Pollution, 4(4): 707-723, Autumn 2018
DOI: 10.22059/poll.2018.255031.430
Print ISSN: 2383-451X Online ISSN: 2383-4501
Web Page: https://jpoll.ut.ac.ir, Email: jpoll@ut.ac.ir

Wastewater Remediation via Modified Activated Carbon: A Review

Hasan, M. B.* **and Hammood, Z. A.**

Environmental Engineering Department, Faculty of Engineering, Mustansiriyah University Baghdad 10047, Iraq

Received: 26.03.2018 Accepted: 19.06.2018

ABSTRACT: The magnetic derivative of Activated Carbon (AC) is a promising new technique to isolate and recover consumed adsorbent. In this light, the current research seeks to summarise the magnetisation rout of AC and its applications, while identifying both benefits and drawbacks of different synthetic routs. Several methods, such as chemical co-precipitation, hydrothermal, impregnation, ball milling, and one-step synthetic routs, have been studied by previous researchers. Among these methods, chemical co-precipitation is simple, extensively adapted for Magnetic Activated Carbon (MAC) syntheses. In general, the magnetic derivatives of AC show a reduction in the surface area and pore volume, due to introduction of magnetic nanoparticles. Magnetisation enhances contaminants' adsorption, despite the reduction in surface area. It allows elimination of contaminants, barely treated by pristine AC due to the introduction of magnetic materials. Developments in synthetic procedures could overcome the destructive influence of acidity on MAC, providing a shield against it. MAC has been used in several applications, including organic and inorganic contaminant removal. Medically, MAC is used to lead drugs to a specific organ and, thus, reduce damages to non-affected organs. It can be said that the preparation method did not obstruct MAC application for specific contaminant adsorption. MAC regeneration has been reported for several sorption cycles, making the process sustainable and cost-effective. Future work could further develop the synthetic route and enhance the characteristics of the produced composite. It also may consider the influence of iron on the treated water, depending on its proposed usage.

Keywords: Adsorption, Sorbent, Synthesised, magnetisation, Magnetic activated carbon.

INTRODUCTION

Recently, remediation of industrial effluents and polluted sites have emerged as one of the greatest environmental challenges (Oliveira et al., 2002). Growing concern about protection of environmental quality and human lives has led to innovation and development of various water and wastewater remediation methods (Chowdhury et al., 2004), with many techniques being used for wastewater treatment via advanced oxidation (Hasan, 2017), chemical precipitation, ion exchange and filtration (Dickhout et al., 2017), coagulation, and filtration (Karbassi and Pazoki, 2015). Nevertheless, they are quite expensive and require secondary treatment. Adsorption as a remediation method is more favourable than conventional methods for removal of pollutants, otherwise impossible to be removed via conventional techniques (Tran et al., 2017).

---

* Corresponding Author Email: manar@uomustansiriyah.edu.iq

Adsorption has evolved as the main defence line for remediation of organic and inorganic contaminants, with AC being the most widely used adsorbent (Lin & Juang, 2009). Due to its large surface area, surface chemistry, and porous structure, AC has shown excellent efficiency for contaminants' removal in the liquid phase (Tseng et al., 2003). To become a sustainable process and to reduce the preparation costs of AC, waste materials like walnut shells (Hatami and Faghihian, 2015), pine cones (Mokhtari & Faghihian, 2015), palms (Younas et al., 2016), almond wastes (Thitame & Shukla, 2016), pomegranate peels (Senthilkumar et al., 2017), orange peels (Hai, 2017), and leaves (Zolgharnein et al., 2016) have been used in order to prepare AC.

In addition, diverse chemical treatments like acid and base can be considered capable of increasing pore volume, adsorption selectivity, and functional groups (Yin et al., 2007). Agricultural waste-based AC have been treated by HCl, HNO_3, and H_3PO_4 (Gomez-Tamayo et al., 2008; Abd El-Latif et al., 2010a; Kuppireddy et al., 2014; Tezcan Un et al., 2015), as well as $ZnCl_2$ (Tezcan Un et al., 2015) and NaOH (Abd El-Latif et al., 2010b). Granular and powdered AC can be used for contaminants' adsorption with the latter having greater adsorption kinetics than the former. However, recovery of powdered AC from the liquid phase is a challenging process (Ahn et al., 2005). What is more, preparation and reactivation costs of AC are relatively high (Minceva et al., 2007; Tseng et al., 2003). Thus, an increasing amount of research is being directed to the recovery of powdered AC from aqueous environment.

A promising new technology is the magnetisation of AC, which allows easy recovery from an aqueous solution (Oliveira et al., 2004; Mehta et al., 2015; Theydan and Ahmed, 2012). It has been first developed to overcome difficulties associated with the filtration of nonmagnetic adsorbents. The recovery of MAC from the aqueous environment can be simply applied using magnetic rods, external magnetic fields, and electromagnets (Oliveira et al., 2002) with the magnetization process involving the incorporation of nano- or micro-magnetic particles into the porous structure of AC on its surface. These magnetic particles include magnetite, maghemite, metallic iron, and different forms of ferrites. The magnetization process includes coating adsorbent surface with $CoFe_2O_4$ particles (Reddy and Lee, 2014), Fe_3O_4 (Baig et al., 2014), and γ-Fe_2O_3 (Wang et al., 2015), and can be chemically achieved to introduce magnetic nano or micro particles to the surface of the adsorbents, so the adsorbents can be easily recovered from contaminated water, carrying away undesired contaminants (Arcibar-Orozco et al., 2012; Cho et al., 2017b; Cho et al., 2017c). Magnetic biosorbents include magnetic saccharomyces cerevisiae (Patzak et al., 1997), magnetic sugarcane bagasse (Yamamura et al., 2011), magnetically-modified spent coffee grounds (Safarik et al., 2012), and slow pyrolysis magnetic biochar (Zhang et al., 2013).

Mubarak et al. (2013) conducted a comparative study to assess magnetic biochar and carbon nanotubes for Zn^{2+} elimination. The adsorption capacities were 1.18 and 1.05 mg/g for magnetic biochar and carbon nanotubes, respectively. Mohan et al. (2014) synthesized a magnetic oak bark (MOBBC) as well as a magnetic oak wood (MOWBC) for Pb^{2+} and Cd^{2+} elimination. The magnetization process was conducted in an aqueous solution of ferric and ferrous salts, followed by addition of NaOH to precipitate iron oxide. They found that MOBBC and MOWBC were much better than the nonmagnetic biochar in removal of Pb^{2+} and Cd^{2+} from aqueous solutions. Reguyal et al. (2016) synthesized a magnetic composite, known as MPSB, using pine sawdust biochar for sulfamethoxazole (SMX) elimination. The spent MPSB could be easily reactivated using non-polar solvents. Reguyal et al. (2016) observed a great saturation magnetisation of 47.8 A.m^2/kg. Due to their separation characteristics along with tiny size, magnetic particles have different interesting applications, e.g. in medicine, environment, biosciences, etc. (Safarik & Safarikova, 2009). Several procedures for modification of AC into its magnetic form have been reported in scientific literature. The core objective of this study has been to review the most widely used techniques for the magnetization of AC and identify the advantages and disadvantages of synthetic routs, while identifying any environmental and medical applications.

Preparation Techniques of MAC

MAC can be synthesised, using a variety of methods, the most widely-used of which include chemical co-precipitation, hydrothermal, impregnation, one-step, and ball milling.

Chemical co-precipitation

This technique has been extensively used by previous researchers, and is usually conducted in an alkaline solution via the precipitation of ferric and ferrous salts at the presence of AC. This is usually followed by heating the prepared solution to precipitate iron oxides into the pores of AC. Maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) are usually formed by this technique. The latter is formed as shown in equation (1). At a pH rate, ranging between 8 and 14, it is quite expected of Fe_3O_4 to be created in a non-oxidizing setting, wherein the ratio of Fe^{3+} to Fe^{2+} is equal to 2:1 (Jolivet et al., 2004). Due to the sensitivity and instability of magnetite at the presence of O_2, it is likely to get converted into maghemite (γ-Fe_2O_3). Equation (2) shows that the creation of γ-Fe_2O_3 may be related to ion or electron transfer, affected by pH level. Several factors can be modified to control MAC characteristics. Jolivet et al. (2004) studied the impact of temperature, ionic strength, salt nature (i.e., nitrate, chlorides, and sulfates), pH, and iron salts ratio. They found that these factors had a great influence on magnetic particles in terms of shape, composition, and size.

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \text{ -------- } Fe_3O_4 + 4H_2O \qquad (1)$$

$$Fe_3O_4 + 2H^{+} \text{ ---------------} \gamma\text{-}Fe_2O_3 + Fe^{٢+} + H_2O \qquad (2)$$

Size control of nanoparticles during the formation of Fe_3O_4 is affected by the addition of polymer surface complexing agents such as polyvinyl alcohol, dextran, carboxydextran, or chelating organic anions, such as carboxylate ions including citric, gluconic, or oleic acid (Laurent et al., 2008). Babes et al. (1999) studied the impact of Fe^{2+}/Fe^{3+} ratio, temperature, and oxygen on the size and magnetic characteristics of the composite in the chemical co-precipitation process, finding that by increasing Fe^{2+}/Fe^{3+} ratio, one could maximize the average particle size, though this would reduce the produced quantity. The average particle size is also highly correlated to ionic strength and the acidity of the environment, both of which influence the electrostatic surface charge of the particles; consequently, high ionic strength and pH level reduce particle size (Tartaj et al., 2006). Great quantities of the iron particles can be produced via this method, but only limited control over particle size dispersal is obtained due to its correlation to kinetic factors (Laurent et al., 2008). According to Sun & Zeng (2002), higher reaction temperature can reduce the creation yield of magnetic particles.

Yang et al. (2008) produced a magnetic-based Rice Husk RHC. Hydrophilic properties were acquired after modification with HNO_3. It was then suspended in a solution of $Fe(NO_3)_3$, followed by heating for 3 hr at 750 °C. Consequently, Fe_3O_4 precipitated into the pores of AC. The authors found that surface hydrophilic properties enhanced the formation of

Fe_3O_4. Yang et al. (2008) attained a mean pore size of 3.1 nm, saturation magnetisation of 2.78 emu/g, and surface area of 770 m^2/g.

Zhang et al. (2007) studied the influence of different ratios of $CuFe_2O_4$ to AC in the preparation of a magnetic composite. The AC was suspended in a solution of $FeCl_3$ and $CuCl_2$, followed by dropwise addition of NaOH to precipitate iron oxide in the pores of AC. The thermal treatment was then conducted for 2 hr at about 98-100 °C. The magnetisation saturation sharply declined for smaller $CuFe_2O_4$ content, showing smaller reduction in the surface area and pore volume, though it was less than the anticipated value and would not block AC pores. Nakahira et al. (2007) studied the influence of air and H_2 treatment on the produced composite. A suspension of charcoal in a solution of ferric and ferrous sulfate was prepared, followed by the addition of NaOH to raise the pH value. The magnetic adsorbent was thermally treated for 2 hr at 473 K in air or H_2 atmosphere. They observed a similar microstructure for both composites.

Castro et al. (2009) and Oliveira et al. (2002) prepared a suspension of AC in a solution of $FeCl_3$ and $FeSO_4$ to manufacture a sorbent of AC/iron oxide, followed by dropwise addition of NaOH to the suspension to precipitate iron oxide, and drying for 3 hours at 100°C. They observed the presence of a cubic iron oxide phase. The core magnetic phase formed in their studies was maghemite with lesser quantities of magnetite, goethite, and hematite. Castro et al. (2009) found that increasing the ratio of AC to iron oxide increased the crystallinity of the sorbent. The magnetic composite was highly sensitive to low pH levels, below 3, and was likely to result in complete dissolution of the product (Oliveria et al., 2002). The magnetisation of the sorbent can be developed by reducing Fe_2O_3 to Fe_3O_4 oxides (Oliveria et al., 2002).

Further development in synthesis procedures involve the stabilisation of magnetic particles. Oh et al. (2015) stabilised magnetic particles, produced via a chemical co-precipitation method, by a calcination step. They achieved a magnetic composite of $CuFe_2O_4$/AC (MACC) through a chemical co-precipitation calcination process. The desired quantities of $Cu(NO_3)_2$ and $Fe(NO_3)_3$ were dissolved in deionized water with different ratios of AC added to the previous mixture ($CuFe_2O_4$) and mixed for 1 hour. Afterwards, the pH level was adjusted between 10 and 11, followed by getting heated for 4 hours at 95-100 °C. Finally, the product was calcined in an oven at 300 °C for 1 hour to stabilise the impregnated $CuFe_2O_4$.

The researchers found that the surface area and total pore volume were negatively affected by reducing the weight ratio of $CuFe_2O_4$ to AC due to the deposition of $CuFe_2O_4$ on the large pore size. They also found that an additional calcination stage increases the magnetism value. Zainol et al. (2017) employed co-precipitation method to prepare a magnetic composite of oil palm frond-magnetic particles (OPF-MP) as well as oil palm frond activated carbon-magnetic particles (OPFAC-MP) for Pb^{2+}, Zn^{2+}, and Cu^{2+}. The OPFAC-MP was characterized by amorphous structure, great surface area of 700 m^2/g, and magnetic properties of 2.76 emu/g. The adsorption capacity of OPFAC-MP was about 15 mg/g, greater than that of OPF-MP. The adsorption capacity of the pristine material was compared to that of the magnetic composite to evaluate the impact of magnetic particles. Zainol et al. (2017) highlighted the role of magnetic particles in enhancing metal ion's elimination, compared to their parent materials. Saroyan et al. (2017) synthesised MAC through iron precipitation on AC, using NaOH as a precipitation agent, followed by heating it to 60°C under N_2 atmosphere. They observed a reduction in the surface area of the composite. Despite the simplicity of this method, one can notice a reduction in the surface area or pore blocking, which affects the adsorption process (Oliveira et al., 2002).

Hydrothermal Synthesis

Fe_3O_4 nanoparticles can be fabricated via a hydrothermal reaction which usually occurs under both high pressure and temperature in an autoclave or a reactor. Hydrothermal reaction can produce ferrites via either hydrolysis or neutralization of metals hydroxide (Laurent et al., 2008). The final product is highly affected by reaction conditions, such as time, the solvent, and temperature (Laurent et al., 2008). Researchers noticed that longer reaction times increased the magnetic particle size. Furthermore, the precipitation of larger particles was positively related to water content. with magnetisation properties of MAC being strongly related to the shape and size control of the nanoparticles. It was proposed that the formation of well-crystallised Fe_3O_4 particles depended on hydrothermal conditions, capable of intensifying the saturation magnetisation of iron particles. The hydrothermal technique is highly effective for creating magnetic crystals.

Wu et al. (2006) synthesised bamboo charcoal/$Ni0.5Zn0.5Fe_2O_4$ and $Ni0.5Zn0.5Fe_2O_4$ composites. A suspension of bamboo charcoal was prepared in a solution of $Zn(NO_3)_2$ and $Ni(NO_3)_2$, followed by getting heated for 2 hours at 180 °C. They observed a spherical polydispersed particle for $Ni0.5Zn0.5Fe_2O_4$ composite with a diameter of 8 to 15 nm. Similar polydispersion was observed for bamboo charcoal/$Ni0.5Zn0.5Fe_2O_4$. Xuan et al. (2007) mixed glucose, $FeCl_3$, and urea in 40 ml of water for 10 minutes. The mixture was then autoclaved at 180 °C for 14 hours to produce a composite carbon-encapsulated Fe_3O_4 core/shell. Wang et al. (2011a) synthesised a magnetic sorbent by hydrothermal rout with H_2O_2. In their study, ferrocene acted as the precursor. Zhang & Kong (2011) prepared Fe_3O_4/C nanospheres coated with AC via a hydrothermal rout. In this method, sodium acetate anhydrous was added to a solution of ethylene glycol and $FeCl_3$ and reacted vigorously, creating a transparent solution. The blend was autoclaved at 200 °C for 8 to 16 hours. This technique was also modified by incorporating ethylene glycol into the system (Zheng et al., 2012).

Wu et al. (2014) employed a hydrothermal process to synthesise magnetic nanoparticles of iron (NPs). In their study, the precursor was produced directly via precipitation, and the crystallisation of iron was accomplished during glucose dehydration. Glucose was added to a solution of $FeCl_2$ and $FeCl_3$ with a mole ratio of 1 to 1.5 at pH = 12. The mixture was stirred for half an hour and sonicated for 5 minutes followed by 6 hours of heat treatment at 160 °C. The produced sorbent was used to adsorb methylene blue (MB). Glucose showed a significant influence on controlling particle size and the morphology of the composite. Zhu et al. (2014) fabricated magnetic porous composite (MPC) from the hydrochar material. Hydrochar was occupied in a solution of $FeCl_3$. After 12 hours, it got separated and dried for 2 hours at 353 K. This was followed by perolyzation for 1 hour at 973 °C under N_2 atmosphere. The produced material was washed and sieved in order to attain a particle size less than 0.15 mm. Qu et al. (2015) optimised the hydrothermal reaction, using sodium borate as a catalyst, and achieved a higher composite porosity. Thus, this method was robust, showing some development in size control and morphology of the produced nanoparticles to form the required structure.

Impregnation

This technique is based on thermal treatment of AC, impregnated with nickel or iron salts. Numerous factors affect composite properties, including temperature, magnetic modifiers, and salts. Thermal treatment is crucial for particle size control, achieving great levels of monodispersity of magnetic particles (Laurent et al., 2008). Gorria et al. (2006) conducted a versatile technique to synthesise magnetic carbon. Due to its low coercivity (0.1 kOe), the composite can be separated easily within an external magnetic field. In this study, nanoparticles of nickel (around 8-15nm) were used to introduce the magnetic properties of the composite. The magnetic properties were introduced to the pores of AC via thermal treatment at 600 °C for 3 hr in N_2 atmosphere. This composite was categorised by large surface area and protection against acidity due to the introduction of Ni magnetic particles.

Paul et al. (2004) revealed that using polyethylene glycol (PEG) in iron oxide production could raise its dispersion and biocompatibility. Thus, advanced production of magnetic composite involves the use of polyols, contributing to iron oxide stabilisation. High temperature treatment causes better degradation of polyols (Laurent et al., 2008). Polyols can be included in the fabrication line via in situ or post-synthesis coating (Laurent et al., 2008). Non-aggregate magnetic composite can be synthesised through coating iron oxide with PEG, dextran, chitosan, carboxydextran, etc. (Laurent et al., 2008).

Ao et al. (2008) synthesised magnetic adsorbent. The pores of AC were filled with iron nitrate in a solution of ethanol, later to be impregnated with PEG so that Fe(III) could be reduced to Fe(II), crucial for the creation of iron oxide ferrites. Later it received 2 hours of heat treatment at 350 or 450 °C, under N_2 atmosphere. They found a sharp reduction in the surface area and pore volume of the AC as a result of magnetic particles' generation. This reduction was positively correlated with the quantity of iron oxide. Okamoto et al. (2011) impregnated coconut shell-based AC with an aqueous solution of ferric nitrate in a vacuum, followed by 1 hour of treatment at 800 °C in an N_2 atmosphere. Afterwards, a second thermal treatment was conducted for 1.5 hours at 850 °C in CO_2 atmosphere. They found that increasing the treatment time of CO_2 treatment maximised the composite magnetisation to reach 17.6 emu/g. In addition, magnetic particles were created uniformly in AC pores.

Saroyan et al. (2017) synthesised MAC by adding Fe_3O_4 into a sonicated dispersion of AC in distilled water. In this study, they found that the impregnation method resulted in a superior-magnetic composite, in comparison to a magnetic composite, prepared by a co-precipitation method. They acquired a saturation magnetisation of 18 emu/g, and the magnetic modification reduced the removal ability. Thus, researchers observed control over magnetic particle dispersity alongside a reduction in surface area via this technique.

One-step Synthetic

Yang et al. (2010) studied the influence of diverse quantities of Fe_3O_4 in the production of a magnetic composite from Datong bituminous coal. They noticed that the creation of mesopores in the composite was highly affected by the presence of Fe_3O_4 in raw materials. They found greater magnetism and higher magneto conductivity when using a suitable quantity of Fe_3O_4 in the raw material. Specifically, 10% of Fe_3O_4 in the raw material was appropriate to obtain 76% of mesopore volumes. Zhang et al. (2011) synthesised a magnetic composite, using coal-based AC at presence of $Ni(NO_3)_2$. $Ni(NO_3)_2$ additive plays a vital rule in the development of meso and macro pores of AC due to the acceleration of AC combustion. The surface area, pore volume, coercivity, and saturation magnetisation were 1074 m^2/g, 0.5792 cm^3/g, 43.26 Oe, and 1.6749 emu/g, respectively. This low coercivity allowed easy magnetic separation of the composite. Zhang et al. (2015) studied the influence of activation temperature and time on the composite. They found that the activation temperature had the greatest influence on Fe_3C formation. Pore development within the composite was positively related to the activation temperature and time.

Guo et al. (2017) synthesised magnetic nanoparticles, modified with L-arginine (MNPs-L), by adding L-arginine to a mixture of $FeSO_4$ and $Na_2S_2O_3$, followed by heating at 413 °C. Magnetisation saturation was 26.98 emu/g due to L-arginine modification; however, one could achieve magnetic separation; in other words, different modifiers can significantly affect the characteristics of the produced magnetic composite. Wang (2017) investigated the influence of different activation temperatures on the synthesis of MAC, using AC-based pomelo peels. AC was impregnated with HCL for 12 hours and activated afterwards at different temperatures for 1 hour. The composites were denoted based on the activation temperature as MAC-573, MAC-773, and MAC-973.

Wang (2017) observed that highest surface area (760 m^2/g) and lowest pore size (5.4 nm) were obtained at the highest activation temperature of 973 K, proving that this technique makes it possible to produce MAC with greater magnetism and higher magneto conductivity.

Ball Mill

In contrast to other methods, milling exploits mechanical energy to stimulate chemical reactions and can be regarded as an environmentally-friendly procedure (Fernández-Bertran, 1999). This method can efficiently produce ultrafine magnetic powders (Lemine et al., 2014), involving mixing powders of iron and AC, followed by a high-temperature treatment in a ball mill. Wang et al. (2011b) manufactured submicron-sized (0.72 μm) AC by ball milling, presenting a higher removal of bisphenol in comparison with conventional AC. Ramanujan et al. (2007) investigated the impact of AC concentration and milling time on the produced magnetic adsorbent by a ball-milling technique. They found that the magnetic properties were highly affected by milling time and the mixing ratio of AC and iron. The milling process reduced the mean particle size, narrowing down particle distribution. The greater carbon ratio demonstrated higher adsorption characteristics and the magnetic features were almost constant during milling. They concluded that the composite with the higher AC ratio was proper for Magnetically Targeted Carrier (MTC) applications due to its better properties.

Shan et al. (2016) obtained a magnetic biochar and AC including biochar/Fe, biochar/Fe_3O_4, biochar/Fe_2O_3, AC/Fe, AC/Fe_2O_3, and AC/Fe_3O_4 by ball milling in a planetary ball (diameter = 5.60 mm). The biochar and iron were first mixed and added to vials. The ball mill apparatus was then operated for 6 hours at 550 rpm with the optimum milling time ranging between 1 and 7 hours for composite preparation. The produced sorbents turned out to be great at eliminating carbamazepine (CBZ), effortlessly separated by applying an external magnetic field. They noticed dramatic increments in the surface area and pore volume of the biochar/Fe_3O_4 in comparison to the control, which may be related to the milling of Fe_3O_4 into the biochar and the creation of new pores.

A remarkable reduction in particle size was observed, unlike AC/Fe_3O_4, wherein a great reduction in the pore volume and surface area was noticed due to pore blockage of AC by Fe_3O_4, reducing the adsorption ability.

In summary, chemical co-precipitation, hydrothermal, impregnation, one-step, and ball-milling methods could be used to synthesise MAC, the synthetic rout of which depends on several factors that can significantly affect the properties of the synthesised MAC. These synthetic procedures could efficiently produce MAC that can be easily separated from an aqueous medium; however, MAC production is compliant with a reduction in the adsorption capacity of the composite due to a reduction in surface area and pore volume, occupied by magnetic nanoparticles. So far, researchers have not provided a clear estimation of the synthesised quantities. The production yield has not been large enough to be consumed commercially or employed in a large-scale application. Limited research has been conducted to compare different synthetic methods, making it quite inappropriate to clearly identify the best preparation method.

However, good magnetic composite was achieved with large surface area and high adsorption capacity. Thanks to its simplicity, the chemical co-precipitation method is the most widely-used approach, while hydrothermal and one-step synthetic procedures allow good control over magnetic particle size, and one-step synthetic methods maintain a great surface area and pore volume for magnetic derivatives of AC, as well as good magnetic properties. Mohan et al. (2014) highlighted the lack of cost studies in the literature, also highlighting the difficulties of comparing different adsorption aptitudes due to the inconsistency of data in the scientific literature.

The Environmental Application of MAC

AC has been widely used for contaminant elimination. Recently, the magnetic derivative of AC has been considered a promising remediation technique. The magnetisation of the adsorbent allows easy separation by an external magnetic field. In comparison with other treatment techniques like flocculation, it produces no contaminants and can remediate a large quantity of wastewater within a short period of time. Magnetic adsorbents have been employed for dye and heavy metal removal as well as biomedical organic and inorganic contaminant remediation.

Thangamani et al. (2017) synthesized a magnetic composite of Goat Dung Activated Carbon-Cobalt Ferrite Magnetic Composite (GDAC-CFMC) for Reactive Red 152 (RR152) and Direct Brown 2 (DB2) elimination from aqueous solutions. They found that anionic dye can be effectively removed, using GDAC-CFMC as an adsorbent. Table 1 gives a brief summary of the literature on organic contaminant removal, while Table 2 presents heavy metal removal of magnetically-characterised sorbents. The use of MAC is considered a sustainable remediation technique due to the reusability of the spent adsorbent. Moreover, regeneration or reactivation can be conducted to restore the adsorbed material and reactivate the spent adsorbent. The reactivated MAC can be used several times, making the process eco-friendly and economic. Magnetisation of AC reduces both the remediation time and the cost of wastewater remediation.

The magnetisation process allows the contaminants, barely treated by pristine AC, get eliminated, which is due to the introduction of magnetic materials, such as germanium extraction combined with arsenic contamination. Xiong et al. (2015) suggested that the conversion of As^{3+} to As^{5+}, followed by adsorption process could tackle this issue. In this study, AC was carbonised and activated with KOH, to be doped with manganese dioxide and iron hydroxide. A great adsorption capacity was achieved by the magnetic derivative of AC, which was about 75.82 mg/g. Arsenic removal was proposed due to the chelation of the contaminant with the adsorbent surface or electrostatic interaction between hydroxyl/carboxylic groups on As^{5+} and AC. It was also found that the existence of germanium had no influence on the adsorption process of As. Thus, arsenic removal, by means of magnetically-modified AC, is a promising technique.

Table 1. Summary of organic matter removal by means of MAC

Composite	Contaminants	Remediation efficiency	References
Magnetic composite of $CuFe_2O_4$/AC	Acid orange II	Adsorption aptitude declined from 199 to109 mg/g after five regeneration cycles.	Zhang et al. (2007)
Fe_3O_4/AC-based rice husk	MB	Removal capability of 321 mg/g of the contaminant was achieved	Yang et al. (2008)
Magnetic composite of alginate beads and AC denoted as (AC-MAB)	Methyl orange and MB	About 50% of MB and methyl orange were adsorbed after 10 min and 17 min, respectively. The pH level had a moderate influence on dye adsorption.	Rocher et al. (2008)
AC/$CoFe_2O_4$	Malachite green dye	An adsorption capacity of about 89.29 mg/g was obtained. Three regeneration cycles by alcoholic solution were conducted. Desorption capacity reduced with each cycle and the composite retained high magnetic sensitivity	Ai et al. (2010)
Developed magnetic composite of Fe_2MnO_4/AC-H	Methyl orange	In 2 hours, complete degradation and 59% of total organic carbon elimination of contaminant was accomplished.	Nguyen et al. (2011)
Synthesised AC/Fe_3O_4	Methyl orange	The highest adsorption capacity was 242 mg/g. After five regeneration cycles with H_2O_2 the composite retained good adsorption ability	Do et al. (2011)
Synthesised non-magnetic and magnetic sorbent of AC-based almond shells	2,4,6-trinitrophenol (TNP)	The adsorption capability highly depended on pH values. Methanol and hot water successfully desorbed 97% of TNP	Mohan et al. (2011)
Synthesised magnetic sorbent	4-octylphenol and 4-n-nonylphenol	Adsorption capacity was about 95%	Borghi & Fabbri (2014)
MAC	Dye	Maximum adsorption ability was 445.294 mg/g. Greater adsorption occurred at pH = 10 Thermal regeneration at 200 °C effectively reactivate the spent composite with greater adsorption capability.	Saroyan et al. (2017)
Composite mixture of adsorption features of Fe_3O_4, AC, and sodium alginate, denoted as MSA-AC	MB	Highest adsorption was 222.3 mg/g. The adsorption capacity declined as dye concentration increased.	Li et al. (2017)
Acorn shell-based AC combined with iron oxide, denoted as Fe-AC	MB	Highest adsorption capacity was 370.4 mg/g. Methanol and acetic acid were successfully used to reactivate the spent Fe-AC for 4 cycles with a recovery yield greater than 94%.	Altntıg et al. (2017)
Prepared MAC, using AC-based pomelo peels at three activation temperatures, namely 573, 773, and 973 K	Phenol	The greatest adsorption capacity was 1.1×10^2 mg/g at 298 K.	Wang (2017)

The influence of introducing magnetic particles on AC for chromate ion elimination was examined by Maneechakr & Karnjanakom (2017), who synthesised AC through physical and chemical activation, showing a moderate adsorption capacity for chromate ions. They found that magnetic modification sharply increased the adsorption affinity towards chromate ions due to the increment of positive charge on the surface of the adsorbent. This also means that introducing the appropriate functional group for adsorption of a specific contaminant is more advantageous than increasing the surface area of the adsorbent. Consequently, further research is required to identify the influence of different functional groups on the adsorption capacity of MAC towards different contaminants. Naushad et al. (2017) prepared a magnetic composite, denoted as $NiFe_2O_4$-NC, using polymer bimetal complexes for Hg^{2+} elimination. The greatest adsorption aptitude of Hg^{2+} was 476.2 mg/g, which was a higher rate of Hg^{2+} removal in comparison with that of other magnetic composites, used for Hg^{2+} removal (Özcan et al. (2004); Xue et al. (2009); Figueira et al. (2011); Ghasemi et al. (2014); Carolin et al. (2017)). Naushad et al. (2017) also found that the best Hg^{2+}

recovery could be obtained from using 0.01 M HCl. Son et al. (2018) prepared a magnetic composite chitosan of modified magnetic kelp biochar (Chi-KBm) for Cu^{2+} elimination. The surface area of Chi-KBm was 6.17 m^2/g, 6 times greater than that of the pristine magnetic kelp biochar KBm. Son et al. (2018) observed the creation of new functional groups, like NH and C-N groups, which enhanced Cu^{2+} elimination.

Table 2. Summary of heavy metal removal, using MAC

Composite	Contaminants	Remediation efficiency	References
Magnetic composite of clay and iron oxide	Cd^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+}	Adsorption capacity of Cd^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} were 74, 40, 75, and 50 mg/g, respectively. Over a wide range of pH rates, great magnetic stability was observed.	Oliveira et al. (2003)
AC, carbon nanotubes (CNTs), and carbon encapsulated magnetic nanoparticles (CEMNPs),	Co^{2+} and Cu^{2+}	CNTs and CEMNPs had significantly greater adsorption ability than AC. Complete regeneration was acquired, simply by using HCl.	Pyrzyńska & Bystrzejewski (2010)
Fabricated a magnetic bead (MBs) and MAC	Hg^{2+}	About 6.3 mg/g of the contaminant was removed from the solution, using MBs in less than 1 min. Regeneration of MBs was easily conducted using dithiothreitol, allowing MBs' reuse. The use of MAC adsorbed about 38.3 mg/g of the contaminant in less than 1 min. Regeneration of MAC was possible through heat-treatment at 600 °C.	Okamoto et al. (2011)
MAC	Hg^{2+}	They achieved a removal efficiency of 96.3% with the magnetization of the composite allowing convenient separation.	Faulconer et al, (2012)
Magnetic biochar	Zn^{2+}	The highest adsorption capacity was 1.18 mg/g for an initial concentration of 1.1 mg/l of Zn^{2+}.	Mubarak et al. (2013)
Polymer carbon composite (PAA-MMC)	Cd^{2+}	The maximum adsorption capacity was 406.6 mg/g. Regeneration with ethylenediaminetetraacetic (EDTA) acid was efficient and about 85.2% of the adsorption capacity was retained after five cycles.	Zeng et al. (2015)
Magnetic chitosan coating on the surface of graphene oxide (MCGO)	Pb^{2+}	The maximum removal capability was about 79 mg/g. The composite could be used efficiently up to 5 times. Efficient Pb^{2+} recovery occurred at pH = 1 and 2, giving an efficiency greater than 90%	Wang et al. (2016)
Magnetic cellulose-based beads (MCB) incorporating modified AC	Cu^{2+}, Pb^{2+} and Zn^{2+}	Contaminant removal was in the following order: $Pb^{2+} > Cu^{2+} > Zn^{2+}$ from aqueous solution.	Luo et al. (2016)
Combined Plum stone-based AC and Fe_3O_4	Cu^{2+} and Pb^{2+}	Optimal pH for removal was 5.5 and the greatest adsorption capability was 48.31 mg/g for Cu^{2+} and 80.65 mg/g for Pb^{2+}.	Parlayıcı & Pehlivan (2017)
MAC/tungsten nanocomposite (AC/Fe/W)	Al^{3+}	Adsorption capacity of Al^{3+} was 184.12 mg/g. Regeneration with HCl was effective. Only 16% of the adsorption desorption efficiency was lost after five cycles.	Saleh et al. (2017)
Tri-amino-functionalized Fe_3O_4@TMAOH	Cd^{2+}, Cr^{3+} and Co^{2+}	The highest adsorption aptitudes were 286 for Cd^{2+}, 370 for Cr^{3+}, and 270 for Co^{2+} in mg/g. The composite was effectively regenerated, using HCl solution.	Alqadami et al. (2017)
Magnetic AC from Combretum quadrangulare Kurz. (500 _C/H3PO4/addition of Fe)	$Cr_2O_7^{2-}$	The highest adsorption aptitude was 1.68 mg/g	Maneechakr & Karnjanakom, (2017)
Fe2O3/Arena nut AC composite (H3PO4/400 _C, N2/addition of Fe2O3)	F_	The highest adsorption aptitude was 4.8 mg/g	Joshi & Pradhananga, (2017)
Aluminium Iron Amended Activated Bamboo Charcoal ($AlCl_3FeCl_3$/400 _C)	F^- fluoride	The highest adsorption aptitude was 21.1 mg/g. About 85.7% of the contaminant was desorbed using NaOH. The adsorption efficiency declined to 82% after the second regeneration cycle, highlighting the reusability of the composite	Wendimu et al. (2017)
$NiFe_2O_4$-NC	Hg^{2+}	The highest adsorption aptitude was 476.2 mg/g. 0.01 M HCl	Naushad et al. (2017)
Magnetic palygorskite (MPG)	Hg^{2+} and CH_3Hg	The highest adsorption capacities were 211.93 and 159.73 mg/g for Hg^{2+} and CH_3Hg, respectively. The composite was effectively regenerated, using HCl solution, and could be used efficiently up to 7 times.	Saleh et al. (2018)

The Medical Applications of MAC

The depletion of freshwater is threatening humanity and attracting global attention. A magnetic derivative of AC provides great adsorption capacity of contaminants, sometimes even better than the original AC. A variety of methods have been implemented for drag elimination from wastewater, such as advanced oxidation processes (Hasan, 2017), coagulation, and filtration (Ding et al., 2016). However, adsorption as a remediation technique is gaining popularity (Tian et al., 2018). AC has been efficiently used for the elimination of six classes of antibiotics (Zhang et al., 2016). Nonetheless, separation of AC from an aqueous media is inconvenient, and filtration as a separation technique could block the filter (Ai et al., 2010). MAC has been used efficiently for xenobiotic adsorption. Antibiotic contamination causes bacteria resistance that complicates treatment processes (Mohammadi et al., 2015).

Biomedical applications employing magnetic nanoparticles have been reported by scientific literature, e.g., cellular capture and separation, hyperthermia, biosensing, and drug delivery (Wu et al., 2015). Their affinity towards precipitation and aggregation inside the biological vessel enabled these nanoparticles to reduce efficiency and biocompatibility. Combining AC with magnetic particles in biomedical applications could overcome the limitation of the magnetic particles due to the production of hybrids (Modugno et al., 2015). MAC have beem used in the separation of biomolecules including DNA (Song et al., 2013), protein (Diao et al., 2012) and antigens (Tang et al., 2011). Shi et al. (2015) employed magnetite, coated with GO quantum dots (GOQDs), to capture rare circulating tumour cells. The GOQDs were used for the isolation of anti-Glypican-3 GPC3-expressed Hep G2 hepatocellular carcinoma tumour cells and enrichment from an infected blood samples. A capture capacity of 91% was achieved in a 5 ml infected sample of 10 tumour cell/ml. Moreover, MAC have also been used in the removal as well as in vivo magnetic enrichment of circulating bacteria cells from infected blood (Galanzha et al., 2012). During the 1970s, the idea of Magnetic Drug Targeting (MDT) became an attractive field of study. The concept was to trap or adsorb drugs by means of a magnetically responsive material comprising bounds. By means of an external magnetic field, this magnetic drug would be controlled to target a specific tumour. Table 3 gives a brief summary of the literature on the medical use of MAC.

Table 3. Summary of the medical application of MAC

Composite	Contaminants	Remediation efficiency	References
Fabricated MTCs combining the properties of AC and iron	Adsorption of methotrexate, doxorubicin, 9AC, camptothecin, mitomycin C, and verapamil onto MTCs.	The drug-loaded composite can be localized and maintained with the tumour.	Rudge et al. (2001)
Composite (CMNP-DOX) combining carbon and iron features in a nanoparticles (CMNP) followed by immobilising doxorubicin (DOX) on the CMNP surfaces.	magnetic carrier for targeted drug-delivery applications.	The composite preserves reactivity of the immobilised DOX	Ma et al. (2006)
MTC merging the adsorption characteristics of AC and iron particles	Theophylline	AC serves as the drug carrier and iron the magnetically prone component. Higher adsorption capacity was positively related to higher AC content in the composite.	Ramanujan et al. (2007)
Magnetic-activated carbon/chitosan (MACC)	Hazardous antibiotics ciprofloxacin, erythromycin, and amoxicillin	The uptake values of ciprofloxacin, erythromycin, and amoxicillin were 90.10, 178.57, and 526.31 mg/g, respectively.	Danalıoğlu et al. (2017)

CONCLUSIONS

To sum up, this paper provided a literature review of the synthetic procedures and application of currently-used MAC. MAC were synthesised via several techniques. Introducing nano- or micro-magnetic particles into the pores of AC allows easy magnetic separation via an external magnetic field. The magnetic derivatives of AC showed great adsorption capacity; however, it complies with a reduction in the adsorption capacity of the composite due to the reduction in surface area and pore volume occupied by magnetic nanoparticles. The magnetisation of AC enhanced its environmental and medical uses. Synthetic procedures do not constitute an obstacle against its application. Chemical co-precipitation techniques are among the most common uses in the synthesis of MAC. The spent MAC can be recycled several times, maintaining great adsorption capacity, thereby making water treatment processes cost-effective and sustainable.

Future work could further develop the synthetic route and enhance the characteristics of the produced composite. Future work could also consider the influence of iron on the treated water, depending on its proposed usage and estimating the amount of the recovered composite after each cycle.

ACKNOWLEDGMENT

The authors acknowledge the faculty of Engineering, Mustansiriyah University (www.uomustansiriyah.edu.iq), for their valuable support. No financial support was received from funding agencies or non-profitable agencies.

REFERENCES

Abd El-Latif, M. M., Ibrahim, A. M. and El-Kady, M. F. (2010a). Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using biopolymer oak sawdust composite. Am. J. Sci., 6(6), 267-283.

Abd El-Latif, M. M., and Ibrahim, A. M. (2010b). Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from oak sawdust. Desalin. Water Treat., 20, 102-113.

Ahn, S., Werner, D., Karapanagioti, H. K., Mcglothlin, D. R., Zare, R. N. and Luthy, R. G. (2005). Phenanthrene and pyrene sorption and intraparticle diffusion in polyoxymethylene, coke, and activated carbon. Environ. Sci. Technol., 39(17), 6516-6526.

Ai, L., Huang, H., Chen, Z., Wei, X. and Jiang, J. (2010). Activated carbon/$CoFe_2O_4$ composites: Facile synthesis, magnetic performance and their potential application for the removal of malachite green from water. Chem. Eng. J., 156(2), 243-249.

Alqadami, A. A., Naushad, M., Abdalla, M. A., Ahamad, T., Abdullah Alothman, Z., Alshehri, S. M. and Ghfar, A. A. (2017). Efficient removal of toxic metal ions from wastewater using a recyclable nanocomposite: A study of adsorption parameters and interaction mechanism. J. Cleaner Prod., 156, 426-436.

Altıntıg, E., Altundag, H., Tuzen, M. and Sarı, A. (2017). Effective removal of methylene blue from aqueous solutions using magnetic loaded activated carbon as novel adsorbent. Chem. Eng. Res. Des., 122, 151-163.

Ao, Y., Xu, J., Fu, D. and Yuan, C. (2008). A simple route for the preparation of anatase titania-coated magnetic porous carbons with enhanced photocatalytic activity. Carbon., 46(4), 596-603.

Arcibar-Orozco, J. A., Avalos-Borja, M. andRangel-Mendez, J. R. (2012). Effect of phosphate on the particle size of ferric oxyhydroxides anchored onto activated carbon: as (V) removal from water. Environ. Sci. Technol., 46, 9577-9583.

Babes, L., Denizot, B., Tanguy, G., Le Jeune, J. J. and Jallet, P. (1999). Synthesis of Iron Oxide Nanoparticles Used as MRI Contrast Agents: A Parametric Study. J Colloid Interface Sci., 212(2), 474-482.

Baig, S. A., Zhu, J., Muhammad, N., Sheng, T. and Xu, X. (2014). Effect of synthesis methods on magnetic Kans grass biochar for enhanced As (III, V) adsorption from aqueous solutions. Biomass Bioenergy., 71, 299-310.

Borghi, C. C. and Fabbri, M. (2014). Magnetic recovery of modified activated carbon powder used for removal of endocrine disruptors present in water. Environ. Technol., 35(8), 1018-1026.

Carolin, C. F., Kumar, P. S., Saravanan, A., Joshiba, G. J. and Naushad, M. (2017). Efficient Techniques for the Removal of Toxic Heavy Metals from Aquatic Environment: A Review, J. Environ. Chem. Eng., 5(3), 2782-2799.

Castro, C. S., Guerreiro, M. C., Goncalves, M., Oliveira, L. C. and Anastacio, A. S. (2009). Activated carbon/iron oxide composites for the removal of atrazine from aqueous medium. J Hazard Mater., 164(2-3), 609-14.

Cho, D. W., Kwon, G., Yoon, K., Tsang, Y. F., Ok, Y. S., Kwon, E. E. and Song, H. (2017b). Simultaneous production of syngas and magnetic biochar via pyrolysis of paper mill sludge using CO_2 as reaction medium. Energy Convers. Manag., 145, 1-9.

Cho, D. W., Yoon, K., Kwon, E. E., Biswas, J. K., and Song, H. (2017c). Fabrication of magnetic biochar as a treatment medium for As(V) via pyrolysis of $FeCl_3$-pretreated spent coffee ground. Environ. Pollut., 229, 942-949.

Chowdhury, A. N., Jesmeen, S. and Hossain, M. (2004). Removal of dyes from water by conducting polymeric adsorbent. Polym. Adv. Technol., 15(11), 633-638.

Danalıoğlu, S. T., Bayazit, Ş. S., Kerkez Kuyumcu, Ö. and Salam, M. A. (2017). Efficient removal of antibiotics by a novel magnetic adsorbent: Magnetic activated carbon/chitosan (MACC) nanocomposite. J. Mol. Liq., 240, 589-596.

Diao, X., Chen, H., Zhang, G., Zhang, F. and Fan, X. (2012). Magnetic carbon nanotubes for protein separation. J. Nanomaterials., 2012, 57.

Dickhout, J. M., Moreno, J., Biesheuvel, P. M., Boels, L., Lammertink, R. G. H. and De Vos, W. M. (2017). Produced water treatment by membranes: A review from a colloidal perspective. J Colloid Interface Sci., 487, 523-534.

Ding, H., Wu, Y., Zou, B., Lou, Q., Zhang, W., Zhong, J., Lu, L. and Dai, G. (2016). Simultaneous removal and degradation characteristics of sulfonamide, tetracycline, and quinolone antibiotics by laccase-mediated oxidation coupled with soil adsorption. J Hazard Mater., 307, 350-8.

Do, M. H., Phan, N. H., Nguyen, T. D., Pham, T. T. S., Nguyen, V. K., Vu, T. T. T. and Nguyen, T. K. P. (2011). Activated carbon/Fe_3O_4 nanoparticle composite: Fabrication, methyl orange removal and regeneration by hydrogen peroxide. Chemosphere., 85, 1269-1276.

Faulconer, E. K., Von Reitzenstein, N. V. H. and Mazyck, D. W. (2012). Optimization of magnetic powdered activated carbon for aqueous Hg(II) removal and magnetic recovery. J. Hazard. Mater., 199, 9-14.

Fernández-Bertran, J. F. (1999). Mechanochemistry: an overview. Pure Appl. Chem., 71(4), 581-586.

Galanzha, E. I., Shashkov, E., Sarimollaoglu, M., Beenken, K. E., Basnakian, A. G., Shirtliff, M. E., Kim, J.-W., Smeltzer, M. S. and Zharov, V. P. (2012). In Vivo Magnetic Enrichment, Photoacoustic Diagnosis, and Photothermal Purging of Infected Blood Using Multifunctional Gold and Magnetic Nanoparticles. PLoS One., 7(9), e45557.

Figueira, P., Lopes, C. B., Daniel-da-Silva, A. L., Pereira, E., Duarte, A. C. and Trindade, T. (2011). Removal of mercury (II) by dithiocarbamate surface functionalized magnetite particles: Application to synthetic and natural spiked waters, Water Res., 45, 5773-5784.

Ghasemi, M., Naushad, M., Ghasemi, N. and Khosravi-fard, Y. (2014). A novel agricultural waste based adsorbent for the removal of Pb(II) from aqueous solution: Kinetics, equilibrium and thermodynamic studies. J. Ind. Eng. Chem., 20, 454-461.

Gomez-Tamayo, M. d. M., Macias-Garcia, A., DiazDiez, M. A. and Cuerda-Correa, E. M. (2008). Adsorption of Zn(II) in aqueous solution by activated carbons prepared from evergreen oak (Quercus rotundifolia L.). J. Hazard. Mater., 153, 28-36.

Gorria, P., Sevilla, M., Blanco, J. A. and Fuertes, A. B. (2006). Synthesis of magnetically separable adsorbents through the incorporation of protected nickel nanoparticles in an activated carbon. Carbon., 44(10), 1954-1957.

Guo, S., Jiao, P., Dan, Z., Duan, N., Chen, G. and Zhang, J. (2017). Preparation of L-arginine modified magnetic adsorbent by one-step method for removal of Zn(Ⅱ) and Cd(Ⅱ) from aqueous solution. Chem. Eng. J., 317, 999-1011.

Hai, T. N. (2017). Comments on effect of temperature on the adsorption of methylene blue dye onto sulfuric acid–treated orange peel. Chem. Eng. Commun., 204, 134-139

Hasan, M. B. (2017). Solar photocatalytic treatment of simazine from synthetic wastewater. J. Eng. Sustainable Dev., 21(5), 200-212.

Hatami, F. and Faghihian, H. (2015). Modification of activated carbon by 4-(8 hydroxyquinoline-azo) benzamidine for removal of Hg^{2+} from aqueous solutions. Environ. Prog., 34, 1562-1567.

Joshi, S. and Adhikari Pradhananga, M. (2017). Removal of Fluoride Ions by Adsorption onto Fe_2O_3/Areca Nut Activated Carbon Composite. J. Inst. Eng., 12(1), 175-183.

Jolivet, J.-P., Chanéac, C. and Tronc, E. (2004). Iron oxide chemistry. From molecular clusters to extended solid networks. Chem. Commun., 5, 481-483.

Karbassi, A. and Pazoki, M. (2015). Optimization of coagulation/flocculation for treatment of wastewater. J. Environ. Treatment Tech., 3(2), 170-174.

Kuppireddy, S. K. R., Rashid, K., Shoaaibi, A. A. and Srinivasakannan, C. H. (2014). Production and characterization of porous carbon from date palm seeds by chemical

activation with H_3PO_4: Process optimization for maximizing adsorption of methylene blue. Chem. Eng. Commun., 201, 1021-1040.

Laurent, S., Forge, D., Port, M., Roch, A., Robic, C., Vander Elst, L. and Muller, R. N. (2008). Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. Chem. Rev., 108(6), 2064-2110.

Lemine, O. M., Ghiloufi, I., Bououdina, M., Khezami, L., M’hamed, M. O. and Hassan, A. T. (2014). Nanocrystalline Ni doped α-Fe_2O_3 for adsorption of metals from aqueous solution. J. Alloys Compd., 588, 592-595.

Li, C., Lu, J., Li, S., Tong, Y. and Ye, B. (2017). Synthesis of Magnetic Microspheres with Sodium Alginate and Activated Carbon for Removal of Methylene Blue. Materials, 10(1), 84.

Lin, S.-H. and Juang, R.-S. (2009). Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review. J. Environ. Manage., 90(3), 1336-1349.

Luo, X., Lei, X., Cai, N., Xie, X., Xue, Y. and Yu, F. (2016). Removal of Heavy Metal Ions from Water by Magnetic Cellulose-Based Beads with Embedded Chemically Modified Magnetite Nanoparticles and Activated Carbon. ACS Sustainable Chem. Eng., 4(7), 3960-3969.

Ma, Y., Manolache, S., Denes, F., Vail, D., Thamm, D. and Kurzman, I. (2006). Plasma synthesis of carbon-iron magnetic nanoparticles and immobilization of doxorubicin for targeted drug delivery. J. Mater. Eng. Perform., 15(3), 376-382.

Maneechakr, P. and Karnjanakom, S. (2017). Adsorption behaviour of Fe(II) and Cr(VI) on activated carbon: Surface chemistry, isotherm, kinetic and thermodynamic studies. J. Chem. Thermodyn., 106, 104-112.

Mehta, D., Mazumdar, S. and Singh, S. K. (2015). Magnetic adsorbents for the treatment of water/wastewater. J. Water Process Eng., 7, 244-265.

Minceva, M., Markovska, L. and Meshko, V. (2007). Removal of Zn^{2+}, Cd^{2+} and Pb^{2+} from binary aqueous solution by natural zeolite and granulated activated carbon., Maced. J. Chem. Chem. Eng., 26(2), 125-134.

Modugno, G., Menard-Moyon, C., Prato, M. and Bianco, A. (2015). Carbon nanomaterials combined with metal nanoparticles for theranostic applications. Br. J. Pharmacol., 172(4), 975-91.

Mohammadi, A., Kazemipour, M., Ranjbar, H., Walker, R. B. and Ansari, M. (2015). Amoxicillin Removal from Aqueous Media Using Multi-Walled Carbon Nanotubes. Fullerenes, Nanotubes and Carbon Nanostructures., 23(2), 165-169.

Mohan, D., Sarswat, A., Singh, V. K., Alexandre-Franco, M. and Pittman, C. U. (2011). Development of magnetic activated carbon from almond shells for trinitrophenol removal from water. Chem. Eng. J., 172(2-3), 1111-1125.

Mohan, D., Kumar, H., Sarswat, A., Alexandre-Franco, M. and Pittman Jr, C.U. (2014). Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. Chem. Eng. J., 236, 513-528.

Mokhtari, Sh. and Faghihian, H. (2015). Modification of activated carbon by 2,6-diaminopyridine for separation of Hg^{2+} from aqueous solutions. J. Environ. Chem. Eng., 674, 1-7.

Mubarak, N. M., Alicia, R. F., Abdullah, E. C., Sahu, J. N., Haslija, A. A. and Tan, J. (2013). Statistical optimization and kinetic studies on removal of Zn^{2+} using functionalized carbon nanotubes and magnetic biochar. J. Environ. Chem. Eng., 1(3), 486-495.

Nakahira, A., Nagata, H., Takimura, M., Fukunishi, K., M., C. S., D., Y. S. and M., L. B. (2007). Synthesis and evaluation of magnetic active charcoals for removal of environmental endocrine disrupter and heavy metal ion. J. Appl. Phys., 101(9), 09J114.

Naushad, M., Ahamad, T., Al-Maswari, B. M., Alqadami, A. A. and Alshehri, S. M. (2017). Nickel ferrite bearing nitrogen-doped mesoporous carbon as efficient adsorbent for the removal of highly toxic metal ion from aqueous medium. Chem. Eng. J., 330, 1351-1360.

Nguyen, T. D., Phan, N. H., Do, M. H. and Ngo, K. T. (2011). Magnetic Fe_2MO_4 (M:Fe, Mn) activated carbons: Fabrication, characterization and heterogeneous Fenton oxidation of methyl orange. J. Hazard. Mater., 185, 653-661.

Oh, W.-D., Lua, S.-K., Dong, Z. and Lim, T.-T. (2015). Performance of magnetic activated carbon composite as peroxymonosulfate activator and regenerable adsorbent via sulfate radical-mediated oxidation processes. J. Hazard. Mater., 284, 1-9.

Okamoto, T., Tachibana, S., Miura, O. and Takeuchi, M. (2011). Mercury removal from solution by superconducting magnetic separation with nanostructured magnetic adsorbents. Physica C: Superconductivity and its Applications., 471, 1516-1519.

Oliveira, L. C. A., Petkowicz, D. I., Smaniotto, A. and Pergher, S. B. C. (2004). Magnetic zeolites: a new adsorbent for removal of metallic contaminants from water. Water Res., 38(17), 3699-3704.

Oliveira, L. C. A., Rios, R. V. R. A., Fabris, J. D., Garg, V., Sapag, K. and Lago, R. M. (2002). Activated carbon/iron oxide magnetic composites for the adsorption of contaminants in water. Carbon., 40, 2177-2183.

Oliveira, L. C. A., Rios, R. V. R. A., Fabris, J. D., Sapag, K., Garg, V. K. and Lago, R. M. (2003). Clay–iron oxide magnetic composites for the adsorption of contaminants in water. Appl. Clay Sci., 22, 169-177.

Özcan, A. S., Erdem, B. and Özcan, A. (2004). Adsorption of Acid Blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite, J. Colloid Interface Sci., 280, 44-54.

Parlayıcı, Ş. and Pehlivan, E. (2017). Removal of metals by Fe3O4 loaded activated carbon prepared from plum stone (Prunus nigra): Kinetics and modelling study. Powder Technol., 317, 23-30.

Patzak, M., Dostalek, P., Fogarty, R. V. Safarik, I. and Tobin, J. M. (1997). Development of magnetic biosorbents for metal uptake. Biotechnology Techniques., 11, 483-487.

Paul, K. G., Frigo, T. B., Groman, J. Y. and Groman, E. V. (2004). Synthesis of ultrasmall superparamagnetic iron oxides using reduced polysaccharides. Bioconjugate Chem., 15, 394-401.

Pyrzyńska, K. and Bystrzejewski, M. (2010). Comparative study of heavy metal ions sorption onto activated carbon, carbon nanotubes, and carbon-encapsulated magnetic nanoparticles. Colloids Surf., A., 362, 102-109.

Qu, L., Han, T., Luo, Z., Liu, C., Mei, Y. and Zhu, T. (2015). One-step fabricated Fe_3O_4@C core–shell composites for dye removal: Kinetics, equilibrium and thermodynamics. J. Phys. Chem. Solids., 78, 20-27.

Ramanujan, R. V., Purushotham, S. and Chia, M. H. (2007). Processing and characterization of activated carbon coated magnetic particles for biomedical applications. Mater. Sci. Eng., C., 27, 659-664.

Reddy, D. H. K. and Lee, S. M. (2014). Magnetic biochar composite: facile synthesis, characterization, and application for heavy metal removal. Colloids Surf. A Physicochem. Eng. Asp., 454, 96-103.

Rocher, V., Siaugue, J.-M., Cabuil, V. and Bee, A. (2008). Removal of organic dyes by magnetic alginate beads. Water Res., 42, 1290-1298.

Rudge, S., Peterson, C., Vessely, C., Koda, J., Stevens, S. and Catterall, L. (2001). Adsorption and desorption of chemotherapeutic drugs from a magnetically targeted carrier (MTC). J. Control. Release., 74(1-3), 335-340.

Safarik, I. and Safarikova, M. (2009). Magnetic nano- and microparticles in biotechnology. Chem. Pap., 63, 497-505.

Safarik, I. Horska, K., Svobodova, B. and Safarikova, M. (2012). Magnetically modified spent coffee grounds for dyes removal. Eur. Food Res. Technol., 234, 345-350.

Saleh, T. A., Tuzen, M. and Sarı, A. (2017). Magnetic activated carbon loaded with tungsten oxide nanoparticles for aluminum removal from waters. J. Environ. Chem. Eng., 5(3), 2853-2860.

Saleh, T.A., Tuzen, M. and Sarı, A. (2018). Polyamide magnetic palygorskite for the simultaneous removal of Hg (II) and methyl mercury; with factorial design analysis. J. Environ. Manage., 211, 323-333.

Saroyan, H. S., Giannakoudakis, D. A., Sarafidis, C. S., Lazaridis, N. K. and Deliyanni, E. A. (2017). Effective impregnation for the preparation of magnetic mesoporous carbon: application to dye adsorption. J. Chem. Technol. Biotechnol., 92, 1899-1911.

Senthilkumar, T., Chattopadhyay, S. K. and Miranda, L. R. (2017). Optimization of activated carbon preparation from pomegranate peel (Punica granatum peel) Using RSM. Chem. Eng. Commun., 204, 238-248.

Shan, D., Deng, S., Zhao, T., Wang, B., Wang, Y., Huang, J., Yu, G., Winglee, J. and Wiesner, M. R. (2016). Preparation of ultrafine magnetic biochar and activated carbon for pharmaceutical adsorption and subsequent degradation by ball milling. J. Hazard. Mater., 305, 156-163.

Shi, Y., Pramanik, A., Tchounwou, C., Pedraza, F., Crouch, R. A., Chavva, S. R., Vangara, A., Sinha, S. S., Jones, S., Sardar, D., Hawker, C. and Ray, P. C. (2015). Multifunctional Biocompatible Graphene Oxide Quantum Dots Decorated Magnetic Nanoplatform for Efficient Capture and Two-Photon Imaging of Rare Tumor Cells. ACS Appl. Mater. Interfaces., 7, 10935-10943.

Son, E. B., Poo, K. M., Mohamed, H. O., Choi, Y. J., Cho, W. C. and Chae, K. J. (2018). A novel approach to developing a reusable marine macro-algae adsorbent with chitosan and ferric oxide for simultaneous efficient heavy metal removal and easy magnetic separation. Bioresour. Technol., 259, 381-387.

Song, Z. L., Zhao, X. H., Liu, W. N., Ding, D., Bian, X., Liang, H., Zhang, X. B., Chen, Z. and Tan, W. (2013). Magnetic graphitic nanocapsules for programmed DNA fishing and detection. Small., 9, 951-7.

Sun, S. and Zeng, H. (2002). Size-controlled synthesis of magnetite nanoparticles. J. Am. Chem. Soc., 124, 8204-8205.

Tang, J., Tang, D., Niessner, R., Chen, G. and Knopp, D. (2011). Magneto-Controlled Graphene Immunosensing Platform for Simultaneous Multiplexed Electrochemical Immunoassay Using Distinguishable Signal Tags. Anal. Chem., 83, 5407-5414.

Tartaj, P., Morales, M. P., Veintemillas-Verdaguer, S., Gonzalez-Carreño, T. and Serna, C. J. (2006). Synthesis, properties and biomedical applications of magnetic nanoparticles. Handbook of magnetic materials., 16, 403-482.

Theydan, S. K. and Ahmed, M. J. (2012). Adsorption of methylene blue onto biomass-based activated carbon by $FeCl_3$ activation: Equilibrium, kinetics, and thermodynamic studies. J. Anal. Appl. Pyrol., 97, 116-122.

Tezcan Un, U., Ates, F., Erginel, N., Ozcan, O. and Oduncu, E. (2015). Adsorption of Disperse Orange 30 dye on to activated carbon de rived from Holm Oak (Quercus Ilex) acorns: A 3^k factorial design and analysis. J. Environ. Manage., 155, 89-96.

Thangamani, K.S., Andal, N.M., Kumar, E.R. and Saravanabhavan, M. (2017). Utilization of magnetic nano cobalt ferrite doped Capra aegagrus hircus dung activated carbon composite for the adsorption of anionic dyes. J. Environ. Chem. Eng., 5(3), 2820-2829.

Thitame, P. V., and Shukla, S. R. (2016). Porosity development of activated carbons prepared from wild almond shells and coir pith using phosphoric acid. Chem. Eng. Commun., 203, 791-800.

Tian, G., Wang, W., Zhu, Y., Zong, L., Kang, Y. and Wang, A. (2018). Carbon/Attapulgite Composites as Recycled Palm Oil-Decoloring and Dye Adsorbents. Materials, 11(1), 86.

Tran, T. V., Bui, Q. T. P., Nguyen, T. D., Le, N. T. H. and Bach, L. G. (2017). A comparative study on the removal efficiency of metal ions (Cu^{2+}, Ni^{2+}, and Pb^{2+}) using sugarcane bagasse-derived $ZnCl_2$-activated carbon by the response surface methodology. Adsorption Sci. Technol., 35, 72-85.

Tseng, R.-L., Wu, F.-C. and Juang, R.-S. (2003). Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons. Carbon., 41, 487-495.

Wang, F. (2017). Novel high performance magnetic activated carbon for phenol removal: equilibrium, kinetics and thermodynamics. J. Porous Mater., 24, 1309-1317.

Wang, H., Chen, Q.-W., Chen, J., Yu, B.-X. and Hu, X.-Y. (2011a). Carboxyl and negative charge-functionalized superparamagnetic nanochains with amorphous carbon shell and magnetic core: synthesis and their application in removal of heavy metal ions. Nanoscale., 3, 4600-4603.

Wang, W., Zhang, H., Zhang, L., Wan, H., Zheng, S. and Xu, Z. (2015). Adsorptive removal of phosphate by magnetic Fe_3O_4@C@ZrO_2. Colloids Surf. A., 469, 100-106.

Wang, Y., Li, L., Luo, C., Wang, X. and Duan, H. (2016). Removal of Pb^{2+} from water environment using a novel magnetic chitosan/graphene oxide imprinted Pb^{2+}. Int. J. Biol. Macromol., 86, 505-511.

Wang, Y., Rao, G. Y. and Hu, J. Y. (2011b). Adsorption of EDCs/PPCPs from drinking water by submicron-sized powdered activated carbon. Water Sci. Technol.: Water Supply., 11, 711-718.

Wendimu, G., Zewge, F. and Mulugeta, E. (2017). Aluminium-iron-amended activated bamboo charcoal (AIAABC) for fluoride removal from aqueous solutions. J. Water Process Eng., 16, 123-131.

Wu, K. H., Shin, Y. M., Yang, C. C., Wang, G. P. and Horng, D. N. (2006). Preparation and characterization of bamboo charcoal/Ni0.5Zn0.5Fe_2O_4 composite with core-shell structure. Mater. Lett., 60, 2707-2710.

Wu, R., Liu, J.-H., Zhao, L., Zhang, X., Xie, J., Yu, B., Ma, X., Yang, S.-T., Wang, H. and Liu, Y. (2014). Hydrothermal preparation of magnetic Fe_3O_4@C nanoparticles for dye adsorption. J. Environ. Chem. Eng., 2, 907-913.

Wu, W., Wu, Z., Yu, T., Jiang, C. and Kim, W. S. (2015). Recent progress on magnetic iron oxide nanoparticles: synthesis, surface functional strategies and biomedical applications. Sci. Technol. Adv. Mater., 16, 023501.

Xiong, W., Hu, X., Wu, X., Zeng, Y., Wang, B., He, G. and Zhu, Z. (2015). A flexible fiber-shaped supercapacitor utilizing hierarchical $NiCo_2O_4$@polypyrrole core-shell nanowires on hemp-derived carbon. J. Mater. Chem. A., 3(33), 17209-17216.

Xuan, S., Hao, L., Jiang, W., Gong, X., Hu, Y. and Chen, Z. (2007). A facile method to fabricate carbon-encapsulated Fe_3O_4 core/shell composites. Nanotechnology, 18, 035602.

Xue, Y., Hou, H. and Zhu, S. (2009). Competitive adsorption of copper(II), cadmium(II), lead(II) and zinc(II) onto basic oxygen furnace slag, J. Hazard. Mater., 162, 391-401.

Yamamura, A. P. G., Yamaura, M. and Costa, C. H. (2011). Magnetic biosorbent for removal of uranyl ions. Int. J. Nucl. Energy Sci. and Technol., 6, 8-16.

Yang, M., Xie, Q., Zhang, J., Liu, J., Wang, Y., Zhang, X. and Zhang, Q. (2010). Effects of coal rank, Fe3O4 amounts and activation temperature on the preparation and characteristics of magnetic activated carbon. Min. Sci. Technol. (China)., 20, 872-876.

Yang, N., Zhu, S., Zhang, D. and Xu, S. (2008). Synthesis and properties of magnetic Fe_3O_4-activated carbon nanocomposite particles for dye removal. Mater. Lett., 62(4-5), 645-647.

Yin, Ch. Y., Kh. Aroua, M., Ashri, W. F., and Daud, W. (2007). Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. Sep. Purif. Technol., 52, 403-415.

Younas, M., Leong, L. K., Mohamed, A. R., and Sethupathi, S. (2016). CO_2 adsorption by modified palm shell activated carbon (PSAC). Chem. Eng. Commun., 203, 1455-1463.

Zeng, G., Liu, Y., Tang, L., Yang, G., Pang, Y., Zhang, Y., Zhou, Y., Li, Z., Li, M., Lai, M., He, X. and He, Y. (2015). Enhancement of Cd(II) adsorption by polyacrylic acid modified magnetic mesoporous carbon. Chem. Eng. J., 259, 153-160.

Zhang, G., Qu, J., Liu, H., Cooper, A. T. and Wu, R. (2007). $CuFe_2O_4$/activated carbon composite: A novel magnetic adsorbent for the removal of acid orange II and catalytic regeneration. Chemosphere., 68, 1058-1066.

Zhang, J., Xie, Q., Liu, J., Yang, M. and Yao, X. (2011). Role of $Ni(NO_3)_2$ in the preparation of a magnetic coal-based activated carbon. Min. Sci. Technol. (China)., 21, 599-603.

Zhang, M. Gao, B. Varnoosfaderani, S. Hebard, A. Yao, Y. Inyang, M. (2013). Preparation and characterization of a novel magnetic biochar for arsenic removal, Bioresource Technology., 130, 457-462.

Zhang, S., Tao, L., Jiang, M., Gou, G. and Zhou, Z. (2015). Single-step synthesis of magnetic activated carbon from peanut shell. Mater. Lett., 157, 281-284.

Zhang, X., Guo, W., Ngo, H. H., Wen, H., Li, N. and Wu, W. (2016). Performance evaluation of powdered activated carbon for removing 28 types of antibiotics from water. J. Environ Manage., 172, 193-200.

Zhang, Z. and Kong, J. (2011). Novel magnetic Fe_3O_4@C nanoparticles as adsorbents for removal of organic dyes from aqueous solution. J. Hazard. Mater., 193, 325-329.

Zheng, J., Liu, Z. Q., Zhao, X. S., Liu, M., Liu, X. and Chu, W. (2012). One-step solvothermal synthesis of Fe_3O_4@C core–shell nanoparticles with tunable sizes. Nanotechnology., 23(16), 165601.

Zhu, X., Liu, Y., Qian, F., Zhou, C., Zhang, S. and Chen, J. (2014). Preparation of magnetic porous carbon from waste hydrochar by simultaneous activation and magnetization for tetracycline removal. Bioresour. Technol., 154, 209-214.

Zolgharnein, J., Shahmoradi, A., Zolgharnein, P. and Amani, S. (2016). Multivariate optimization and adsorption characterization of As(III) by using fraxinus tree leaves. Chem. Eng. Commun., 203, 210-223.