Activated charcoal–magnetic nanocomposite for remediation of simulated dye polluted wastewater
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ABSTRACT

Herein, we report a straightforward way to fabricate activated charcoal–magnetic nanocomposite (AC–MNC) by chemical precipitation for the sequestration of methylene blue (MB) from a simulated solution. The synthesised nanocomposite was characterised by Fourier transform infra-red (FTIR), Brunauer–Emmett–Teller (BET), transmission electron microscope (TEM) and vibrating sample magnetometer (VSM) techniques. A good uniformity in the spherical AC–MNC particles is observed from a TEM image with an average particle size diameter of around 25 nm. AC–MNC possesses a specific surface area of 387.28 m² g⁻¹ with easy dispersibility and magnetic separation. The nanocomposite demonstrates an MB sequestration capacity of 147.71 mg g⁻¹. The high efficiency of the nanocomposite is rationalised on the basis of H-bonding and electrostatic interaction between the electropositive N-atom of MB and electronegative oxygen-containing functional groups on the composite surface. Moreover, the exhausted AC–MNC can be efficiently regenerated by microwave irradiation followed by elution with methanol. The renewed nanocomposite showed good reusability. Thus, the synthesised AC–MNC proved to be an interesting and potential material for the remediation of MB-contaminated aqueous solution.

Key words | chemical elution, magnetic separation, methylene blue-sequestration, microwave irradiation, nanocomposite

INTRODUCTION

Widespread application of synthetic dyes in the textile, paper, printing, paint and plastic industries impart colour to the effluents causing water pollution (Xie et al. 2014). Toxic organic dyes in effluents cause an environmental hazard to diverse ecosystems, biodiversity and aquatic systems (Xie et al. 2014). The potential toxicity of methylene blue (MB), an industrially relevant cationic dye, on flora, fauna and humans are well documented in the literature (Ghorai et al. 2014). Thus, the remediation of dye-polluted aqueous streams by straightforward, efficient and greener technologies is gathering substantial attention. Adsorption is one of the best dye-remediation techniques because of its simple operation, high efficiency and extensive applications (Cheng et al. 2014).

The use of various adsorbents, such as activated carbon, agricultural waste, polymeric materials, zeolites and carbon nanotubes for sequestration of dyes have been established by other researchers (Zhang et al. 2013). However, their industrial applications are limited because of inconveniences encountered during separation, especially in their powdered form. Moreover, the use of commercially available adsorbents is not viable from an economic standpoint. Hence, it is necessary to exploit new and promising low-cost adsorbents for the sequestration of dyes from wastewater. In this regard, considerable attention has been focused on magnetic nanomaterials for their promising sequestering efficiency and easy magnetic separation (Ambashta & Sillanpaa 2010). Several magnetic nanomaterials have been reported in the literature for the removal of dyes (Ali 2012). So far, activated charcoal (AC) has not been used for the fabrication of magnetic nanocomposites. Herein, the authors report a single-step synthesis of AC–magnetic nanocomposite by chemical precipitation. The fabricated magnetic nanocomposite can efficiently remove MB from aqueous solution.

MATERIALS AND METHODS

Synthesis and characterisation of magnetic nanocomposite

The co-precipitation technique was employed for the synthesis of magnetic nanocomposite with modification in
the procedure described elsewhere (Lasalle et al. 2011). Briefly, 15.1795 g of FeCl₃ and 6.9502 g FeSO₄·7H₂O was dissolved in 400 mL ultra-pure water; 4 g of AC was added to the resulting solution and vigorously stirred. Thereafter, 100 mL 5 M NaOH was added slowly with constant stirring at 70°C for 30 minutes. The colour of the mixture changed from brown to black with the formation of precipitate. The black precipitate was separated by a magnet and repeatedly washed with 50% ethanol–water solution to remove impurities. The black solid was then dried in a vacuum for 12 hours, pulverised and sieved to 150 micron. The material thus synthesised was referred to as activated charcoal–magnetic nanocomposite (AC–MNC). The AC used in the present study had the following characteristics: form = powder; auto-ignition temperature = 824.78°C; melting point = 3,550°C; resistivity = 1,375 μΩ-cm, 20°C (graphite); particle size = 150 μ; impurities = < 0.5% water soluble, < 12% moisture; and vapour pressure = < 0.1 mm Hg (20°C). AC with a high surface area, carbon density, adsorption capacity and microporous/mesoporous pore-size distribution, depending on the applications of the nanocomposite, would be beneficial from the viewpoint of AC–MNC synthesis.

The surface functional groups of AC–MNC were confirmed by Fourier transform infra-red (FTIR) spectroscopy on a MAGNA-550 FTIR spectrometer ( Nicolet, Madison, WI, USA). The magnetic properties were analysed using a vibrating sample magnetometer (VSM; Lakeshore 7410, Wasterville, OH, USA) and microscopic investigation by transmission electron microscope (TEM; EOL JEM – 2100, Tokyo, Japan). The calculation of average particle size from the TEM image was done with the aid of Image J (version: 1.48) software. The specific surface area was estimated by N₂ adsorption at 77.71 K in an ASAP 2010 Surface Area Analyser (Micromeritics, Atlanta, GA, USA).

### Experimental approach for sequestering MB from simulated solution

The sequestration of MB from aqueous solution was carried out in a batch system. The experiments were performed in a temperature-controlled incubator-cum-shaker (shaking speed = 140 rpm) at 303 K. At stipulated time intervals, the samples were withdrawn and magnetically separated. The supernatant was analysed for residual MB concentration (λ_max = 663 nm) on a GENESYS 10S UV–Visible Light Spectrophotometer, Waltham, MA, USA. The percentage removal and adsorptive uptake of MB were computed using mass-balance equations (Ahmaruzzaman et al. 2014):

\[
\text{Percentage removal of MB} = \left(1 - \frac{C_e}{C_0}\right) \times 100 \quad (1)
\]

\[
\text{Adsorptive uptake of MB per g of the nanocomposite} = \frac{(C_0 - C_e)V}{m} \quad (2)
\]

where \(C_0\) and \(C_e\) are the initial and equilibrium MB concentration (mg L⁻¹), \(V\) is the volume (L) of the MB sample taken and \(m\) is the weight (g) of the AC–MNC.

The test conditions assessed for parameter optimisation were nanocomposite load (\(m = 0.15–1.0\) g L⁻¹), interaction time (\(t = 0.03–12\) hours), initial concentration (\(C_0 = 10–500\) mg L⁻¹) and temperature (\(T = 293–313\) K). All the experiments were repeated thrice and the average values were reported for quality assurance (QA)/quality control (QC).

### RESULTS AND DISCUSSION

#### Characterisation of magnetic nanocomposite

The functional groups on the surface of the AC–MNC are depicted by the FTIR spectra shown in Figure 1(a). The characteristic bands at around 589 cm⁻¹ and 500–750 cm⁻¹ can be ascribed to (Fe–O) vibrations (Ai et al. 2011; Zhang et al. 2013), which confirms the formation of magnetic oxide. The presence of oxygen-containing functional groups are confirmed from the characteristic absorption bands at

![Figure 1](https://iwaponline.com/wst/article-pdf/71/9/1361/468651/wst071091361.pdf)

Figure 1 | FTIR spectra of (a) blank and (b) MB-laden AC–MNC.
3,410 cm\(^{-1}\) (hydroxyl group, H-bonded OH-stretching mode), 1,550 cm\(^{-1}\) (C\(-\)O-stretching mode of carboxylate) and 1,320 cm\(^{-1}\) (C\(-\)O-stretching mode) (Ai et al. 2011). Figure 2(a) depicts the room-temperature magnetisation curve of AC–MNC. The corresponding results of VSM show remanent magnetisation (\(M_r\)), saturation magnetisation (\(M_s\)) and coercivity (\(H_c\)) lower than bare magnetite nanoparticles (\(M_r = 7.4\) emu.g\(^{-1}\), \(M_s = 58.94\) emu.g\(^{-1}\) and \(H_c = 160.1\) Oe; Nguyen et al. 2011). The value of \(M_r\) (0.16 emu.g\(^{-1}\)) signifies super-paramagnetic characteristics (Darezereshki et al. 2013) and easy dispersibility in solutions for reuse. Moreover, reduced \(M_s\) (14.87 emu.g\(^{-1}\)) indicates narrow particle size distribution as well as good crystallinity of the nanocomposite (Darezereshki et al. 2013). The \(H_c\) value (12.12 Oe) implied the easy separation of AC–MNC by an applied magnetic field (Nguyen et al. 2011). Figure 2(b) illustrates the easy magnetic separation of AC–MNC (post-MB-adsorption) by a magnet (aqueous dispersion by ultra-sonication for 10 minutes and external magnetic field for 2 minutes). It is worth to mentioning that the decrease in the magnetisation parameters of AC–MNC is because of the presence of AC and the smaller particle size of the magnetic material. Thus, it could be inferred that AC–MNC is a potential magnetic nanocomposite that shows easy separation, recovery and reuse. The formation of the magnetic nanocomposite is supported by the TEM image illustrated in Figure 3(a). The figure illustrated a uniform distribution of spherical magnetic nanocomposite particles. The particle-size diameter ranges from 15 to 30 nm with an average particle size of around 25 nm (Figure 3(b)). Thus, the straightforward approach of synthesis could successfully avoid the agglomeration of nanocomposite particles, even those with lower engineered particle size. This is unlike the nanomaterials and nanocomposite synthesised by several researchers (Yang et al. 2008; Afkhami et al. 2010; Lasalle et al. 2011). The smaller particle size and its narrow distribution as inferred from magnetisation data are in good agreement with the elucidations from TEM. The specific surface area (387.28 m\(^2\) g\(^{-1}\)) of the nanocomposite was estimated from \(N_2\) adsorption data in conformity to the BET surface area model.

**Interaction of MB in simulated solution with AC–MNC**

The interaction of MB with AC–MNC was investigated under optimum operating conditions (nanocomposite loading, \(m = 1.0\) g L\(^{-1}\); interaction time, \(t = 4\) hours; initial dye concentration, \(C_0 = 100\) mg L\(^{-1}\) and reaction temperature, \(T = 303\) K). The dye-sequestering efficiency of 99.38% was observed. The adsorption isotherm of MB uptake is illustrated in Figure 4, which shows the Type II Class of isotherms as classified by International Union of Pure and Applied Chemistry (IUPAC), depicting strong adsorbate-adsorbent interaction (Ahmed & Ahmaruzzaman 2014). The adsorption profile is characterised by a sharp knee and a fairly horizontal plateau portraying a Langmuir isotherm type. The monolayer adsorption capacity (\(q_m\)) and separation factor (\(R_L\)) were computed from the Langmuir isotherm (Ahmed et al. 2014). The monolayer coverage of MB onto the AC–MNC surface demonstrates a high sequestration capacity of 147.71 mg g\(^{-1}\) (of the nanocomposite) and an \(R_L\) factor of 0.037 indicates the feasibility of sequestration, as \(R_L < 1\).

![Figure 2](https://iwaponline.com/wst/article-pdf/71/9/1361/468651/wst071091361.pdf)
Insight into the retention mechanism of MB onto AC-MNC

The FTIR spectroscopic analysis of blank and MB-laden nanocomposite provides insight into the retention mechanism of MB. Figure 1(a) and (b) depict the characteristic peaks of blank and MB-laden AC-MNC, respectively. On the basis of the aforesaid results, AC-MNC is characterised by some prominent peaks at 3,410 cm\(^{-1}\) (\(\nu_{\text{O-H}}\)), 1,550 cm\(^{-1}\) (\(\nu_{\text{C-O}}\)) and 1,320 cm\(^{-1}\) (\(\nu_{\text{C-O}}\)). After the adsorption of MB, the peak at 3,410 cm\(^{-1}\) shifted to 3,420 cm\(^{-1}\), which indicates the involvement of H-bonding. The intensity of the band at 1,320 cm\(^{-1}\) decreases to 1,315 cm\(^{-1}\) with peak broadening, which signifies \(\nu_{\text{C-O}}\). Furthermore, the adherence of MB onto the nanocomposite surface is confirmed by new absorption bands at 1,630 cm\(^{-1}\), which corresponds to aromatic-ring stretching (C=C-C). The band at around 1,360 cm\(^{-1}\) may be ascribed to the aromatic tertiary amine, CN-stretching of MB molecules (Ai et al. 2011). Hence, it is clear that the electropositive N-atom of MB can easily adhere to the negatively charged AC-MNC surface by electrostatic interaction. The change in stretching frequencies of the oxygen-containing functional group justifies the involvement of hydrogen-bonding and electrostatic force in the retention of MB onto the nanocomposite surface.

Integrated desorption approach to restore retention efficiency of exhausted magnetic nanocomposite

To diminish waste production and operational expenditure, regeneration of the exhausted AC-MNC was explored. An integrated desorption approach was adopted for regeneration where the exhausted nanocomposite was subjected to microwave (MW) irradiation followed by chemical elution. The exhausted nanocomposite was oven-dried at 383 K for 1 hour and then MW irradiated (2.45 GHz, 360 W) for 5 minutes. The MW-treated material was thereafter subjected to chemical elution by desorbing solvents.
such as methanol, ethanol, acetonitrile and acetic acid. It was observed that acetic acid and ethanol showed a desorption efficiency of 55.50% and 63.47%, respectively. However, acetonitrile and methanol proved to be better desorbing solvents with a high desorption efficiency of 92.06% and 99.53%, respectively. Thus, the optimum conditions for regeneration of AC–MNC are: drying temperature = 383 K; drying time = 1 hour; MW irradiation = 360 W; MW irradiation time = 5 minutes; and desorbing solvent = methanol. On a larger scale, the exhausted adsorbents can be dried and passed through an MW reactor connected in-line with the regeneration pathway. Thereafter, MW-irradiated materials can be flushed with desorbing solvent and dried to regenerate the adsorbents. The advantage of the integrated approach is the fact that, due to MW irradiation, the adsorbate molecules come easily to the surface of the exhausted nanocomposite and chemical elution can remove them efficiently. Unlike conventional heating by convection where gases at high temperature depart from the surface to the centre of materials, MW heats the material from the inner core, which develops a decreasing temperature gradient towards the surface (Liao et al. 2013). Hence, quick and easy transport of the desorbed molecules from the higher temperature core region to the lower-temperature surface takes place. This in turn results in better conservation of textural characteristics of the material by reducing coke deposits in the porous domain, unlike convection heating where decomposition of desorbed molecules occurs, resulting in the rupture of pore walls (Ania et al. 2005).

Comparative assessment of the sequestration capacity of fresh and renewed AC–MNC

The MB-sequestration capacity of fresh AC–MNC was 99.38 mg g⁻¹. The renewed AC–MNC (MW irradiated at 360 W for 5 minutes and eluted with methanol) was re-explored for MB-sequestration capacity under similar experimental conditions (C₀ = 100 mg L⁻¹). The sequestration capacity of the renewed nanocomposite was 98.66 mg g⁻¹, almost similar to the fresh one. However, on increasing the MW irradiation to 540 W and 720 W (during regeneration), MB sequestration capacity decreases to 95.82 mg g⁻¹ and 90.16 mg g⁻¹, respectively. This may be attributed to the fact that under higher temperature there may occur partial decomposition of the desorbed molecules, resulting in coke deposits and pore blockage. Moreover, due to high temperature, there may be an intense decrease in the oxygen-containing surface functional groups (Ania et al. 2005). These may lead to a decrease in the sequestering capacity of the renewed nanocomposite with increasing MW irradiation.

Exploitation and disposal tactics of MB-laden magnetic nanocomposite

The dye-laden nanocomposite was exploited for energy recovery in terms of higher heating value (HHV = 6.43 MJ kg⁻¹). Thus, the exhausted dye-laden AC–MNC can be dried, and then employed for fabricating fuel briquettes to be used in furnaces/boilers/incinerators. The remaining bottom ash post-energy recovery can be exploited for the construction of building blocks/fire bricks. Accordingly, the exhausted nanocomposite can be renewed by integrated desorption and utilised for repeated adsorption-desorption cycles. After the significant loss in sequestering efficiency, energy can be recovered and bottom ash can be utilised for construction purposes (Ahmed et al. 2014a). Thus, secondary pollution caused by the MB-laden nanocomposite can be effectively checked.

CONCLUSIONS

The AC–MNC was successfully synthesised by a straightforward chemical precipitation technique with narrow particle-size distribution and without any agglomeration. The synthesised AC–MNC has a strong magnetic sensitivity to the external magnetic field, thereby nullifying any separation hazard for widespread application. The present study substantiates the practical utility of the material for a better sequestering efficiency of MB from aqueous solution. The effective regeneration of the exhausted nanocomposite and good reusability of the renewed material confirms its potential for industrial application and waste minimisation. The energy recovery from the exhausted material (after repeated regeneration and reuse) and exploitation of the remaining bottom ash for partial replacement of construction materials substantiate the complete utilisation of AC–MNC. The cost of the AC used in this study is approximately USD 8.73. From an economic perspective, agricultural/industrial waste materials can be used for the fabrication of nanocomposites and this will be a better approach to low-cost dye wastewater treatment. The potential of AC–MNC can also be explored for the sequestration of other toxic pollutants from wastewater for a clean and healthy environment.
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