Synthesis of Magnetic Materials from Natural Carbon Precursors – a Review

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Summary

Preparation methods, properties and utilization of magnetic materials based on natural carbon precursors are summarized in this short review. Magnetic material is defined as the composite material consist of carbon substance coming from natural precursor such as coal/biomass and magnetic substance. Various processes can be applied to prepare magnetic materials. Pyrolysis of the biomass/coal together with iron ions and coprecipitation of Fe^{2+}/Fe^{3+} with charcoal are mostly used methods for synthesis of magnetic biochar. The pyrolysis is defined as a thermal degradation in the absence of oxygen, which converts a raw material into different reactive intermediate products: solid (char), liquid and gaseous products. Especially, microwave pyrolysis of natural materials with iron ions is one of the best techniques offering homogenous, rapid and energetically efficient heating system to produce magnetic material. After the synthesis, iron particles are incorporated to the pore carbon structure and can form (especially in thermal process) microparticles as well as nanosized particles with defined structure possessing magnetic properties, high pore volume and high specific surface area. Magnetic carbon is used mainly as an excellent sorbent material mainly for organic pollutants and heavy metals. Moreover, solid/liquid magnetic separation as a rapid and effective technique can be applied in removal of used magnetic biochar from aqueous solution after sorption process. After sorption and pre-concentration, the magnetic sorbent can be effectively regenerated e.g. by high temperature (organic pollutants such as azodyes, pesticides) and leaching methods (inorganic contaminates).

Keywords: magnetic materials, biomass, microwave pyrolysis, sorption

Introduction

Natural wastes (derived from coal and biomass) coming from industry after burning process, pyrolysis and extraction are still suitable material for additional smart utilization. For example, pyrolytic carbon char with high content of carbon, high porosity and high surface area is valuable material for environmental, agricultural and chemical applications such as sorbent of organic and inorganic (heavy metals) pollutants in water treatment technologies. Additionally, biochars improve cation-exchange capacity for enhanced soil fertility and thus they are effective host for microorganisms in soil (Warnock et al. 2007). It is also suitable material for reduction of greenhouse gases (Spokas et al. 2009) and carbon storage capacity (Yanai et al. 2007). Modification (chemical, biological, magnetic) of biochars leads to the improvement of chemical and physical properties. On the other side, in many cases the process is time consuming and it is not cost effective. It is well known that the low cost activated carbon or biochar is one of the best sorbent material especially for organic pollutants as well as inorganic contaminants from water. This sorbent is thermally stable, and it can be used over a broad pH range (Zhang et al. 2007). However, after the sorption process, the material must be renewable and it must be easily separable from aqueous solution. In this step, there are several limitations e.g. activated carbon could cause the blockage of filters or the loss of carbon. This phenomenon makes a problem mainly in the industry sector, because the sorbent cannot be removed effectively from the water (Lata et al. 2008). Afterwards, activated carbon is simply discarded as a sludge (Clifford et al. 1983).

Magnetic biochar

Compared to the conventional separation method, magnetic filtration is rapid and effective technique. Magnetic separation has been used not only in mineral processing or environmental technologies but also in analytical chemistry, biochemistry, cell biology etc. Magnetic biochar is a charcoal modified usually with iron oxides. There are several ways to synthesize magnetic char.

Magnetic biochar prepared by pyrolysis

One of the procedures is mixing of Fe (III) and/or Fe (II) ions with natural waste (biomass, coal).

After that, the mixture is pyrolysed at defined temperature to obtain charcoal with magnetic iron oxide particles.

Mubarak et al. (2014) synthesized magnetic biochar by microwave pyrolysis. In contrast to conventional heating, where the material is heated from surface to core with the cost ineffectiveness and time consuming, microwaves works in the whole volume and material is heated very fast with quick thermal reaction (Lovás et al. 2011). Microwaves offer homogenous and energetically efficient heating system. On the other hand, microwaves need suitable material, which absorbs microwave energy. Since the material is heated very fast, the problem with process controlling is occurred. Intact biomass is heated by microwaves very slow. Therefore, in this case, carbon or metal oxide catalyser as the susceptor-material can be used for heating. Thereafter, a high temperature can by reached during short time.

The pyrolysis process comprise of two steps: First step consist of absorption of microwave energy of absorber and subsequent heating of whole material. In step two, carbonization of biomass organic component is occurred, which causes more effective microwave heating. The scheme of microwave pyrolysis system designed and used at Institute of Geotechnics (Slovak Academy of Sciences) is showed in Figure 1.

In the paper of Mubarak et al. (2007), biomass were mixed with different concentration $FeCl_3$ and then pyrolyzed in microwave muffle under nitrogen flow at various temperatures. Results show that microwave heating leads to production of magnetic biochar with high surface area (890 m^2/g) and high porosity. Prepared sorbent is highly effective to remove organic pollutant - methylene blue (99.9%) from water.

Chen et al. (2011) prepared magnetic sorbent by coprecipitation of Fe^{2+}/Fe^{3+} on orange peel powder with subsequent conventional pyrolysis under different temperatures. It results in nanosized magnetite formation with amorphous biochar. In comparison to non-magnetic biochar, magnetic char demonstrates better sorption capacity to remove organic pollutants and phosphate in water.

Magnetic biochar prepared by coprecipitation

A novel magnetic sorbent ($CuFe_2O_4$/active coal - active coal is added to the solution of Cu (II) and Fe (III) ions) for removal of organic dye (acid orange II) were developed using coprecipitation (Zhang et al. 2007). Magnetic component did not significantly affect pore structure and specific surface area and magnetic sorbent is regenerated during the process of pyrolysis after several adsorption - regeneration cycles. Moreover, it was proven that the regeneration temperature is lower (500ºC) in comparison to unmodified activated carbon (around 800ºC) (Clifford et al. 1983).

Magnetic carbon, iron modified zeolites prepared by coprecipitation and two samples of aluminosilicates were tested as sorbent of arsenate and arsenite (Payne and Abdel-Fattrah, 2005). Iron modified activated carbon is better sorbent of As (V) and As (III) in comparison to naturally occurred iron modified zeolites and aluminosilicates. Of course, ionic strength, temperature and pH strongly affected sorption capacity. There is also a responsible mechanism for removal of As (V) and As (III) for iron treated absorbents:

Simplified mechanism for arsenate (1) and arsenite (2) (Payne and Abdel-Fattrah, 2005):

(1) Carbon-FeOH + H_3AsO_4 → Carbon -Fe-H_2AsO_4 + H_2O

(2) Carbon-FeOH + H_3AsO_3 → Carbon -Fe-H_2AsO3 + H_2O

Kahani at al., (2007) prepared magnetic carbon (Fe_3O_4 + activated carbon) by homogenous and heterogeneous method. Homogenous method consists of precipitation of $FeCl_3$ and $FeCl_2$ with NH_4OH in aqueous solution to obtain Fe_3O_4. After washing and drying, doping of activated carbon with magnetite was performed. It means, that magnetite and commercial activated carbon was stirred in water. After 5 hours, the doping is complete. For heterogeneous method, goethite, $FeCl_2 .4H_2O$, activated carbon and NaOH was used. The mixture was heated to the boiling point, and refluxed (1-2 hours). A black precipitate was formed on activated carbon surface. Magnetic carbon active applied as magnetic carriers that could be used as an extraction agent of precious metals such as gold from cyanide solutions (Kahani at al., 2007). Based on results, the extraction of gold up to 99% can be achieved. Thus, conversion of activated carbon into a magnetically-active material would provide an excellent magnetic filtration aid.

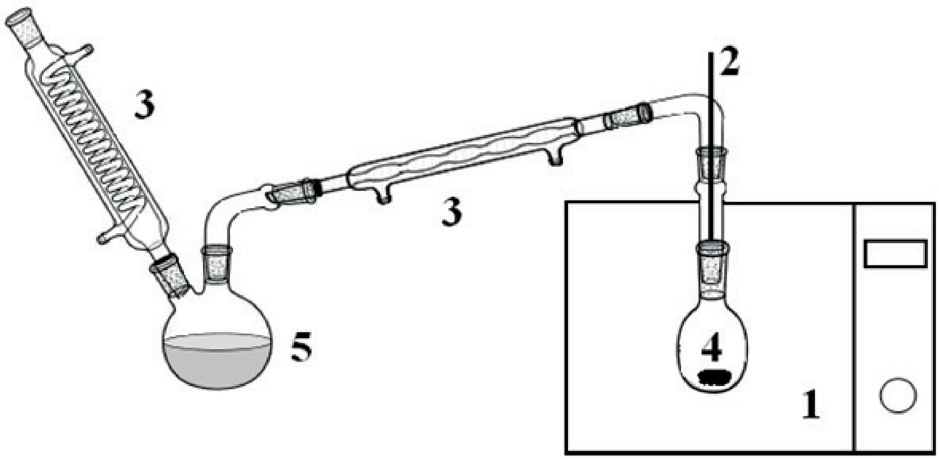

Fig. 1 Scheme of microwave pyrolysis system (1 - microwave oven, 2 – gas flow, 3 – reflux, 4 – biomass briquette, 5 - collector).
Rys. 1 Schemat systemu mikrofalowego pirolizy (1 - kuchenka mikrofalowa, 2 - przepływ gazu, 3 - powrót, 4 - brykiet z biomasy, 5 - kolektor)

A novel magnetic polysaccharide - calcium alginate was used as a sorbent of organic arsenate (Lim at al. 2009). The interaction characteristics between the organic arsenate and magnetic sorbent were studied by applying FT-IR and XPS analyses. It is shown that the functional groups of sorbent (-COOH and Fe-O) are involved in the adsorption process.

Magnetic carbon nanocomposites

At the present, carbon as a nanocomposite is one of the most studied materials. There are many morphologies of carbon (for example: activated carbon, carbon nanofibers, graphene, fullerene, carbon nanotubes, graphite) owing unique chemical, mechanical and physical properties. Thus, magnetic carbon as a nanocomposite can be defined as material composed of an inorganic magnetic component and organic carbon as the hosting matrix (Zhu et al. 2013). Knowledge about chemical, physical and other properties of magnetic carbon have been studied in limited extent.

Pyrolytic process of natural wastes can lead to formation of magnetic and non-magnetic carbon nanocomposites. Final pyrolytic biochar product is usually a mixture of nanosized particles together with microparticles. Moreover, iron, iron oxides and iron minerals (e.g. in coal milling and pyrolysis) can promote creation of nanoparticles with defined nanostructure (Zubrik and Hredzák, 2008). Zhu et al. (2014) synthesized by microwave heating in nitrogen atmosphere magnetic carbon nanocomposite fabrics with highly porous structure for removal of Cr (VI) from water. Material prepared by microwave assisted heating system adsorbed quickly (minutes) in comparison to conventionally available adsorbents e.g. biomass, active carbon (hours).

A magnetic multi-wall carbon nanotube synthesized by the in situ chemical coprecipitation of Fe (II) and Fe (III) in alkaline solution was used as an adsorbent for removal of cationic dyes (methylene blue, neutral red and brilliant cresyl blue) from aqueous solutions (Gong et al. 2009). The prepared magnetic multi-wall carbon nanotube adsorbent indicated the main advantage of separation convenience compared to other adsorbents.

Carbon-encapsulated iron nanoparticles synthesized from wood char using thermal treatment method with iron nanoparticles were used as a catalyst (Mun et al. 2013). After thermal synthesis in argon, a magnetic separation was used to obtain magnetic and non-adhered fraction. Both fractions were studied in detail. It was found that Fe-carbonized materials had a significant lower quantity in amorphous carbon compared to the non-adhered materials and carbon graphitic layers encapsulated on iron nanoparticles.

Conclusion

Cost effective magnetic biochar can replace active carbon due to its high surface area, high microporosity and high absorption capacity for removing of heavy metals, organic pollutants and organic toxins from polluted soils and water. Afterwards, magnetic sorbent can be effectively separated by magnetic separating technique.

Acknowledgements

This work has been supported by Science and Scientific Grant Agency VEGA (project No 2/0114/13 and project No 2/0175/11), by the Slovak Research and Development Agency under the contract SK-RO-0026-12 and FP7-People-IAPP-612250-WaSClean.

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Synteza materiałów magnetycznych z naturalnych prekursorów węgla - przegląd

W tym krótkim przeglądzie streszczono metody przygotowywania, właściwości i wykorzystanie materiałów magnetycznych opartych na maturalnych prekursorach węgla. Materiały magnetyczne są zdefiniowane jako materiał kompozytowy składający się z substancji węglowej pochodzących z naturalnych prekursorów takich jak węgiel/biomasa i substancji magnetycznej. Różne procesy mogą być zastosowane do przygotowania materiałów magnetycznych. Piroliza biomasy/węgla wraz z jonami żelaza i współstrąceniem Fe^{2+}/Fe^{3+} z węglem drzewnym są najczęściej używanymi metodami syntezy magnetycznego biowęgla. Piroliza jest zdefiniowana jako rozkład termalny bez udziału tlenu, który przetwarza surowiec w różne reaktywne produkty pośrednie: stałe (karbonizat), płynne i gazowe produkty. Szczególnie piroliza mikrofalowa materiałów naturalnych z jonami żelaza jest jedną z najlepszych technik oferującą homogeniczny, szybki i energetycznie efektywny system ogrzewania do produkcji materiałów magnetycznych. Po syntezie, jony żelaza są włączane do struktury porowatej węgla i mogą tworzyć (szczególnie w procesach termicznych) mikrocząsteczki jak i nanocząsteczki o zdefiniowanej strukturze posiadające właściwości magnetyczne, dużą objętość porów i dużą powierzchnię właściwą. Węgiel magnetyczny jest używane głównie jako doskonały sorbent głównie dla organicznych zanieczyszczeń i metali ciężkich. Ponadto, magnetyczna separacja substancji stałych od ciekłych może być zastosowana jako szybka i efektywna technika usuwania zużytego biowęgla magnetycznego z roztworów wodnych po procesie sorpcji. Po sorpcji i wstępnej koncentracji, sorbent magnetyczny może być efektywnie zregenerowany np. za pomocą wysokiej temperatury (zanieczyszczenia organiczne takie jak barwniki azowe, pestycydy) i metodami ługowania (zanieczyszczenia nieorganiczne).

Słowa kluczowe: materiały magnetyczne, biomasa, piroliza mikrofalowa, sorpcja