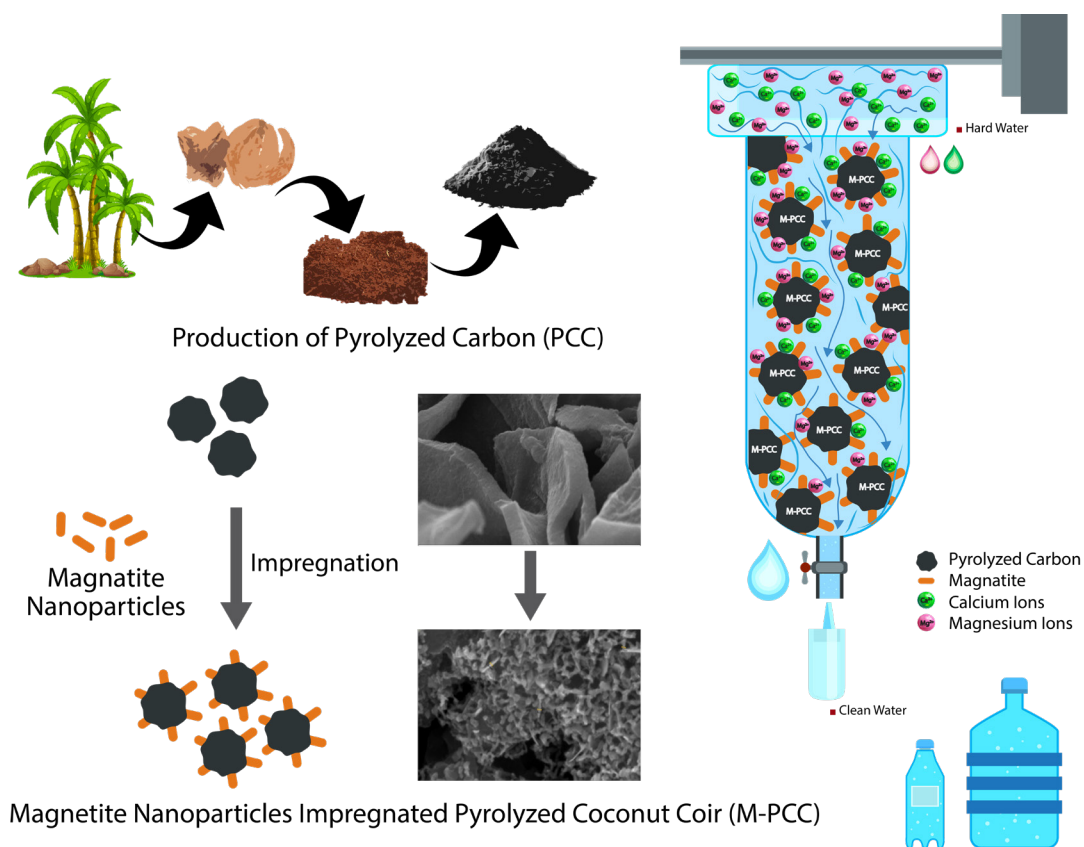# Magnetite nanoparticles impregnated pyrolysed coconut coir for water softening applications

B.M.D.S. Balasuriya, S.R.W.M.I.S. Bandara, N. Kottegoda and A.D.L.C. Perera*

Production of Pyrolyzed Carbon (PCC)

Magnatite Nanoparticles

Impregnation

Magnetite Nanoparticles Impregnated Pyrolyzed Coconut Coir (M-PCC)

Hard Water

M-PCC

Pyrolyzed Carbon
Magnatite
Calcium Ions
Magnesium Ions

Clean Water

Highlights

- One-pot *in-situ* synthesis of magnetite nanoparticles impregnated pyrolyzed coconut coir (M-PCC) is reported.
- PXRD, FT-IR, SEM and EDX validated the impregnation of magnetite into pyrolyzed coconut coir.
- Double filtration at pH of 6-8 reduced over 80% of the total hardness in natural hard water.
- M-PCC is more efficient in water softening than activated coconut coir.

RESEARCH ARTICLE

Magnetite nanoparticles impregnated pyrolysed coconut coir for water softening applications

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Abstract: Development of novel advanced materials for water softening applications is a timely need. Water softening efficiency of activated and pyrolyzed coconut coir (PCC) was found to be higher than that of activated carbon derived from coconut shell charcoal. For further enhancing the water softening capacity of PCC, magnetite nanoparticles impregnated pyrolyzed coconut coir (M-PCC) was synthesized by an *in-situ* one-pot synthesis method. In this approach, the raw coconut coir was dipped in a solution of 1.00 mol dm^{-3} FeCl$_3$, 1.00 mol dm^{-3} FeSO$_4$.7H$_2$O and 5.00 mol dm^{-3} NaOH followed by pyrolysis at $450\ °C$ under N$_2$ gas flow and evaluated its efficiency in water softening applications. The process parameters, including contact time, adsorbent dose and pH, were optimized using a representative natural water sample (total hardness - 370 mol L^{-1}). Characterization studies confirmed the successful impregnation of magnetite nanoparticles into pyrolyzed coconut coir. Powder X-ray diffraction and Fourier transform infrared spectroscopy confirmed the formation of magnetite phase and provided information on interactions with the carbon matrix. M-PCC thus prepared was capable of removing total hardness of natural hard water over 80% with an adsorbent dose of 0.6 g/50 mL at a water pH of 6–8 by double filtration. Therefore, it can be claimed that magnetite nanoparticles impregnated pyrolyzed coconut coir is suitable as an adept adsorption material in developing next-generation methodologies for restoring water softness.

Keywords: Coconut coir; magnetite nanoparticles; pyrolyzed coconut coir; water hardness.

INTRODUCTION

Hardness of water caused by excessive amounts of calcium and magnesium ions has led to a multitude of health and economic impoverishments worldwide. It adds unpalatability to the water and reduces the water quality, making people evade utilizing hard water. Therefore, it is crucial to remove hardness and improve palatability (Mengesha *et al*., 2018). Water hardness also induces many health issues and causes damage to electrical appliances and pipes (Gabrielli *et al*., 2006). Furthermore, excessive amounts of calcium produce kidney stones, whereas extreme quantities of magnesium cause diarrhoea and laxative effects (Akram and Rehman, 2018).

Therefore, reducing hardness in water has become a critical factor, and many methods such as membrane technology (Park *et al.*, 2007), electrochemical techniques (Zhi and Zhang, 2014), ion exchange (Li *et al.*, 2016), nano-filtration (Izadpanah and Javidnia, 2012) and adsorption (Sepehr *et al.*, 2013) have been widely used. Adsorption techniques are celebrated as an excellent strategy to remediate water hardness at present. The drawbacks of the other technologies include the requirement of higher capital and maintenance cost making them difficult to be implemented in rural areas. Furthermore, due to the non-selectivity of these techniques, they not only remove the required ions but also all others which require additional resources, yet producing excess solute-rich waste. In this regard, activated carbon is identified as an excellent candidate in treatment of hard water due to its high surface area, excellent porosity and desirable surface activity (Menéndez *et al.*, 1996). However, commercial activated carbon (AC) made of coconut shell charcoal is less effective in hardness removal. Although AC has been widely used as an adsorbent in water purification, especially, to remove toxic organic matter, colour and odour, it inherits some drawbacks, such as low adsorption rates and low efficiency, when adapted to water softening applications. Therefore, the development of low-cost novel advanced adsorbent materials for water softening is a timely need.

It has been reported that hardness removal efficiency of coconut shell activated carbon at nearly neutral pH of 6.3 for both synthetic and field collected water samples were 60% and 55%, respectively (Rolence *et al.,* 2014). Dev Bharadwaj *et al*. (2016) also reported that coconut shell activated carbon reduced the hardness of water by 52%. Further Hettiarachchi *et.al*. (2017) has reported that water softening efficiency of activated carbon derived from coconut coir dust (PCC) is higher than that derived from coconut shell.

Coconut coir dust is a widely available carbonaceous material in Sri Lanka as a by-product from coconut-based industries. Higher percentage of lignin present in coconut coir allows to maintain its framework even after pyrolysis by giving rise to the porous structure consisting of improved meso- and micro-pore structures and oxygen containing functional groups (Hettiarachchi *et al.*, 2016; Correa *et al.,* 2017). Viable alternatives for further enhancement of the

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adsorption capacity of the above locally derived PCC are to introduce effective surface modification approaches. Protonation, heat treatment and impregnation of metals and metal oxides are some surface modification methods reported to improve adsorption efficiency (Bhatnagar *et al.*, 2013). Impregnation of nanoparticles of metals/ metal oxides is another approach which modifies the surface of activated carbon by increasing the amount of surface oxygen atoms on activated carbon, providing more binding sites to different pollutants (Park *et al.*, 2019). Impregnation of metals, such as copper (Nastas *et al.*, 2013), iron (Shah *et al.*, 2015), silver (Chen *et al.*, 2017) and aluminium (Kazeem *et al.*, 2018) shows significantly high adsorption capacity. Among the metal oxide nanoparticles, magnetite (Fe_3O_4) has been gained immense attention due to its low production cost, eco-friendliness, non- toxicity, high photo stability and high efficiency. Magnetite has been used in previous studies to remove cations while it induces magnetic properties which offers added practical advantage in separating the filtered water (Azari *et al.*, 2015). Here, the development of magnetite nanoparticles impregnated pyrolyzed coconut coir, M-PCC is disclosed, as an efficient adsorbent material for remediation of water hardness. The synergistic quantum effects arising at the nano scale due to the surface functionalization of pyrolyzed coconut coir with magnetite nanoparticles have awarded these nano-hybrids enhanced adsorption properties and ease of removal after adsorption (Kahani *et al.,* 2007). The aim of this study is to synthesize magnetite nanoparticles impregnated pyrolyzed coconut coir (M-PCC), assess its applicability as an adsorbent for efficient water softening and compare with activated and pyrolyzed coconut coir (PCC) made by KOH activation (Balasuriya *et al.*, 2020).

MATERIALS AND METHODS

Materials

Coconut coir dust purchased from the local market in Peradeniya was used as the carbonaceous precursor for preparing M-PCC. Water samples were collected from three different locations in Sri Lanka, namely,Mahawa (GPS:7°49'13.19"N, 80°16'24.00"E), Thambuttegama (GPS: 8°9'40.67"N, 80°18'0.19"E) and Matale (GPS: 7°18'37.18"N, 80°37'53.94"E) having hardness values of about 370, 230 and 100 mg L^{-1} $CaCO_3$ equivalent, respectively. Unless otherwise indicated, all chemicals used were of analytical grade and were used as received. Metal ion salts $FeCl_3$ (98% assay), $FeSO_4.7H_2O$ (97% assay), and NaOH (98% assay) were used without further purification.

Preparation of adsorbent

The M-PCC was synthesized using *in-situ* one-pot synthesis method of precipitation reported by Le *et al.* (2019) with slight modifications. First, raw coconut coir was washed thoroughly with distilled water until the effluent color became clear and, dried in an oven at 105 °C for 24.0 h. Then, 200.00 mL of 1.00 mol L^{-1} $FeCl_3$ and 200.00 mL of 1.00 mol L^{-1} $FeSO_4.7H_2O$ were mixed well with dried coconut coir (30.00 g). The pH was adjusted to 9-11 by adding 5.00 mol L^{-1} NaOH solution dropwise and boiled

for one hour. The resultant product was separated and pyrolyzed at 450 °C for 1 h in a tube furnace under N_2 environment to obtain magnetite impregnated pyrolyzed coconut coir (M-PCC). Finally, the product was cooled and washed thoroughly with distilled water until the pH of the filtrate reached near seven and oven dried at 100 °C for 48 h before use.

Characterization of the adsorbent

Surface morphology analysis of the adsorbent was carried out by Scanning Electron Microscopy (SEM) using SEM Zeiss EVO at an accelerated voltage of 10 kV. Here, the sample set in an epoxy was placed in a high vacuum chamber and bombarded with a finely focused electron beam. Energy Dispersive X-ray (EDX) analysis was performed to identify the elemental composition of the adsorbent. It was carried out on sintered pellets using a Zeiss EVO scanning electron microscope in conjunction with EDX system.

Fourier Transform Infrared (FTIR) analysis to determine functional groups on the surface of adsorbents was carried out using SHIMADZU IR Prestige 21 spectrometer equipped with a Universal ATR accessory. The samples were placed on Diamond/ZnSe crystal plate and scanned from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} at room temperature.

In order to analyze the structure of crystalline materials and the chemical phase of the samples, Powder X-ray diffraction (PXRD) pattern of M-PCC was obtained by using SIEMENS D5000 Powder X-Ray diffractometer equipped with a Cu target metal and a Ni K_β filter operated at 40 kV and 40 mA X-Ray source with 2.00 deg min^{-1} scanning rate from 5.00°–80.00° (2θ) range.

Further, surface characterizations were carried out using zeta potential and point of zero charge. Zeta potential was measured on a zeta-potential analyzer (Horiba – SZ 100). In zeta potential measurement, 50.00 mL of 0.01 mol L^{-1} NaCl solution was added into a series of conical flasks and the solution pH was adjusted from 2.00 to 12.00 with 0.01 mol L^{-1} HCl or NaOH solution; then, 0.05 g of fine-ground M-PCC or PCC was added into each of the flasks, sealed and shaken at 25 °C for 24.0 h before measurements.

Fast titration method was used to determine the point of zero charge where $NaNO_3$ was used as the background electrolyte solution and three titrations were carried out using 30.00 mL of $NaNO_3$ solution of three different concentrations (1×10^{-1}, 1×10^{-2}, and 1×10^{-3} mol L^{-1}) containing 0.600-0.800 g of M-PCC samples. Solution was equilibrated with continuous magnetic stirring at a temperature of 303 K for 1.0 h and pH of the system was adjusted using 0.0443 mol L^{-1} NaOH. Thereafter, the suspension was titrated by addition of 0.0496 mol L^{-1} HNO_3 using auto titrating equipment. Then, the pH was recorded with respective HNO_3 volume added.

In order to obtain quantitative evidence on the porosity and surface area, Auto Flow BET+™ and Flo Win analyzer were used. Sample (0.5000 g) was degassed

at 350 °C for 45 min under N_2 flow at 0.50 mL s^{-1}, and the specific surface area was estimated with the aid of the following Brunauer-Emmett-Teller(BET) equation,

$$\frac{1}{W\left[\left(\frac{P_0}{P}\right)-1\right]} = \frac{1}{W_mC} + \frac{C\text{-}1}{(W_mC)}\left(\frac{P_0}{P}\right)$$

where W is the weight of gas adsorbed at a relative pressure, P/Po, and W_m is the weight of adsorbate constituting a monolayer of surface coverage. The term C, the BET C "constant", is related to the energy of adsorption in the first adsorbed layer and consequently its value is an indication of the magnitude or strength of the adsorbent/adsorbate interactions.

Inductively coupled plasma mass spectrometry (ICP-MS: iCAP™ 7400 ICP-OES Analyzer, Thermo Scientific) was used to determine the extent of impregnation of iron. Thermal digestion method was used to digest in the M-PCC samples. For measuring the leaching content of Fe, 0.200 g of M-PCC/PCC was treated with 10.00 mL of ultra-pure distilled water for 1.0 h. Next, 1.00 mL of the filtrate was diluted up to 5.00 mL and introduced to ICP-MS instrument to determine the contaminated Fe content.

Determination of total hardness using EDTA

A hard water sample was treated with 4.00 mL of pH 10 buffer, two drops of Erichrome Black T indicator and titrated against 0.01 mol dm^{-3} EDTA solution until the colour changed from wine red to sky blue. Total hardness was determined as $CaCO_3$ in ppm using ASTM D-1126 standard method.

$$\text{Total hardness as } CaCO_3 = \frac{(1000)\,(c)}{S}$$

where c = standard EDTA titre in cm^3 (for total hardness determination); S = sample size in cm^3.

Optimization of process parameters

Natural hard water samples collected from Mahawa, and Kurunegala, Sri Lanka were used in batch experiments under static conditions for the optimization of all process parameters. In the optimization experiment of contact time, 0.100 g of M-PCC was stirred at a rate of 150 rpm with 50.0 mL of hard water sample for 10 min. Then, it was filtered and the total hardness in the filtrate was determined using the EDTA titration method. This procedure was repeated at different stirring times (20, 30, 40, 50, 60, 75, and 90 min). In the optimization experiment of M-PCC dose, 0.100 g of M-PCC was stirred at a rate of 150 rpm with 50.00 mL of hard water sample for 30 min (optimized contact time). Then, it was filtered and the total hardness in the filtrate was determined using the EDTA titration method. This procedure was repeated with 0.200, 0.400, 0.500, 0.600, 0.800 and 1.000 g M-PCC dose. In the optimization experiment of pH, the above procedure was repeated with 0.600 g of M-PCC (optimized dose) and 30 min (optimized contact time) by varying the pH of hard water sample from 5–10 using HCl and NaOH solutions.

Single and double filtrations

After optimizing the process parameters, single and double filtration experiments using water samples collected from 3 different areas were carried out under optimized conditions of, 0.600 g of M-PCC in 50.00 mL of water with 30 min stirring time. In the single filtration, natural hard water samples collected from dug wells in Mahawa, Thambuttegama and Mathale areas, where the hardness levels were very high, moderate and low respectively, were treated once with M-PCC under the above optimized conditions, whereas, in the double filtration the filtrate collected in single filtration was treated again with 0.600 g of M-PCC under optimized conditions. For comparison, the above test was repeated using activated and pyrolyzed coconut coir (PCC). All the experiments were carried out at 25 °C in triplicate and natural hard water samples were used in all experiments.

RESULTS AND DISCUSSION

Characterization of M-PCC

Functional group analysis of M-PCC and PCC were carried out, and the results show that the characteristic structural properties of magnetite impregnated and non-impregnated carbon matrix made of coconut coir are very similar to each other. Moreover, the success of the magnetite impregnation in PCC was validated by the characteristic peaks of Fe_3O_4 in PXRD while FTIR further confirms the presence of Fe-O bonds in the surface of M-PCC.

FTIR spectra of M-PCC and PCC shown in Figure 1A indicate the presence of mainly stretching vibrations of O-H (3200 - 3600 cm^{-1}), C=O (1620 - 1830 cm^{-1}), C-O (1000 - 1320 cm^{-1}), and C-N (1080 - 1360 cm^{-1}) bonds. Other than the above-mentioned bands, in M-PCC, a prominent band appears at 580 cm^{-1} which is attributed to the stretching vibration of the Fe-O bond in Fe_3O_4 confirming the presence of magnetite.

PXRD is an effective characterization technique to obtain information on phase purity of materials. PXRD pattern of magnetite nanoparticles is presented in Figure 1B. The 2θ peaks appearing at 30.34°, 35.71°, 43.39°, 53.72°, 57.30°, 62.93° are attributed to the crystal planes (*220*), (*311*), (*400*), (*422*), (*511*), and (*440*) of magnetite respectively. The presence of sharp peaks suggests that magnetite appears as a well-crystalline phase, and the position and the relative intensity of the diffraction peaks match well with the standard PXRD data for magnetite (JCPDS No. 88 - 0866). The structure of crystal is found to be face centred cubic with unit cell parameter, a = 8.371 Å which is in agreement with the reported data (a = 8.393 Å). Using Scherrer's formula, the crystallite size of the synthesized Fe_3O_4 nanoparticles calculated referring to (111) plane is 11 nm. No peaks originating for any other crystalline phases are seen in this pattern, indicating the high purity of the synthesized magnetite nanoparticles. The characteristic broad asymmetric peak present in both observed diffraction profiles (Figure1B) around 23° reveals the amorphous nature of pyrolyzed coconut coir.
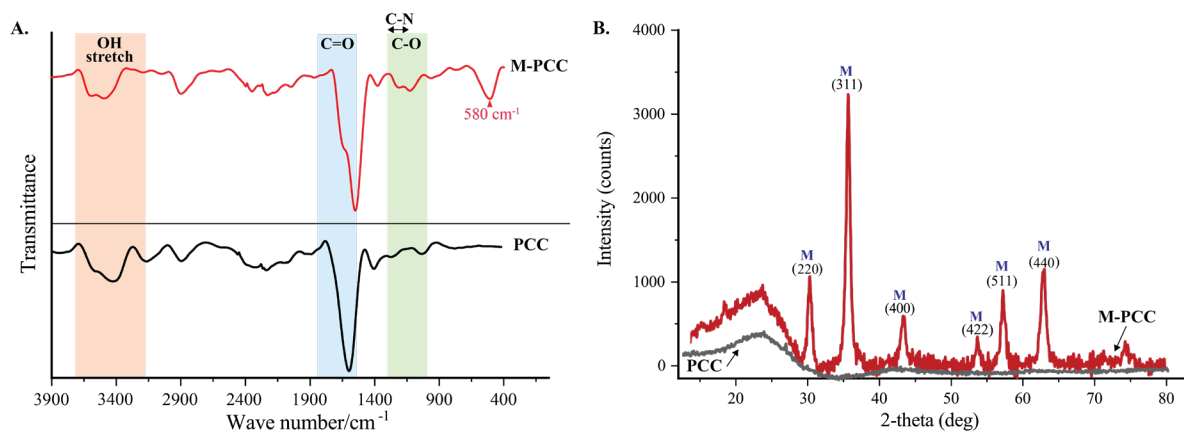
Figure 1: Comparison of the structural features of magnetite nanoparticles impregnated pyrolyzed coconut coir (M-PCC) and activated and pyrolyzed coconut coir (PCC). **A:** FTIR spectra of the M-PCC and PCC; **B:** Powder X-Ray diffraction patterns of M-PCC and PCC.
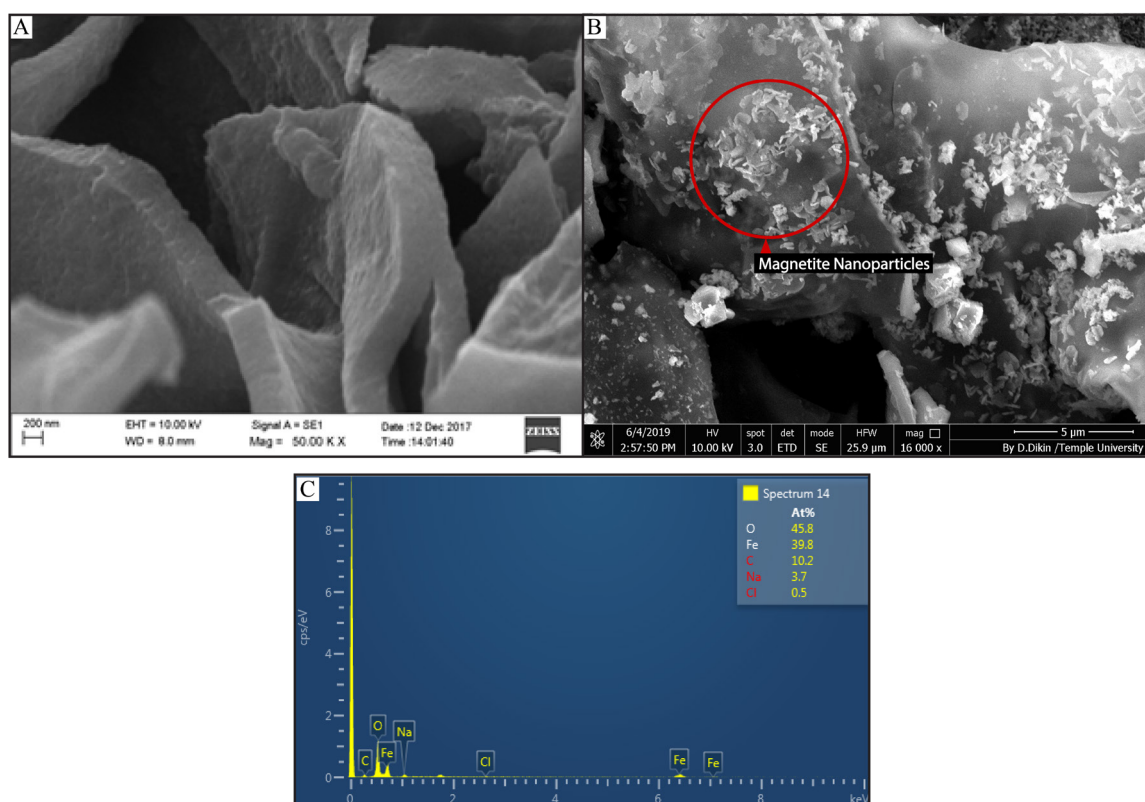

Figure 2: SEM images of activated and pyrolyzed coconut coir (PCC) are compared with magnetite impregnated pyrolyzed coconut coir (M-PCC). (A) PCC under 50,000× magnification; (B) M-PCC image under 16,000× magnification; (C) EDX spectrum of M-PCC.

SEM image of PCC in the absence and presence of magnetite nanoparticles are shown in Figures 2A and 2B respectively. The surface morphology of the PCC shows presence of micro- and meso- pores (Figure 2A) whereas, in M-PCC (Figure 2B) rod shaped magnetite nanoparticles are distributed randomly on the surface of the M-PCC causing a rough and coarse surface. Such surface modification may promote the increase in reactive sites thus leading to higher adsorbent capacity. The average diameter of nanorods is in the range of 28 - 32 nm.

The analysis of EDX (Figure 2C) ensured the presence of elements, such as carbon, oxygen, and iron, in the final product. The peaks for iron in Figure 2C confirm the presence of Fe (39.8%) on the M-PCC surface. The analysis also reveals the presence of 10.2% of C, 45.8% of O and traces of Na (3.7%) and Cl (0.5%). Thus, this analysis suggests that about 39.8% of M-PCC surface be occupied by Fe in the form of Fe_3O_4. All the above data confirm the successful impregnation of magnetite nanoparticles in PCC.
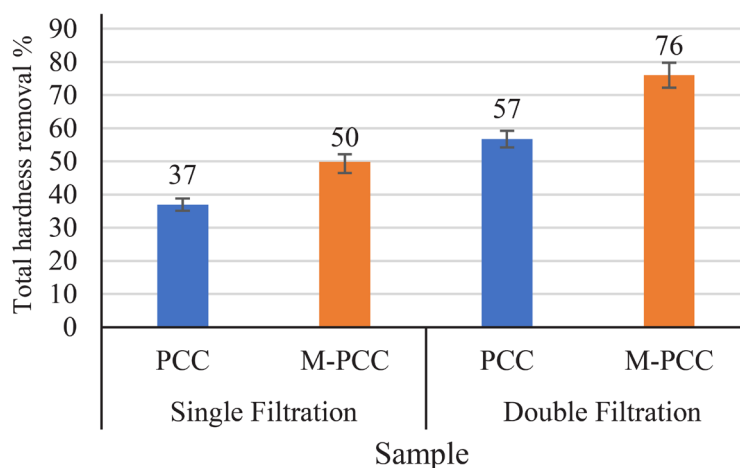
Comparison of the specific surface area obtained from BET isotherms, pH at the point of zero charge, zeta potential values, impregnated Fe amount and Fe leaching amount to ultra-pure water obtained by ICP-MS analysis of both M-PCC and PCC (prepared by KOH activation) are shown in Table 1.

Table 1: Surface characteristics and the amounts of Fe impregnated and leaching to water from M-PCC and PCC.

Parameter	M-PCC	PCC
Specific surface area (BET isotherms / $m^2 \, g^{-1}$)	239.969	100.285
pH_{pzc}	5.29	6.58
Zeta potential (mV)	-87	-53
Fe content (ICP-MS Analysis / wt%)	1.5	5.0×10^{-4}
Fe leaching amount (ICP-MS Analysis / mg L^{-1})	9.52×10^{-2}	-

Table 2: Initial pH and % hardness removal by M-PCC in single and double filtrations.

Natural water sample	Initial pH of the sample	Initial hardness / mg L^{-1} ($CaCO_3$ eq)	Hardness removal (%) by single filtration	Hardness removal (%) by double filtration
Mahawa area	8.73	368	43	71
Thambuttegama area	8.15	232	62	81
Matale area	8.11	102	45	76

Figure 3: Comparison of total hardness removal by PCC and M-PCC in single and double filtrations.

The point of zero charge determines the condition when the electrical charge density on a surface is zero (Menéndez *et al.*, 1995). The pH of point of zero charge (pH_{pzc}) of activated carbon depends on the chemical and electronic properties, and the functional groups on its surface. It is clear that magnetization has decreased the pH_{pzc} of the pyrolyzed coconut coir improving the adsorbent capacity for positive ions within a wide range of pH. With the increase in the magnitude of the zeta potential, the stability of the colloidal solution increases. According to Table 1, zeta potential of PCC has increased with the magnetization suggesting an increase in the colloidal stability of M-PCC. The BET theory explains the physical adsorption capacity of gas molecules on a solid surface and serves as the basis for an important analytical technique for the determination of specific surface area of materials. After the modification, the BET surface area of M-PCC has been increased, enhancing the adsorption capacity. ICP-MS data further confirm the impregnation of magnetite particles into PCC. According to WHO standards, highest desirable level of Fe is 0.3 mg L^{-1} in drinking water and the maximum permissible level is 1.0 mg L^{-1}. M-PCC contamination results only 9.52×10^{-2} mg L^{-1} when 1.00 L of water sample is treated with 20.00 g of M-PCC for 1.0 h. Therefore, the contamination levels of water due to leaching of prepared M-PCC are in the safe range.

Optimization of process parameters

Optimization of contact time, amount of adsorbent (M-PCC) and pH on hardness removal were carried out using natural hard water samples collected from Mahawa area. The maximum hardness removal was obtained after 30 min of stirring time. The maximum percentage removal of 44% was achieved with M-PCC dosage of 0.600 g. The total hardness removal increased with the increase in pH. The surface of the adsorbent is surrounded by hydrogen ions and it hinders the adsorption of cations responsible for hardness (Ca^{2+} and Mg^{2+}) on to the binding sites of adsorbent through repulsion. With the increase of pH the number of hydrogen ions decreased and other cations get a higher chance to adsorb into the surface (Rolence *et al.*, 2014). This is also related to the pH of point of zero charge (pH_{pzc}) of the surface, which is 5.29 for M-PCC, and indicates that the optimum pH for hardness removal should be above this point.

Although the highest hardness removal efficiency of 63% was achieved at pH of 10, it does not seem to be practical, economical and safe as it requires an increase of pH of water before softening and neutralize after softening by adding pH adjusting chemicals. Thus, for the sake of providing safe water in an economical way, the water softening efficiency was determined (43 - 62%) at the pH of natural hard water [pH ≈ 8 (Table 2)] in single filtration.

The efficacy of the removal of total hardness using M-PCC was assessed using the representative samples from dug wells in Mahawa, Thambuttegama, and Matale areas. The results (Table 2) show the percentage removal of hardness using M-PCC under the optimized conditions at normal pH of hard water samples. Double filtration has increased the softening efficiency of M-PCC by 19 - 31%.

Comparison of M-PCC with PCC

Figure 3 shows the average percentages of total hardness removal by both PCC (prepared by KOH activation) and M-PCC from the three water samples given in Table 2 under optimum conditions and at initial pH of the collected water samples. It has been determined that M-PCC shows higher performance in removal of hardness than PCC does in terms of both single and double filtrations. This is because magnetite nanoparticles in M-PCC increases the surface oxygen atoms which cause the increment of surface binding sites for the cations in hard water (Park *et al.*, 2019).

CONCLUSION

M-PCC is an effective adsorbent in water softening applications, and therefore, it can be used as an economically feasible filter material for removal of hardness. Moreover, due to its inherent magnetic properties, M-PCC can be easily removed from the filter medium. The results obtained by SEM, EDX, PXRD and FTIR analyses imply that the *in-situ* one-pot synthesis method adapted in the present study has successfully impregnated magnetite nanoparticles in pyrolyzed coconut coir. The contact time of 30 min and an adsorbent dose of 0.600 g per 50 mL of hard water, are the optimized conditions for the maximum total hardness removal (62%) in single filtration, whereas, double filtration enhances the removal of total hardness over 80% at the normal pH of natural hard water. Based on the results obtained in the study, it is clear that M-PCC is more efficient in removal of water hardness than PCC due to the presence of more binding sites.

ACKOWLEDGMENT

DECLARATION OF CONFLICT OF INTEREST

The authors have no conflicts of interest regarding the publication of this paper.

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