A Review on Conversion of Crayfish-shell Derivatives to Functional Materials and Their Environmental Applications

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ABSTRACT

As a new research focus in the field of biological resources, crayfish shells have great potential for development and utilization. In this review, the typical methods and research progress of separating the primary components such as chitosan, protein, and astaxanthin from crayfish shells and converting crayfish shells into functional carbon-based materials are introduced in detail. Then, the application of crayfish shell and typically modified crayfish-shell biochar in adsorption, antibacterial, electrochemical, etc. is reviewed. Finally, the future research outlook is proposed. This review can provide some perspectives on the development of the application of crayfish shells and crayfish-shell derivatives.

Keywords: biological resources, crayfish shells, separation, conversion, application

1. Introduction

Crayfish is one of the common food sources for human. In the traditional process, approximately 80% of crayfish shells have become waste, and approximately 100,000 tons of crayfish shells are generated every year (Peng et al., 2016). On the one hand, random discard of crayfish shells in nature or landfill will lead to environmental pollution (Arvanitoyannis and Kassaveti, 2008). On the other hand, appropriate disposal of such waste can be costly, for example, up to 150 dollar per ton in Australia (Hamed et al., 2016). Notably, the crayfish shell has a unique composition, which contains three basic compounds, namely, protein (20%–30%), calcium carbonate (30%–40%), and chitin (20%–30%) (Rødde et al., 2008). In addition, some minor ingredients are identified, including lipids, astaxanthin, and other minerals. Using the abundant crayfish-shell resources reasonably has attracted increasing attention from researchers (Benhabiles et al., 2012; Cai et al., 2017).

The extraction of useful chemical substances from crayfish shells is an attractive and environment-friendly approach. As the primary component of crayfish shells, chitin is an organic polymer compound second only to cellulose in nature and the only natural alkali polysaccharide found to date (Du et al., 2014; Hamed et al., 2016). Chitin is chemically stable and insoluble and can be converted to chitosan after deacetylation. As the primary product of the comprehensive utilization of freshwater crayfish, chitin is extensively used in many fields, such as in daily chemicals, medicines, and food processing (Riva et al., 2011; Parvez et al., 2012). The astaxanthin contained in crayfish is a widely used carotenoid, which has a strong scavenging effect on free radicals, can resist oxidation, improve immunity, and prevent cancer. Astaxanthin can protect the central nervous system and the visual system (Visioli and Artaria, 2017; Lim et al., 2018), due to the rich protein contained in crayfish shell, primarily aspartic acid and glutamic acid (Huang et al., 2018). Crayfish shells can be processed into nutritious food (Bueno-Solano et al., 2009). In addition, N-acetyl D-glucosamine can also be extracted from crayfish shell and is an effective drug for rheumatism and rheumatoid arthritis in clinical medicine. It also has the ability to strengthen the human immune system and can be used as antioxidant, sweetener, and additive in the food industry (Seyfarth et al., 2008; Azuma et al., 2012).

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Converting crayfish shells to functional materials is another approach in recycling waste. In recent years, some scholars have used crushed crayfish shells and crayfish-shell biochar to remove heavy metal ions from wastewater. The results show that crayfish-shell powder with a natural specific structure and crayfish-shell biochar has a strong ability to remove heavy metal ions (Zheng et al., 2010; Long et al., 2017; Park et al., 2018). Selecting a suitable substance to modify crayfish-shell biochar can effectively improve its adsorption capacity (Long et al., 2017; Yan et al., 2018). In addition, based on the material structure and functional properties of crayfish shells, a series of functional materials have been synthesized and can be used to solve the global challenges (Sini et al., 2007; Yang et al., 2009; Qin et al., 2016).

In the past decades, the huge application potential of crayfish shells and crayfish-shell derivatives has received increasing attention. This review aims to illustrate the latest developments involved in the separation and application of crayfish shell (Fig. 1). First, the typical methods of separating the primary components of crayfish shell and converting it to functional carbon-based materials were introduced. Then, the application of crayfish shell and typical modified crayfish-shell biochar in adsorption, antibacterial, electrochemical, etc. is reviewed.

2. Methods for Crayfish Shell Utilization

2.1. Extraction of chemical substances from crayfish shell

In general, the crayfish shell primarily contained approximately 20%–30% chitin, 30%–40% proteins, 30%–40% calcium carbonate, and some minor ingredients, including lipids, astaxanthin, and other minerals (Table 1). Various methods have been developed to extract those components.

<table>
<thead>
<tr>
<th>Chemical substance</th>
<th>Method</th>
<th>Yield (%)</th>
<th>Reaction time (h)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitin</td>
<td>Chemical method</td>
<td>35%</td>
<td>48</td>
<td>(He et al., 2014)</td>
</tr>
<tr>
<td>Chitin</td>
<td>Chemical method</td>
<td>20%</td>
<td>–</td>
<td>(Abdou et al., 2008)</td>
</tr>
<tr>
<td>Chitin</td>
<td>Biological methods</td>
<td>25.7%</td>
<td>48</td>
<td>(Bautista et al., 2001)</td>
</tr>
<tr>
<td>Chitin</td>
<td>Simultaneous enzymatic hydrolysis and fermentation</td>
<td>20%</td>
<td>48</td>
<td>(Dun et al., 2019)</td>
</tr>
<tr>
<td>Protein</td>
<td>Ultraviolet irradiation combined autolysis method</td>
<td>–</td>
<td>120</td>
<td>(Cao et al., 2014)</td>
</tr>
<tr>
<td>Astaxanthin</td>
<td>Ionic liquid based ultrasonic-assisted extraction</td>
<td>0.0092%</td>
<td>0.2</td>
<td>(Bi et al., 2010)</td>
</tr>
<tr>
<td>Astaxanthin</td>
<td>High-pressure processing methods</td>
<td>0.006%</td>
<td>0.2</td>
<td>(Irma et al., 2018)</td>
</tr>
<tr>
<td>N-acetyl-d-glucosamine</td>
<td>Enzymatic degradation</td>
<td>15.2%</td>
<td>36</td>
<td>(Gao et al., 2015)</td>
</tr>
<tr>
<td>N-acetyl-d-glucosamine</td>
<td>Pretreatment with high pressure homogenization before biological methods</td>
<td>15.6%</td>
<td>1.5</td>
<td>(Wei et al., 2017)</td>
</tr>
</tbody>
</table>

Note: a, yield of obtained substance was based on the dry weight of raw crawfish shell.

2.1.1. Chitin and its derivatives

Two types of methods were available for obtaining chitin: traditional chemical methods and biological (microbial) methods. For the traditional chemical method, the strong acids or bases were used to remove the protein and minerals in crayfish shells. Abdou et al. (2008) used hydrochloric acid and sodium hydroxide in demineralization and deproteinization, respectively. The actual yield of chitin in crayfish shells was approximately 20%, demonstrating that the crayfish can be an economic source of chitin. Recently, Kaya et al. (2015) modified the traditional chemical methods by introducing sodium hypochlorite treatments before demineralization and deproteinization. This modified method can highly reduce the time required for demineralization and deproteinization, and the total time of chitin extraction was reduced from 1 d to 1 h. In addition, the yield and quality of chitin
obtained by the modified method were similar to those by the traditional method. The chemical methods had short processing time and high extraction efficiency, making them the commonly used commercial processing methods. However, the large amounts of toxic waste without effective treatment were detrimental to the environment, and the alkali treatment might affect the quality of chitin (Hamed et al., 2016). Thus, the biological extraction method has attracted increasing attention because of its advantages of being environmentally benign and cost effective.

In the biological extraction process, the proteolytic microorganisms or enzymes were used in the demineralization and deproteinization of crayfish shell. Bautista et al. (2001) used Lactobacillus pentosus to extract chitin from crayfish shells. After 50 h, the protein and mineral content of crayfish shells were obviously decreased (81.5% and 90.1%, respectively). To enhance the demineralization and deproteinization rate and shorten the fermentation time, Dun et al. (2019) combined enzymatic hydrolysis and fermentation for the extraction of chitin from crayfish-shell wastes by using Bacillus coagulans and proteinase, and the deproteinization rate and demineralization rate reached 91% and 94% after 48 h of fermentation, respectively. However, the biological method of extracting chitin from crayfish shells has been limited to laboratory research and cannot be applied on a large scale in actual production (Kaur and Dhillon, 2015).

The chitosan can be obtained by removing the acetyl groups of chitin. The degrees of deacetylation and the physicochemical properties of chitosan can be affected by the component of the raw materials and preparing method. Kumari et al. (2017) prepared different chitosan via the deacetylation of chitin by 40% NaOH, and the physicochemical properties of the obtained chitosan indicated that the shrimp shells were the best choice for the extraction of chitosan among fish, crab, and shrimp shells. Bajaj et al. (2011) investigated the effect of deacetylation conditions on the viscosity of chitosan and found that the high viscosity of chitosan obtained after deacetylation was primarily determined by the purification of chitin.

2.1.2. N-Acetyl-D-glucosamine

The extraction of N-acetyl-D-glucosamine from shrimp shells has drawn increasing interest because of its large market demand. Currently, the N-acetyl-D-glucosamine is primarily produced through acid hydrolysis of chitin pre-extracted by a chemical method, which is not environmentally friendly. Recently, Gao et al. (2015) used an efficient chitinolytic bacterium for the enzymatic hydrolysis of crayfish shell, and an approximately 100% N-acetyl-D-glucosamine yield could be obtained from crayfish shell under optimal conditions. Wei et al. (2017) found that high pressure homogenization pretreatment can decrease the crystallinity of crayfish shell and enhance the efficiency of enzymatic hydrolysis for the production of N-acetyl-D-glucosamine.

2.1.3. Protein

Enzymatic hydrolysis methods are extensively used to recover the protein fraction of crayfish-shell wastes, and the obtained hydrolysate contained bio-active peptides, which can be used as pharmaceutical tools or aquaculture feeds (Oliveira Cavalheiro et al., 2007; Cheung and Li-Chan, 2010). Gildberg and Stenberg (2001) used commercially available protease (Alcalase) to hydrolyze shrimp waste, and a protein hydrolysate with a high content of essential amino acids was obtained. Apart from the additive enzymatic hydrolysis methods, many inherent hydrolytic enzymes (proteases and lipases) were found in crayfish wastes. Such enzymes will hydrolyze the tissues spontaneously under certain conditions, and this phenomenon is called “autolysis” (Bezerra et al., 2008). Although the autolysis of crayfish wastes avoided the addition of expensive enzymes, the naturally occurring autolysis was inefficient, and the reaction process was slow. Cao et al. (2014) found that the activated endogenous enzymes from biological materials by ultraviolet radiation can accelerate the autolysis of shrimp waste and improve the reclamation of proteins from shrimp waste. However, the activation mechanism of endogenous enzymes by UV treatment has not been investigated, and further research is necessary for the optimization of autolysis technology and efficient extraction of useful components in shrimp.

2.1.4. Astaxanthin

Astaxanthin is the primary and most valuable carotenoid in crayfish shells. It has been applied in the cosmetic and food industries and has the potential to be an anti-cancer agent (de Holanda & Netto, 2006; Benhabiles et al., 2012). Various methods, such as an enzymatic process, fermentation process, and chemical extraction, have been proposed to extract astaxanthin from crayfish shells (Armenta-López et al., 2002; Sachindra and Mahendrakar, 2005; Sachindra et al., 2006; Sachindra et al., 2007). For instance, Handayani et al. (2008) extracted the astaxanthin from shrimp waste through palm oil. Compared with the conventional organic solvents, ionic liquid can improve the extraction yields of bioactive compounds and alleviate environmental pollution. Bi et al. (2010) used ionic liquid for the extraction of astaxanthin from shrimp waste, and the amount of extracted astaxanthin was double that of the conventional method under optimized extraction conditions. Recently, Irna et al. (2018) developed a high-pressure processing method for the extraction of astaxanthin from shrimp shells, which increased the yield of astaxanthin from 29 µg/g (dried weight) to 60 µg/g compared with chemical extraction.
2.2. Transformation of crayfish shell to carbon-based materials

Despite the tremendous efforts that have been made to recycle valuable chemical substances in crayfish shells, these techniques were costly or time consuming, and the amount of crayfish-shell wastes recycled by these technologies was extremely limited. Therefore, developing new, economical, and facile technologies was necessary to effectively recycle crayfish shells. Carbon materials have been extensively utilized in adsorption, catalysis, and energy storage because of their large pore size, large surface area, and high conductivity (Liang et al., 2008; Navalon et al., 2014). The conversion process from crayfish shells to carbon materials was simple, and it can be used to dispose a large amount of crayfish-shell wastes. To date, crayfish-shell wastes have been used to prepare carbon materials, such as calcium-rich biochar, nitrogen-doped porous carbon, and carbon dots (Table 2).

<table>
<thead>
<tr>
<th>Material</th>
<th>Synthetic method</th>
<th>Application</th>
<th>Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crayfish powder</td>
<td>Mechanical milling</td>
<td>Adsorbent</td>
<td>Adsorption was completed within 2 h, with a maximum chromium adsorption of 9.84 mg/g.</td>
<td>(Morris et al., 2012)</td>
</tr>
<tr>
<td>Calcium-rich biochar</td>
<td>Pyrolysis</td>
<td>Adsorbent</td>
<td>Obtained biochar can adsorb Pb(II) with a sorption capacity of 190.7 mg/g.</td>
<td>(Xiao et al., 2017)</td>
</tr>
<tr>
<td>Modified biochar</td>
<td>Pyrolysis and modified with ZnCl₂</td>
<td>Adsorbent</td>
<td>Modified biochar with a maximum As(V) adsorption capacity of 17.2 mg/g.</td>
<td>(Yan et al., 2018)</td>
</tr>
<tr>
<td>Nitrogen doped porous carbon</td>
<td>Hydrothermal activation and pyrolysis</td>
<td>Lithium ion batteries and supercapacitors</td>
<td>Material shows a high specific capacity of 1507 mA·h/g for Li-ion batteries, and 99.4% capacitance retained after 5000 cycles for super capacitor electrode.</td>
<td>(Mondal et al., 2017)</td>
</tr>
<tr>
<td>Nitrogen doped porous carbon</td>
<td>KOH activation and pyrolysis</td>
<td>Lithium sulfur battery</td>
<td>Obtained mesoporous carbon cathode shows great cycle stability with 90% retention within 100 cycles.</td>
<td>(Qu et al., 2016)</td>
</tr>
<tr>
<td>Carbon dots</td>
<td>Hydrothermal treatment</td>
<td>Fluorescence determination</td>
<td>The NO₃⁻ detection by obtained carbon dots fluorophores can achieve an analytical detection linear range from 1.0 μM to 1.0 mM.</td>
<td>(Zhang et al., 2016b)</td>
</tr>
<tr>
<td>Carbon dots and SiO₂ composite</td>
<td>Hydrothermal treatment</td>
<td>Oxygen reduction reaction</td>
<td>Obtained material exhibits an excellent catalytic activity with an onset potential of −0.06 V, a half wave potential of −0.21 V, and a large limiting current density of 3.3 mA/cm²</td>
<td>(Liu et al., 2016)</td>
</tr>
</tbody>
</table>

2.2.1. Calcium-rich biochar

The calcium-rich biochar is a porous carbon-rich solid produced by pyrolyzing biomass materials in the absence of air and usually has rich surface functional groups (C—O, —COOH, C=O, —OH, etc.) (Liu et al., 2015). In the pyrolysis process, the inorganic elements in the crayfish shell, particularly the high content of Ca, can effectively promote the formation of biochar, which can produce more gaseous compounds such as H₂, CO, CO₂, and CH₄ during the pyrolysis process, thereby promoting the cracking of biochar (Yaman, 2004; Bridgewater, 2012). Park et al. (2018) investigated the effect of pyrolysis temperature on the characteristics of biochar obtained from crawfish. The element composition results showed that calcium content in biochar obtained at 800 °C was 41.2%, which was higher than that of raw crawfish (17.0%). The Fourier transform infrared spectroscopy (FT-IR) results showed that calcium carbonate will be decomposed to calcium oxide at 800 °C.

2.2.2. Nitrogen-doped porous carbon

The introduction of nitrogen into carbon materials can enhance their adsorption capacity and electrochemical and catalytic activity (Wang et al., 2010). The commonly used methods for the preparation of nitrogen-doped carbon were the processing of nitrogen-containing precursors (urea, ammonia, or melamine) at high temperatures or direct carbonization of nitrogen-containing precursors (pyrrole and polyaniline). Shrimp shells are rich in chitin, an excellent precursor for nitrogen-doped porous carbon, thereby enabling the conversion of shrimp-shell waste to nitrogen-doped porous carbon. Wang et al. (2014) successfully synthesized nitrogen-doped porous carbon from crawfish shells through a facile hydrothermal method, and the CaCO₃ in porous carbon was removed by acetic acid solution. As such, uniform sheet-by-sheet paper-like porous carbon can be obtained. The nitrogen content of the porous carbon was approximately 4.1%, including pyridine N, pyrrolic N, and graphite N. The obtained nanosheet material contained macroporous and mesoporous structures, and the Brunauer-Emmett-Teller (BET) surface area was 304.4 m²/g. To increase the surface area of porous carbon, Mondal et al. (2017) prepared nitrogen-doped porous carbon by the hydrothermal activation of waste shrimp shells with KOH before carbonization. The nitrogen content in porous carbon was 2.86% and was homogeneously distributed in porous carbon. The BET surface area of the obtained nitrogen-doped porous carbon was 1271 m²/g. The large surface area of the obtained materials can provide sufficient interface for charge or ion accumulation, which can improve adsorption and catalytic performance.
2.2.3. Carbon dots
Fluorescence assay methods based on carbon dots, with the advantages of rapidity, high sensitivity, and simple sample preparation, are extensively used for sensing many metals (Aragay et al., 2011). However, the commonly used approaches for preparing carbon dots were limited by the disadvantages of environmental poisoning, low yield, and complex process (Wang et al., 2011a). Zhang et al. (2016a) synthesized carbon nanodots from prawn shells through hydrothermal carbonization, and the mass yield of carbon nanodots was approximately 18%. The transmission electron microscopy results showed that carbon nanodots were relatively uniform with an average size of 3 nm and rich in O- and N-containing functional groups. Those highly polar groups (amino group) can enhance the stability and hydrophilicity of the carbon nanodots in the aqueous systems. Recently, Devi and Dhamodharan (2018) modified the shrimp waste treatment method by adding 2% aqueous urea solution in the hydrothermal process. This method can be used to synthesize carbon nanodots and to separate chitin from shrimp wastes. The obtained carbon nanodots were quasi-spherical, and the sizes were in the range of 7–15 nm. In addition, the quality of the separated chitin was better than the chitin obtained from the traditional chemical method.

3. Environmental Application of Crayfish Shell and Derived Biochar

Crayfish shells have excellent adsorption and processing properties and are used as cheap and abundant adsorbents or mesoporous carbon supports in chemical reactions. This section provides some application examples.

3.1. Adsorption of heavy metal ions

The calcium carbonate component and certain surface functional groups in crayfish-shell powder are very important for the adsorption performance of heavy metal ions. Tudor et al. (2006) found that Ca ions in crayfish-shell powder can be directly exchanged with metal ions. Lee et al. (2004) found that calcium carbonate can be rapidly dissolved under acidic conditions, and precipitates are formed between dissolved carbonate ions and heavy metal ions. Therefore, when heavy metal ions are adsorbed by the crayfish-shell powder, ion exchange will be formed between Ca\(^{2+}\) and M\(^{2+}\), and the heavy metal ions were removed by the formation of metal carbonate precipitates on the surface of the crayfish crust. Simultaneously, the functional groups on the surface of the crayfish shell will undergo a complex reaction with M\(^{2+}\) to remove heavy metal ions. Zheng et al. (2010) investigated the adsorption process of Cu, Cd, Zn, and Pb by crayfish-shell powder and obtained the following adsorption amount: 93.765, 112.671, 61.455, and 82.574 mg/g. In addition, crayfish powder can obtain better results by removing different heavy metal ions at different pH values in the acidic range, which has great practical importance (Zheng et al., 2010; Zhao et al., 2016).

As a natural and excellent adsorbent, crayfish shells have been used on a large scale to remove metal ions from actual water bodies (Zhou et al., 2004). The adsorption of various metal ions by natural crayfish shells shows satisfactory results in removing metal ions from surface runoff, reaching the excellent removal effect on Fe (63.4%) and Cr (62.2%). Fresh crayfish shells are alkaline due to the abundance of Ca and chitin; thus, the pH slightly increases after surface runoff adsorption. The surface runoff after treatment is basically neutral and will not have a harmful effect on the environment (Rech et al., 2019). Gamage and Shahidi (2007) pointed out that the chitin and chitosan in crayfish shells are excellent chelating agents for certain metal ions. Particularly in the treatment of industrial wastewater with pH 7, chitin and chitosan exhibit an effective removal effect on metal ions such as Pb, Cu, Hg, Fe, and Ni. In the treatment of acidic wastewater, such as mine-affected water (pH between 2 and 4), the crayfish shell still has a good metal-ion-removal effect, and CaCO\(_3\) in the crayfish shell as an acid neutralizer can improve the pH of water (Núñez-Gómez et al., 2017).

The crayfish-shell biochar, as an adsorbent, has a high adsorption capacity for heavy metal ions, such as lead, copper, and arsenic, showing its high efficiency in wastewater purification and in the removal of heavy metal ions (Xiao et al., 2017; Yan et al., 2018). The advantages of using crayfish-shell biochar are summarized as follows: 1) large adsorption capacity and fast adsorption speed, 2) a wide tolerance range for the concentration of metal ions, and 3) strong tolerance to pH (Varma et al., 2004; Xiao et al., 2017).

Xiao et al. (2017) investigated the adsorption of Pb\(^{2+}\) by crayfish-shell biochar generated at different calcination temperatures from 300 °C (CS300) to 600 °C (CS600). Based on the Langmuir model, CS600 showed the highest Pb\(^{2+}\) adsorption capacity of 190.7 mg/g, which was more than the maximum Pb\(^{2+}\) adsorption capacity of crayfish-shell powder. Guo et al. (2019) showed that when the activated crayfish-shell biochar adsorbed a ternary metal mixture of Cu\(^{2+}\), Cd\(^{2+}\), and Cr\(^{6+}\), the maximum total adsorption amount was 560 mg/g. Based on the reports, the ZnCl\(_2\) was used to modify the crayfish-shell biochar and increase the specific surface area, which may be due to the introduction of Zn and improved reforming of organic compounds during calcination (Yao et al., 2011). These factors have further improved the adsorption capacity of the modified crayfish-shell biochar.
3.2. Recovery of phosphorus

Phosphorus, as a non-renewable and indispensable resource in the development of industry and agriculture, currently has a sharp reduction in reserves that can no longer meet the needs of economic development. Therefore, phosphorus removal in water bodies has been standardized from simple phosphorus removal to resource utilization (Yin et al., 2017). Crayfish-shell biochar has high adsorption capacity for phosphorus (Park et al., 2018).

Phosphate adsorbed on crayfish-shell biochar is closely related to Ca content and is primarily affected by pH. With the increase of pyrolysis temperature from 200 °C to 800 °C, the primary component of Ca in crayfish-shell biochar increases from 17.0% to 41.2%, and the pH of crayfish-shell biochar increases markedly from 8.7 to 12.1 (Park et al., 2018). In addition, the maximum adsorption capacity of crayfish-shell biochar for phosphate increases from 9.5 mg/g to 70.9 mg/g, which has evident advantages compared with other adsorbents (Oguz, 2005; Prochaska and Zouboulis, 2006; Chen et al., 2007; Xiong et al., 2008; Bozorgpour et al., 2016). At lower pH or neutral pH conditions, the adsorption of hydrolysis products of phosphate ions (H$_2$PO$_4^-$, HPO$_4^{2-}$) is primarily carried out by the dissolved Ca on the surface of crayfish-shell biochar to form a phosphate precipitate. At higher pH conditions, the precipitate is primarily formed by the reaction of PO$_4^{3-}$ and the dissolving free Ca of CaO and Ca(OH)$_2$.

The crayfish-shell biochar saturated with phosphorus adsorption is applied to the soil as phosphate fertilizer, and the phosphorus is slowly released to promote plant growth, thereby achieving the purpose of resource utilization (Yao et al., 2013; Zhang et al., 2016b).

3.3. Electrochemical performance

3.3.1. Solid oxide fuel cells

Solid oxide fuel cells (SOFC) is an efficient power generation equipment that directly converts chemical energy of fuel into electrical energy at operating temperature (Brett et al., 2008). In fuel cells, alkaline earth metal additives (such as CaCO$_3$) are often added to enhance the stability and durability of the electrolyte (Huang et al., 2007; Wang et al., 2011b). The large amount of natural CaCO$_3$ contained in the crayfish shell provides a basic strategy for the development of electrolytes that increase the cost-effectiveness of new SOFC (Sugawara et al., 2006).

Cai et al. (2017) prepared crayfish-shell biochar through calcination and proved that the crayfish shell calcined at 600 °C (CWS600) has the most stable CaCO$_3$ polycrystalline structure (Fig. 2). Then, the prepared CWS600 was compounded with a perovskite-type La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (LSCF) and a layered LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (LNCA) by wet ball milling and calcination to obtain an electrolyte sample. The single-cell device assembled by CWS600 can achieve a peak power density of 166 Mw/cm$^2$ at 550 °C, and the peak power of the electrolyte material obtained after compounding with LSCF and LNCA has been significantly improved, which can reach 330 and 256 mW/cm$^2$, respectively.

![Fig. 2 Schematic illustration of formation process of fuel cells from crayfish-shell](Reprinted with permission from Cai et al. (2017) Copyright 2017 American Chemical Society.)
3.3.2. Lithium-ion battery (LIB)
The anode material is one of the important materials of lithium-ion battery (LIB) and directly affects the overall performance of the LIB (Xu et al., 2017; Zuo et al., 2017). When used as the negative electrode of a lithium-ion battery, the porous structure of the biochar material provides shorter transport channels and more storage sites for lithium ions (Xu et al., 2014; Elizabeth et al., 2016). The crayfish shell-derived biochar has abundant heteroatoms (O and N) and a unique porous structure, making it a potential material in the field of lithium-ion batteries (Mondal et al., 2017).

Elizabeth et al. (2016) demonstrated that the crayfish-shell biochar calcined at 750 °C under argon atmosphere by using NaOH as the activator has a high nitrogen content (5.3%) and a unique porous structure. Such biochar can withstand the storage space and transmission channel provided by Li/Na ions. As the anode of the LIB, the crayfish-shell biochar can maintain a specific capacity of 740 mA/g at a current density of 0.1 A/g after 150 cycles, which reflects its excellent electrochemical performance. Wang et al. (2014) calcined the crayfish shell at 750 ℃ in an N\textsubscript{2} atmosphere and then removed the excess CaCO\textsubscript{3} with acetic acid to generate a porous crayfish-shell biochar material with a large specific surface area and rich nitrogen elements (Fig. 3). At a current density of 100 mA/g, the initial capacitance released by the material is 1223 mA·h/g. After 100 cycles, the high reversible capacity of 1060 mA·h/g can still be maintained, which is higher than the capacity of a single N-doped crayfish-shell biochar or Co\textsubscript{3}O\textsubscript{4}.

![Fig. 3 Fabrication process of crawfish shell-derived PC-Co\textsubscript{3}O\textsubscript{4} nanocomposites](Reprinted with permission from Wang et al. (2014) Copyright 2014 American Chemical Society.)

3.4. Antibacterial properties

Chitosan is a deacetylated product of natural biopolysaccharide chitin, which has a series of excellent biological characteristics, such as biocompatibility, biodegradability, and antibacterial. Considerable literatures have reported that chitosan has a broad spectrum of antibacterial properties and a good inhibitory effect on a variety of bacteria, fungi, and some viruses (Kohsari et al., 2016; Verlee et al., 2017). Crayfish shells are an excellent source of chitosan; thus, exploring the antibacterial properties of chitosan extracted from crayfish shells has gradually become a focus of investigation (Mahdy Samar et al., 2013; Taher et al., 2019).

Results from Samar et al. (2013) showed that the antibacterial activity of chitosan is primarily affected by its solution concentration, degree of deacetylation, and molecular weight. Chitosan remarkably inhibited the growth of the tested bacteria, and the inhibitory effect of chitosan on Gram (−) bacteria was greater than that of Gram (+) bacteria. In addition, the Taher's research group demonstrated that chitosan extracted from crayfish shells has a remarkable inhibitory effect on the proliferation of human breast cancer cells (Taher et al., 2019). Therefore, chitosan and its nanoparticles are considered to be potential natural compounds in the treatment of human breast cancer. Moreover, attaching Ag-TiO\textsubscript{2} nanoparticles to the crayfish-shell biochar carrier optimizes its antibacterial ability and facilitates recycling (Zeng et al., 2019).
3.5. Fluorescence detection

Carbon quantum dots have advantages of low toxicity, easy molecular modification, good water solubility, and good photoluminescence, making them ideal substitutes for traditional fluorescent nanomaterials (Zhang et al., 2016a). Considering that the crayfish shell contains N elements, cheap and rich N-doped carbon nanodots (N-CNDs) can be prepared from crayfish shells, which have great potential in fluorescence detection of environmentally harmful ions. Wang et al. (2011a) explored the application of shrimp shell-derived N-CNDs as fluorophores for sensitive and selective detection of nitrite in water. The experimental results showed that the detection limit of NO$_2^-$ by the fluorescence quenching of N-CNDs is 1.0 μmol/L, which is below the detection limit of 3.0 mg/L for the NO$_2^-$ maximum limit in drinking water specified by the World Health Organization.

3.6. Activated persulfate (PS) oxidation

The activated persulfate (PS) oxidation method can improve the removal effect of organic matter by generating sulfate radicals (SO$_4^{2-}$) with high oxidation potential. It is an emerging advanced oxidation technology that has been extensively used, and the use of biochar-based materials as activators has become the focus of most research in recent years (Fang et al., 2015; Wang et al., 2017). Carbon configuration and porosity are two key influencing factors for improving the catalytic performance of biochar during PS oxidation. The abundance of calcium in the crayfish shell can be used as a natural pore template, and the configuration of carbon can be adjusted by changing the calcination temperature (Yu et al., 2020).

4. Conclusions and Outlooks

As a new research focus in the field of biological resources, crayfish shells have great potential for development and utilization. Crayfish shells and their derivatives provide a cost-effective and sustainable platform for the functional utilization of biological materials. The primary components, such as chitin, protein, and N-acetyl-d-glucosamine, can be separated by modified chemical or biological methods. Furthermore, crayfish shells can be converted into functional carbon-based materials, which are extensively used as cheap and abundant adsorbents or mesoporous carbon supports in chemical reactions. However, based on the limited research on crayfish shells and their derived functional materials, more research attention is needed to solve the scientific and technical challenges of crayfish-shell utilization.

First, when the chemicals are separately extracted from the crayfish shell, it should be carried out without destroying other ingredients as much as possible. Second, little research has been focused on the cost of crayfish-shell utilization, including the cost of collection, transportation, and disposal; thus, more detailed investigations on the costs and benefits of extracting chemical materials from crayfish shells and transforming them into functional materials are necessary, which help to maximize the benefits of crayfish-shell utilization. Finally, little research has been focused on lobster shell biochar in the fields of electrochemistry and catalysis, and further modification is needed to improve its performance.

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References


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