Simple synthesis of bacterial cellulose/magnetite nanoparticles composite for the removal of antimony from aqueous solution

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Abstract
The progress of efficient wastewater treatment predominantly depends on materials fabrication. Polygonal magnetite nanoparticles (MNPs) were fabricated with 6–14 nm diameter by a developed co-precipitation approach, using non-toxic biotemplate bacterial cellulose (BC), biosynthesized by Gluconacetobacter xylinus (ATCC® 10245). The fabricated BC/MNPs composite was used for the removal of antimony (Sb (III)) from aqueous solution for the first time. The fabricated BC/MNPs-C was structurally characterized by Fourier-transform infrared spectrum (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). BC/MNPs-C has a saturation magnetization of 55.15 emu g⁻¹, surface area and pore size of 85.68 m² g⁻¹ and 60 nm, respectively, as determined using the Brunauer–Emmett–Teller method. Networks were basically mesoporous with pore sizes mostly <60 nm and pore size distribution centered around 27 nm. Adsorption data were modeled using four adsorption isotherms, including Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R) models. The experimental data fitted Langmuir isotherm and followed pseudo-second-order kinetic model, indicating that the Sb (III) adsorption process occurred on homogenous monolayer, and it is chemically controlled via electrostatic attraction. The Sb (III) adsorption reached its equilibrium status within 60 min. EDXS analysis confirmed the presence of Sb (III) on the BC/MNPs-C surface. The fabricated BC/MNPs-C showed considerable regeneration capability and high performance after four successive cycles, with almost the same efficiency (88.7–93%). The overall work provides a green/simple method for bio-based nanocomposite preparation with excellent magnetic properties for the removal of antimony. As a result, the fabricated BC/MNPs-C could have important applications in many environmental and biological fields.
Graphical Abstract

Keywords  Bacterial cellulose · Biotemplate · Heavy metals · Nanocomposite

Introduction

According to the World Health Organization, more than 10 million people suffered from various infections because of water contamination (Ali and Aboul-Enein 2006; Ali et al. 2009; Gnanasekaran et al. 2017). Various human activities play a growing role in impairing water scarceness by contaminating water sources, in both industrialized and developing countries. As a result, wastewater from various industries, such as mining, chemical manufacturing, textiles, plastics, electroplating, pesticides, contains many toxic heavy metals, which are not biodegradable and likely accumulate in living organisms, causing severe diseases (Santhosh et al. 2016). In general, water pollution creates major environmental and health problems; therefore, wastewater remediation before its discharge is essentially important for both human and environment, and it represents a global challenge (Ali et al. 2016a, b, 2017a and 2018; Gupta et al. 2017; Saravanan et al. 2015). For that reason, the worldwide environmental concern is extensively growing for the development of new methodologies that can be used in wastewater treatment (Ali et al. 2017b; Gupta et al. 2017; Santhosh et al. 2016; Su 2017). Antimony (Sb) is a hazardous toxic metal with various industrial applications, such as semiconductors, lead batteries, pipe metal, infrared detectors and diodes (Lee et al. 2016). Although it occurs widely in the environment as a result of various human activities, it is considered as a toxic element with similar effects to lead and arsenic, causing harmful effects to the central nervous system, as well as sterility, abortions and neonatal mortality; however, it is rarely investigated (Lee et al. 2016). Antimony and its derivatives are classified as a high-priority pollutant for water due to their toxicity and implications in cancer development (WHO 2017). Therefore, the European Union (EU) and United States Environmental Protection Agency (US EPA) have established a low maximum acceptable level
of 5 and 6 µg L⁻¹, respectively, for Sb species, regarding safe drinking water (EU 2014; US EPA 2012).

On the other hand, there are several methods for the removal of hazardous pollutants from aqueous solution, such as solvent extraction, precipitation, ion exchange, reverse osmosis, coagulation/flocculation/ultrafiltration, ultrasonic waves, photocatalysis and adsorption (Ali et al. 2016a, c; Dehghani et al. 2016; Gupta et al. 2017; Nikfar et al. 2016; Santhosh et al. 2016; Su 2017). However, the adsorption method is the most commonly used one, since it is considered eco-friendly, efficient, inexpensive and simple in its application (Nagarajah et al. 2017). Importantly, the design and application of non-toxic adsorbents for the removal of huge amounts of hazardous material in short time are crucial requirements in wastewater treatment (Asfaram et al. 2015; Gnanasekaran et al. 2017). Therefore, many adsorbents were studied for their possibility to remove hazardous materials; these adsorbents included activated carbon, carbon nanotube, zeolite, chitin, low-cost adsorbents, barley straw, lignin, switchgrass biochar, nanocomposites and graphene oxide (Essandoh et al. 2017; Fakhrri et al. 2016; Gupta et al. 2017; Saravanan et al. 2016). The positive point of choosing these materials is the lower cost and green synthesis involved in the whole process. However, there is a continuous need to search for new economical and effective adsorbents (Gupta et al. 2017). Moreover, with the recent progress of nanotechniques, new classes of nanoparticles (NPs) have emerged (Agarwal et al. 2017; El-Baz et al. 2016a, b; Giraldo et al. 2013; Gnanasekaran et al. 2017; Nekouei et al. 2015). In this respect, magnetic nanoparticles (MNPs) have attracted much interest, because of their extraordinary magnetic/optic properties that made them used in many applications, such as food, agriculture and medicine (Ali et al. 2017a, b; Essandoh et al. 2017; Nagarajah et al. 2017). Furthermore, MNPs are being extensively studied and have been successfully used to solve many environmental problems (Nagarajah et al. 2017). The main advantage of using MNPs is the possibility of their co-aggregation, because of the interparticles dipolar forces; therefore, using BC nanofibers networks as biotemplate can prevent their aggregation and facilitates the formation/deposition of the MNPs along its nanofibers with uniform coating of the BC (Stoica-Guzun et al. 2016). For the aforementioned reasons, the main objective of this study is to fabricate a new nanomaterial using an eco-friendly and cost-effective precursors, via simple synthesis route. The present work describes a new BC/MNPs-C approach by modified co-precipitation route, using BC nanofibers as a non-toxic biotemplate. The fabricated BC/MNPs-C was structurally characterized using FTIR, SEM, TEM and XRD analyses and was used for Sb (III) ions removal from aqueous solution for the first time. The adsorption reaction, isotherms and diffusion model which facilitate understanding the reaction mechanism were concisely discussed. Adsorption kinetics and the reusability of the fabricated BC/MNPs-C for Sb (III) ions removal using AAS and EDX were also investigated. Research was carried out throughout this study in 2016/2017, at University of Sadat City, Egypt.

Materials and methods

Chemicals

Hydrochloric chloride (HCl), sodium hydroxide (NaOH) and ammonium hydroxide (NH₄OH) are of analytical grade. Cadmium and antimony standards (1000 ppm) were obtained from (Merck, Germany). Ferrous chloride (FeCl₂·4H₂O) and ferric chloride (FeCl₃·6H₂O) were obtained from oxford (India), whereas sodium chloride (NaCl), yeast extracts, d-glucose, sodium phosphate (Na₃HPO₄), citric acid, calcium carbonate (Ca₃CO₃) and agar were purchased from SAS chemical CO (MUMBAI). All aqueous solutions were prepared using milli-Q water (18 MΩ).

Biosynthesis and purification of the bacterial cellulose (BC)

_Gluconacetobacter xylinus_ (ATCC® 10245) was inoculated into Hestrin-Schramm (HS) growth medium having the following composition (g/L): 20 d-glucose, 5 yeast extract, 5 peptone, 2.7 Na₂HPO₄ and 1.15 citric acid in deionized
water (DI). Growth medium pH was adjusted to 6.0–6.2 using 1 N NaOH/1 M HCl. Stock culture was maintained on a DSMZ (Deutsche Sammlung von Mikroorganismen und Zellkulturen) 105 medium slants containing, 10% d-glucose, 2% calcium carbonate, 1% yeast extract, 1.5% agar, and cultures renewal was made every 30 days. Ten milliliters of 3-days-old culture (3 × 10⁶ CFU/mL) was used to inoculate 100 mL of HS medium in Erlenmeyer flask and incubated statically at 30 °C for 5 days. The cellulose ribbons were developed and harvested after 72 h, boiled in double deionized water at 70 °C for 3 h, then immersed in 2% NaOH for 1 h and dried at 70 °C prior to use (Masaoka et al. 1993).

Preparation of the bacterial cellulose magnetite nanoparticles composite (BC/MNPs-C)

The co-precipitation method of Khalafalla and Reimers (1980) with some modifications was used for the preparation of the BC/MNPs-C, where two equivalents of the ferrous chloride (FeCl₂·4H₂O) were added to three equivalent of the ferric chloride (FeCl₃·6H₂O) in 100 mL of milli-Q water (18 M Ω) containing 500 mg of the harvested BC. The mixture was stirred for 15 min, and then 50 mL of NaCl (0.2 M) was added while stirring for an extra 1 h at 25 °C. Finally, 200 mL of NH₄OH (30% V/V) was dispensed while stirring for 15 min to form a black precipitate which was then washed several times with 5% NH₄OH, collected and air-dried.

Characterization of BC/MNPs-C

The crystalline structure and particles size measurement of the fabricated BC/MNPs-C were conducted by X-ray diffraction (XRD) at 25–28 °C with a D8 Advance X-ray diffractometer (Bruker–Germany) of nickel (Ni) filter using CuKα (λ = 1.54184 Å) radiations as an X-ray source. Fourier-transform infrared spectrum (FTIR) of the samples was examined using Nicolet 6700 (Thermo scientific—USA). Atomic force microscopy (AFM) and field emission transmission electron microscopy (FETEM, JSM-2100F, JEOL Inc.) at an accelerating voltage of 15 and 200 kV. The magnetic properties were investigated using vibrating sample magnetometer (VSM, Lakeshore, Model-7410, USA). Surface area of the BC/MNPs-C was measured by micromeritics surface analyzer (NOVO Series 2000, USA) using nitrogen (99.99%) adsorption/desorption at 77 K. The adsorbents were outgassed at 378.15 K under a vacuum of < 10 mmHg for 24 h as a minimum time. Porosity distribution was calculated using the density functional theory (Rangel-Mendez and Streat 2002).

Adsorption kinetics and isotherms

The adsorption kinetic experiments were performed according to Nassar et al. (2011) method to examine the effect of the reaction time on the heavy metal adsorption onto the BC/MNPs-C. Fifty milligrams of BC/MNPs-C was added to 50 mL of 200 mg L⁻¹ Sb (III) solution, and the mixture was agitated at 150 rpm at 28 °C for 150 min, where samples were withdrawn every 10 min. The BC/MNPs-C was magnetically separated, and the residual Sb (III) concentration in the supernatant was determined by atomic absorption spectrometry (AAS) (Savant AA-GB Scientific Equipment, Australia). Kinetic models were used to fit the experimental data, and the adsorption equilibrium isotherms were determined at 28 °C following the aforementioned procedure. After determination of the residual Sb (III) concentration, the amount adsorbed per unit mass (qₑ, mg g⁻¹) was calculated by the mass balance and the removal percentage % was calculated using Eqs. (1) and (2) (Rajput et al. 2016). Comparison of the experimental adsorption equilibrium data with theoretical isotherms was carried out.

\[ Q_e = \frac{(C_0 - C_e)}{m} V, \tag{1} \]
\[ \% = \frac{(C_0 - C_e)}{C_0} \times 100, \tag{2} \]

where \( C_0 \) and \( C_e \) are the initial and equilibrium heavy metal concentrations in the solution (mg L⁻¹), respectively, \( m \) is the dry mass of the contacted adsorbent solid (g), and \( V \) is the volume of solution (L). The effect of pH ranging from 2 to 12 was also investigated by adjusting the pH with 0.5 M HCl or NaOH, in order to determine the adsorption mechanism. Adsorption of Sb (III) ions by BC/MNPs-C was modeled using four adsorption isotherms (Nagarajah et al. 2017). The Langmuir isotherm was performed by fitting experimental data to Eqs. (3) and (4), where \( C_e \) is the equilibrium concentration of the heavy metal in mg/L, \( q_e \) is the adsorbed heavy metal ions at equilibrium in mg g⁻¹, \( q_o \) and \( b \) are Langmuir constants related to adsorption capacity, \( R_L \) is the Langmuir constant and \( C_o \) is the initial concentration of metal ions in (mg/L).

\[ \frac{C_e}{q_e} = \frac{C_o}{q_o} + \frac{1}{b q_o}, \tag{3} \]
\[ R_L = \frac{1}{1 + b C_o}. \tag{4} \]

The value of \( R_L \) (dimensionless separation parameter) indicates the isotherm shape or type. Adsorption isotherm defines sorbate molecules fraction that are partitioned...
between the liquid and solid phases at equilibrium; isotherm will be linear if \( R_t = 1 \), irreversible if \( R_t = 0 \), favorable if \( 0 < R_t < 1 \) and unfavorable if \( R_t > 1 \) (Biswa et al. 2007).

The **Freundlich** isotherm is applicable for both the monolayer (chemisorption) and the multilayer adsorption (physiosorption), and it assumes that the adsorbate adsorbs onto the heterogeneous surface of the adsorbent. Freundlich linear form equation can be expressed as in Eq. (5):

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e, \tag{5}
\]

where \( K_f \) and \( n \) are Freundlich isotherm constants associated with adsorption capacity and intensity, respectively, and \( C_e \) is the equilibrium concentration (mg L\(^{-1}\)) (Freundlich 1926; Tan and Xiao 2009). The **Temkin** isotherm model presumes that the adsorption energy linearly decreases with the surface coverage due to adsorbent–adsorbate interactions. The linear form of Temkin isotherm model is given by the following equation (Eq. 6):

\[
q_e = \frac{R_T}{b} \ln K_t + \frac{R_T}{b} \ln C_e, \tag{6}
\]

where \( b \) is Temkin constant related to the heat of sorption (J mol\(^{-1}\)) and \( K_t \) is Temkin isotherm constant (L g\(^{-1}\)) (Boparai et al. 2011).

The **Dubinin–Radushkevich** (D-R) isotherm model is a semiempirical equation, and adsorption follows a pore-filling mechanism. It assumes that the adsorption has a multilayer character, involving van der Waals forces, and is applicable for physical adsorption processes (Boparai et al. 2011). The linear form for D-R isotherm model can be expressed by Eqs. (7) and (8):

\[
\ln q_e = \ln q_d - \beta \varepsilon^2, \tag{7}
\]

\[
\varepsilon = R_T \ln [1 + 1/C_e], \tag{8}
\]

where \( q_d \) is the D-R constant (mg g\(^{-1}\)), \( \varepsilon \) is the constant related to free energy, and \( \beta \) is the Polanyi potential as shown in Eq. (8). All experiments were duplicated, with an experimental error margin of < 5%. In order to predict the Sb (III) ions removal rate, kinetic data were fitted by least-square procedures to kinetic models extensively used in the literature, which consider pseudo-first-order and pseudo-second-order rate expressions referred to the solid capacity (Eqs. 9 and 10), assuming that the sorption capacity is proportional to the number of active sites occupied on the sorbent (Nagarajah et al. 2017).

\[
\ln (q_e - q_t) = \ln q_e - k_1 t, \tag{9}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \tag{10}
\]

where \( q_e \) (mg g\(^{-1}\)) and \( q_t \) (mg g\(^{-1}\)) are the adsorbent quantity at equilibrium and the adsorption quantity at time \( t \) (min), respectively. \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the kinetics rate constants for the pseudo-first-order equation and the pseudo-second-order equation, respectively. Both the slope and intercept of the pot of \( \ln (q_e - q_t) \) versus \( t \) were used to determine the pseudo-first-order rate constant \( k_1 \) and \( q_e \). The slope and intercept of \( t q_t \) versus \( t \) plot were used to calculate the pseudo-second-order rate constant \( k_2 \) and \( q_e \). In case of heavy metals removal, the limiting step and thus the kinetic order of this reaction is two with respect to the number of adsorption sites available for exchange. To study the mechanism and rate-controlling step of adsorption, the kinetic experimental results were tested with Weber’s intraparticle diffusion model (Biswa et al. 2007) which is expressed by Eq. (11):

\[
q_t = k_t t^{1/2} + C, \tag{11}
\]

where \( q_t \) is the amount of solute on the surface of the adsorbent at time \( (mg \ g^{-1}) \), \( k_t \) is the intraparticle diffusion rate constant (mg g\(^{-1}\) min\(^{-1}\)), and \( C \) is the intercept (mg g\(^{-1}\)) and gives an idea of boundary layer thickness (Biswa et al. 2007). The slowest step in the adsorption process can be determined by plotting the kinetic data using Bangham equation (Eq. 12) which is expressed as:

\[
\log \log \left( C_o/C_0 - q_t \right) = \log \left( k_0 m/2.303 V \right) + \alpha \log t, \tag{12}
\]

where \( C_o \) is the initial concentration of the solute in the solution (mg/L), \( V \) is the volume of the solution, \( L \), \( m \) is the weight of the adsorbent used per liter of the solution (g/L), and \( q_t \) is the amount of the adsorbent retained at time \( t \) (mg g\(^{-1}\)); \( \alpha \) and \( k_0 \) are constants. In addition, the Boyd plot predicts the actual rate-determining step involved in the adsorption process (Biswa et al. 2007) and is expressed by the following equation (Eq. 13):

\[
B_t = -0.4977 - \ln \left( 1 - F \right), \tag{13}
\]

where \( F \) represents the fraction of solute adsorbed at any time and \( B_t \) is a mathematical function of the fraction of solute adsorbed at any time (Biswa et al. 2007).

**Regeneration of the fabricated BC/MNPs-C**

To investigate the BC/MNPs-C adsorption/desorption reliability, 100 mg L\(^{-1}\) of BC/MNPs-C was agitated in 25 mL solution containing 500 mg L\(^{-1}\) Sb (III) at 150 rpm for 1 h. The BC/MNPs-C was magnetically separated using magnetic bar; 1M HCl was used as an eluent for the heavy metal ions desorption by shaking at 150 rpm for 1 h at room temperature, and then washed several times with ultra-pure water to remove the unabsorbed heavy metals ions (Hu et al. 2006). The regenerated BC/MNPs-C was repeatedly used for Sb (III) ions adsorption/desorption for 4 successive times.
Statistical analysis

Statistical analyses of the values for all the adsorption experiments were expressed as mean ± standard deviation of triplicate independent experiments. The experimental data were analyzed using student’s t test (Microsoft Excel, Microsoft Corporation, USA).

Results and discussion

BC/MNPs-C fabrication

BC/MNPs-C was fabricated by developing the co-precipitation method at room temperature without atmospheric nitrogen by changing the Fe$^{+2}$/Fe$^{+3}$ molar ratio from 1/2 to 2/3, thus improving the fabrication process without affecting the efficiency of magnetization momentum resulting from the small-sized NPs (Abdalla et al. 2011). In the present study, more simple and economic method was developed using ammonia and no nitrogen was needed as compared to using NaOH as previously described by Mascolo et al. (2013). Ammonium hydroxide reacts with water and dissociates into ammonia gas and hydroxide ions, and then the hydroxide ions precipitate the MNPs, while the ammonia gas provides the atmospheric nitrogen, preventing oxygen from oxidizing the iron salts into hematite (Abdalla et al. 2011). Furthermore, BC nanofibers were used as non-toxic biotemplate for the facile fabrication of novel BC/MNPs-C through one-step method, and the BC nanofibers were uniformly coated with Fe$\text{3O}_4$-NPs in aqueous suspension using the Cl$^-\text{ions}$. 0.2 M sodium chloride (NaCl) was added to the reaction forming a uniform net-like BC/MNPs-C with smooth surface. It is probably suggested that the thick coating of the MNPs is due to the reduction in zeta potentials ($\zeta$) of Fe$^{+2}$ and Fe$^{+3}$ in the presence of Cl$^-\text{ions}$. The negatively charged Cl$^-\text{ions}$ have a significant affinity to the iron salts surface, whereas the MNPs are positively charged; thus, they coordinate and stabilize the nanofibers to form thickly coated BC/MNPs-C. Also, the positive charge of iron ions binds to the hydroxyl group surface of BC via hydrogen bond and electrostatic attraction. However, if a halide ion (Cl$^-\text{ions})$ is present in the reaction suspension, it reduces the $\zeta$ of the iron ions and hence results in a large number of iron ions coating the BC nanofibers (Zhang et al. 2010).

Characterization of BC/MNPs-C using FTIR spectroscopy

FTIR spectrum of the bacterial cellulose (Fig. 1A) shows a strong absorption band at 3396.1 cm$^{-1}$ representing the hydroxyl OH group, and at 1638 cm$^{-1}$ that confirms the presence of carboxylic acid group (COOH). The band at 750 cm$^{-1}$ indicates its pure crystalline cellulose I$\beta$ structure (Foresti et al. 2017; Szymańska-Chargot et al. 2011). FTIR spectrum of the magnetite loaded on the BC (Fig. 1b) shows H–O–H bending vibration at about 1617 cm$^{-1}$, typical for the H$_2$O molecule (Nassar et al. 2011). The sample exhibits two intense bands, at 579.8 and 630.4 cm$^{-1}$ probably as a result of the stretching vibration mode that is associated with the metal–oxygen absorption band (Fe–O bonds) in the crystalline lattice of Fe$\text{3O}_4$ (Ahn et al. 2003) and characteristics of the $\alpha$-Fe$_2$O$_3$ (Barrón and Torrent 1996). These bands are characteristic for all spinel structures, especially for ferrites. The band at 1400.6 cm$^{-1}$ is characteristic to the $M_{\text{Tetrahedral}}$ resonance with oxygen which is related to the Fe–O group (Sun et al. 2007). The broadband at 3361.5 cm$^{-1}$ is assigned to OH adsorption on the Fe$_2$O$_3$ surface; the decrease in the hydrogen bonding band at 2360.4 cm$^{-1}$ is probably due to the formation of magnetite on the BC surface (Fig. 1b). The overall results obtained for the FTIR pattern confirmed the existence of MNPs on the BC nanofibers (Fig. 1).

X-ray diffraction and crystal structure pattern

Crystallinity of the bacterial cellulose (BC) in the nanocomposites was partly destroyed because of the formation of nanoparticles (Zhou et al. 2009). The X-ray diffraction pattern (XRD) of the fabricated magnetite nanoparticles (MNPs) (Fig. 1c) showed peaks at 2$\theta$ = 18.362, 30.344, 35.634, 43.415, 57.264 and 62.866 that is assigned to 111, 220, 311, 222, 400 and 511, respectively, and match with the standard magnetite diffraction pattern of magnetite Fe$\text{3O}_4$ according to the Joint Committee on Powder Diffraction standards (JCPDS, reference 88-0315) (Almeida et al. 2014). In addition, Zhou et al. (2009) reported that the relative intensity of diffraction for the MNPs increases with increasing the concentration of its precursors (FeCl$_2$ and FeCl$_3$), indicating an increase in the nanophase loading in the cellulose matrix. Similar XRD data for the MNPs were previously described by Giraldo et al. (2013) and Zhou et al. (2009). The resulting MNPs mean particle diameter was 14 nm as calculated from the Scherrer equation with characteristics of the bulk magnetite crystallite phase, suggesting the nanocrystallite nature of the fabricated MNPs (Zhou et al. 2009).

Magnetic properties of the fabricated BC/MNPs-C

Typical magnetization loops of the fabricated MNPs with no reduced remanence and coercive (Fig. 2a) were obtained from the VSM hysteresis curve at 250 °C (Cudennec and Lecerf 2006). It shows the magnetic hysteresis loops at 0 K saturation moments, whereas Ms value, the indicator of the magnetic properties, was 55.15 emu g$^{-1}$ at 25 kOe. The complete reversibility of the magnetization process confirms
the super-paramagnetic behavior of the fabricated MNPs (Cudennec and Lecerf 2006).

**Surface area and pore size of the fabricated BC/MNPs-C**

The specific surface area and pore volume were measured by Brunauer–Emmett–Teller method (BET) and found to be 85.68 m$^2$ g$^{-1}$ and 0.217 cm$^3$ g$^{-1}$, respectively. Results in Fig. 2 show the nitrogen sorption isotherms of the MNPs along with the Barrett–Joyner–Halenda (BJH) pore size distribution plot, which suggest that the networks were basically mesoporous with pore sizes mostly < 60 nm and a pore size distribution centered around 27 nm (Fig. 2). According to the International Union of Pure and Applied Chemistry (IUPAC) classification, MNPs have a type II sorption pattern. These results indicate that the sorption relation of MNPs-C can be represented by a sigmoidal shape, which is characteristic of type II isotherm (Fig. 2).
The adsorption amount of N\(_2\) for MNPs increased gradually with an increase in relative pressure in the region of 0 < \(P/P_0\) < 0.8, and in this region the adsorption/desorption curves were overlapped, revealing the presence of small micropores with monolayer adsorption. Then, N\(_2\) adsorption increased sharply at \(P/P_0 > 0.8\) due to the mesoporous structure of the BC almost disappeared; this has been probably attributed to the in situ co-precipitation of MNPs inside the micropores of the BC matrix (Fig. 3b), and because of the strong interaction between the MNPs and the BC matrix, the MNPs were dispersed in the BC forming a stable cluster structure (Guan et al. 2012; Zhou et al. 2009). SEM of the fabricated BC/MNPs-C using BC as a biotemplate (Fig. 3b) showed that the addition of MNPs made the surface of the adsorbent composite denser and compact than that of pure BC.

Briefly, during MNPs fabrication, the BC was immersed into a mixture of aqueous FeCl\(_2\) and FeCl\(_3\); the iron ions effectively diffuse and then adsorbed into the BC micropores; these ions were connected to the hydroxyl groups of BC by hydrogen bonds and other coordinating bonds (Zhou et al. 2009). When the BC/adsorbed iron ions were immersed in the NH\(_4\)OH solution, the basic hydrolysis of the iron ions led to the formation of an iron oxide NPs colloidal solution, and the BC turned darker because of the formation of MNPs. The microporous structure and the abundance of OH groups in BC matrix played an important role in the growing and stabilization of the MNPs and prevented the growth of larger particles. Therefore, the Fe\(_3\)O\(_4\) nanocomposite formed a compact morphology (Fig. 3b); these results were consistent with XRD for the standard Fe\(_3\)O\(_4\) pattern (JCPDS, reference 88-0315). Similar SEM images and XRD pattern of the iron oxide nanocomposite were obtained by Guan et al. (2012) and Zhou et al. (2009). TEM analyses of the fabricated BC/MNPs-C showed a polygonal-shaped BC/MNPs-C with an average diameter of 6–14 nm (Fig. 3c, d). Overall, the unique microporous structure and the presence of ether and hydroxyl groups of BC nanofibers constitute an effective nanoreactor for in situ synthesis of MNPs (Guan et al. 2012). These results are in agreement with those obtained from the Scherrer equation and with the XRD pattern presented in Fig. 1.

### Effect of pH and contact time

The pH of an aqueous solution is a controlling parameter for the adsorption process of heavy metals (Giraldo et al. 2013; Santhosh et al. 2016). The adsorption efficiency of Sb (III) ions increased from 20 to 75% by increasing the pH value...
from 2 to 11 (Fig. 4). The magnetite surface is covered with hydroxyl groups (Fig. 1); at pH values higher than the point of zero charge (PZC), the adsorbent surface becomes negatively charged, and by increasing the pH values it becomes more negative. Therefore, the positively charged Sb (III) species can ion exchange and/or complex with the oxygenated surface functional groups (Rangel-Mendez and Sreat 2002). Giraldo et al. (2013) reported that the proton ion concentration in the media has great effect on the removal process of heavy metals. This has been probably attributed to the formation of surface complexes between the functional groups of the sorbent (Fe-OH) and the Sb (III) ions. At $pH_{\text{pzc}}$ lower than 6, the adsorbent surface is positively charged and the adsorption depends on ion exchange due to the size of hydrated ionic radii (Leng et al. 2012). $\text{Sb}^{3+} < \text{H}^+$ and, hence, Sb (III) ions have the lowest hydrated ionic radius and highest capability to complete proton, consequently the highest comparative adsorption capacity; therefore, the adsorption of Sb (III) ions is strong at high pH value of 11 (Leng et al. 2012). On the other hand, when $pH_{\text{pzc}}$ is higher than 6 the MNPs surface is negatively charged and the Sb (III) ions are attached to the adsorbent surface via electrostatic attraction as previously reported (Leng et al. 2012). Moreover, the magnetite is an amphoteric solid, which can develop charges in the protonation/deprotonation reactions of the Fe-OH on the surface (Wang et al. 2010). Surface hydroxyl groups

Fig. 3 SEM image of bacterial cellulose nanofibers produced by *Gluconacetobacter xylinus* (a), Fe$^{2+}$ and Fe$^{3+}$ co-precipitate in the BC micropores to form dense cluster nanocomposite (a'), fabricated BC/MNPs-C (b), and TEM image of fabricated BC/MNPs-C (c, d)
protonate/deprotonate to generate surface charge (FeOH$_2^+$ or FeO$^-$) that functions at pH values below or above the $pHpzc$, respectively. At $pHpzc$, the charge of MNPs is neutral due to equal number of FeO$^-$ and FeOH$_2^+$ groups. At pH < $pHpzc$, the FeOH$_2^+$ groups dominate over the FeO$^-$ groups, while at pH > $pHpzc$, the number of FeO$^-$ increases and the MNPs may adsorb either negatively or positively charged species by electrostatic attraction depending on the medium pH (Giraldo et al. 2013; Rajput et al. 2016; Wang et al. 2010). Nevertheless, Shan et al. (2014) reported that the removal of Sb (III) ions using hematite-coated MNPs was not obviously affected over a wide pH ranging from 3 to 11.

Additionally, the equilibrium time is considered as one of the major engineering parameters for economical/practical applications, such as wastewater treatment (Leng et al. 2012). Results in Fig. 4 showed that Sb (III) ions removal takes place in two phases; initially, the metal uptake rate increased significantly from 50 to 61% within 30 min. Then, it increased slowly by time, and the removal rate gradually approached an equilibrium condition within 60 min, and 75% total removal after 120 min. The initial rapid adsorption is probably due to external surface adsorption; since nearly all of the adsorption sites of BC/MNPs-C exist on the exterior of adsorbent (Zhang et al. 2010). After 60 min, Sb (III) ions removal tends to be in equilibrium, where the surface adsorption sites were exhausted and the remaining vacant sites were difficult to be occupied by the cation due to repulsive forces between the adsorbate on both the solid and bulk phases (Lee et al. 2016; Zhang et al. 2010). In contrast, Leng et al. (2012) reported longer equilibrium time (> 4 h) using graphene as an adsorbent for the Sb (III) ions from aqueous solution. Similar results were reported by Lee et al. (2016) for the removal of As (V) and Sb (V) using MNPs-supported layered hydroxide nanocomposites where their removal process reached equilibrium within 120 min.

**Kinetic studies, adsorption isotherm and mechanism**

The kinetic models are quite helpful to explain the mechanism of metal adsorption onto the adsorbent surface. Adsorption mechanism and the rate-controlling step of metal ions can be explained by different kinetic models, including pseudo-first-order, pseudo-second-order, diffusion or intraparticle diffusion kinetic models (Nagarajah et al. 2017). The obtained adsorption data (Fig. 5) do not fit the pseudo-first-order kinetic model, whereas the pseudo-second-order

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**Fig. 4** Effect of contact time (A) and pH (B) on the adsorption of Sb (III) ions by fabricated bacterial cellulose/magnetite nanoparticles composite (BC/MNPs-C), at $T=28^\circ$C

**Fig. 5** Pseudo-first-order kinetic for the adsorption of Sb (III) ions on fabricated BC/MNPs-C. (A) pseudo-second-order kinetic for the adsorption of Sb (III) ions (B) at $T=28^\circ$C
was able to adequately describe the adsorption with 
\( R^2 = 99.93\% \) (Fig. 5 and Table 1) and constant \( K_2 = 0.23 \text{ g mg}^{-1} \text{ min}^{-1} \). The obtained results (Fig. 5) indicate that the adsorption of Sb (III) ions onto the BC/MNPs-C may be attributed to the chemisorption forces, involving valence forces through the exchange or sharing of electrons between the nanosized metal oxide and the heavy metal ions (Araneda et al. 2008). On the other hand, Gupta et al. (2017) reported that a novel binary chitosan–SnO\(_2\) nanocomposite was prepared and used as photocatalyst to degrade 2 model dyes, such as rhodamine B and methyl orange under different UV wavelengths. The prepared binary chitosan–SnO\(_2\) (50:50) nanocomposite showed superior degradation efficiency compared with pure SnO\(_2\) and binary chitosan–SnO\(_2\) (75:25) nanocomposite owing to its high crystallinity and surface area with small particle size; the photocatalysis kinetics data followed the first-order model. Similarly, Rajput et al. (2016) reported that the adsorption kinetics of lead and chromium using MNPs fitted pseudo-second-order kinetic model and the adsorption rate was dependent on the number of MNPs surface sites.

Four adsorption isotherm models, including Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R), were discussed comparatively to describe the adsorption process of Sb (III) ions onto the BC/MNPs-C (Fig. 6 and Table 1). The Langmuir adsorption equation (Eq. 3) is one of the most commonly used isotherm equations for modeling equilibrium data in the solid–liquid systems (Kumar et al. 2016). Adsorption isotherm of Sb (III) ions onto the BC/MNPs-C follows Langmuir isotherm (Fig. 6), which assumes uniform energies of adsorption on the surface.

### Table 1 Adsorption isotherm and kinetics models of Sb (III) ions on BC/MNPs-C at \( T = 28\,\text{°C} \), adsorbent concentration = 50 mg, Sb (III) concentration = 200 mg/L

<table>
<thead>
<tr>
<th>Isotherm model parameters</th>
<th>Kinetic model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir isotherm</strong></td>
<td><strong>Pseudo-first-order model</strong></td>
</tr>
<tr>
<td>( q_m )</td>
<td>( k_1 )</td>
</tr>
<tr>
<td>( K_L )</td>
<td>( q_e )</td>
</tr>
<tr>
<td>( R_L )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>18.69</td>
<td>0.0026</td>
</tr>
<tr>
<td>0.147</td>
<td>17.7</td>
</tr>
<tr>
<td>0.13</td>
<td>99.73</td>
</tr>
<tr>
<td>98.35</td>
<td></td>
</tr>
<tr>
<td><strong>Freundlich isotherm</strong></td>
<td><strong>Pseudo-second-order model</strong></td>
</tr>
<tr>
<td>( K_F ) (L g(^{-1}))</td>
<td>( K_2 )</td>
</tr>
<tr>
<td>( n )</td>
<td>( q_e )</td>
</tr>
<tr>
<td>( R^2 )</td>
<td></td>
</tr>
<tr>
<td>229.72</td>
<td>0.0059</td>
</tr>
<tr>
<td>−1.4532</td>
<td>38.6</td>
</tr>
<tr>
<td>97.92</td>
<td>99.93</td>
</tr>
<tr>
<td><strong>Temkin isotherm</strong></td>
<td><strong>Intraparticle diffusion model</strong></td>
</tr>
<tr>
<td>( b )</td>
<td>( K_1 )</td>
</tr>
<tr>
<td>( K_T ) (L/mg)</td>
<td>( C ) (mg g(^{-1}))</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>( \alpha )</td>
</tr>
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<td>24.257</td>
</tr>
<tr>
<td>1.0337</td>
<td>0.1396</td>
</tr>
<tr>
<td>98.91</td>
<td>k(_0)</td>
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<tr>
<td></td>
<td>20.309</td>
</tr>
</tbody>
</table>

### Fig. 6 Langmuir isotherm for the adsorption of Sb (III) ions on BC/MNPs-C (a), Freundlich isotherm (b), Temkin isotherm (c), Dubinin–Radushkevich isotherm (d) at \( T = 28\,\text{°C} \)
with no lateral interaction between the adsorbate molecules (Kumar et al. 2016). The Langmuir sorption capacity of Sb (III) was 18.69 mg g\(^{-1}\) at 28 °C (Table 1) which is comparable to that of the commercial Fe\(_3\)O\(_4\) nanoparticles (Shan et al. 2014). Similarly, Yu et al. (2016) reported that the Langmuir sorption capacity of Co (II) and Cd (II) was 18.85 and 14.15 mg g\(^{-1}\), respectively, at 20 °C using magnetite/sepiolite composite. However, Shan et al. (2014) reported that the sorption capacity of Sb (III) was 36.7 mg g\(^{-1}\) using hematite-coated MNPs. In the present study, the adsorption capacity of the fabricated BC/MNPs-C was higher than some adsorbents, such as multi-walled carbon nanotubes (0.33 mg g\(^{-1}\)) < bentonite (0.56 mg g\(^{-1}\)) < Fe\(_2\)O\(_3\)-modified carbon nanotubes (6.23 mg g\(^{-1}\)) < graphene (8.06 mg g\(^{-1}\)) followed by hydrous oxide of iron (12.2 mg g\(^{-1}\)) and hydrous oxide of manganese (17.1 mg g\(^{-1}\)) (Leng et al. 2012; Shan et al. 2014). The separation factor “\(R_L\)” and regression coefficient “\(R^2\)” calculated by Langmuir isotherms model were 0.13 (< 1) and 0.983, respectively (Fig. 6 and Table 1), indicating a favorable and monolayered coverage of the Sb (III) ions onto the BC/MNPs-C surface as reported previously by Kumar et al. (2016) using SnO\(_2\)-NP adsorbents to remove lead and cadmium from aqueous solution. Similarly, Nagarajah et al. (2017) reported that heavy metals such as lead, copper and cadmium were adsorbed onto homogeneous functional groups of nanostructured magnesium oxide-coated magnetite composite, and their adsorption isotherm follows Langmuir isotherm model. In addition, Nekouei et al. (2015) prepared a new nanoadsorbent, namely copper oxide NPs, loaded on activated carbon and used it to remove acid blue 129 dye; the pseudo-second-order kinetic equation described the adsorption data, and the Langmuir model provides a better correlation of the experimental data. Similarly, the adsorption processes of Auramine-O by ZnS:Cu nanoparticles loaded on activated carbon was investigated by Asfaram et al. (2015) and also the kinetics data followed Langmuir isotherm and pseudo-second-order model.

The Freundlich isotherm constants (\(K_F\)) and \(n\) were determined from the intercept and slope of log \(q_e\) versus log \(C_e\) plot (Fig. 6, Table 1). Isotherms with \(n > 1\) are classified as L-type isotherms that reflect a high affinity between both the adsorbent and adsorbate which is indicative of chemisorption (Tan and Xiao 2009). The poor agreement between experimentally observed equilibrium adsorption and that derived using Eq. (3) suggests that the adsorption of Sb (III) ions onto the BC/MNPs-C did not follow Freundlich or Temkin isotherms (Tan and Xiao 2009). The D-R isotherm parameters \(\beta\) and \(q_d\) were calculated using the slope and intercept of plots of \(\ln q_e\) versus \(e^2\). The \(q_d\) values are not consistent with the \(q_m\) values that were determined for the Langmuir isotherm (Table 1 and Fig. 6). The correlation coefficients magnitude for D-R isotherm was low (0.87) which suggests that Sb (III) ions adsorption onto BC/MNPs-C is not a physical process (Boparai et al. 2011). Furthermore, Weber–Morris intraparticle diffusion model has been used to determine if intraparticle diffusion is the rate-limiting step (Unuabonah et al. 2007). According to this model, a plot of \(q_t\) versus \(t^{1/2}\) (Fig. 7a) should be linear if intraparticle diffusion is involved in the adsorption process and if the plot passes through the origin, then intraparticle diffusion is the sole rate-limiting step. It has also been suggested that in instances when \(q_t\) versus \(t^{1/2}\) is nonlinear, then two or more steps govern the adsorption process (Unuabonah et al. 2007). The multilinearity of the plot for the adsorption of Sb (III) ions onto the BC/MNPs-C (Fig. 7a) suggests that adsorption occurred in three phases. The initial steeper section represents surface or film diffusion; the second linear section represents a gradual adsorption stage
where intraparticle or pore diffusion is rate-limiting; and, the third section is the final equilibrium stage. Since the $q_t$ versus $t$ plot did not pass through the origin, the intraparticle diffusion was not the sole rate-limiting step. Accordingly, there were three processes controlling the adsorption rate, but only one was rate-limiting in any particular time range (Unuabonah et al. 2007). The slope of the second linear section was used to calculate the intraparticle diffusion rate constant ($k_i$). The value of the intercept $C$ provides information correlated with the thickness of the boundary layer. Larger intercepts propose that surface diffusion has a greater role as the rate-limiting step. Also, it is essentially important to determine the slowest step in the adsorption process which is a rate-controlling step. The Bangham plot (Fig. 7b and Table 1) suggests that the intraparticle diffusion was of a consequence, but was not the sole rate-determining step. Nevertheless, the Boyd plot (Fig. 7c and Table 1) confirms that the external mass transfer was rate-controlling step since the plots did not pass through the origin (Kumar et al. 2016).

**Regeneration studies**

Regeneration of the adsorbent is an essential parameter in the adsorption process, due to cost-rising of raw materials used in wastewater treatment (Hu et al. 2006). For recovery studies, results shown in Fig. 8 reveal that the adsorption efficiency of Sb (III) ions onto the fabricated BC/MNPs-C was not affected and it remained approximately constant for 4 successive cycles, which indicates that the active sites on the fabricated BC/MNPs-C surface are reversible (Hu et al. 2006). Therefore, the fabricated BC/MNPs-C exhibited great potential for repeated removal of Sb (III) ions from contaminated water with a simple and convenient magnetic separation process.

**EDXS analysis and adsorption mechanism**

To confirm the elements present in the sample, a typical energy-dispersive X-ray spectrometry (EDXS) measurement of the BC/MNPs-C was done, and Sb (III), Fe and O were clearly detected (Fig. 9). The adsorption mechanism of Sb (III) ions was investigated using EDXS. The amount mass percentage of the Sb (III) was 12.8% of the total mass. The mechanism of Sb (III) ions adsorption onto the surface of BC/MNPs-C is proposed via the electrostatic attraction at high pH (Wang et al. 2007). When pH > pH_{ZPC}, excess of OH$^{-1}$ ions exists in aqueous solution and Sb (III) ions react with the OH$^{-1}$ to form Sb (OH)$_3$ as shown in Eq. (14) and Sb (OH)$_3$ precipitate.

$$\text{Sb}^{(III)^{3+}} + 3\text{OH}^{-1} \rightarrow \text{Sb(OH)}_3\downarrow \quad (14)$$

However, at pH < pH_{ZPC}, the surface is positively charged and the adsorption of Sb (III) ions on the surface of BC/MNPs-C occur by the electron affinity. If Sb (III) ions affinity is higher than that of H$^+$, Sb (III) ions can replace H$^+$ from the hydrolyzed magnetite surface and ion exchange participates in this process (Giraldo et al. 2013; Rangel-Mendez and Streat 2002).

In addition, the ether oxygen and the hydroxyl group of BC nanofibers not only anchor Sb (III) ions tightly on the BC/MNPs-C surface via ion–dipole interactions, but also stabilize the Sb (III) ions by strong interaction with their surface hydroxyl groups (Guan et al. 2012). The Sb (III) ions could be adsorbed on BC/MNPs-C mainly by electrostatic attraction and surface complexation (Guan et al. 2012). Similar mechanism was proposed by Guan et al. (2012) for the adsorption of cadmium ions using cellulose/magnetite nanocrystals. The SEM analysis (Fig. 9) verifies the adsorption of Sb (III) ions onto the surface of BC/MNPs-C with a white amorphous Sb (III) existing on the surface of BC/MNPs-C, confirming that the adsorption process depends on electrostatic attraction (Wang et al. 2007).

**Conclusion**

- In this work, BC/MNPs-C was fabricated using BC nanofibers as non-toxic biotemplate and was used for antimony removal from aqueous solution for the first time.
- The complete reversibility of the magnetization process confirms the super-paramagnetic behavior of the fabricated BC/MNPs-C.
- The fabricated BC/MNPs-C exhibited great potential for repeated removal of antimony in a relative short
time (≤ 60 min) with a simple, convenient magnetic separation process.

- The adsorption efficiency of antimony increased from 20 to 75% by increasing the pH from 2 to 11.
- Antimony was adsorbed on BC/MNPs-C mainly by electrostatic attraction and surface complexation.
- Regenerated BC/MNPs-C was reusable with nearly the same efficiency after 4 successive cycles.
- Overall, the fabricated BC/MNPs-C provides a new adsorbent material and it is expected to offer a cost-effective process for environmental pollution cleanup, due to its simple synthesis, eco-friendly process and reusability.

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Conflict of interest All authors declare that there are no financial/commercial conflicts of interest.

Abbreviations Sb (III): Antimony; AAS: Atomic absorption spectrometry; BC: Bacterial cellulose; EDX: Energy-dispersive X-ray; FETEM: Field emission transmission electron microscopy; FTIR: Fourier-transform infrared spectrum; Fe₃O₄: Magnetite; BC/MNPs-C: Bacterial cellulose/magnetite nanoparticles composite; SEM: Scanning electron microscope; XRD: X-ray diffraction

References


Fig. 9 The EDX spectra (a) and SEM image for Sb (III) adsorbed onto the BC/MNPs-C (b)


Mascolo MC, Pei Y, Ring TA (2013) Room temperature co-precipitation synthesis of magnetite nanoparticles in a large pH window with different bases. Materials 6(12):5549–5567


Rajput S, Pittman CU, Mohan D (2016) Magnetic magnetite (Fe3O4) nanoparticle synthesis and applications for lead (Pb2+) and chromium (Cr6+) removal from water. J Colloid Interface Sci 468:334–346


