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Fabrication of advance magnetic carbon nano-materials and their potential applications: A review

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ABSTRACT

Novel magnetic carbon nano-materials have attracted great interest in recent years due to their potential applications in many areas that exploit the combined advantage of magnetic with nano-scale properties. These materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. This is due to some of amazing properties that allow them to be utilized multiple functionalities including high porosity, distinguished structures, uniform morphologies, high stability, high magnetic properties and high conductivity. This paper provides a comprehensive summary of promising methods for synthesis of magnetic carbon nano-materials and their applications.

1. Introduction

The phenomenal capability of nano-sized materials to exhibit unique physio-chemical characteristics in contrast to bulk material, has opened new gateways for fabrication of novel materials for new applications that were not possibly evident in the past [1,2]. Despite of various applications of carbon nanomaterials, an overlay of magnetic properties on the carbon nano-materials provide an additional dimension of valuable attributes that enhance performance [3–9]. In particular, a dramatic enhancement was observed while the attention on production of magnetic nano-particles was influenced by the theory established by Brown on magnetization relaxation for different ferromagnetic and ferri-magnetic materials [10]. Magnetic carbon nanomaterials are capable to be used in various areas including catalysis, super capacitance, adsorption, enzymes immobilization, CO_2 capture and biosensor [11–16]. In particular, magnetic nanoparticles have been deployed in medical sciences for hyperthermia treatment, magnetic resonance imaging (MRI), efficient drug and gene delivery, and cancer imaging and therapy [17]. Furthermore, the study on concerned area depicts that the BET surface area of the nano-structure material and porosity have also been enhanced through processing. A key feature of magnetic nano-materials is the ease of directing their movement and separating them from other media using magnetic fields [14]. Furthermore, integerating magnetic nanoparticles with the porous carbon nanomaterials such as graphene have demonstrated outstanding performance as electrodes in super capacitors [18–20]. Recently, magnetic nanoparticles bestowed on polymer have exhibited amazing performance in the lithium ion batteries which ultimately enhanced overall capacitance and electrical conductivity. In view of all the facts, the magnetic carbon nano-materials are creating a revolution in terms of their potential applications. The next decade will likely to witness a considerable rise in production of magnetic carbon nano-material.

Arc discharge, chemical vapour deposition, laser pyrolysis, microwave plasma, metal-catalysed methods and metallic reduction-pyrolysis-catalysis are some of the processing methods have been deployed [21–26]. However these processes typically have drawbacks due to complexity and high energy costs. Thus, processing methods that are cost effective and efficient are needed to facilitate widespread adoption of the materials and processes.

This paper analyses resource and energy-efficient techniques used for fabrication of magnetic carbon nano-materials and discusses key areas of applications of these materials that can open new doors for future industrial advancements. These methods are convenient to process and able to fabricate various morphological structures that can be

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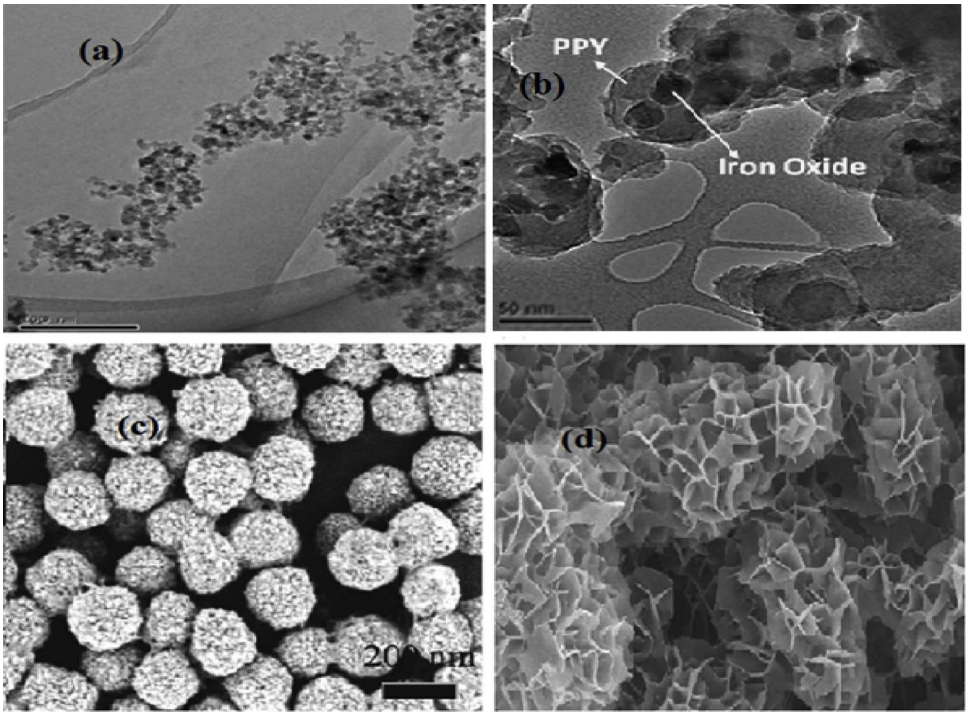

Fig. 1. TEM Images of various magnetic nano-materials; a) magnetic carbon nano-composite [49], b) magnetic polypyrrole nano-composite [50] c) magnetic carbon nano-clusters [51] d) magnetic carbon nano- flowers [21].

utilized to design materials having extra ordinary features including high surface area, highly controlled structure and unique morphology.

2. Materials

2.1. Magnetic source

Different kinds of metals can be used including Iron (Fe), Nickel (Ni) and Cobalt (Co) based compounds. However, iron based magnetic media is usually preferred due to their greater magnetic characteristics and lower cost [27]. Earlier studies used a variety of Fe based compounds including ferric chloride ($FeCl_3$), ferrous oxide (Fe_2O_3), ferric oxide $(Fe_3O)_4$, ferrous sulphate ($FeSO_4$), ferric nitrate $Fe(NO_3)_3$ and iron ores such as maghemite and magnetite [28]. The optimum performance of magnetic nano-material was observed to be influenced by the size of nano-particles [29]. It was reported that performance was enhanced using nano-materials with ultrafine size of 20 nm in medical therapy [30].

2.2. Carbon precursor

Different carbon sources have been used for the production of carbon-based magnetic nano-structures including acetylene, oleates, acetate, low density polyethylene, yeast alcohol dehydrogenase, polyurethane and nitro-phenol [24,31–38]. An attractive feature of using carbon based materials in conjunction with magnetic nanoparticles is the possibility of using renewable biomass as raw material. Various types of organic residues are available from industrial, agricultural and domestic waste materials, that have no proper utilization [27,39]. Among these starting materials, biomass from agricultural waste has the advantages of low cost, abundance and with a range of functional groups linked to the feedstock [40,41]. In addition, these materials are also arising from renewable resources thus making their utilization further attractive apart from resource recovery from waste. A possible source for the carbon support is biochar which is a carbonaceous material produced by pyrolysis of biomass (including agricultural waste) in an inert environment which is used in soil remediation. Biochar is also capable of eliminating the heavy metals and other pollutants from wastewater through adsorption process with the core advantage of low cost [42].

2.3. Magnetic nanoparticles incorporated on biomass

Common problems in using biochar is related to its low adsorption capability, low porosity and extremely difficult separatation. Thus, the utilization of magnetic nano-materials in the biomass matrix can easily overcome all three of above mentioned problems. Inclusion of magnetic properties enhances the adsorption capacity of the material with moderate surface area. Furthermore, these magnetic particles can easily be separated by use of the magnetic field therefore operations which were involved in dealing with separation of biochar through filtration and centrifugation are no more required. In this way, overall process cost is reduced by the use of magnetic medium [43,44].

Consequently, the synthesis of magnetic nano-material by using agricultural waste sources is a practical, cost effective and environmentally friendly solution to eliminate the pollution with relation to removing heavy metals from water [45]. In addition, the selection of right biomass is also an important factor that positively impacts the properties of end product. Agri-waste biomass is a low cost precursor and taking advantage of this aspect, hydrochar was utilized for the production of cost effective magnetic carbon nano-composite materials [46]. Recently, bagasse was used to produce magnetic nano-structure material using microwave assisted pyrolysis [47]. Also activated carbon is considered as a versatile material but the difficult separation is always associated with its processing while using it as catalyst or adsorbent. A research conducted that utilized chemical co-precipitation for synthesis of magnetic activated carbon using activated carbon produced from rice husk with magnetite (Fe_3O_4), goethite FeO(OH) and maghemite (Fe_2O_3) and the composite was successfully applied for triclosan removal [48].

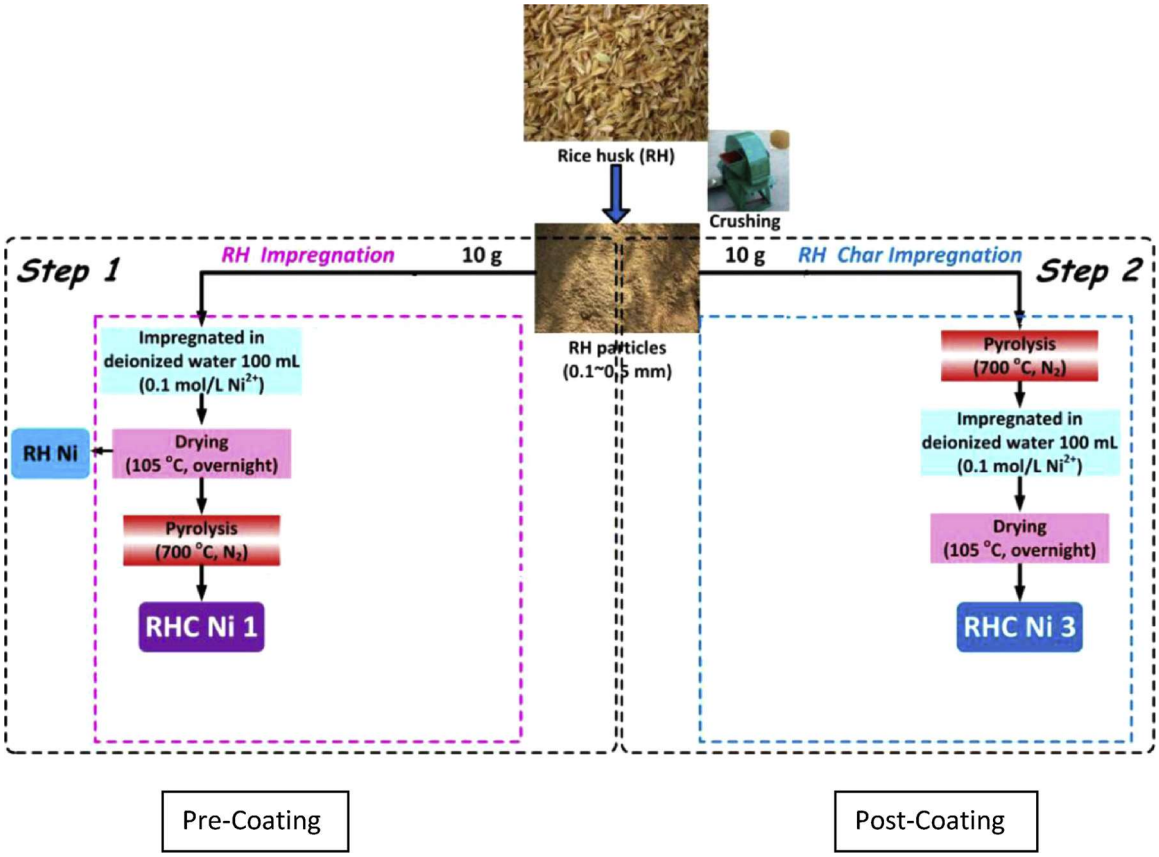

Fig. 2. Process for magnetic carbon nano-material production through precoating and postcoating pyrolysis methods [34].

3. Synthesis of magnetic carbon nano-materials

The processing methods used for producing carbon-based magnetic nano-materials aim to use the carbonaceous material as the support and impart magnetic properties by inclusion of magnetically active components in the matrix. Pyrolysis, chemical co-precipitation, hydrothermal carbonization and ultra-sonication are inexpensive and operationally efficient methods for producing magnetic nano-materials. Each method brings unique modifications to the end product and also have specific limitations and disadvantages. Structural collaboration of different carbon and magnetic materials can lead to design various morphological magnetic carbon nano-materials produced by these methods are shown in Fig. 1.

3.1. Pyrolysis

Pyrolysis is a thermochemical method which decomposes carbon-based materials at temperatures greater than 400 °C in an inert atmosphere converting them into fuel such as bio-oil, bio-gas and biochar [52–54]. It is widely used and considered as a proficient method due to its simplicity and low cost [55–57]. Pyrolysis takes place as a two-step process. Removal of moisture takes place in the first step and as the temperature increases, further degradation of hemicellulose and cellulose components occurs, resulting in removal of volatile components and production of bio-gas by the action of heat transfer through convection and conduction [58]. As hemicellulosic and cellulosic materials are degraded from the biomass in the first step, pores are produced in the surface of biomass due to elimination of volatile material [59]. In the second step, the pores enlarge and carbon content increases by simultaneous effect of further volatilization and continuous heat transfer [39,60]. The incorporation of magnetic components can take place by pre or postcoating pyrolysis.

3.1.1. Precoating pyrolysis

In this process, $FeCl_3$, $FeSO_4$ or $Fe(NO_3)_3$ is mixed with the carbon precursor in a defined ratio for a defined time so that the magnetic component is impregnated on carbon and feedstock is pyrolyzed under different process conditions. Recently, Jung et al. [61] used electromagnetisation pyrolysis by utilizing marine microalgae immersed in water with Fe_3O_4 magnetic components under continuous stirring with an electrode base current of 42.46 mA for half an hour. After drying, it was heated in a horizontal furnace at 600 °C for 1 h with heating rate of 10 °C/min under inert environment with a 25 ml/min nitrogen flow for the production of magnetic nano-composite. A considerable development of porosity was found from the experimental research and also 382 mg/g maximum adsorption capacity was achieved for acid orange. The most important parameter of pyrolysis process which can affect the nano- size, yield and product is process temperature [62]. In a study, magnetic nano-fibres and nano-tubes were successfully produced by the catalytic pyrolysis of ethylene as the organic precursor at temperature ranging from 500 to 800 °C [32]. The size of the magnetic nano-fibre, developed was 60 to 80 nm at 650 °C. It was also observed from the results that increasing temperature from 710 °C to 800 °C, synthesis of magnetic nano-tubes was dominant. Process temperature was the most significant factor to produce the specific nano-materials either magnetic nano-fibre or nano-tube. One more advantage of this technique is production of nano-size material of unique morphology and complex structure. In a pyrolysis study using pine resin and iron nitrate, a complex core shell type magnetic nano-cage material of size 20 to 100 nm was produced [63]. Furthermore, this unique structure nano-material exhibited higher adsorption capacity for arsenic removal from wastewater. Some of the researchers focused this method for the production of ultrafine nano-catalysts. Furthermore, magnetic saturation from precoating pyrolysis method was also reported to be higher [64].

3.1.2. Postcoating pyrolysis

Another approach of using pyrolysis for the production of magnetic nano-materials is by mixing of the magnetic solution after charring through pyrolysis. Recently, a study utilized paper mill sludge together with iron and nickel to produce magnetic carbon nano-composite that exhibited higher surface area modification with efficient removal of pentachlorophenol [65]. Singh et al. worked on production of carbon nano-composite magnetic material using postcoating pyrolysis method by combining the magnetic property with activated carbon [66]. A coconut based biomass was used to obtain magnetic nano-composites that displayed high ability to adsorb rhodamine B solution. Comparative analysis on both precoat and postcoat pyrolysis methods for magnetic nano-material production was conducted by Shen et al. in which Ni was used as a magnetic medium as shown in Fig. 2. Rice husk was used as precursor for both methods [34]. Exactly same quantity of Ni based magnetic material was inserted in precoat and postcoat methods. Both methods utilized same conditions for pyrolysis. The produced magnetic nano-material showed different characteristics in terms of BET and magnetic loadings. Precoating method exhibited higher BET surface area compared with postcoating method. On the other hand, the magnetic loading of nickel was found slightly higher for the case of postcoating method. These produced composites were later utilized successfully in adsorption process. Table 1 shows the research summary of production of magnetic nano-materials from pyrolysis method.

3.2. Chemical co-precipitation

Chemical co-precipitation is one of the most common methods used for producing magnetic nano-materials. The main reason is separation of nucleation and slow growth of nuclei that results in uniform particle size of the product [67–69]. In this technique, precipitation of solute takes place, separating it from the solution hence, the solute is bound with the solution instead of dissolving. The binding of solute follows one of these three techniques in the precipitation process including occlusion, inclusion and surface adsorption [70]. If the carrier is fully trapped by the solute during the formation of crystal lattice it is known as occlusion but in the inclusion process the crystal matrix of solute is integrated partially with the crystal matrix of carrier. However, in the surface adsorption, the solute is attached to the surface of the carrier completely leaving the solution creating a larger surface area [58]. This method is efficient to produce highly ultrafine controlled size up to 5–8 nm of magnetic nano-material production by using chemical co-precipitation technique [71].

Generally, chemical co-precipitation is a combination of two steps: alkaline precipitation of magnetic media with carbonaceous feedstock, and activation at a specific temperature. The carbon source is dipped in the solution containing the magnetic components for a specific time at fixed temperature under continuous agitation. The pH is continuously adjusted during the process by the use of alkaline compounds such as KOH, NaOH or NH_4OH. In this way, the magnetic ions precipitate out and bind with the solution using occlusion, inclusion or surface adsorption and form nanoparticles of different shapes, sizes and character. A general process for producing magnetic nanomaterials is shown in Fig. 3.

The co-precipitation method has been employed for producing carbon-encapsulated magnetic nano-particles using glucose as an organic precursor with a combination of ferric chloride ($FeCl_3{\cdot}4H_2O$) and ferrous chloride ($FeCl_2{\cdot}6H_2O$) as magnetic media [72]. The product exhibited extraordinary magnetic characteristics with a maximum saturation magnetization value of 123 emu/g and high surface area. This technique is also being utilized to enhance the capabilities of functional nano-materials. In another study, magnetic multi-walled carbon nanotubes were synthesised by co-precipitation of $FeCl_3$, carbon nanotubes and MnO_2 [73]. The novel magnetic nano-composite showed unique structure and properties, and displayed great performance in removal of hexavalent chromium.

A combination of magnetic properties with mixture of inorganic/organic polymer composites for the fabrication of novel hybrid nanomaterials is also possible by use of chemical co-precipitation. The size of the final product depends on process materials, additives, temperature, time, pH, and the type and quantity of magnetic material used. A novel composite of polypyrrole and Fe_3O_4 was formed in a single step precipitation process through in-situ polymerization of pyrrole monomer using $FeCl_3$ as the magnetic medium. 10 nm sized particles with BET area 1206.53 m^2/g were obtained by this process and utilized for adsorption of fluoride from water [50]. Recently, a novel metal organic framework (MOF) nano-composite was synthesised by the mixture of toluene and dithizone through chemical co-precipitation that showed high BET surface area and porous structure [74]. A comparative analysis of the use of the chemical co-precipitation technique for producing magnetic carbon nano-materials is provided in Table 2.

3.3. Hydrothermal carbonization (HTC)

HTC is known as an efficient technique for the fabrication of nanomaterials [80,81]. Recently it has attracted considerable interest to develop complex nano-structures with distinct characteristics. It is interesting to note that this method originated in the last century with the aim of producing charcoal [82]. Considerable improvements to the process were implemented since then, making it efficient to transform complex polysaccharides into solid products under a range of processing temperatures [83]. The process variables for HTC range from 150 to 350 °C, 2–10 MPa and few hours of process time, depending on the type of material and end product required [84–86]. It utilizes water as catalyst which possesses a high ionization constant and therefore accelerates hydrolysis and disintegration of material [87,88]. As it is a wet process, drying of feedstock is not required, thus making it an energy efficient process. The hydrothermal treatment process enhances solubility, melts the crystalline matrix, accelerates physiochemical interactions of carbon materials and solvents, enables acid/base complex reactions, and improves the carbon content in the end product [89]. The HTC technique is also well-known for synthesis of controlled mono-

Table 1
Research summary of synthesis of magnetic carbon nano-material using pyrolysis process.

Organic material	Temp. (°C)	Time (h)	Magnetic medium	Precoat /Postcoat method	Reactor Type	Product type	Ref.
Acetylene	650	0.5	Iron particles with nickel	Pre	Tube reactor	Magnetic nano-fibre	[32]
Acetylene	800	0.5	Iron particles with nickel	Pre	Tube reactor	Magnetic nano-tubes	[32]
Cotton wood	600	1	$FeCl_3$	Pre	Furnace	Magnetic nano-composite	[64]
Paper mill sludge	700	–	$FeSO_4$ + $NiCl_2$	Post	Furnace	Magnetic nano-composite	[65]
styrene + ethylene glycol	600	–	$Co_2(CO)_8$	Pre	Furnace	Magnetic carbon nano-sphere	[23]
Coconut shell	750	1	$Fe(NO_3)_3$	Post	–	Magnetic nano-composite	[66]
Polyacrylate	500	3	$Fe(NO_3)_3$ + $Ni(NO_3)_2$	Pre	Furnace	Nano- crystalline spinel ferrites	[35]
Rice Husk	700	–	$Ni(NO_3)_2$	Pre		Magnetic carbon nano-particles	[34]
Rice Husk	700	–	$Ni(NO_3)_2$	Post	–	Magnetic carbon nano-particles	[34]
Brown Microalgae	600	1	Fe_3O_4	Pre	Horizontal furnace	Magnetic nano-composite	[61]

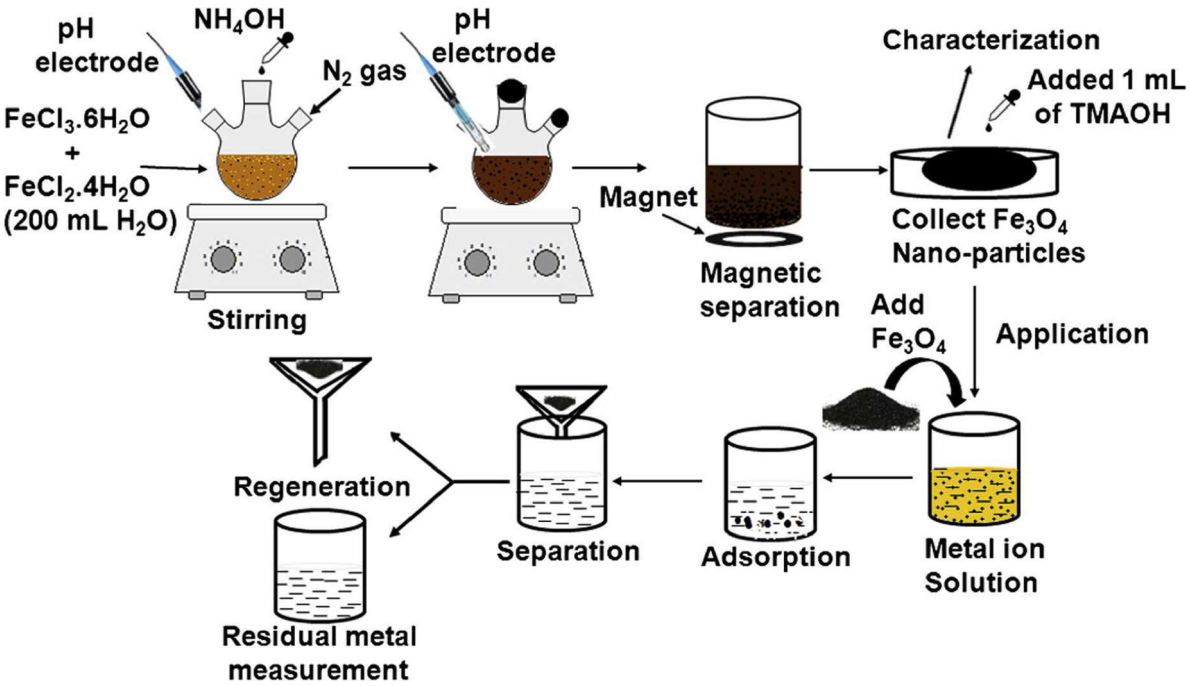

Fig. 3. A general method for producing magnetic nano-particles and its utilization for adsorption of metal ion [75].

dispersed carbonaceous nano-spheres from starting materials that undergo degradation as a result of dehydration, condensation, polymerization and aromatization [90,91]. HTC facilitates higher reactivity with higher oxygenated functional groups (OFG) that favours development of porosity which is a key performance indicator for application in catalysis, adsorption, super-capacitance and carbon capture [92]. The porosity of the product is also dependent on process temperature and is reported to increase with temperature up to 240 °C, while further increase in process temperature enhances mechanical stability of the material but reduces porosity [93,94]. Catalysts have a significant role in HTC process; Cui et al. reported that presence of iron oxide nano-particles in HTC promotes formation of hollow carbonaceous spheres [95]. Fig. 4 shows the process for conversion of ligno-cellulosic materials into magnetic carbon nano-materials through HTC. Zhang et al. used glucose and iron oxide used to design quasi-spherical structures with uniform particle size of magnetic nano-materials [96]. These exhibited higher adsorption capacity for polycyclic aromatic hydrocarbons. Lim et al. used the same material to form a 3D porous magnetic nano-composite electrode [97]. The magnetic nano-composites possessed symmetrical shapes and size with a super-capacitance of 259.3 F/g with a potential window of 1.8 V. The surface area of the nano-composite was significantly improved to1712.8 m^2/g. Recently, Nickel-iron based hydrochar (Ni/Fe-HC) nano-particles were successfully synthesized by HTC and utilized for adsorption of lead with 99.5% removal of lead [98]. The particle size of the nano-material in HTC is mainly influenced by process time, concentration of the precursor, catalyst and microwave power in the process [99,100].

A facile microwave HTC method was used to generate single-crystalline Fe_3O_4 nano-wires within 15 min at 150 °C [101]. These magnetic carbon nano-wires of 20–50 nm size showed higher performance in lithium ion batteries. Recently, Gai et al. studied the effect of various concentrations of Fe with pinewood sawdust as precursor to understand key characteristics of magnetic hydrochar nano-particles [26]. The study showed that concentration of Fe^{3+} may affect the nano-particles size of magnetic media and the structure and due to formation of surface complexes structures can really affect the catalytic activity and its performance. The magnetic hydrochar nano-composite produced in this study was utilized as a nano-catalyst for the decomposition of phenol. Table 3 summarizes the various magnetic nano-structures produced through HTC.

Table 2
Research summary of magnetic carbon nano-materials using chemical co-precipitation.

Precursor material	Magnetic medium	Alkaline	Process Temp. (°C)	Time (h)Product	Product	Ref
Poly-vinyl alcohol + phenoxy resin	$FeCl_3$ + $FeCl_2$	NaOH	–	2	Magnetic carbon nano-composite particles	[76]
Toluene + Dithizone	Fe_3O_4	–	–	12	Magnetic nano-composite	[74]
Pectin	$FeCl_3$ + $FeCl_2$	NH_4OH	90	24	Magnetic nano-composite	[77]
Tetraethoxysilane + Ethyl alcohol	$FeCl_3$ + $FeCl_2$	NH_4OH	50	24	Magnetic nano-composite	[78]
Sugarcane hydrochar	$FeSO_4$ + $FeCl_3$	NaOH	100	3	Magnetic carbon composites	[46]
Graphene Oxide	$(NH_4)_2Fe(SO_4)$ + $NH_4Fe(SO_4)_2$	NH_4OH	50	–	Graphene magnetic nano-composite	[79]
Polypyrrole	$FeCl_3$	–	–	3	Magnetic nano-composite	[50]
Multi-walled carbon nano-tube	$FeCl_3$ + MnO_2	NH_4OH	65	2	Magnetic multi-walled carbon nano-tube	[73]

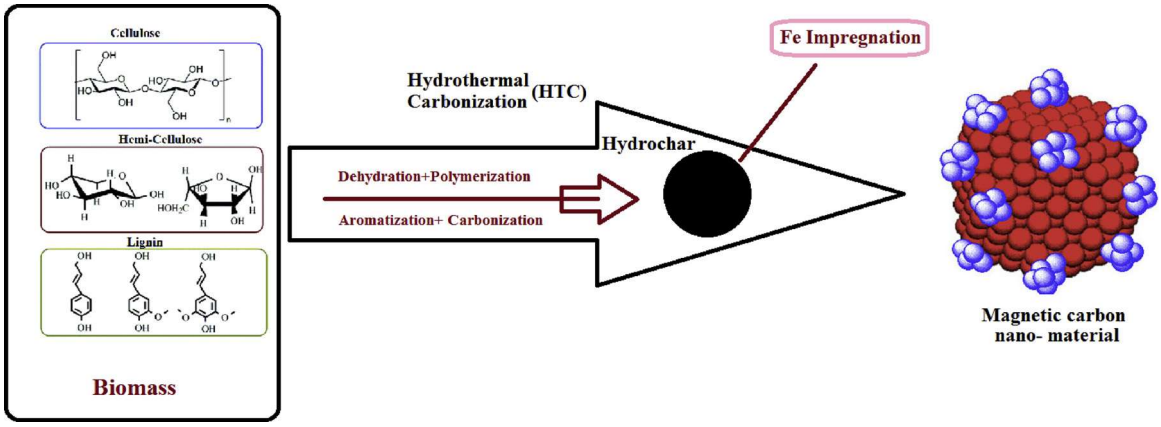

Fig. 4. Conversion of ligno-cellulosic materials into magnetic carbon nano-materials using HTC.

3.4. Ultra-sonication

Ultra-sonication method is an innovative technique has been extensively utilized in various chemical processes. Sound waves used in the process are of high frequencies (greater than 20 KHz) that facilitate intensification of force for mixing. The sound waves create a large number of micro vacuum bubbles in the liquid medium within micro seconds that develop and collapse at the same time. This cavitation delivers large hydrodynamic shear forces that can be used for fabricating and sizing nanostructures [105–108].

Guo et. al, used two different approaches for the fabrication of magnetic nano-composites conventional direct sonication and surface initiated polymerization sonication using similar quantities of chemicals [24]. In the conventional direct sonication method, monomers, catalyst and accelerator were added with ultrasonic stirring for half an hour. In the surface initiated polymerization sonication, initially a surface adsorption was made iron-oxide (Fe_2O_3) nano-particles with tetra-hydro furan solution then it was mixed with the catalyst and promoter solution under ultra-sonication. The magnetic carbon nano-materials produced by surface initiated polymerization/co-precipitation exhibited higher iron loading, better quality and more controlled size of the magnetic carbon nano-material, which were utilized in giant magneto-resistance sensor.

The ultrasonic process is also capable of enhancing the characteristics of magnetic materials. It has been used for the production of polyvinyl alcohol (PVA) based magnetic nano-composite material that showed saturation magnetization of 66 emu/g and a coercivity of 39 Oe [109]. The final product size from ultrasonic method is dependent on the parameters including ultrasonic power, process time; catalyst used and post treatment method. Caruso et al. fabricated, magnetic hollow sphere nano-particles of 22 nm size, using ultra-sonication technique followed by calcination at 500 °C [110]. In another study, 10 nm hollow spheres of magnetic Polypyrrol (ppy/Fe_3O_4) based nano-composites were fabricated by ultrasonic irradiation at 750 W and 30 min of process time that shows the simplicity and versatility of ultra-sonication process to formulate unique structures with highly controlled morphology [111].

While there are still some challenges in the process, such as uniformity in size, particle size and shape control, crystalline structure, and the alignment with substrate, but still it is attractive due to simplicity of operation [112]. Table 4 summarizes production of magnetic nano-material produced using ultra sonication.

4. Potential applications of magnetic carbon nano-materials

Combining magnetic characteristics with the nano-materials makes it very special and interesting that allows it to be used in various dimensions. Potential applications of magnetic carbon nano-materials are given in this section.

4.1. Catalysis

Use of magnetic nano-materials is an innovative approach for highly efficient, cost effective, fast and easy isolation of catalysts thereby avoiding conventional separation techniques such as filtration, liquid–liquid extraction, chromatography and centrifugation [14]. Fig. 5 shows a simple separation scheme of magnetic carbon nano-materials in the catalyst. Yi et al. produced magnetic nano-clusters of size 20 nm using $Fe_2O_3/SiO_2/Pd$ by pyrolysis using a microwave reactor which was successfully applied as a catalyst for hydrogenation reaction for nitrobenzene showed highest conversion rates of 99% with great consistency on replication [117]. The size of the end product also depends on the catalyst or the material utilized in the process therefore the platinum nano-particles also played an efficient role to achieve a high symmetrical ultrafine nano-material which showed an effective conversion during the reaction. Recently, magnetic nano-particle encapsulated biochar was found efficient as a catalyst for the conversion of bio-gas into liquid hydrocarbon products [118].

There are significant benefits of using magnetic materials as a catalyst. One advantage is that, it can perform additional functions apart

Table 3
Research summary for magnetic nano-material production through HTC.

Carbon Precursor	Reaction Temp. (°C)	Reaction Time (h)	Magnetic medium	Product type	Ref
Pinewood Sawdust	200	1	Fe	Magnetic hydrochar nano-particles	[26]
Glucose hydrochar	180	6	Fe_3O_4	3D magnetic carbon nano-composite	[97]
Biogas residue	250	3	$Ni(NO_3)_2 + FeSO_4$	magnetic hydrochar nano-particles	[98]
Polysaccharides	180	0.3	Fe_3O_4	magnetic carbon nano-wires	[101]
Glucose	180	16	Fe_3O_4	magnetic carbon nano-particle	[102]
Starch	180	12	$Fe(NH_4)_2(SO_4)_2$	magnetic carbon nano-particle	[95]
Glucose, fructose, xylose and starch	180	24	$FeCl_4$	magnetic carbonaceous nano-material	[103]
Ethylene glycol	200	20	$FeCl_3$	magnetic coaxial nano-material	[104]

Table 4
Research summary of magnetic nano-materials produced using ultra-sonication.

Carbon cursor	Magnetic material	Power W	Time Mins	Method	Product	Ref
Polystyrene	Magnetite	–	10	Sonication Followed by calcination	Magnetic carbon hollow sphere nano-particles	[110]
Polypyrrole	$FeCl_3$ + $FeSO_4$	750	30	Ultrasonic irradiation	Magnetic polypyrrole/Fe_3O_4 composite	[111]
Amino benzyl alcohol + (nitro phenyl) propynone	Cobalt	–	2160	Ultrasonic irradiation	Magnetic C/Co Nano-particles	[113]
PVA	Fe_3O_4	60	20	Sonochemical method	PVA based magnetic nano-material	[109]
carbodiimide	$FeCl_3$ + $FeCl_2$	–	10	Sonication	LHRH magnetic nano-particles	[114]
Oleic acid	$Co_2(CO)_8$ + $Fe(CO)_5$	60	6	Thermal sonication method	Magnetic encapsulated nano-particles	[115]
yeast alcohol dehydrogenase (YADH)	Fe_3O_4	–	30	Sonication	YADH-bound magnetic nano-particles	[37]
Candida rugosa lipase	Fe_2O_3	–	10	Enzymatic sonication	Enzymatic magnetic nano-particles	[116]

from its role as a catalyst. Other catalytic components including metal oxides, enzymes, other complex materials on magnetic nano-materials can be immobilized with magnetic materials [119]. Furthermore, coating of a noble metal with a magnetic material can protect against oxidation, as indicated by higher stability for co-coated platinum nanoparticles [120]. Rossi et al. reported the following outstanding advantages of magnetic nano-catalysts over conventional catalysts (1) effective, fast separation of magnetic material from other materials (2) energy efficient; (3) no solvent is required for separation (4) reduced water requirement in washing (5) No chance of air exposure during separation and (6) low possibility of mass loss during transformation [14].

4.2. Environment remediation

The use of agricultural waste to produce magnetic carbon nano-material will provide opportunity for better utilization of the waste resources that are highly abundant. Furthermore, proper utilization of these waste resources is also helpful in the reduction of harmful gases caused by direct burning [121]. Utilization of these residues will also lower the overall production cost of magnetic carbon nano-materials. Due to the special ability of magnetic material to attract many pollutants, this quality makes it highly appropriate for adsorption due to high affinity [44]. Specifically, the broad carbon functional group range and magnetic characteristics of easy separability of these novel materials are highly suitable for the adsorption of heavy metals from wastewater [27].

Since nano-materials have shown incredible effectiveness in dealing with the environmental hazards but concerns are still there about the disposal and its exposing effects to health and environment [122]. There may be chances that due to ultrafine sizes, these can be included in waste stream and can cause damage to health of sea species and humans. However, utilizing such nano-materials having magnetic properties can be fully recovered using magnetic field and hence the technology is quite safe and efficient. Wu et al. successfully removed arsenic from water with the aid of novel mesoporous magnetic encapsulated carbon [123]. Recently, magnetic carbon nano-cages exhibited significant ability to adsorb arsenic with high adsorption capacity of 363 mg/g with a low surface area of 177 m_2/g [63]. Graphene based magnetic nano-composites showed high capacity to adsorb thiazole fungicides from water [124]. Magnetic activated carbon has exhibited enhanced adsorption capabilities for many organic components including phenol, chloroform, chloro benzene and dyes and without the need for separation [125]. The study also revealed that combining 4 different forms of iron including Fe_3O_4 (magnetite), γ-Fe_2O_3 (maghemite), α-Fe_2O_3 (hematite) and α-FeO(OH) (goethite) has a positive effect on the overall magnetization that ultimately has an impact on separation capability.

Magnetic carbon nano-composites are also being investigated for gas adsorption that leads its utilization in biosensing. Suri et al. utilized magnetic carbon nanomaterials (composite of polypyrrole and iron oxide nanoparticles for adsorption of gases including CO_2, N_2 and CH_4

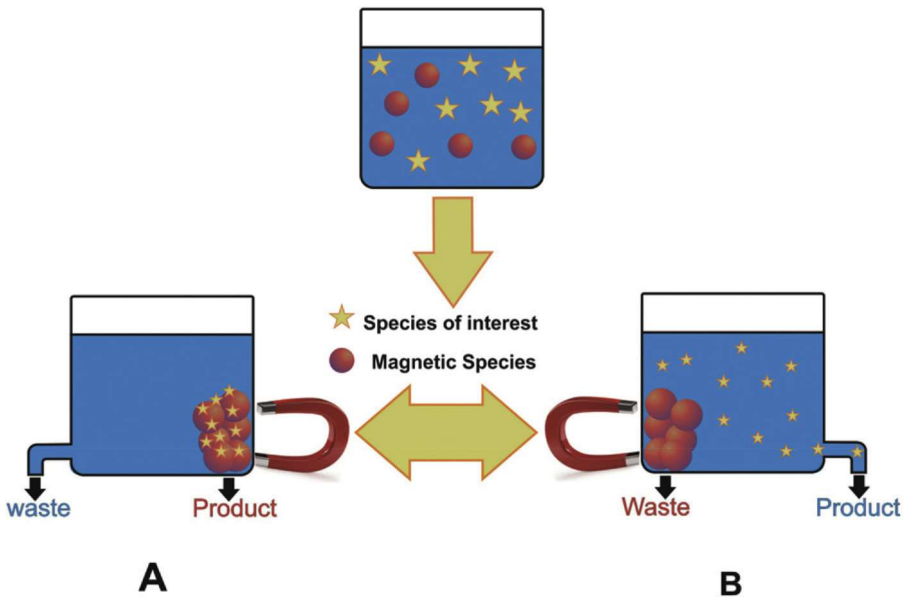

Fig. 5. Simple separation of magnetic carbon nano-materials as catalyst [14].

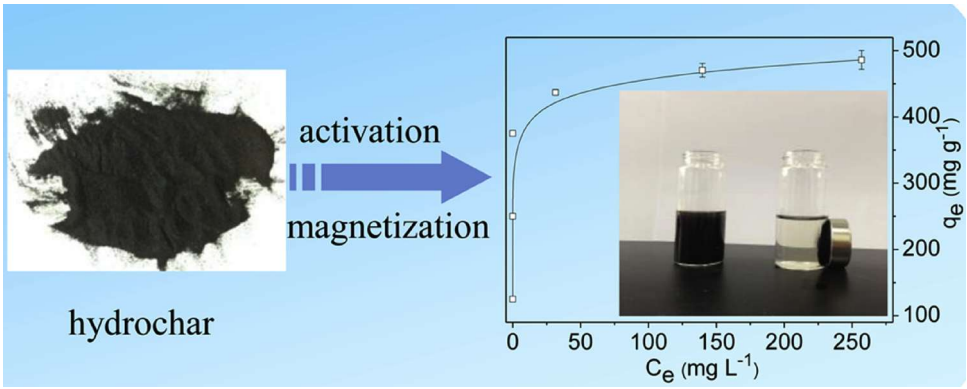

Fig. 6. Potential application of magnetic carbon nanomaterial in adsorption [127].

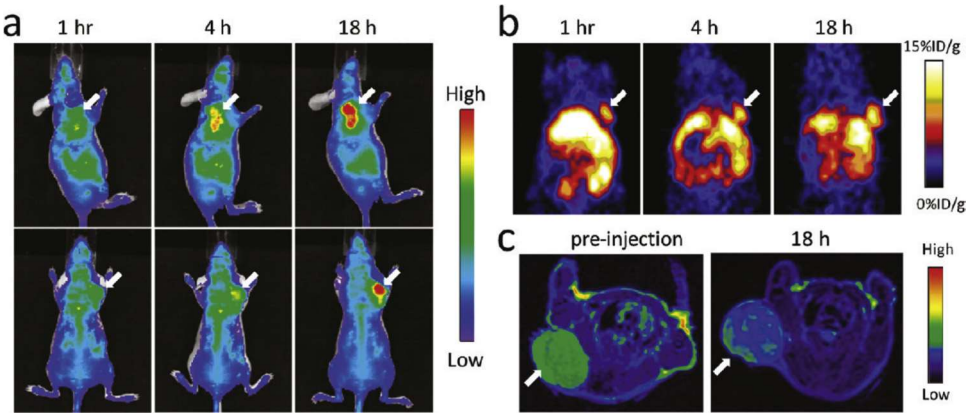

Fig. 7. Use of magnetic nano-materials in tumour detection through MRI technique [140].

and the nano-composites have shown an outstanding competency for adsorbing these gases with varying pressures [126]. Fig. 6 shows the potential adsorption and separation capability of magnetic carbon nano-material for heavy metal from water.

4.3. Energy storage

Iron based materials have a relatively lower energy storage capacity and do not find much utility in energy storage applications; however, combination of magnetic properties with carbon materials can boost the capability extensively. A powerful electrostatic interaction between negatively charged carbon and positively charged magnetic nano-particles enables greater electrical stability and faster electron transfer by reducing the resistance, which is highly suitable for super-capacitance applications [128]. Magnetic carbon nano-wire electrodes have shown excellent electrical durability with specific capacitance of 259.3 F/g, maximum energy density of 29.2 Wh/kg at a power density of 1.2 kW/kg that successfully completed 5000 cycles along with capacitance retention of 95.1% [97]. Magnetic carbon nano-wires have also shown high performance as anode materials in lithium ion batteries. In addition to high energy capacity, lower cost, non-toxic nature, super electromagnetic properties and high surface area [129–132] are other attributes that are favourable for deployment of magnetic carbon materials for energy storage applications.

Another unique characteristic of these materials that has increased interest is the giant magneto-resistance (GMR) effect that causes higher electrical resistivity drop when the material is brought near a magnetic field, and it is highly suitable for magnetic storage devices and sensors [133]. Guo et al. fabricated a novel magnetic nano-material using surface initiated polymerization sonication method that is suitable to be utilized in giant-magneto resistor [24]. An active area of investigation is the search for magnetic carbon nano-materials with high coercivity that is important for stability and resistance to demagnetization [134]. Recent experiments were conducted to produce magnetic microspheres having flower like structures using L-cysteine (C_3H_7NS) that showed promising capacity for hydrogen storage [135].

4.4. Medical sciences

Nano-materials are contributing significantly in health care for many years. One key issue that is being faced in using conventional nano-materials is the challenge of getting them to the targeted areas of the body. The introduction of magnetic nano-materials facilitates guidance to specific locations by simple use of a magnetic field during treatment, followed by efficient removal subsequent to delivery [30]. One well-established field is imaging of musculo-skeletal structure including soft tissue by use of magnetic resonance imaging (MRI) that uses contrast agents, which are responsible for higher quality images [136]. Magnetic nano-materials specially (iron oxide based nano-materials) are suitable to be used as high contrast agents during MRI scanning [137]. These nano-particles have higher permeability and higher retention time and therefore they are able to detect tumours more effectively (Fig. 7).

One of the most important uses of magnetic nano-materials is as a drug carrier. Some researchers were successful in non-viral effecting transfection of nano-magnetic materials into cells for gene therapy [138]. Successful cytotoxic drug delivery has been reported on different animals using magnetic nano-materials [139]. Researchers are focusing to improve novel magnetic nano-material carrier systems and by using surface engineering techniques for application as a drug delivery agent [140]. On the other hand, considerable development is also done in the field of biosensor and biochips using magnetic nano-materials [141].

5. Future scope and challenges for magnetic carbon nano-materials

The interest and demand of magnetic carbon nano-materials having unique magnetic characteristics and porous structure is increasing due to their applications in diverse fields. Apart from the ongoing challenges of delivering performance, one of the key issues would be selection of raw material. One key obstacle that can arise may be encountered through fabrication of advanced magnetic carbon nanomaterials by controlling the overall structure, morphology, homogeneous design and controlled properties. In this way, the methods should be carefully analysed in depth considering each of the process parameter making it possible to avoid every chance of negligence and error. However, one problem of this field is agglomeration of magnetic nanoparticles when it is chemical bonded with the carbon nano-tubes, it can adversely affect the overall performance by capturing few sites resulting in destroying of few features including lowering surface area, porosity and surface chemistry of composite and lowering its efficiency. Therefore it is highly recommended that the controlled process design should be efficient enough to deal with issues like this and that can affect positively providing the composite with exceptional properties and enhancing overall performance and its application.

Availability and cost of raw material and processing cost are key factors that will govern choice of starting material and processing methodology. Utilization of waste biomass as starting material for producing carbon nanomaterial substrates provides a highly attractive, environmentally friendly option that would neutralize the negative effects of improper disposal of these waste residues. While the abundance and reduced cost are highly advantageous features, challenges remain in developing lower-cost processes that deliver high-performance products. Other issues include scale up issues, product and process optimization. One other interesting area, which is a research gap and needs to be filled is the applications of these materials in special fields mainly radioactive and optical imaging methods that are interestingly involved in some bio-nanotechnology research as in multifunctional diagnosis and therapy. Existing tactics using the magnetic materials in optic kerr effect, electron microscopy and x-ray and have few boundaries that need some improvement to achieve ultra-high spatial resolutions. Magneto-optical response of an array with negatively-charged nitrogen-vacancy spins in diamond may potentially enhance the overall spatial resolution using all-optical spin contrast imaging approach play its role in achieving overall effectiveness in the current system. This approach needs to be studied in depth that can lead to some ground breaking outcomes.

6. Conclusion

The present study has provided a comprehensive overview on synthesis methods for novel magnetic carbon nano-materials. These techniques are also capable to enhance morphological and physio-chemical features, enabling the material for the application in broad areas. These advance materials have extensive applications in the area of catalysis, super-capacitance, environmental remediation and biomedical applications. The use of biomass such as agricultural waste contains abundant functional groups that are able to produce novel nano-materials, which can significantly reduce its production cost and render the application environmentally friendly and sustainable. There are some challenges in the field of fabrication of magnetic carbon nanomaterials with higher controlled morphology, homogeneous nanostructure and controlled properties. As well as their applications in certain areas including optical imaging, by utilizing and designing optimal optical spin contrasting image method using array of inert nitrogen vacancy spins in diamond can enhance the overall performance and leads to ground breaking results in the field.

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