popular kinetic models, which are widely used to study the adsorption of metals and dyes using most adsorbents, are: (i) the pseudo-first-order kinetic model; (ii) the pseudo-second-order kinetic model; and (iii) the intra-particle diffusion model. These kinetic models provide valuable information related to adsorbent surface, chemical reaction, and/or diffusion mechanisms, which controls the adsorption process. On the other hand, analysis of isotherm data is important to develop an equation that accurately represents the results, which could be used for design purposes and to optimize the operating procedure. The most common isotherms in solid/liquid systems due to their straightforwardness and easy interpretability are the theoretical equilibrium isotherms; Langmuir and Freundlich models.

4. Applications of agricultural waste as adsorbent

Contamination of wastewater by metal ions, such as cadmium, chromium, arsenic, nickel, and zinc is an on-going problem due to their toxicity. One of the major problems caused by industrial activities is the rising water pollution problem. Hence, water pollution control is needed towards preserving the ecosystem for the future. Nowadays, the removal of hazardous metal ion pollutants using the adsorption method is widely applied [10,16,18,23,29,30,46,58,60–65]. The application of activated carbon and biochar as adsorbents have been widely studied [8,11,16,20,31,32,62,66–70]. Because they are low cost, porous, rich in carbon, and have the ability to adsorb metal ions, biochar and activated carbon have been widely used in water pollution control [11,13,16,19,69,71,72].

Oak wood and barks were used as precursors to produce magnetic biochar for removing cadmium and lead ions. It was proven that these magnetic biochars can remediate Pb^{2+} and Cd^{2+} better than their corresponding nonmagnetic biochars [14]. Activated carbon prepared from palm kernel shells, via phosphoric acid impregnation and microwave activation, was found to be an effective adsorbent for the removal of Cr(VI) from water [47]. The novel magnetic biochar was synthesized using the single-stage microwave heating technique, using EFB in the presence of ferric chloride hexahydrate, for the removal of cadmium, with 265 mg/g adsorption capacity [73].

The growing number of manufacturing industries in Malaysia is observed as the major contributor for metal pollution in the environment due to various processes, such as metal-finishing and mining. High concentrations of heavy metals, such as cadmium, lead, zinc, nickel, copper, and arsenic, have been identified as major sources of wastes produced by these industries. This has led to a sharp increase in water contamination, which has affected the various uses of water. The parameters applied in this current study have been restricted to a few heavy metals, such as Ni, Cd, Pb, and As with regard to the water quality status from the report produced by the DOE [74–80].

A comparison of heavy metals removal by various adsorbents is summarized in Tables 2 and 3. To overcome the growing pollution problems, adsorbents from various sources have been widely studied. A summary of heavy metals removal by sugarcane bagasse is presented in Table 4.

4.1. Removal of nickel

Nickel is a nonbiodegradable and toxic heavy metal ion, which is present in wastewater. The main sources of nickel pollution in water include galvanization, smelting, mining, dyeing operations, battery manufacturing, and metal finishing. Nickel is beneficial to humans as an activator for various enzyme systems at trace amounts, but if it is beyond the normal levels, different types of diseases can occur, such as lung cancer, renal edema, skin dermatitis, and gastro intestinal disorder. Thus, the World Health Organization (WHO) has set up 0.02 mg/L of Ni(II) as the permissible level. Thus, removing nickel from wastewater is mandatory towards maintaining a safe ecosystem. Sugarcane bagasse pith activated carbon, produced via the physical activation method, was proven to be more effective for the adsorption of Ni(II) from aqueous phase [8].

Sugarcane bagasse pith activated carbon has the highest surface area (536.50 m^2/g), followed by commercial activated carbon, and raw sugarcane bagasse pith. These activated carbons have a porous structure and hence, have good adsorption capacities towards various elements [27]. Apart from having high surface area and porosity, sugarcane bagasse pith also has the highest cation exchange capacity (3.96 meq/g) among other materials, which would consequently help with the nickel sorption process. It was proven that the surface area of raw sugarcane bagasse pith is lower compared to those that have been converted into activated carbon. This might be due to the decomposition of organic substances and the formation of micropores during the pyrolysis process [4,71]. The FTIR spectra of these samples clearly show that sugarcane bagasse pith-activated carbon has functional groups that play important roles in adsorbing heavy metals [11].

Additionally, the amount of nickel adsorbed by sugarcane bagasse pith-activated carbon had increased with time, with the capacity of 140.85 mg/g in aqueous solutions at pH 6.5. The two main factors that can influence the pattern of adsorption at various solution pH, are the pH_{zpc} of sugarcane bagasse pith-activated carbon and Ni(II) speciation in solution as a function of pH. pH_{zpc} is the pH value for the materials when the surface charge density equals zero. Thus, it was confirmed that the surface carries positive charges below the pH 5.6 and negative charges above pH 5.6, which is consistent with experimental data that indicated the low adsorption percentage at pH below 5.6. This phenomenon occurred due to the repulsion of Ni(II) species by the positively charged adsorbent surface. However, due to the inter ionic attractions at above pH 5.6, where the surface is negatively charged, the amount of adsorption had increased. The Ni(II) speciation also favours the adsorption process at pH > 5.6 due to the presence of Ni^{2+} species, which was consistent with Garg et al. [12], and as explained by [58,59]. Thus, based on the observation and experimental data presented, it was concluded that the mechanism involved in the removal of Ni(II) was most likely cation exchange due to the reduced pH from before and after adsorption [8].

4.2. Removal of cadmium

Cadmium is one of the heavy metals used in industrial processes, such as metal plating, batteries, phosphate fertilizers, mining, pigments, stabilizers, and alloys. This type of heavy metal can affect blood pressure, kidney, testicular tissues, and red blood cells of humans. In India, the permissible limit of cadmium for wastewater discharge is 0.1 mg/L. Various researches have been done to find the best solution to remove cadmium in wastewater. In 2008, the feasibility of various agricultural wastes, including sugarcane bagasse (SCB), maize corncob (MCC), and Jatropha oil cake (JOC) for the removal of Cd(II) from aqueous solution, under different experimental conditions, was demonstrated using native sugarcane bagasse, without any treatment or activation method [11]. The maximum metal removal was observed at pH 6.0, with 20 g/L adsorbent dose at 250 rpm stirring speed for 60 min' contact time. Significant effect of pH on the sorption of Cd(II) on different adsorbents was confirmed. In another study, Cd(II) removal was examined using succinic anhydride-chemically modified sugarcane bagasse, where the carboxylic acid functions introduced into the material were used to anchor polyamines, which contributed to the maximum adsorption capacity of cadmium of 313 mg/g [10]. They concluded that metal ion adsorption efficiency is proportional to the number of amine functions introduced into the material.

In another work, ferric oxide magnetic biochars derived from mangosteen peels had exhibited good removal efficiency compared to woody-based biomasses [14,81]. In particular, the removal percentage of Cd (II) was 49% at pH 2, which reached a maximum adsorption of 97% at pH 8. The Cd(II) adsorption exhibited a decreasing trend when the pH gradient moved towards the alkaline region, and had resulted in very low adsorption percentage of 30% at pH 12. Similar results, to improve the rate of Cd(II) removals, were also reported for magnetic biochar from oak bark [14], iron oxide tangerine peel extracts [82], and magnetic biochar derived from coconut shells [83].

4.3. Removal of lead

According to ATSDR, lead is the second top priority hazardous substance. Due to its nonbiodegradability, lead has the tendency to accumulate in blood, soft tissues, and bones. Acute diseases, such as brain damage, kidney damage, gastrointestinal distress to humans, and damage to the central nervous centre are some of the effects of long-term consumption of water containing Pb(II). Hence, the United States Environmental Protection Agency has set up the maximal permissible limit to 0.0015 mg/L (15 ppb), while WHO recommended a limit of 10 μg/L of lead in drinking water. Data from several studies have identified that low-cost adsorbents have significant effect on lead removal in aqueous solution [16,65,68]. Sugarcane bagasse biochars, which were synthesised using conventional pyrolysis method without any activating agent, were found

Table 2
Comparison of adsorption capacity of adsorbents for heavy metals.

Adsorbent(s)	Adsorbate(s)	Adsorption capacity (mg/g)		pH	Temp. (°C)	Kinetic model	Isotherm	Ref.
Activated carbon from sugarcane bagasse pith	Ni(II)	140.85		6.5	–	PSO	Langmuir	[8]
Sugarcane bagasse (chemical activation)	Cr(III)	77.5 mg/L		8.58	40	PSO	Langmuir	[9]
Sugarcane bagasse	Cu(II)	133		6	–	PSO	Langmuir	[10]
	Cd(II)	313						
	Pb(II)	313						
Sugarcane bagasse with succinic acid	Cd(II)	–		6	–	–	Langmuir	[11]
Sugarcane bagasse	U(II)	17.15		5	27	PSO	Langmuir	[12]
Miscanthus Sacchariflorus	Cd(II)	13.24		6		PSO	Langmuir	[13]
Oak wood (OW) and oak bark (OB)	Cd(II)	OB	OW					[14]
		8.33	3.04	5	45	PSO	SIPS	
	Pb(II)	55.91	8.92					
Switchgrass biochar	Cu(II)	Cu: 31		5	23	–	–	[15]
	Cd(II)	Cd: 34						
Xanthation of sugarcane	Cd(II)	2.04 mol/kg		4–6	30	PSO	Langmuir	[16]
	Pb(II)	1.69						
	Ni(II)	2.80						
	Zn(II)	2.54						
	Cu(II)	3.13						
Corn straw	Cd(II)	858		7	25	–	Freundlich	[18]
Orange peel	Phosphate	1.24		–	25	–	Langmuir	[19]
Dairy-manure	Pb(II)	583 mmol/kg		–	–	–	Langmuir	[23]
Sugarcane bagasse	Cr(VI)			2	25	–	–	[88]
Pine bark waste	Cd(II)	17.793		5	–	PSO	SIPS	[28]
	Pb(II)	29.699		5	–	PSO	SIPS	
Empty fruit bunch	Cd(II)	265		–	30	N/A	N/A	[72]
Almond shell	Ni(II)	Ni: 22.22		7	40	PSO	Langmuir	[29]
	Co(II)	Co: 28.09		7	40	PSO	Langmuir	
Cotton wood	Ar(V)	3.147		–	22	PFO	Langmuir	[31]
Magnetic cobalt ferrite microparticles	Pb(II)	44.58		–	25	PSO	Langmuir	[34]
		76.22		–	35	PSO	Langmuir	
		80.32		–	45	PSO	Langmuir	
Aluminon functionalized magnetic nanoparticles	Cr(VI)	Cr(VI): 263.2		1	25	PSO	Langmuir	[36]
	Cr(III)	Cr(III): 400		7	25	PSO	Langmuir	
Sea Buckthorn stone	Pb(II)	51.81		6	25	–	SIPS	[45]
Palm kernel fibre	Cr (VI)	19.1		3	50	PSO	Freundlich	[46]
Bagasse	Pb(II)	–		–	22	PSO	Langmuir	[70]
Potato peel	Cu(II)	62.76		6	25	PSO	Langmuir	[59]
Alternanthera philoxeroides	Pb(II)	257.12		5	25	PSO	Langmuir	[60]
Marine Algal biomass (*Sargassum sp. Padina sp.,*)		S	P					[57]
	Pb(II)	1.16	1.25	5	22	–	Langmuir	
	Cu(II)	0.99	1.14	5.5	22	–	Langmuir	
	Cd(II)	0.76	0.75	5.5	22	–	Langmuir	
	Zn(II)	0.61	0.81	5.5	22	–	Langmuir	
	Ni(II)	0.50	0.63	5.5	22	–	Langmuir	
Iron-doped activated carbon	Ar(V)	–		8	25	–	–	[61]
Microporous AC (jute stick)	Ar(V)	1320		–	25	–	–	[62]
Pine wood (PW)	Pb(II)	PW: 4.25		5	25	PSO	Langmuir	[64]
Rice husk (RH)		RH: 2.40		5	25	PSO	Langmuir	
Iron oxide/hydroxide nanoparticles	Pb(II)	Lepidocrocite: 847.81		5.2	25	–	Langmuir and SIPS	[65]
		Goethite: 820.165		5.2	25	–	Langmuir and SIPS	
Acrylamide–titanium nanocomposites	Cd(II)	322.58		8	30	PSO	SIPS	[66]
TSNT	Pb(II)	184.32		7	25	PSO	Langmuir	[67]
Biochar-alginate capsule	Pb(II)	263.15		5	27	PSO	Langmuir	[68]
Lignin	Cu(II)	ACM: 1.541 mmol/g		6	28	PSO	Langmuir	[71]
		ACS: 1.152		6	28	PSO	Langmuir	
C. Vulgaris	Cd(II)	111.1		4	20	PSO	SIPS	[58]
MWCNT	As(V)	–		–	–	–	–	[84]
Sugarcane bagasse	As(III)	As (III): 28.57		7	–	PFO	SIPS	[85]
	As(V)	As (V): 34.48		7	–			
Sugarcane bagasse	As(V)	22.1		4	22	–	Langmuir	[86]
Sugarcane bagasse	Cd(II)	Cd: 1.1 mmol/g		5	Room temp.	PFO	Langmuir	[91]
	Pb(II)	Pb: 1.2 mmol/g		5		PSO		

** PFO, pseudo-first-order; PSO, pseudo-second-order.

to be effective in removing Pb(II) from aqueous solution [71]. From the FTIR spectra analysis, several peaks that could be attributed to metal binding were present in the biochar. The presence of –OCH$_3$ groups can be attributed to lignin structure in sugarcane bagasse [11]. They had also identified that sugarcane bagasse has oxygen-containing functional groups, which was consistent with findings by Garg et al. [11]. Ding et al. [71] have determined the zeta potential to characterize the surface charge. They found that sugarcane bagasse biochars produced at 500 °C gave the highest value of cation exchange capacity. In a subsequent research, the charred xanthate sugarcane bagasse (CXSB) can be used as a selective adsorbent for the removal of lead ions from wastewater due to its high adsorption capacity and kinetic results [16].

4.4. Removal of arsenic

Arsenic is also one of the top poisonous heavy metals, which contaminates water sources around the world. It will lead to high

Table 3
Comparison of adsorption capacity of sugarcane bagasse waste for range of heavy metal.

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Isotherm	Ref.
Activated carbon from sugarcane bagasse pith	Ni(II)	140.85	Langmuir	[8]
Sugarcane bagasse (chemical activation)	Cr(VI)	77.5 mg/L	Langmuir	[9]
Sugarcane bagasse	Cu(II)	133	Langmuir	[10]
	Cd(II)	313		
	Pb(II)	313		
Sugarcane bagasse	Uranyl	17	Langmuir	[12]
Xanthation of sugarcane	Cd(II)	1.95 mol/kg	Langmuir	[16]
	Pb(II)	1.58 mol/kg		
	Ni(II)	2.52 mol/kg		
	Zn(II)	2.40 mol/kg		
	Cu(II)	2.91 mol/kg		
Sugarcane bagasse	Cr (VI)	69.06		[88]
Sugarcane bagasse	As(V)	22.1	Langmuir	[86]
Sugarcane bagasse	Cd(II)	1.1 mmol/g	Langmuir	[91]
	Pb(II)	1.2 mmol/g		

Table 4
Comparison of adsorption capacity of various magnetic bio-char for the removal of lead and cadmium.

Adsorbent	Adsorption capacity (mg/g)		pH	Temp. (°C)	Kinetic model	Isotherm model	Ref.
Sugarcane bagasse	Cd(II): 313		5–6	–	PSO	Langmuir	[10]
	Pb(II): 313						
Sugarcane bagasse with succinic acid	Cd(II)		6	–	–	Langmuir	[11]
Miscanthus sacchariflorus	Cd(II): 13.24		6	–	PSO	Langmuir	[13]
Oak wood and oak bark	Cd(II): 8.33		5	45	PSO	SIPS	[14]
	Pb(II): 3.04						
Switchgrass biochar	Cd(II): 34		5	23	–	–	[15]
Xanthation of sugarcane	Cd(II): 1.95 mol/g		4–6	30	PSO	Langmuir	[16]
	Pb(II): 1.58						
Pomelo skin	Cd(II): 585		7	25	–	Freundlich	[18]
Dairy-manure	Pb(II): 583 mmol/kg		–	–	–	Langmuir	[23]
Pine bark waste	Cd(II): 2.889		5	–	PSO	SIPS	[28]
	Pb(II): 3.296						
Empty fruit bunch	Cd(II): 265		–	30	–	–	[72]
almond shell	Co(II): 28.09		7	30	PSO	Langmuir	[29]
Magnetic cobalt ferrite microparticles	44.58		–	25	PSO	Langmuir	[34]
	76.22		–	35			
	80.32		–	45			
Sea Buckthorn stone	Pb(II): 51.81		6	25	–	SIPS	[45]
Bagasse	Pb(II):			22	PSO	Langmuir	[70]
Alternanthera philoxeroides	Pb(II) 257.12		5	25	PSO	Langmuir	[60]
Marine Algal biomass *(Sargassum sp.(S), Padina sp.(P))*	S	P					[57]
	Pb(II): 1.16 mmol/g	Pb(II): 1.25 mmol/g	5	22	–	Langmuir	
	Cd(II): 0.76 mmol/g	Cd(II): 0.75 mmol/g		5.5			
Pine wood	PW: 4.25		5	25	PSO	Langmuir	[64]
Rice husk	RH: 2.40						
Iron oxide/hydroxide nanoparticles	Pb(II): 847.81		5.2	25	–	Langmuir and SIPS	[65]
Acrylamide–titanium nanocomposites	Cd(II): 322.58		8	30	PSO	SIPS	[66]
TSNT	Pb(II):184.32		7	25	PSO	Langmuir	[67]
Biochar-alginate capsule	Pb(II): 263.15		5	27	PSO	Langmuir	[68]
C. Vulgaris	Cd(II): 111.1		4	20	PSO	SIPS	[58]
Sugarcane bagasse	Cd(II): 1.1 mmol/g		5	Room temp	PFO and PSO	Langmuir	[91]
	Pb(II): 1.2 mmol/g						

**PFO, pseudo-first-order; PSO, pseudo-second-order.

profile public health problems among communities that depend on underground water sources for drinking. Consumption of water contaminated with arsenic can cause fatal diseases, such as skin cancer, lung cancer, urinary bladder cancer, chronic bronchitis, and cardiovascular diseases [84]. Thus, due to its high risk to public health, the World Health Organization (WHO) and the Environmental Protection Agency (EPA) have suggested a maximum permissible arsenic concentration in drinking water of 10 ppb. Currently, due to its low cost, good performance, and relatively low waste generation, numerous researchers have proposed that adsorption is one of the best options for arsenic removal [85].

Gupta et al. [86] reported that sugarcane bagasse is a versatile adsorbent among other low cost sorbents, which can adsorb a maximum of 28.57 mg/g As(III) and 34.48 mg/g As(V), with the higher values compared to another low cost sorbent reported in

the literature. They had introduced thiol functional group into sugarcane bagasse. They had also confirmed that the adsorption of arsenic ions was closely related to sulphur ligands, where the bonding of sulphur and arsenic molecules had reduced the intensity of disulphide linkage bands. They revealed that when the pH (2–7) was increased, the adsorption capacity had also increased due to the electrostatic force between the protons present in $-SH^+$ group and the existence of As(V) as the negative charge. However, when pH was further increased, the biomass surface became negatively charged, which reduced the adsorption capacity. In the aspect of dosage and contact time, both had the same effect on the adsorption capacity. Adsorption capacity was increased when both parameters were increased. Hydrated ferric oxide (HFO)-treated sugarcane bagasse was used as adsorbents for As(V), and the maximum removal of 98% was reached at pH 4 [87]. The electrostatic

force had taken place in the adsorption mechanism and played an important role [86].

Recently, a new environmentally friendly and low-cost adsorbent, to remove As(V) from industrial wastewater, was synthesized from a mixture of chestnut shells and magnetic gelatin, which produced the maximum adsorption capacity of 45.8 mg/g. This value was higher than that of unmodified adsorbent mixture (17.5 mg/g) and other biochars [88].

5. Future of sugarcane bagasse biomass magnetic biochar

Only a few researches have been conducted since 1997 to synthesize activated carbons from sugarcane bagasse. This is apparent from the limited works on magnetic biochar from sugarcane bagasse. In fact, heavy metal removal studies using sugarcane bagasse biochars have not been applied widely. The potentials of sugarcane bagasse magnetic biochars can be further developed using various types of syntheses and catalysts. This is because different syntheses could produce different properties for the magnetic biochars, as well as producing different adsorption effects based on different catalysts used. Based on the above review, the properties of activated carbons can produce greater sorption capacity for heavy metals, if the functional groups of the components are suitable for certain metal ions.

Extensive studies should be concentrated on removing major heavy metals in wastewater, such as lead, nickel, cadmium, arsenic, and mercury from industrial activities since they may harm many lives due to their high toxicity. Furthermore, the feasibility of using sugarcane bagasse as magnetic biochars should also be extensively studied. Determining optimum parameters and suitable synthesis should be the focus in the study of heavy metals removal using magnetic biochars from sugarcane bagasse.

6. Conclusion

The synthesis and applications of agricultural waste-based magnetic adsorbents for the removal of various types of heavy metals from water have been reviewed. Agricultural waste-based magnetic adsorbents offer various attractive features, such as outstanding adsorption capacity for various heavy metals, low-cost, non-toxic, and biocompatible. Although available literature on the application of agricultural waste-based magnetic adsorbents in water and wastewater treatments is steadily increasing, there are still several gaps that require attention, such as the enhancement of biosorption capacity through the modification of magnetic adsorbents, assessment of magnetic adsorbents under multicomponent pollutants, validating these materials with real industrial effluents, recovery of metal ions, regeneration studies, and continuous flow of studies. Furthermore, these adsorbents can be magnetized using eco-friendly chemicals to avoid secondary pollution. As evidenced by the literature reviewed in this paper, chemical modification can increase the number of active binding sites in the adsorbents; thereby, improving their ion exchange properties and form new functional groups that favour pollutant uptake. Studies should also be extended to pilot and full scales using agricultural waste-based magnetic adsorbents to examine their potential in treating real wastewaters. However, significant financial and technological efforts are required to scale up this study to a larger scale. Despite the various drawbacks and challenges that currently exist, a widespread progress in this area can be expected in the future. Overall, agricultural waste-based magnetic adsorbents offer significant advantages over the current expensive, commercial activated carbons for water pollution control. In addition, it can also contribute to an overall waste minimization strategy.

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