



Review

Biochar-based nano-composites for the decontamination of wastewater: A review



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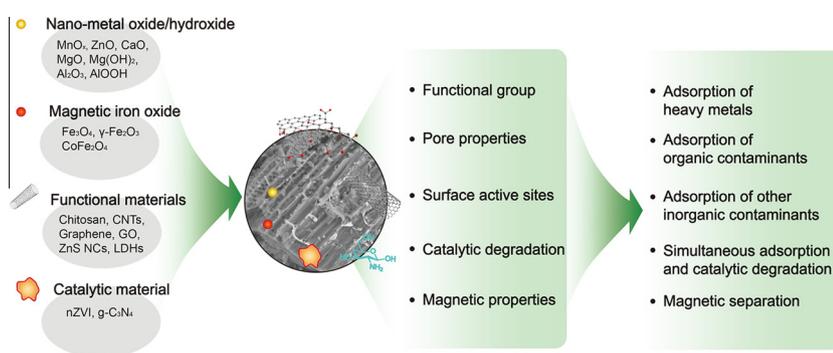
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HIGHLIGHTS

- Recent studies on synthesis of biochar-based nano-composites are reviewed.
- Biochar-based nano-composites combine the advantages of biochar with nano-materials.
- Nano-particles improve biochar's physicochemical properties and serve as active sites.
- Multiple mechanisms are involved in contaminants removal.
- Knowledge gaps in the future development should be studied.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesizing biochar-based nano-composites can obtain new composites and combine the advantages of biochar with nano-materials. The resulting composites usually exhibit great improvement in functional groups, pore properties, surface active sites, catalytic degradation ability and easy separation. These composites have excellent abilities to adsorb a range of contaminants from aqueous solutions. Particularly, catalytic material-coated biochar can exert simultaneous adsorption and catalytic degradation function for organic contaminants removal. Synthesizing biochar-based nano-composites has become an important practice for expanding the environmental applications of biochar and nanotechnology. This paper aims to review and summarize the various synthesis techniques for biochar-based nano-composites and their effects on the decontamination of wastewater. The characteristic and advantages of existing synthesis methods are summarized and discussed. Application of biochar-based nano-composites for different contaminants removal and the underlying mechanisms are reviewed. Furthermore, knowledge gaps that exist in the fabrication and application of biochar-based nano-composites are also identified.

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1. Introduction

Biochar is a carbon-rich solid derived by pyrolyzing biomass with little or no oxygen (Lehmann and Joseph, 2012), it can be applied to soil for both agricultural and environmental gains (Sohi, 2012). Biochar is usually produced from crop residues, wood biomass, animal litters, and solid wastes via various thermochemical processes, including slow pyrolysis, fast pyrolysis, hydrothermal carbonization, flash carbonization, torrefaction and gasification (Meyer et al., 2011). Biochar research is originated from the soils called terra preta (“dark earth”) in the Amazon Basin, which contain high fertility and carbon content (Marris, 2006). During the past several years, application of biochar into soil has become a new exciting biotechnology with the benefits of using biochar in terms of soil amendment, enhancing of crop yield, mitigating global warming and carbon sequestration (Sohi, 2012).

Recently, considerable research efforts have also been conducted on biochar-based adsorbents for removal of aqueous contaminants, which can exert beneficial win–win effects for both carbon sequestration and water pollution control (Ahmad et al., 2014; Tan et al., 2015). Biochar has exhibited a great potential to adsorb water contaminants due to its wide availability of feedstocks, low-cost and favorable physical/chemical surface characteristics (Tan et al., 2015). However, the applications of biochar for water treatment are also restricted due to its limited functionalities, inherited from the feedstock after pyrolysis. The removal ability of biochar for various contaminants depends on its physical and chemical properties, which are greatly affected by the feedstocks, pyrolysis technologies and pyrolysis conditions (Ahmad et al., 2014; Tan et al., 2015). The raw biochar has limited ability to adsorb contaminants from aqueous solutions (Yao et al., 2013a), particularly for high concentrations of polluted water. In addition, the powdered biochar is difficult to be separated from

the aqueous solution due to its small particle sizes (Chen et al., 2011; Reddy and Lee, 2014).

In order to overcome these unfavorable factors mentioned above, a plenty of investigations have also been carried out to produce engineered biochars with novel structures and surface properties (Zhang et al., 2013b; Gan et al., 2015). Recently, considerable research interest has been focused on synthesis of biochar-based nano-composites to remove aqueous contaminants. Synthesizing a biochar-based nano-composite is not a method just to improve the physical or chemical properties of biochar, but to obtain a new composite and combine the advantages of biochar with other nano-materials. Recently, different substrates based nanocomposite materials were developed for decontamination of wastewater even the nuclear wastewater (Awual et al., 2014, 2015, 2016a,b; Lau et al., 2015; Shahadat et al., 2015; Awual, 2016). Compared with other nanocomposite materials, multiple advantages of using biochar as the substrates material for nano-composites production are existed. Firstly, the feedstocks of biochar production are abundant and low-cost, which mainly obtained from agricultural biomass and solid waste (Lehmann and Joseph, 2012; Sohi, 2012). Furthermore, the biochar production is cheap with low energy requirements, which is usually produced at relatively low temperatures (<700 °C) (Meyer et al., 2011). In addition, the thermochemical treatment of biomass can generate biofuels and syngas accompanied with biochar production (Lehmann and Joseph, 2012). Therefore, synthesizing biochar-based nano-materials may achieve four integrated goals, including pollutants removal, waste management, carbon sequestration, and energy production (Sohi, 2012; Tan et al., 2015).

The categories of different methods for the fabrication of biochar-based nano-materials are shown in Fig. 1. In general, these biochar-based nano-composites can be classified into the following three categories, namely, nano-metal oxide/hydroxide-biochar

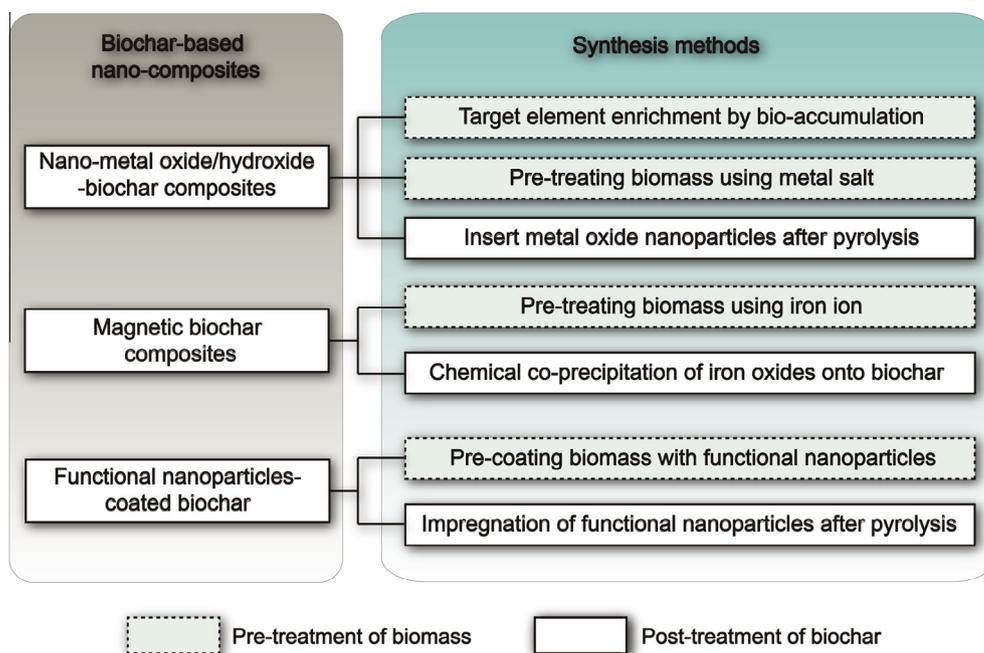


Fig. 1. The categories of different methods for the fabrication of biochar-based nano-composites.

composites, magnetic biochar composites, and functional nanoparticles-coated biochar (Fig. 1). This classification is based on the various kinds of nano-materials that are used to functionalize biochar, i.e., nano-metal oxide/hydroxide, magnetic iron oxide and functional nanoparticles (eg., chitosan, graphene, graphene oxide, carbon nanotubes, ZnS nanocrystals, layered double hydroxides, nanoscale zero-valent iron, graphitic C_3N_4), respectively. Each kind of composite can be produced by different synthesis methods, which are reviewed and discussed in the following sections. Two treatment processes are mainly involved in these methods, i.e., either pre-treatment of biomass or post-treatment of biochar (Fig. 1).

The resulting composites usually showed great improvement in the factors affecting the contaminants removal due to the introduction of nano-materials, including specific surface area, pore-size distribution, pore volume, presence of surface active sites, catalytic degradation ability and easy to separation. The adsorption experiments demonstrated that these composites had excellent abilities to adsorb a range of contaminants from aqueous solutions, including heavy metals, organic contaminants, and other inorganic contaminants (Zhang et al., 2012b, 2013a; Yan et al., 2014). In addition, biochar-based nano-composites with different catalytic material dispersed on biochar surface can remove organic contaminants via simultaneous adsorption and degradation (Devi and Saroha, 2014, 2015; Jung et al., 2015; Kastner et al., 2015). Thus, impregnation of foreign materials onto raw biochars to get biochar-based nano-composites has become an important practice for expanding the environmental applications of biochar and nanotechnology. However, apart from their advantages, the environmental and biological toxicity of nano-materials are also need to be considered (Kahru et al., 2008; Aruoja et al., 2009; Jiang et al., 2009). Furthermore, apart from the studies available, knowledge gaps are existed in the future development.

This paper aims to review and summarize the various synthesis techniques for biochar-based nano-composites and their effects on the decontamination of wastewater. The characteristic and advantages of existing synthesis methods are discussed. The research needs for potential synthesis method are proposed along with the review process. Application of biochar-based

nano-composites for different contaminants removal and the underlying mechanisms are summarized and discussed. Furthermore, knowledge gaps, uncertainties, and future research needs that exist in the fabrication and application of biochar-based nano-composites are also identified.

2. Nano-metal oxide/hydroxide-biochar composites

Three kinds of synthesis methods are applied to produce nano-metal oxide/hydroxide-biochar composites, including target element enrichment by bio-accumulation, pre-treating biomass using metal salt, and insert metal oxide nanoparticles after pyrolysis (Fig. 2a). The first two methods are concentrated on the treatment of biomass by impregnation of target metal into biomass before pyrolysis. The later one is tried to directly introduce nano-metal oxide/hydroxide into the biochar pyrolyzed from biomass (Table 1, Fig. 2a).

2.1. Target elements enrichment by bio-accumulation

Target chemical elements can be enriched by bio-accumulation in biomass, which can be further used to produce engineered biochar with desired properties (Table 1, Fig. 2a). The metal elements enriched in the biomass can be turned into nano-metal oxide/hydroxide after thermal treatment. An innovative engineered biochar from Mg enriched tomato tissues was produced through slow pyrolysis (Yao et al., 2013a,b). The tomato plants grown in a peat-based medium were irrigated with Hoagland solution containing 25 mM Mg twice a week to enrich Mg content. The resulting Mg-biochar composites showed commendable adsorption ability to phosphate in aqueous solutions. The nanoscale $Mg(OH)_2$ and MgO particles presented on the surface of Mg-biochar served as the main adsorption sites for phosphate. So far, there is little research about modifying the biomass feedstock by bio-accumulating target chemicals to obtain biochar with remarkable physiochemical properties. Therefore, it should be noted that there exists significant potential for further research about the bio-accumulation of other foreign chemicals, such as Al, Zn, Ca, Fe,

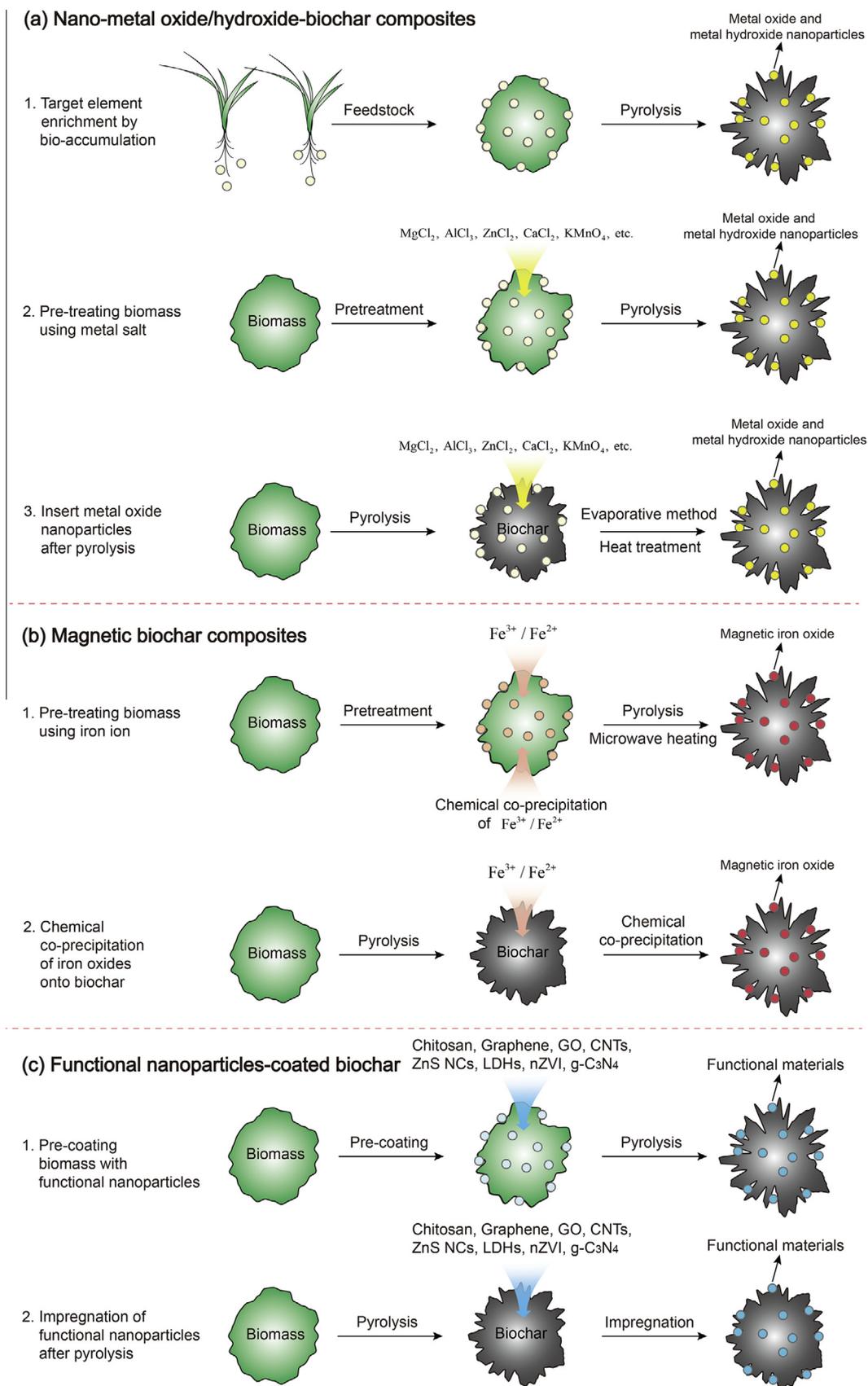


Fig. 2. The schematic diagram of synthesizing biochar-based nano-composites.

Table 1
Recent researches on synthesis, characteristic, and application of nano-metal oxide/hydroxide-biochar composites.

Feedstock	Pyrolytic conditions ^a	Technique used	Characteristic and advantages	Contaminants	Effect on removal capacity	References
Tomato plants tissues	600 (1 h)	Pyrolysis of Mg-enriched plant tissues	Nanoscale Mg(OH) ₂ and MgO particles were presented on the biochar surface	Phosphate	Biochars with high Mg level removed greater percent of Phosphate	Yao et al., (2013a,b)
Corn	300, 450 and 600 (3 h)	Pyrolysis of MgCl ₂ -pretreated biomass	Increased numerous magnesium nanoparticles	Phosphate	More effective than pristine biochar	Fang et al. (2014)
Corn cob	300, 450, and 600 (3 h)	Pyrolysis of Ca/Mg-treated biomass	Rich in organic functional groups and CaO and MgO nanoparticles	Phosphate	The maximum P adsorption amounts were 294.22, 315.33, and 326.63 mg g ⁻¹ , respectively	Fang et al. (2015)
Cotton Wood	600 (1 h)	Pyrolysis of AlCl ₃ -pretreated biomass	Biochar/AlOOH nanocomposite with carbon-nanoparticle structure	Arsenic, methylene blue and phosphate	Excellent adsorption abilities for various contaminants	Zhang and Gao (2013)
Hickory wood	600 (1 h)	Pyrolysis of KMnO ₄ -treated biomass	Biochar covered with MnOx ultrafine particles with more surface oxygen-containing functional groups and much larger surface area	Pb(II), Cu(II), and Cd(II)	2.1 times higher for Pb(II); 2.8 times higher for Cu(II); 5.9 times higher for Cd(II) than pristine biochar	Wang et al. (2015a)
Lotus stalks	300, 350 and 400 (1 h)	Pyrolysis of zinc borate-pretreated biomass	Enhanced biochar yield and promoted biochar surface oxygen content	Ni(II)	3–10 times higher than pristine biochar	Liu et al. (2014)
Marine macroalgae (<i>Laminaria japonica</i>)	600 (1 h)	Pyrolysis of biomass treated by electro-assisted modification method with MgCl ₂ as an electrolyte	Nano-sized Mg–Al oxide/hydroxide were uniformly dispersed on the biochar surface	Phosphate	As high as 887 mg g ⁻¹	Jung et al. (2015)
Marine macroalgae (<i>Laminaria japonica</i>)	600 (1 h)	Pyrolysis of biomass treated by combined electrochemical modification method, using a graphite electrode-based electric field and MgCl ₂ as electrolyte	Nano-sized MgO particles with a highly crystalline structure	Phosphate	As high as 620 mg g ⁻¹	Jung and Ahn (2016)
Pecan nut shells	600 (4 h)	Pyrolysis of calcium salts-pretreated biomass	Increased the micropore volume and the total pore volume	Dyes (acid blue 74 and reactive blue 4)	More efficient than the pristine biochar	Aguayo-Villarreal et al. (2014)
Pine wood	600 (1 h)	Pyrolysis of MnCl ₂ ·4H ₂ O-treated biomass	Presences of manganosite	As(V) and Pb (II)	Near 2 times higher for As(V) and Pb(II) than pristine biochar	Wang et al. (2015d))
Sewage sludge	500 (1 h)	One-step pyrolytic process with citric acid–ZnCl ₂ mixed fabricating-pore agents	More micropores and mesopores, and higher surface area	Benzene derivatives	Effectively sorb many kinds of benzene derivatives in aqueous solution	Kong et al. (2014)
Sugar beet tailings and peanut shells	600 (1 h)	Pyrolysis of MgCl ₂ -pretreated biomass	The MgO nano-flakes dispersed uniformly on the biochar matrix	Phosphate and nitrate	Increased to 835 mg g ⁻¹ for phosphate and 95 mg g ⁻¹ for nitrate	Zhang et al. (2012a)
Sugarcane bagasse	450 (1 h)	Pyrolysis of zinc nitrate-pretreated biomass	Higher surface areas and total volumes pore	Cr(VI)	1.2–2.0 times higher than that of pristine biochar	Gan et al. (2015)
Corn straws	600 (3 h)	KMnO ₄ modification under high temperature (600 °C)	Layered structures of micro/nano-MnOx were formed	Cu(II)	Much higher than pristine biochar	Song et al. (2014)
Hickory chips	600 (2 h)	Directly hydrolyzes iron salt onto biochar	Iron hydroxide particles were formed	As(V)	Much better than the pristine biochar	Hu et al. (2015)
Peeled pine wood	700 (3 h)	Conventional wet impregnation method	Amorphous hydrous manganese oxide was loaded onto biochar	Pb(II)	5 times higher than pristine biochar	Wang et al. (2015b)
Pine wood	600 (1 h)	KMnO ₄ precipitation method	Presences of birnessite	As(V) and Pb (II)	More than 4 times higher for As (V) and 20 times higher for Pb (II) than pristine biochar	Wang et al. (2015d)
Rice husks	450–1050 (30 min)	Amended with iron oxides using dissolved ferric nitrate	Increased surface area	Arsenic	Nearly 2 times higher than those reported for iron oxide amended sand	Cope et al. (2014)

^a Pyrolytic temperature (residence time).

Mn, on biomass feedstock, which may further have impact on the physiochemical properties of the resulted biochar and introduce nano-metal oxide/hydroxide into resulted biochar due to the enrichment of target element. In addition, the application of hyper-accumulator plant may enhance the bio-accumulation of target element, which should be demonstrated in the further study.

2.2. Pre-treating biomass using metal salt

Another method is pre-treating biomass using chemical reagent before pyrolysis (Table 1, Fig. 2a). Metal salts are usually chosen as the chemical reagents for the pretreatment of biomass. The metal ions may attach onto the surface or get into the interior of biomass after it is dipped into the metal salts solution. After pyrolysis, the metal ions will transform into nano-metal oxide or metal hydroxide, and the biomass impregnated with metal ions will become biochar based nanocomposites (Yao et al., 2013a,b). Particularly, magnetic biochar based adsorbent can be fabricated by the pyrolysis of iron ion treated biomass (Zhang et al., 2013a). AlCl₃ (Zhang and Gao, 2013), CaCl₂ (Fang et al., 2015; Liu et al., 2016), MgCl₂ (Zhang et al., 2012a; Fang et al., 2015), KMnO₄ (Wang et al., 2015a), MnCl₂ (Wang et al., 2015d), and ZnCl₂ (Gan et al., 2015) are the commonly applied metal salts for the pretreatment of biomass, which result in the formation of Al₂O₃, AlOOH, CaO, MgO, MnO_x, and ZnO nanoparticles on biochar surface. For instance, highly porous MgO-biochar nanocomposites could be synthesized by slow pyrolysis of MgCl₂-pretreated biomass (Zhang et al., 2012a). The results indicated that the MgO nano-flakes dispersed uniformly on biochar surface, and the MgO-biochar nanocomposite showed excellent removal efficiencies to phosphate and nitrate. Biochar/AlOOH nanocomposite could be fabricated via thermal pyrolysis of AlCl₃ pre-treated biomass (Zhang and Gao, 2013). The nanosized polycrystalline AlOOH flakes grown on biochar surfaces dramatically increased the reactive area and sites to attract heavy metals, organic, and inorganic contaminants from water. ZnCl₂ were also applied to produce ZnO-biochar nanocomposites (Gan et al., 2015). It was reported that zinc-biochar nanocomposites produced from ZnCl₂-pretreated sugarcane bagasse had much higher BET specific surface area and total pore volume (TPV) (BET = 21.28 m² g⁻¹ and TPV = 0.0325 m³ g⁻¹) than those of the pristine biochar (BET = 1.98 m² g⁻¹ and TPV = 0.0037 m³ g⁻¹), which exhibited 1.2–2.0 times higher removal efficiency for Cr (VI) (Gan et al., 2015).

2.3. Insert metal oxide nanoparticles after pyrolysis

Biochar-based composites with metal oxide nanoparticles attached onto biochar matrix can also be synthesized after the pyrolysis of biomass (Table 1, Fig. 2a). Evaporative method (Cope et al., 2014), heat treatment (Song et al., 2014), conventional wet impregnation method (Wang et al., 2015b), and directly hydrolyzes (Hu et al., 2015) are the commonly used methods for the treatment of biochar in the presence of metal salt. For instance, biochar could be amended with iron oxides by Fe(NO₃)₃·9H₂O via an evaporative method (Cope et al., 2014), which showed approximately 2.5 orders of magnitude higher surface area. The heat treatment of the mixture of biochar and KMnO₄ could synthesize a novel composite composed of porous biochar and micro/nano-MnO_x (Song et al., 2014). The formation of surface complexes with MnO_x and oxygen-containing function groups were the key factors for increasing the removal capacity of Cu²⁺ on the MnO_x-loaded biochar. Hydrous-manganese-oxide-loaded biochar was prepared by a conventional wet impregnation method, that amorphous hydrous manganese oxide loaded onto biochar contributed to the higher sorption ability for Pb(II) (Wang et al., 2015b). Iron (Fe)-impregnated biochar, prepared through direct hydrolysis of

iron salt onto hickory biochar, and results suggested that iron hydroxide particles on the biochar surface served as the main sites for As sorption (Hu et al., 2015).

3. Magnetic biochar composites

Considering its difficulty to be separated from the aqueous solution, biochar can also be converted into magnetic materials by two synthesis methods, i.e., pre-treating biomass using iron ion and chemical co-precipitation of iron oxides onto biochar (Fig. 2b). By these methods, nanosized magnetic iron oxide including Fe₃O₄ (Baig et al., 2014), γ-Fe₂O₃ (Wang et al., 2015e), and CoFe₂O₄ particles (Reddy and Lee, 2014) can be coated on the surface of biochar, resulting in the introduction of magnetism and active sites of iron oxide for contaminants removal (Table 2). The magnetic biochar could be easily separated from solution by an external magnetic field and its adsorption capacity could also be enhanced with the impregnation of magnetic iron oxides (Chen et al., 2011; Zhang et al., 2013a).

3.1. Pre-treating biomass using iron ions

The first method is impregnating with Fe³⁺/Fe²⁺ or chemical co-precipitation of Fe³⁺/Fe²⁺ on biomass and subsequently pyrolyzing or microwave heating under different conditions (Table 2, Fig. 2b). A novel magnetic biochar based adsorbent with colloidal or nanosized-Fe₂O₃ particles embedded in porous biochar matrix were synthesized through thermal pyrolysis of FeCl₃ pretreated biomass (Zhang et al., 2013a). The resulting composite showed wonderful ferromagnetic properties (saturation magnetization = 69.2 emu g⁻¹) and good adsorption ability for As(V) in aqueous solution. Similarly, Chen et al. (2011) produced a magnetic biochar by chemical co-precipitation of Fe³⁺/Fe²⁺ on orange peel powder before pyrolysis. TEM, SAD and XRD analyses of resulted biochar confirmed the existence of magnetic iron oxide in magnetic biochar. Microwave heating technique can be used as an effective technique in preparing magnetic biochar (Mubarak et al., 2014). The magnetic biochar synthesized from a FeCl₃-impregnated palm oil empty fruit bunch by microwave heating technique was effective in removing methylene blue with a maximum adsorption capacity of 265 mg g⁻¹ due to its high surface area of 890 m² g⁻¹ (Mubarak et al., 2014). Magnetic biochar can also be synthesized by pretreatment of biomass using Fe accompany with other ions. Reddy and Lee (2014) synthesized a magnetic biochar via slow pyrolysis of Co(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O pretreated biomass. Their results indicated that the spinel-type lattice of cobalt ferrite on biochar's surface seemed to enhance its Pb(II) and Cd(II) adsorption capacity. Furthermore, the treatment of biomass by naturally-occurring hematite mineral can also be used to produce magnetic biochar (Wang et al., 2015e). In comparison to the pristine biochar, the hematite modified biochar exhibited stronger magnetic property and the γ-Fe₂O₃ particles on the carbon surface served as sorption sites for arsenic.

3.2. Chemical co-precipitation of iron oxides onto biochar

Another method for magnetic biochar composites production is directly chemical co-precipitation of Fe³⁺/Fe²⁺ on biochar which is firstly pyrolyzed from biomass (Table 2, Fig. 2b). Recent researches have also produced magnetic biochar by the impregnation of magnetic particles into biochar after pyrolysis. Chemical co-precipitation of iron oxides onto biochar was the most commonly used method (Mohan et al., 2014b; Han et al., 2015b; Ren et al., 2015). In this synthesis process, biochar was firstly produced by pyrolysis of biomass, then aqueous biochar suspension was mixed with aqueous ferrous/ferric solution, followed by aqueous NaOH

Table 2
Recent researches on synthesis, characteristic, and application of magnetic biochar composites.

Feedstock	Pyrolytic conditions ^a	Technique used	Characteristic and advantages	Contaminants	Effect on removal capacity	References
Cotton Wood	600 (1 h)	Pyrolysis of FeCl ₃ -treated biomass	Magnetic biochar containing colloidal/nano-sized Fe ₂ O ₃ particles in porous char structures	As(V)	Comparable to or that of many commercial adsorbents	Zhang et al. (2013a)
Empty fruit bunch	– (–)	Single stage microwave heating technique in the presence of ferric chloride hexahydrate	Magnetic biochar with a high surface area of 890 m ² g ⁻¹	Methylene blue	The maximum adsorption capacity was 265 mg g ⁻¹	Mubarak et al. (2014)
Loblolly pine wood	600 (1 h)	Pyrolysis of hematite-treated biomass	Magnetic γ-Fe ₂ O ₃ particles on the biochar surface	As(V)	Near 1.6 times higher than pristine biochar	Wang et al. (2015e)
Orange peel	250, 400 and 700 (6 h)	Chemical co-precipitation of Fe ³⁺ /Fe ²⁺ on orange peel powder	Nano-size magnetite particles and amorphous biochar	HOcs and phosphate	Higher sorption capability than the non-magnetic biochars	Chen et al.(2011)
Pine bark waste	950 (2 h)	Pyrolysis of Co(NO ₃) ₂ ·6H ₂ O and Fe(NO ₃) ₃ ·9H ₂ O pretreated biomass	Spinel-type lattice of cobalt ferrite formed on its surface	Pb(II) and Cd (II)	–	Reddy and Lee (2014)
Rice husk and the organic fraction of municipal solid wastes	300 (1 h)	The biomass was impregnated with calcium and iron agents before pyrolysis	Increased Fe and Ca content in its mineral impurities	As(V) and Cr (VI)	Much better As(V) removal capacity compared to the non-impregnated biochars	Agrafiori et al. (2014)
Corn stalks	400 (2 h)	Chemical co-precipitation	Biochar coated with magnetic Fe ₃ O ₄ nanoparticles	Crystal violet	Near 20 times higher than pristine biochar	Sun et al. (2015)
Oak wood and oak bark	400, 450 (–)	Chemical co-precipitation of iron oxides onto the char	Magnetic biochar with increased surface area	Pb(II) and Cd (II)	Better/comparable to other biochars reported earlier	Mohan et al. (2014a)

^a Pyrolytic temperature (residence time).

treatment (Han et al., 2015b; Sun et al., 2015). Oak bark and oak wood biochars were successfully converted into magnetic biochars via chemical co-precipitation of iron oxides onto the biochar (Mohan et al., 2014a). Similar chemical co-precipitation method was applied for magnetic biochar preparation from eucalyptus leaf residue (Wang et al., 2014, 2015c).

A comparison of two synthesis methods (chemical co-precipitation of iron oxides onto biochar after pyrolysis and chemical co-precipitation of iron oxides onto biomass before pyrolysis) for preparing magnetic biochars was studied by Baig et al. (2014). The results suggested that the physiochemical properties (Fe₃O₄ loading content, saturation magnetization and thermal stability) and As(III, V) adsorption efficiency of the biochars prepared using chemical co-precipitation of iron oxides onto biomass before pyrolysis were higher than the former method.

4. Functional nanoparticles-coated biochar

The coating of functional nanoparticles (eg., chitosan, graphene, graphene oxide, carbon nanotubes, ZnS nanocrystals, layered double hydroxides, nanoscale zero-valent iron, graphitic C₃N₄) onto biochar surface can fulfill an affordable composite material capable of removing various contaminants by combining the advantages of biochar matrix and functional nanoparticles (Fig. 2c). These functional nanoparticles may make a great improvement in surface functional groups, surface area, porosity, and thermal stability of biochar, which contribute to better performance of contaminants removal (Table 3). Particularly, biochar-based nano-composites with different catalytic and oxidative/reductive nanoparticles (such as nanoscale zero-valent iron and graphitic C₃N₄) dispersed on biochar surface can exert simultaneous adsorption and degradation ability for removing organic contaminants.

4.1. Pre-coating biomass with functional nanoparticles

Several functional nanoparticles were applied to pretreat biomass before pyrolysis (Table 3). Generally, biomass can be converted to biochar based functional composites following a dip-coating procedure. Specifically, functional nanoparticles suspensions were prepared by adding functional nanoparticles into deionized water. The resulted suspensions were homogenized by sonication using ultrasonicator. Then the biomass was dipped into the suspension and oven dried for later pyrolysis. A new engineered graphene-coated biochar was created through anneal of graphene/pyrene-derivative treated biomass feedstock. Experimental results indicated that the graphene “skin” could improve the thermal stability of the biochar, and the graphene-coated biochar had excellent adsorption ability of methylene blue (Zhang et al., 2012b). Similarly, a graphene/biochar composite was synthesized via slow pyrolysis of graphene pretreated wheat straw, and the results suggested that graphene was coated on the surface of biochar mainly through π–π interactions, resulting in a larger surface area, more functional groups, greater thermal stability, and higher removal efficiency of phenanthrene and mercury compared to pristine biochar (Tang et al., 2015). Multi-walled carbon nanotube (CNT)-coated biochars were synthesized by dip-coating biomass in varying concentrations of carboxyl-functionalized CNT solutions prior to slow pyrolysis (Inyang et al., 2014, 2015). The results indicated that the surface area, porosity, and thermal stability of the biochars were enhanced by additions of carbon nanotubes (CNTs).

4.2. Impregnation of functional nanoparticles after pyrolysis

Impregnation of functional nanoparticles onto raw biochar after pyrolysis to get biochar-based composites can also combine the

Table 3
Recent researches on synthesis, characteristic, and application of functional nanoparticles-coated biochar.

Feedstock	Pyrolytic conditions ^a	Technique used	Characteristic and advantages	Contaminants	Effect on removal capacity	References
Cotton wood	600 (1 h)	The biomass was pretreated with graphene/pyrene-derivative	Graphene coated on biochar, and the thermal stability of the biochar was improved	Methylene blue	More than 20 times higher than pristine biochar	Zhang et al. (2012b)
Hickory chips and sugarcane bagasse	600 (1 h)	Dip-coating biomass in carboxyl-functionalized CNT solutions prior to slow pyrolysis	Better thermal stabilities, higher surface areas, and larger pore volumes	Methylene blue	Almost twice those of their respective unmodified biochar	Inyang et al. (2014)
Hickory chips and sugarcane bagasse	600 (1 h)	Dip-coating biomass in carbon nanotube (CNT) suspensions with sodium dodecylbenzenesulfonate (SDBS)-aided dispersion before pyrolysis	Surfactant SDBS promote the distribution and stabilization of individual CNT nanoparticle on the biochar surface	Pb(II) and sulfapyridine	Much higher than pristine biochars	Inyang et al. (2015)
Wheat straw	600 (1 h)	Slow pyrolysis of graphene-pretreated biomass	Larger surface area, more functional groups, and greater thermal stability,	Phenanthrene	Near 2 times higher than pristine biochar	Tang et al. (2015)
Bamboo	300, 450 and 600 (–)	Chitosan was used as a dispersing and soldering reagent to attach fine ZVI particles onto bamboo biochar surfaces	Loaded with large amount of the chitosan and ZVI	Pb(II), Cr(VI), As (V), phosphate and methylene blue	Excellent ability to remove various contaminants	Zhou et al. (2014b)
Bamboo, sugarcane bagasse, hickory wood and peanut hull	600 (2 h)	Coating of chitosan on biochar surfaces	Chitosan coated on the biochar surfaces with additional amine groups	Pb(II), Cu(II), and Cd(II)	Enhanced removal of three metals from solution	Zhou et al. (2013)
Chestnut leaves	900 (2 h)	Condensation reaction of melamine at 520 °C	C ₃ N ₄ existed in the composites	Methylene blue	Sustaining decontamination by simultaneous adsorptive and photocatalytic processes	Pi et al. (2015)
Chicken droppings, wood, and old car tire	– (–)	Neutral hydrogel matrix loaded with biochars	Hydrogel-Biochar composites with neutral hydrogel matrix loaded on biochars	Phenol	Comparable or even better absorption characteristics than activated carbons	Karakoyun et al. (2011)
Cotton Wood	600 (1 h)	Mg/Al-LDH deposited biochar composites was synthesized by a spontaneous self-assembly method	Increased Mg/Al-LDH particles on the carbon surfaces	Phosphate	Higher than that any other LDH adsorbents	Zhang et al. (2013b)
<i>Eichornia crassipes</i>	600 (1 h)	Chitosan coated on biochar/ γ -Fe ₂ O ₃	Magnetism and abundant functional groups	Cr(VI)	4 times higher than pristine biochar	Zhang et al. (2015)
Paper mill sludge	700 (–)	Impregnation of the Zero-valent iron (ZVI) on the biochar surface	Impregnation of ZVI with improved pore structures	Pentachlorophenol	Much higher compared to biochar and ZVI alone	Devi and Saroha (2014)
Paper mill sludge	700 (–)	Impregnation of the Zero-valent iron (ZVI) on the biochar surface, followed by the doping of Ni	Impregnation of Ni and ZVI with higher surface area	Pentachlorophenol	Simultaneous adsorption and dechlorination	Devi and Saroha (2015)
Rice hull	400 (5 h)	Deposition of ZnS nanocrystals (NCs) on magnetic biochar in a polyol solution	Magnetic biochar coated with ZnS nanocrystals	Pb(II)	10 times higher than that of reported magnetic biochar	Yan et al. (2014)
Rice husk	500 (–)	Synthesis of biochar supported nZVI	Increase in the dispersion and reactivity of nZVI	Methyl orange	Near 13 times higher than pristine biochar	Han et al. (2015a)

^a Pyrolytic temperature (residence time).

advantages of biochar with the properties of functional nanoparticles (Table 3, Fig. 2c). Hydrogel (Karakoyun et al., 2011), Mg/Al LDH (Zhang et al., 2013b), chitosan (Zhou et al., 2013; Zhang et al., 2015), zerovalent iron (ZVI) (Devi and Saroha, 2014, 2015; Zhou et al., 2014a; Yan et al., 2015), and ZnS nanocrystals (Yan et al., 2014) were commonly used in this synthesis process. These particles of functional materials were deposited on the carbon surface within the biochar matrix, which could serve as the active sites to adsorb contaminants from aqueous solutions. The resulted composites have superior functions and properties inherited from both functional nanoparticles and biochar. However, functional nanoparticles coated on the biomass feedstock may also cause the partial blockage of pores of biochar. Fortunately, the superior properties of functional nanoparticles may overcome this potential shortcoming. For instance, chitosan-modified biochars were synthesized by coating chitosan onto biochar surfaces (Zhou et al., 2013). It was found that this modification combined the advantages of biochar's porous network as well as relatively large surface area with the high chemical affinity of chitosan. However, the surface area of the biochar decreased dramatically due to the blockage of partial pores by the chitosan after the synthesis with the chitosan. Therefore, specific researches should be conducted to minimize the undesirable effect of a synthesis method on the other properties while introducing the target nano-materials.

5. Application for decontamination of wastewater

5.1. Adsorption of heavy metals

The removal of heavy metals has been one of the main research interests in application of biochar-based nano-composites for decontamination of wastewater. Adsorption characteristics of biochar-based nano-composites exposed to various heavy metals are presented in Table 4. Metals whose studies of adsorption on biochar-based nano-composites have been published at least once include As(III, V) (Zhang et al., 2013a; Baig et al., 2014; Cope et al., 2014; Hu et al., 2015; Wang et al., 2015e), Cd(II) (Reddy and Lee, 2014; Wang et al., 2015a), Cr(VI) (Gan et al., 2015; Zhang et al., 2015; Huang et al., 2016), Cu(II) (Song et al., 2014; Wang et al., 2015a), Hg(II) (Tang et al., 2015), and Pb(II) (Yan et al., 2014; Inyang et al., 2015; Wang et al., 2015b,d). Of which, As(V) and Pb(II) are the two most commonly studied metals (Table 4). The Langmuir maximum adsorption quantity of As(V) by various biochar-based nano-composites range from 0.4287 to 3.147 mg g⁻¹. The magnetic biochar/ γ -Fe₂O₃ composites synthesized by thermal pyrolysis of FeCl₃-pretreated biomass had the highest adsorption ability (Zhang et al., 2013a). The adsorption capacity of Pb(II) by various biochar-based nano-composites range from 4.913 to 367.65 mg g⁻¹, and the magnetic biochar/ZnS composites synthesized by deposition of ZnS nanocrystals (NCs) on magnetic biochar exhibited the best performance (Yan et al., 2014).

Many isotherm models have been employed to analyze experimental data and describe the equilibrium of heavy metals adsorption onto biochar-based nano-composites. The most popular and widely used of these are: Langmuir, Freundlich, Langmuir–Freundlich, Temkin, Redlich–Peterson, and BET models. As evidenced by the collected data, all of these equations can be used to describe the equilibrium adsorption of heavy metals by biochar-based nano-composites (Table 4), of which, Langmuir, Freundlich and Langmuir–Freundlich are used more frequently than others. Similarly, several kinetic models have been used to study the adsorption of contaminants by biochar-based nano-composites: pseudo-first-order, pseudo-second-order, Elovich, *n*-th-order and intra-particle diffusion model. As shown in Table 4,

the removal processes of heavy metals were well followed pseudo-second-order and Elovich model in most cases. The results of isotherm and kinetic study vary widely depending on the synthesis methods, properties of biochar-based nano-composites, and the target heavy metals. As well as, multiple mechanisms are involved in the adsorption of heavy metals by different biochar-based nano-composites.

Fig. 3(a) presents the effects and mechanisms of different nano materials on the adsorption of heavy metals. Their effects are mainly manifested in the following aspects: (1) influence on the surface functional groups of biochar; (2) improvement or deterioration on the pore property of biochar; (3) serving as active sites themselves. Compared with pristine biochar, the amount of oxygen-containing functional groups (such as carboxylate, –COOH; and hydroxyl, –OH and carboxyl, –C=O) may increase on the surface of the biochar after the introduction of nano materials (Song et al., 2014; Wang et al., 2015a). The improvement of functional groups may provide more available bonding sites for heavy metals. And these functional groups might strengthen the interactions between biochar and heavy metals by forming surface complexes, cation- π bonding, electrostatic attraction and ion-exchange (Baig et al., 2014; Song et al., 2014; Wang et al., 2015a,e), which contribute to the higher adsorption ability. Nano materials may also increase the surface area of biochar (Gan et al., 2015; Wang et al., 2015a,d), which can promote the adsorption process. However, several studies reported that nano materials could heavily block and fill the pores and reduce the surface area and pore volume of biochar (Cope et al., 2014; Hu et al., 2015; Wang et al., 2015b,e). This suggested that the influence of nano materials on the pore property of biochar may not be the main aspect determining heavy metals sorption onto biochar (Hu et al., 2015). Nano-metal oxide/hydroxide (eg., MnO_x, ZnO, CaO, MgO, Mg(OH)₂, Al₂O₃, and AlOOH), magnetic iron oxide (eg., Fe₃O₄, γ -Fe₂O₃, and CoFe₂O₄) and other functional nanoparticles (eg., chitosan, CNTs, graphene, GO, ZnS NCs, and LDHs) dispersed on the biochar surface could interact with heavy metals and make biochar have much stronger adsorption capacity for heavy metals (Song et al., 2014; Wang et al., 2015a). For instance, several researches reported that the increased adsorption of different heavy metals is attributed to the formation of surface complexes with nano-metal oxide/hydroxide and magnetic iron oxide (Song et al., 2014; Hu et al., 2015; Wang et al., 2015e). The studies of Pb(II) adsorption onto chitosan-modified biochars and CNTs-coated biochars suggested that lead adsorption on the biochar is mainly through the interactions with the amine functional groups of chitosan (Zhou et al., 2013) and the complexation with oxygen containing functional groups of the CNTs, respectively (Inyang et al., 2015). In general, both the functional groups and the nano particles on the surface of biochar could serve as the main adsorption sites for heavy metal ions in aqueous solutions.

Multiple functional materials can exert synergistic effects on heavy metal removal by coating different functional nanoparticles onto one biochar simultaneously. Magnetic biochar/ZnS composites were successfully synthesized by deposition of ZnS nanocrystals (NCs) on magnetic biochar in a polyol solution (Yan et al., 2014), which exhibited excellent superparamagnetic properties for separation and 10 times higher adsorption capacity for Pb(II) than that of reported magnetic biochar. In this composite, the coating of ZnS NCs and magnetic iron oxides induced the adsorption sites of nanoparticles and magnetism onto biochar. Chitosan modified magnetic biochar was successfully prepared by combining the superiority of chitosan, biochar and γ -Fe₂O₃, which was possessed of the features of low operating cost, easily available biomass resource, magnetic, and abundant functional groups with a high Cr(VI) adsorption capacity (4 times higher than unmodified biochar) (Zhang et al., 2015).

Table 4
Adsorption characteristics of various heavy metals with biochar-based nano-composites.

Feedstock	Pyrolytic conditions ^a	Nano-materials	BET surface area (m ² g ⁻¹)	Adsorption temperature (°C)	Adsorption pH	Adsorbent dosage (g L ⁻¹)	Contaminants	Q _{max} (mg g ⁻¹)	Isotherm ^b	Kinetic model ^c	References
Kans grass	500 (4 h)	Fe ₃ O ₄	31.45	25	7		As(III)	2.004 (L)	L	PSO	Baig et al. (2014)
Cotton Wood	600 (1 h)	γ-Fe ₂ O ₃ particles		22 ± 0.5		2	As(V)	3.147 (L)	L	PSO	Zhang et al. (2013a)
Hickory chips	600 (2 h)	Iron hydroxide particles	16.0	20 ± 2	5.8 ± 0.2	2	As(V)	2.16 (L)	T		Hu et al. (2015)
Kans grass	500 (4 h)	Fe ₃ O ₄	31.45	25	7		As(V)	3.132 (L)	L	PSO	Baig et al. (2014)
Loblolly pine wood	600 (1 h)	γ-Fe ₂ O ₃ particles	193.1	22 ± 0.5	7	2.5	As(V)	0.4287 (L)	L	Elovich	Wang et al. (2015e)
Pine wood	600 (1 h)	Manganosite	463.1, N ₂	22 ± 0.5	7	2.5	As(V)	0.594 (L)	F	Elovich	Wang et al. (2015d)
Pine wood	600 (1 h)	Birnessite	67.4	22 ± 0.5	7	2.5	As(V)	0.932 (L)	F	Elovich	Wang et al. (2015d)
Rice husks	550 (0.5 h)	Iron oxide	77.3, N ₂		6.85 ± 0.23		As(V)	1.15 (L)	L		Cope et al. (2014)
Rice husks	950 (0.5 h)	Iron oxide	220, N ₂		6.85 ± 0.23		As(V)	1.46 (L)	L		Cope et al. (2014)
Hickory wood	600 (1 h)	MnOx	205, N ₂	22 ± 0.5		2	Cd(II)	28.104 (L)	R-P	n-th-order	Wang et al. (2015a))
Pine bark waste	950 (2 h)	Magnetic CoFe ₂ O ₄					Cd(II)	17.793 (L-F)	L-F	PSO	Reddy and Lee (2014)
<i>Eichhornia crassipes</i>	600 (1 h)	Chitosan and γ-Fe ₂ O ₃	90.78, N ₂	20		1	Cr(VI)	151.62 (L)	L	PSO	Zhang et al. (2015)
Sugarcane bagasse	450 (1 h)	ZnO	21.28, N ₂	30		2	Cr(VI)	84.87 (L)	F	PSO	Gan et al. (2015)
Walnut shell	450 (2 h)	Chitosan	82.09, N ₂	25		2	Cr(VI)	124.42 (L)	F	PSO	Huang et al. (2016)
Corn straws	600 (3 h)	MnOx		25	6.0 ± 0.1	5	Cu(II)	160.3 (L)	L		Song et al. (2014)
Hickory wood	600 (1 h)	MnOx	205, N ₂	22 ± 0.5		2	Cu(II)	34.205 (L)	R-P	Elovich	Wang et al. (2015a)
Wheat straw	600 (1 h)	Graphene	17.3	25	7	0.36	Hg(II)	0.853 (BET)	BET	PSO	Tang et al. (2015)
Bamboo	600 (2 h)	Chitosan	166.9, N ₂	22 ± 0.5		2	Pb(II)	14.3 (L)	L	PSO	Zhou et al. (2013)
Hickory chips	600 (1 h)	Carbon nanotubes (CNTs)	359, N ₂		4-5	2	Pb(II)	31.05 (L-F)	L-F	Elovich	Inyang et al. (2015)
Hickory wood	600 (1 h)	MnOx	205, N ₂	22 ± 0.5		2	Pb(II)	153.109 (L)	R-P	n-th-order	Wang et al. (2015a)
Peeled pine wood	700 (3 h)	Hydrous-manganese-oxide		25		0.5	Pb(II)	91.98 (L)	L	PSO	Wang et al. (2015b)
Pine bark waste	950 (2 h)	Magnetic CoFe ₂ O ₄					Pb(II)	29.699 (L-F)	L-F	PSO	Reddy and Lee (2014)
Pine wood	600 (1 h)	Manganosite	463.1, N ₂	22 ± 0.5	5.5	2.5	Pb(II)	4.913 (L)	F	Elovich	Wang et al. (2015d)
Pine wood	600 (1 h)	Birnessite	67.4	22 ± 0.5	5.5	2.5	Pb(II)	47.05 (L)	L	PSO	Wang et al. (2015d)
Rice hull	400 (5 h)	Magnetic iron oxide and ZnS nanocrystals		20	6	0.4	Pb(II)	367.65 (L)	L	PSO	Yan et al. (2014)
Sugarcane bagasse	600 (1 h)	Carbon nanotubes (CNTs)	336, N ₂		4-5	2	Pb(II)	122.63 (L-F)	L-F	PSO	Inyang et al. (2015)

^a Pyrolytic temperature (residence time).

^b Isotherm model: Langmuir (L), Freundlich (F), Langmuir-Freundlich (L-F), Redlich-Peterson (R-P), and BET models (BET).

^c Kinetic model: pseudo-first-order (PFO), pseudo-second-order (PSO).

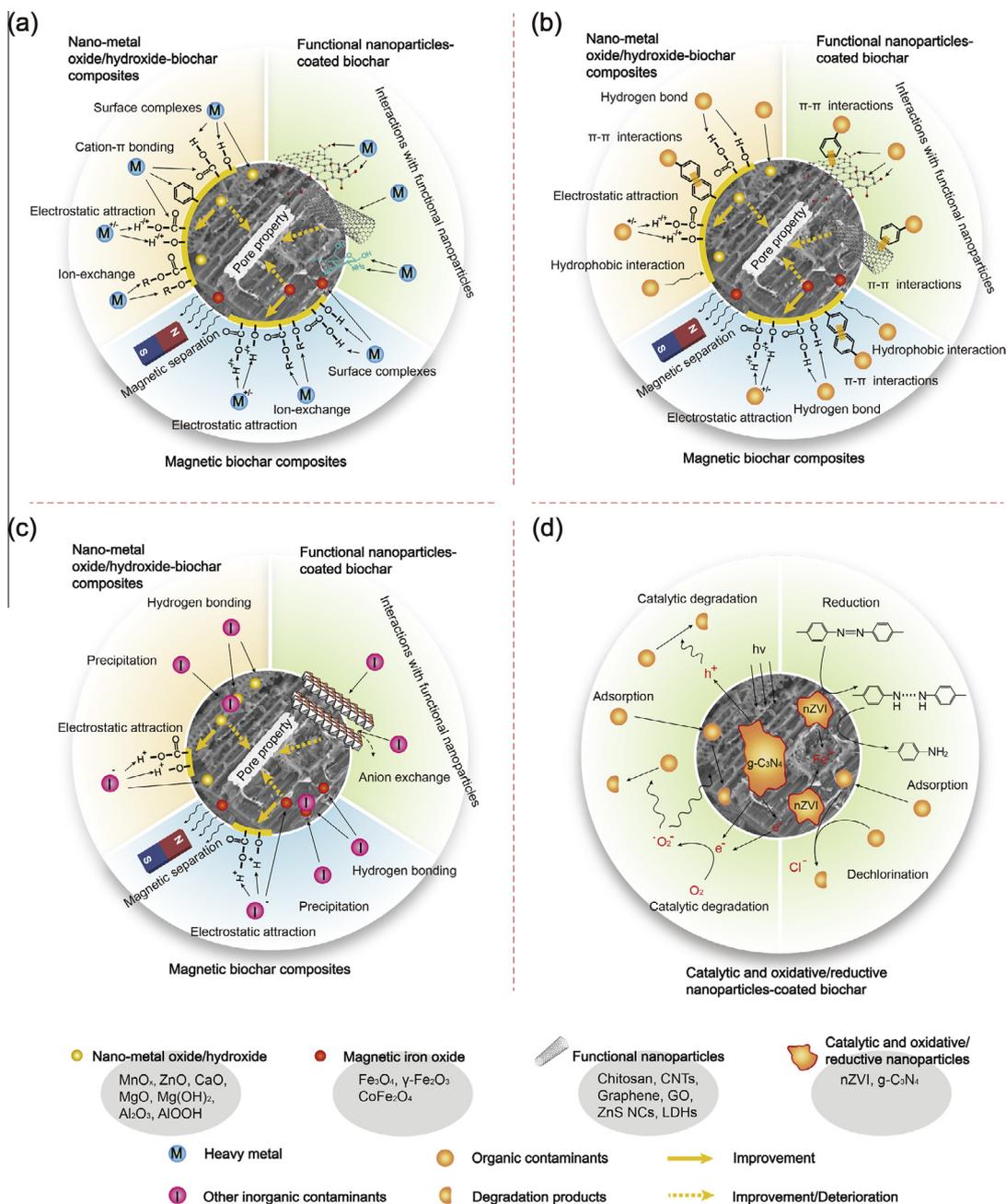


Fig. 3. The effects and mechanisms of different nano-materials on the removal of various contaminants: (a) adsorption of heavy metals, (b) adsorption of organic contaminants, (c) adsorption of other inorganic contaminants, and (d) simultaneous adsorption and degradation of organic contaminants.

5.2. Adsorption of organic contaminants

Biochar-based nano-composites also showed high affinity for organic pollutants. Adsorption characteristics of biochar-based nano-composites exposed to various organic contaminants are presented in Table 5. The concerned organic contaminants include crystal violet (Sun et al., 2015), methylene blue (Zhang et al., 2012b; Zhang and Gao, 2013; Inyang et al., 2014), phenanthrene (Tang et al., 2015), phenol (Karakoyun et al., 2011; Kong et al., 2014), sulfapyridine (Inyang et al., 2015), naphthalene (NAPH) and *p*-nitrotoluene (*p*-NT) (Chen et al., 2011). The adsorption ability of these organic contaminants varied from 2.4 to 278.55 mg g⁻¹ depending on the various nano materials, biochar substrates and target organic contaminants. As shown in Table 5, Langmuir and Langmuir–Freundlich fitted the data better than other isotherm

models. In addition, pseudo-second-order and Elovich were the most commonly used models in simulating sorption kinetics.

The various mechanisms proposed for the interaction of biochar-based nano-composites with organic contaminants are summarized in Fig. 3(b). As for the nano-metal oxide/hydroxide-biochar composites and magnetic biochar composites, several mechanisms might be involved in the adsorption processes by the interactions between organic contaminants and functional groups of biochar, including π - π interactions, hydrogen bond, electrostatic attraction and hydrophobic interaction (Tan et al., 2015). In addition, the coating of nanoparticles on carbon structure could also increase the adsorption sites to attract the organic contaminants from water (Zhang and Gao, 2013; Sun et al., 2015). The other functional nanoparticles (eg., chitosan, CNTs, graphene, GO, ZnS NCs, and LDHs) coated on the surface of biochar may account

Table 5
Adsorption characteristics of various organic contaminants with biochar-based nano-composites.

Feedstock	Pyrolytic conditions ^a	Nano-materials	BET surface area (m ² g ⁻¹)	Adsorption temperature (°C)	Adsorption pH	Adsorbent dosage (g L ⁻¹)	Contaminants	Q _{max} (mg g ⁻¹)	Isotherm ^b	Kinetic model ^c	References
Corn stalks Cotton Wood	400 (2 h)	Fe ₃ O ₄ nanoparticles AlOOH particles/flakes		20	6	1	Crystal violet	278.55 (L)	L	PSO	Sun et al. (2015) Zhang and Gao (2013)
	600 (1 h)			22 ± 0.5	2	85.0 (L)		L	PSO		
Hickory chips Milled cotton wood	600 (1 h)	Hybrid multi-walled carbon nanotube (CNT) Graphene	352, N ₂	22 ± 0.5		2	Methylene blue	2.4 (L–F)	L–F	Elovich	Inyang et al. (2014) Zhang et al. (2012b)
	600 (1 h)			22 ± 0.5	2	174 (L)		L	PSO		
Sugarcane bagasse Wheat straw Wood	600 (1 h)	Hybrid multi-walled carbon nanotube (CNT) Graphene	390, N ₂	22 ± 0.5		2	Methylene blue	5.5 (L–F)	L–F	PSO	Inyang et al. (2014) Tang et al. (2015)
	600 (1 h)			25	0.07	25.3 (L)		L	PSO		
Hickory chips Sugarcane bagasse	600 (1 h)	Hydrogel Carbon nanotubes (CNTs)	359, N ₂	25	7	1	Phenol	23.14 (L)	L	PSO	Karakoyun et al. (2011) Inyang et al. (2015)
	600 (1 h)			25	2	31.05 (L–F)		L–F	Elovich		
		Carbon nanotubes (CNTs)	336, N ₂		6–7	2	Sulfapyridine	122.63 (L–F)	L–F	Elovich	Inyang et al. (2015)

^a pyrolytic temperature (residence time).^b Isotherm model: Langmuir (L), Freundlich (F), Langmuir–Freundlich (L–F), Redlich–Peterson (R–P), and BET models (BET).^c Kinetic model: pseudo-first-order (PFO), pseudo-second-order (PSO).

for the larger surface area, more functional groups, greater thermal stability, and higher removal efficiency of organic contaminants (Zhang et al., 2012b; Inyang et al., 2015; Tang et al., 2015). And the mechanisms are associated well with the properties of the coated functional groups. It was reported that the enhanced adsorption of organic contaminants by the graphene-coated biochar could be mainly attributed to the strong interactions between the organic contaminants molecules and the graphene sheets on the biochar surface through the π - π interactions (Zhang et al., 2012b; Tang et al., 2015). Similarly, π - π interactions and hydrophobic interactions between organic contaminants and graphitic/hydrophobic sites on CNTs contributed to the main sorption mechanism for organic contaminants removal (Inyang et al., 2014, 2015).

5.3. Adsorption of other inorganic contaminants

Apart from heavy metals and organic contaminants, removal ability of biochar-based nano-composites for other inorganic pollutants such as phosphate (Yao et al., 2013a; Zhang and Gao, 2013; Zhang et al., 2013b; Jung et al., 2015; Liu et al., 2016), fluoride (Mohan et al., 2014b), and nitrate (Zhang et al., 2012a) were also investigated. Of which, phosphate is the most commonly studied inorganic contaminants. The adsorption capacity of phosphate by various biochar-based nano-composites ranged from 17.41 to 886.2 mg g⁻¹ (Table 6), and biochar/Mg–Al assembled nanocomposites showed the highest ability (Jung et al., 2015). The sorption of inorganic contaminants on the biochar-based nano-composites could be govern by multiple mechanisms (Fig. 3c). Two main effects of nano-materials on biochar are existed in the process of inorganic contaminants removal: (1) enhancing the surface area of biochar, and (2) impregnating nanocomposites on the biochar surface, which may dramatically increase the adsorption of inorganic contaminants from water (Zhang and Gao, 2013; Jung and Ahn, 2016). The studies found that the colloidal or nanosized nano-materials dispersed on the biochar served as the main reactive sites for inorganic contaminants bonding (Zhang and Gao, 2013; Jung et al., 2015; Jung and Ahn, 2016). Several interactions between nanoparticles in the biochar matrix and the inorganic contaminants were proposed to explain the underlying adsorption mechanisms, including electrostatic attraction, precipitation, hydrogen bonding, and anion exchange (Zhang et al., 2012a; Yao et al., 2013a,b).

5.4. Simultaneous adsorption and degradation of organic contaminants

Biochar-based nano-composites with different catalytic and oxidative/reductive nanoparticles dispersed on biochar surface are synthesized to fulfill an affordable composite material capable of removing organic contaminants via simultaneous adsorption and degradation. These nanoparticles have high catalytic degradation and oxidative/reductive degradation ability toward various contaminants. Nanoscale zerovalent iron (nZVI) and graphitic C₃N₄ are the two most commonly used nanoparticles in the synthesis processes. The zero-valent iron and graphitic C₃N₄ biochar composites were applied to removal various organic contaminants from aqueous solutions, including acid orange 7 (Quan et al., 2014), methylene blue (Pi et al., 2015), methyl orange (Han et al., 2015a), pentachlorophenol (Devi and Saroha, 2014, 2015), tar (Kastner et al., 2015), and trichloroethylene (Yan et al., 2015).

The synthesis of biochar-based catalytic and oxidative/reductive composites combine the advantages of biochar with catalytic and oxidative/reductive nanoparticles (Fig. 3d), which could promote each other's performance (Devi and Saroha, 2014, 2015; Kastner et al., 2015). Three potential effects of biochar on catalytic

Table 6
Adsorption characteristics of various other inorganic contaminants with biochar-based nano-composites.

Feedstock	Pyrolytic conditions ^a	Nano-materials	BET surface area (m ² g ⁻¹)	Adsorption temperature (°C)	Adsorption pH	Adsorption dosage (g L ⁻¹)	Contaminants	Q _{max} (mg g ⁻¹)	Isotherm ^b	Kinetic model ^c	References
Corn stover	600 (30 min)	Magnetic iron oxide	3.61, N ₂	25			Fluoride	4.11 (L)	L	PFO	Mohan et al. (2014b)
Sugar beet tailings	600 (1 h)	MgO	70.0, N ₂	22 ± 0.5		2	Nitrate	95 (L)	L		Zhang et al. (2012a)
Cotton Wood	600 (1 h)	MgAl-LDH		22 ± 0.5		2	Phosphate	410 (L)	L, F and L-F	PSO	Zhang et al. (2013b)
Cotton Wood	600 (1 h)	AlOOH particles/flakes		22 ± 0.5		2	Phosphate	17.41 (L)	F	Elovich	Zhang and Gao (2013)
Marine macroalgae (<i>Laminaria japonica</i>)	600 (1 h)	Mg–Al assembled composites, MgO, spinel MgAl ₂ O ₄ , AlOOH, and Al ₂ O ₃	14.1, N ₂	20	6	1	Phosphate	886.2 (L-F)	L-F	PFO	Jung et al. (2015)
Marine macroalgae (<i>Laminaria japonica</i>)	600 (1 h)	Nano-sized MgO particles	56.42, N ₂	20 ± 2		1	Phosphate	620.658 (L-F)	L-F		Jung and Ahn (2016)
Ramie stem	500 (2 h)	CaO	14.97, N ₂	26 ± 0.5		2	Phosphate	105.406 (L)	L	PSO	Liu et al. (2016)
Sugar beet tailings	600 (1 h)	MgO	70.0, N ₂	22 ± 0.5		2	Phosphate	835 (L)	L		Zhang et al. (2012a)
Tomato leaves	600 (1 h)	Mg(OH) ₂ and MgO particles		22 ± 0.5		2	Phosphate	116.6 (L)	L-F and R-P	n _l -th-order	Yao et al. (2013a)

^a pyrolytic temperature (residence time).

^b Isotherm model: Langmuir (L), Freundlich (F), Langmuir–Freundlich (L-F), Redlich–Peterson (R-P), and BET models (BET).

^c Kinetic model: pseudo-first-order (PFO), pseudo-second-order (PSO).

and oxidative/reductive performance are existed: (1) biochar can serve as a substrate for catalytic and oxidative/reductive nanoparticles, which could increase the dispersion of these particles and the contact area with contaminants (Han et al., 2015a); (2) large specific surface area and oxygen-containing functional groups of biochar may promote the reactivity of catalytic and oxidative/reductive nanoparticles (Yan et al., 2015); (3) biochar can accelerate the mass transfer of the contaminant from ambient solution to the surface of the composites via the adsorption process (Pi et al., 2015). In turn, the coating of catalytic and oxidative/reductive nanoparticles on biochar may also have several benefits for biochar sorption: (1) catalytic and oxidative/reductive nanoparticles may regenerate the biochar by degradation of adsorbed contaminants, and therefore enhances organic contaminants adsorption (Pi et al., 2015); (2) the presence of catalytic and oxidative/reductive nanoparticles may enhance the adsorption of contaminants by preventing the accumulation of contaminants in the biochar matrix (Devi and Saroha, 2015).

6. Knowledge gaps in the future development

As a new exciting field of study, a number of research gaps and uncertainties still exist. More relevant investigations are needed to close these knowledge gaps in the future development.

6.1. Factors affecting the properties of biochar-based nano-composites

Many factors are existed in the biochar-based nano-composites production and synthesis processes, which may have significant influences on the properties of resulted materials. Biochar properties can change with production conditions, making the properties of biochar-based nano-composites vary correspondingly. Biomass type and pyrolysis conditions (thermochemical conversion technology, pyrolysis temperature, residue time, etc.) may affect the properties and adsorption ability of biochar-based nano-composites. Zhang et al. (2012a) prepared various MgO-biochar nanocomposites using five feedstocks to remove phosphate from aqueous solutions, and the adsorption ability followed the order of sugar beet tailings > cottonwoods > sugarcane bagasse > peanut shells > pine woods. Chitosan-modified biochars from bamboo, sugarcane bagasse, hickory wood, and peanut hull were applied for various metals adsorption (Zhou et al., 2013). The results showed that modified bamboo biochar was good at Pb and Cd removal, whereas modified sugarcane bagasse biochar is favor for Cu adsorption. As can be seen from these results, feedstocks played an important role in the fabrication process. This can be mainly attributed to the different composition of various feedstocks types, which determine the properties of biochar, such as the contents of lignin, cellulose, hemicellulose, and inorganic salts. So that, in the future studies, suitable feedstocks with appropriate composition are needed to be chosen to produce biochar-based nano-composites with the greatest adsorption efficiency for specific contaminants. Apart from the composition of feedstock, pyrolysis conditions (thermochemical conversion technology, pyrolysis temperature, residue time, etc.) can also have great influence on the adsorption performance of biochar-based materials (Chen et al., 2011; Liu et al., 2014). However, little information is available about the effects of these factors, which are needed in the further studies.

In addition, the parameters of different synthesis methods may greatly affect the synthesis efficiency. Engineered biochars produced via direct pyrolysis of Mg-accumulated tomato tissues were applied for phosphate removal (Yao et al., 2013b). The results showed that biochars with high Mg level had higher adsorption ability for P from the solution. The zero-valent iron (ZVI) magnetic biochar composites were synthesized using paper mill sludge

biochar and applied for pentachlorophenol adsorption, and the effects of the dosage of chemical agent used in the synthesis process were also studied (Devi and Saroha, 2014). Sodium borohydride (NaBH_4) was applied to reduce Fe(II) to Fe(0) and cetyltrimethylammonium bromide (CTMB) was acted as the surfactant during the synthesis process. The results suggested that the adsorption efficiency increased with the increase of the $\text{FeSO}_4/\text{NaBH}_4$ ratio, the CTMB dosage and the ZVI/biochar ratio. It is certain that there are a range of key factors affecting the characteristics of biochar based composites during the synthesis processes. And these factors can have conspicuous influence on the adsorption efficiency of resulted biochar-based materials correspondingly. Further studies we should provide insight into optimum biochar production conditions and synthesis parameters to produce biochar-based adsorbent with the best properties, so as to enhance adsorption ability economically and effectively.

6.2. Other potential synthesis methods and materials

Apart from the synthesis methods existed and proposed during the review process, there are other potential methods which are suitable for the fabrication of biochar-based nano-composites. It is essential to develop novel and environment-friendly technologies for producing biochar-based nano-composites with suitable properties in a cost-effective way in the future. For instance, inorganic flame retardants (such as $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and inorganic silicon-based flame-retardants) and catalysts can also be chosen as the chemical reagents for pretreatment of biomass. Flame retardants and catalysts may accelerate the dehydration reaction and carbonization of biomass at relatively low pyrolytic temperatures, which can increase the residue yield and surface oxygen-containing functional groups of biochar (Zhao et al., 2013; Liu et al., 2014). In addition, after pyrolysis, these inorganic flame retardants pre-treated biomass may turn into nanoparticles-biochar composite, that the nanoparticles grown on biochar surfaces can increase the specific surface area and sites to adsorb contaminants. Recently, the worldwide application of titanium dioxide as an advanced photo-catalyst may also formulate a new growing branch of titanium dioxide/biochar composite for enhancement of adsorption capacity and degradation of organic pollutants (Leary and Westwood, 2011). Furthermore, the immobilization of different kinds of organic ligands onto biochar for the preparation of novel biochar composite adsorbent may achieve the goal of selective removal of various metal ions from wastewater (Awual et al., 2014, 2015, 2016a).

6.3. Stability and eco-toxicity of biochar-based nano-composites

Unintended release of nanoparticles during their manufacturing and application process has led to public concerns about the potential impacts of these nanomaterials on the ecosystem and human health (Wiesner et al., 2006). Despite of the advantages of nanoparticles-biochar composite, such as the increase of biochar yield, specific surface area and nanoparticles, the potential risk of the environmental and biological toxicity of metal oxide nanoparticles (ZnO , TiO_2 , CuO , MgO , MnO_x , etc.) should be considered (Kahru et al., 2008; Aruoja et al., 2009; Jiang et al., 2009). Therefore, further researches should be conducted to improve the stability of biochar-based nano-composites, and evaluate as well as minimize the potential release of the toxic nanoparticles, so as to promote the beneficial applications of nanomaterials and minimize biochar-based nano-composites' unintended harm to the environment. Before practical applications, physicochemical interactions of biochar-based nano-composites with the environmental media and their potential eco-toxicity should be studied clearly.

6.4. Emerging contaminants removal by biochar-based nano-composites

Recently, non-regulated trace organic emerging contaminant (ECs) including halogenated flame retardants, surfactants, pharmaceuticals, illicit drugs and personal care products have caused increasing public concerns (Marti et al., 2014; Petrie et al., 2015). These ECs have been widely detected and ubiquitous in the aquatic environment, which are mainly derived from the discharge of municipal wastewater effluents. The presence of ECs is of concern on account of their potential toxicological impacts on the environment ecosystem and human health (e.g., endocrine disruption) (Petrie et al., 2015). Therefore, it is imperative to tackle the ECs entering wastewater before discharging into the aquatic environment. Further studies about producing biochar-based nano-composites with appropriate properties for ECs removal from wastewater should be conducted.

6.5. Potential application of biochar-based nano-composites

Considering biochar-based nano-composites combine the advantages of biochar matrix and various nano-materials, many potential applications of biochar-based nano-composites are existed. For instance, biochar-based nano-composites have excellent adsorption ability in water pollutants, that it may be used as a new potential in-situ amendments sorbent for contaminated soil or sediment management (Ghosh et al., 2011). In addition, catalytic materials coated biochar may be applied for simultaneous adsorption and in-situ degradation of contaminants in soil or sediment. Furthermore, biochar-based nano-composites can be applied in other wastewater treatment processes, such as their addition into membrane bioreactor (MBR) may have the benefits of relieving membrane fouling, improving wastewater treatment efficiency, and enhancing membrane life cycle (Skouteris et al., 2015).

6.6. Future practical engineering application of biochar-based nano-composites

For the future practical engineering application of biochar-based nano-composites in industrial scale as cost-effective materials, we should get insight into these important aspects regarding their reuses, the large scale production, pollutant resource recycling and the management of spent biochar. Very little information is available about these aspects, which need further investigations.

The laboratory studies are commonly concentrated on the application of biochar-based nano-composites for simulated wastewater treatment, while their application in actual wastewater treatment is still lacked. The actual wastewater usually consists of divers pollutants, therefore the selective removal and resource recycling of these pollutants are of great significance. During the engineering application process, preparation of biochar-based nano-composites with selective adsorption ability for various pollutants could remove these pollutants separately, followed by desorption of pollutants and regeneration of adsorbent. The regenerated adsorbent can be reused in the next adsorption cycle, and the desorbed pollutants can be recycled for resource utilization. However, the selective removal ability of biochar-based nano-composites for target contaminants is rarely reported. The researchers need to address this point in the future studies. In addition, recycling studies of biochar-based nano-composites after adsorption are largely missing in the literature, with only several available researches. Desorption/regeneration properties are needed to be investigated, which help to determine the reusability of biochar-based nano-composites and evaluate the economic feasibility.

7. Conclusions

In the present review, a wide range of synthesis methods for biochar-based nano-composites and their beneficial influence on enhancing the removal capacity of biochar by combining the advantages of biochar and nano-materials have been presented. Impregnation of nano-materials onto raw biochars has become an important practice for expanding the environmental applications of biochar and nanotechnology. Further studies we should provide insight into choosing suitable feedstocks with appropriate composition, and optimizing production conditions and synthesis parameters to produce biochar-based nano-composites with higher removal ability for specific contaminants. Furthermore, knowledge gaps for this exciting field should be studied in the future.

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