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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.

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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Table 1
Different values of components found in sugarcane bagasse.

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