ประสิทธิภาพการดูดซับด้วยถ่านชีวภาพยูคาลิปตัสแบบยึดติดคอลัมน์เพื่อกำจัดแมงกานีสในน้ำบาดาล

Adsorption performance of eucalyptus biochar fixed-bed column for manganese removal from groundwater

อรชพร วิลามาศ[1*], สร้อยดาว วินิจนันทรัตน์[1,2] และ อนวัช พินิจศักดิ์กุล[3]
Arachporn Wilamas[1*], Soydoa Vinitnantharat[1,2] and Anawat Pinisakul[3]

Received: 18 October 2022 ; **Revised**: 16 December 2022 ; **Accepted**: 13 February 2023

บทคัดย่อ

การกำจัดแมงกานีสในน้ำใต้ดินปนเปื้อนด้วยระบบการกรองเป็นระบบที่นิยมใช้มากที่สุด งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาประสิทธิภาพของคอลัมน์แบบยึดติดกับที่ ที่ใช้ถ่านชีวภาพยูคาลิปตัสและถ่านชีวภาพยูคาลิปตัสที่ปรับปรุงพื้นผิวด้วยด่างทับทิมเป็นสารกรองในการกำจัดแมงกานีสจากน้ำใต้ดินที่ความเข้มข้น 0.723 $\pm$ 0.002 มก./ลิตร โดยป้อนน้ำเข้าสู่ด้านบนของคอลัมน์กรองระดับห้องปฏิบัติการอย่างต่อเนื่องอัตราการไหล 5 ลิตร/วัน เก็บตัวอย่างน้ำที่เวลาต่าง ๆ จนครบ 24 ชั่วโมง ใช้แบบจำลองโธมัสและยุน-เนลสัน เพื่ออธิบายความสามารถในการดูดซับแมงกานีส ผลการศึกษาพบว่าถ่านชีวภาพยูคาลิปตัสมีความสามารถในการดูดซับเท่ากับ 1.812 มก./กรัม สูงกว่าถ่านชีวภาพยูคาลิปตัสที่ปรับปรุงพื้นผิวเนื่องจากมีค่าไอโอดีนนัมเบอร์สูงกว่า โดยความสามารถในการดูดซับเท่ากับ 0.769 มก./กรัม และเวลาดูดซับที่ร้อยละ 50 ของเบรคทรูของถ่านชีวภาพยูคาลิปตัสและถ่านชีวภาพ ยูคาลิปตัสที่ปรับปรุงพื้นผิวมีค่าเท่ากับ 1,020 และ 240 นาที ตามลำดับ มีความสอดคล้องกับแบบจำลองของยุน - เนลสัน การใช้ EB และ MEB เป็นวัสดุกรองจากท้องถิ่นสามารถลดต้นทุนการปรับปรุงคุณภาพน้ำให้กับชุมชนได้

คำสำคัญ: ตัวกรองถ่านชีวภาพ แมงกานีส คอลัมน์แบบยึดติดกับที่ น้ำบาดาล ยูคาลิปตัส

Abstract

Removal of manganese in contaminated groundwater using filtration is one of the most treatment systems. The objective of this research was to study the efficiency of fixed-bed adsorption column using eucalyptus biochar and potassium permanganate-modified eucalyptus biochar as filter media to remove manganese from groundwater. The initial manganese concentration of 0.723 $\pm$ 0.002 mg/L was continuously fed to the top of column at a flow rate of 5 L/d. Water samples were collected periodically within 24 hours. Thomas and Yoon-Nelson models were used to describe the adsorption performance. Results showed that adsorption capacity of eucalyptus biochar was 1.812 mg/g higher than that of modified eucalyptus biochar (0.769 mg/g) as it has higher iodine number. The adsorption times at 50% breakthrough of eucalyptus biochar and modified eucalyptus biochar were 1,020 minutes and 240 minutes, respectively, which were consistent with the Yoon-Nelson model. Use of EB and MEB as local filter media can reduce the cost of improving community water quality.

Keywords: Biochar filter, manganese, fixed-bed column, groundwater, eucalyptus

[1] หลักสูตรเทคโนโลยีสิ่งแวดล้อม คณะพลังงานสิ่งแวดล้อมและวัสดุ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี กรุงเทพฯ 10140
[2] กลุ่มวิจัยการจัดการสิ่งแวดล้อมและพลังงานเพื่อชุมชนและเศรษฐกิจหมุนเวียน มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี กรุงเทพฯ 10140
[3] หน่วยวิจัยเคมีเพื่อสังคมสีเขียวและสุขภาพ, ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี กรุงเทพฯ 10140
[1] Environmental Technology Program, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi, Bangkok, 10140 Thailand
[2] Environmental and Energy Management for Community and Circular Economy (EEC&C) Research Group, King Mongkut's University of Technology Thonburi, Bangkok, 10140 Thailand
[3] Chemistry for Green Society and Healthy Research Group (ChGSH), Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok, 10140 Thailand
[*] Corresponding author Email: arachaporn.wi@mail.kmutt.ac.th

Introduction

Groundwater represents 97% of the world's available freshwater resources (Guppy *et al*., 2018). It is used widely, especially in developing countries in Asia such as Thailand. People in the northeastern region use groundwater because most areas are not in the service area of the Provincial Waterworks Authority. Groundwater quality is dependent on geologic conditions and human activities. Groundwater resources can be contaminated naturally by salt intrusion, and human activities *via* agriculture practices, and heavy metal contamination from industries (Vesselinov *et al*., 2018). In the Chi and Mun river basins, groundwater has iron, manganese, sulfate and fluoride concentrations exceeding the maximum allowable limits of groundwater standards for drinking water. In some areas of Ubon Ratchathani Province, there are high iron and manganese concentrations in groundwater more than 1 mg/L (Department of Groundwater Resources, 2022). Manganese in groundwater is found as the dissolved form of manganese bicarbonate ($Mn(HCO_3)_2$). As groundwater is exposed to air, the dissolved form is oxidized to dark brown insoluble manganese (Mn(IV)) (Henry & Heinke, 1989). This causes the appearance in stored water of a black sediment from manganese, causing stains to sanitary equipment and which may also affect health due to it being a chronic toxin (Rahman *et al*., 2021 ; Schullehner *et al*., 2020 ; Tay *et al*., 2018).

Manganese could be removed by physical, chemical, biological and physicochemical processes (Patil *et al*., 2016). The common and popular methods are the physical processes of adsorption and filtration. Activated carbon is most frequently used as solid adsorbent because it is a very effective adsorbent in various applications (Yin *et al*., 2007). The high surface areas and functional groups of activated carbon could remove Mn(II) from water (Chen *et al*., 1996). Previous research has used a variety of adsorbents such as activated carbon derived from Ziziphus spina-christi seeds (Omri & Benzina, 2012), kaolin (Yavuz *et al*., 2003), manganese oxide-coated zeolite (Alvarez-Bastida *et al*., 2018) and greensand or manganese oxide-coated sand (Benis *et al*., 2020). Potassium permanganate ($KMnO_4$) is an oxidizing agent. It has been reported to be an efficient oxidant to achieve manganese removal of 96% from groundwater (Menard & Demopoulos, 2007). Thus, $KMnO_4$ is widely used as a material coating on adsorbents. Most conventional wastewater treatment plants use manganese oxide-coated media to remove soluble manganese and then subsequent oxidation by free chlorine to MnO_x(s) (Hargette & Knocke, 2001). The filtration method is suitable for rural areas to remove heavy metals and odorous compounds before the distribution system. The filtration process in the community normally uses a combination of sand, anthracite or activated carbon as filter media. The problem encountered with rural filtration systems is the excessive cost of filter media. Thus, biochar can be an alternative low-cost filter media for heavy metal removal. Previous studies have reported the use of biochars for manganese removal in batch experiments with, for example, poultry manure and farmyard manure-derived biochar (Idrees *et al*., 2018), palm waste-derived biochar (Fseha & Yildiz, 2022), and biochar made banana peel and acid-modified banana peel (Kim *et al*., 2020). However, limited documentation is available for heavy metal removal using real groundwater in column studies.

Eucalyptus is an economic crop in Thailand because it is a fast-growing plant, widely cultivated for a variety of uses. Eucalyptus branches are highly productive as charcoal and have low cost. In addition, eucalyptus biochar (EB) has been used as an adsorbent for lead removal in aqueous solution (Singh & Arora, 2018) and manganese in groundwater (Wilamas *et al*., 2022). Activated carbon derived from eucalyptus was reported as effective for removal of cadmium (Venkatesan & Rajam, 2014). However, the removal of manganese in groundwater by eucalyptus biochar filter including modified surface-biochar by $KMnO_4$. has not been reported in any specific studies. Thus, this research used eucalyptus to produce biochar and its surface modification for manganese removal from groundwater. The objectives were to determine the efficiency of fixed-bed adsorption columns filled with eucalyptus biochar and modified eucalyptus biochar (MEB) for manganese removal from groundwater and use of the Thomas and Yoon-Nelson models for prediction of the adsorption performance.

Materials and methods

1. Preparations of filter media

Eucalyptus biochar was produced using ground pits. The eucalyptus branches were cut to a length of 50 cm and put in a hole dug in the ground (60 X 90 cm). Then, it was covered and burnt slowly with limited of oxygen on the top using auxiliary fuel (wood chips) for 6 hours. The temperature was between 400 - 500 °C. After being cooled, EB biochar was crushed and sieved to obtain a uniform size range of 2.0-3.0 mm and used as filter media (Figure 1a). To make the MEB (Figure 1b), the modification method was adapted from Taffarel and Rubio (2009) and Xuwen *et al*. (2010). EB (100 g) was placed in a 1000 ml beaker containing 500 ml of 5% (w/v) $KMnO_4$ solution prepared from $KMnO_4$ (AR grade, Qrec, New Zealand), then the mixture was heated at 90 °C, and stirred for 1 hour. The mixture was then filtered to separate MEB, which was washed with tap water until the rinsed water was colorless. MEB was dried in an oven at 60 °C for 6 hours. Two commercial adsorbents, activated carbon (AC) (Figure 1c) and manganese green sand (Mn-G) (Figure 1d), were bought from a domestic supplier (J.L. Intertrade Co., Ltd.).

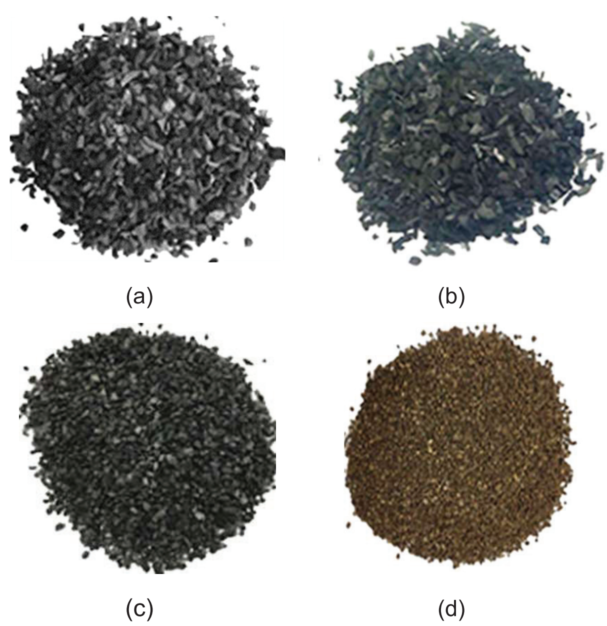

Figure 1 Filter media: (a) eucalyptus biochar (EB), (b) modified eucalyptus biochar (MEB), (c) activated carbon (AC) and (d) manganese green sand.

Adsorbents were tested for adsorption capacity using the standard iodine adsorption method (ASTM D46070). Elemental analysis of adsorbent materials using a Rigaku ZSX Primus model, Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF), Model Rigaku ZSX Primus, Japan. Adsorbents were determined for the external surface structural morphology by scanning electron microscopy (SEM), JEOL Model JSM-7610F Plus.

2. The quality of groundwater

Groundwater was collected from a residential area in NonNhon subdistrict, Warinchamrap district, Ubon Ratchathani province. The pH of groundwater was in the range of 6.78 $\pm$ 0.12, Iron and manganese concentrations of 0.354 $\pm$ 0.022 mg/L and 0.723 $\pm$ 0.002 mg/L, respectively. Mn concentrations were higher than the maximum allowable concentration of 0.3 mg/L, groundwater quality for drinking purpose in Thailand. The total hardness was 420 $\pm$ 0.5 mg/L as $CaCO_3$ which was classified as ‘very hard’ (Saha *et al*., 2019).

3. Column adsorption set up

The filter column for manganese removal was set up using four types of filter media, consisting of EB, MEB, AC and MnG, which were run in duplicate. The size of glass column was 1 cm inner diameter and 76 cm height. The filter media were boiled in tap water for 20 minutes to remove entrapped air in the pores (Ferrara, 1980). Then, 10 g of either EB, MEB, AC or 40 g of MnG were individually packed into a column to a height of 50 cm (Figure 2). The groundwater was continuously fed into the top of the column at a flow rate of 5 L/d. Water samples were collected at delignated time (every hour for 24 hours) for Mn analysis. The breakthrough curve was plotted between the ratio of remaining manganese concentrations at various times and initial manganese concentration (Mn/Mn_0) and times.

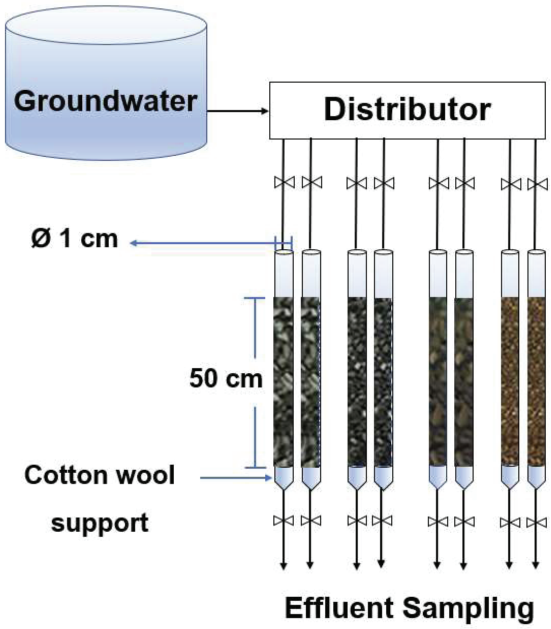

Figure 2 Schematic of filter column system

4. Mathematical models

The general mathematical equations for describing adsorption columns are Thomas and Yoon-Nelson models, which provide widely used theoretical methods to describe column performance (Chen *et al*., 2012). The assumption of the Thomas model is based on the Langmuir kinetics of adsorption-desorption with no axial dispersion. The rate driving force obeys second-order reversible reaction kinetics (Ayoob & Gupta, 2007). The model is described in Equation 1.

$$ln\frac{C_0}{C_t} - 1 = \frac{k_{Th}q_0\,m}{Q} - k_{Th}C_0\,t, \quad (1)$$

where C_O, C_t are initial Mn concentration and concentration at time t (mg/L), respectively. k_{Th} is a Thomas constant (mL/min.mg), t is the total flow time (min), and Q is the volumetric flow rate (mL/min). Adsorption capacity and mass of the adsorbent are denoted as q_0 (mg/g) and m (g), respectively. Plot of $ln\frac{C_0}{C_t} - 1$ versus t gives the value of k_{Th} and q_0.

The Yoon-Nelson model is a simple model which does not require explicitly elaborated information. 50% of the breakthrough time can be predicted from the equation as expressed in Equation 2. (Yoon and Nelson, 1984).

$$ln\frac{C_t}{C_0 - C_t} = k_{YN}t - \tau k_{YN}, \quad (2)$$

The value of k_{YN} was calculated from the slope by plotting the graph between $ln\frac{C_t}{C_0 - C_t}$ and t. Where, k_{YN} is the rate constant (mn^{-1}), is time required for 50% adsorbate breakthrough (min) and t is time (min).

5. Analysis and characterization

Water samples were acidified with nitric acid (pH < 2) after collection and then digested by nitric acid using microwave digestion. The digested samples were filtered through filter paper (Whatman no.42) and were analyzed for manganese concentration using inductively coupled plasma-optical emission spectrometry (ICP-OES, model Optima 8000, Germany). The average of duplicate data is reported for each column.

Results and discussion

1. Characterizations of the adsorbent

The iodine number of EB, AC, MEB and MnG was 152.42, 271.96, 174.67, 6.14 mg/g, respectively, indicating a low number of pores of MnG. Results from WDXRF revealed that there were Mn in EB, AC, MEB and MnG of 2.11, not detected, 69.1, and 8.61%, respectively. MEB had high Mn content after modification by $KMnO_4$ showing that insoluble manganese oxide (MnO_x(s)) was successfully coated onto the EB surfaces.

The external surface structure morphology images before adsorption are shown in Figure 3. The images show that there were pores on the surface of adsorbents, indicating their porosity. The main factors that affect adsorption capacity are particle size, pore diameter, and specific surface area (Wang *et al*., 2010).

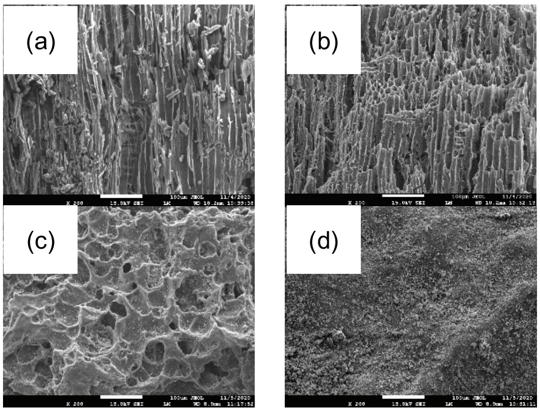

Figure 3 SEM images: (a) eucalyptus biochar (EB), (b) modified eucalyptus biochar (MEB), (c) activated carbon (AC) and (d) manganese green sand.

2. Manganese removal

Manganese removal efficiency from each column ranged from 46.11-63.67%, 30.70-58.72%, 53.29-88.01% and 56.70-68.27%, for EB, MEB, AC and MnG, respectively at 1,440 min (Figure 4). 50% removal of manganese was achieved at for EB, MEB, AC, and MnG at 1,020, 240, 1,140 and 660 min, respectively. Mn(II) was removed by complexation or electrostatic attraction of metal ions to various surface oxygen-containing functional groups in EB (Wilamas *et al*., 2022) and AC (Yin *et al*., 2007, Omri & Benzina, 2012). MnG can be used to remove soluble Mn(II) in filters *via* sorption and oxidation. MnO_x(s) on filter media surfaces of MEB and MnG could oxidize Mn(II) rapidly and Mn(II) was also removed *via* adsorption until all available adsorption sites were occupied (Knocke *et al*. 1990). According to research on the removal of Mn using MnG, which has a MnO_x coating liked MEB on the filter surface.

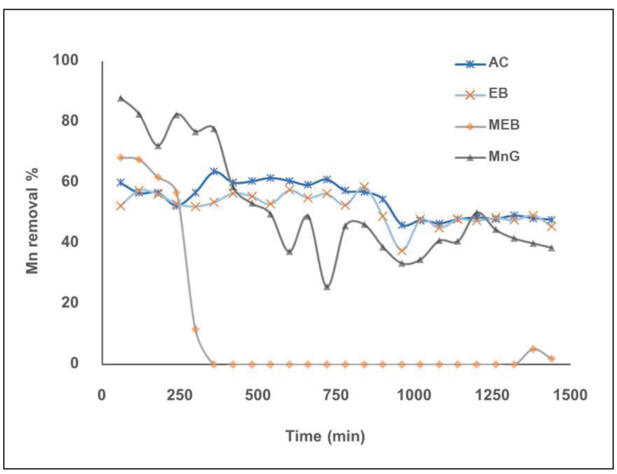

Figure 4 The efficiency of manganese removal

The breakthrough curve of each column was determined by plotting the ratio of Mn/Mn_0 against time as shown in Figure 5.

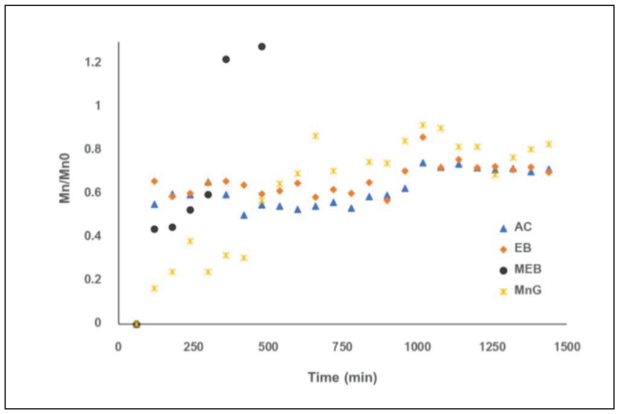

Figure 5 Breakthrough curve

The Mn/Mn_0 ratios for all filter media except MEB did not achieve 0.95 until 5,000 min whereas the Mn/Mn_0 values of MEB were higher than 0.95 at 240 min and followed by MnG at 540 min. of EB was highest at 1,020 min. However, MEB and MnG filters gave high removal efficiencies during the initial period (0-240 min), due to the vacant surfaces of these adsorbents occurring in Mn(IV) oxide (MnO_2) form. Mn^{2+}in groundwater is adsorbed on the surface of adsorbent, as shown in Equation 4. (Letterman, 1999).

$$Mn^{2+} + MnO_2\,(s) \longrightarrow MnO_2(s) - Mn^{2+} \qquad (4)$$

The breakthrough curve enabled determination of the breakthrough time (t_b). The amount adsorbed at breakthrough time is q_b. The length of the unused bed at breakthrough (L_m) is determined by equation 3 (Gabelman, 2017).

$$L_m = L\left(1 - \frac{t_b}{t_f}\right), \qquad (3)$$

where, L is the total bed length (cm), t_f is the midpoint of the real S-shaped breakthrough curve.

However, the maximum allowable Mn concentration for drinking purpose is 0.3 mg/L, thus this present study used the 50% breakthrough time, as shown in Table 1.

Table 1 The constant values from the breakthrough graph.

Filter media	t_b (min)	t_f (min)	L_m (cm)	q_b (mg/g)
EB	1,020	1,938	23.68	1.278
MEB	240	300	10.00	0.342
AC	900	2,166	29.22	1.233
MnG	540	1,254	28.47	0.169

Table 2 shows the constant values of Yoon and Nelson model and Thomas model. The adsorption capabilities predicted by the Thomas model were in good agreement with the experimental results. The correlation coefficient (R^2) ranged from 0.8717 to 0.9709, indicating the best fit of the model with the experimental breakthrough curve. The Thomas model is suitable to describe the adsorption of manganese onto the filter media and aid in the design of columns with the best parameters. From this present study, the value of the Thomas constant (k_{Th}) of MEB was the highest, followed by MnG, which corresponds to the highest removal efficiencies of manganese during the initial period.

From the Yoon-Nelson model, (τ) the time of 50% adsorbed breakthroughs, was consistent with the time of the experiment (t_{exp}). The R^2 values were relatively high (0.8197-0.9709), indicating that this model was effective at forecasting breakthrough time.

In this study, it was revealed that manganese had limited removal efficiency *via* its adsorption onto the adsorbent medium. The Mn removal was effective at alkaline pH values. According to Lefkowitz *et al*. (2013), dissolved Mn(II) is oxidized to insoluble forms of Mn(III) and Mn(IV) and then physically separated by filtration. Due to different removal mechanisms, EB and AC had a longer breakthrough time than MEB and MnG. The iodine number was high in EB and AC indicating adsorption into pores. SEM pore size images of EB and AC confirmed pore size to be a factor in manganese adsorption. Furthermore, from the result of Fourier transform Infrared spectroscopy by Wilamas *et al*. (2022) reported the Mn adsorption by EB surfaces at the hydroxyl functional group.

It was found that the initial manganese removal efficiency of MEB and MnG was high, due to the oxidation and adsorption processes during first 120 min. MEB could not remove Mn after 250 min. This can be explained if the excess Mn on the MEB surfaces was leached out as the groundwater had a low Mn concentration of 0.723 mg/L. It can be seen from WDXRF that Mn content in MEB was 8 times that of MnG. In addition, the removal performance of adsorbents depends on adsorption conditions such as pH, Mn concentration and adsorbent dosage. It is recommended to use low amounts of MEB and MnG in the filter column as Mn may desorb in the case of the groundwater having a low Mn concentration. Biochar filters should be backwashed according to breakthrough time to remove the accumulated fine particles. However, spent biochar cannot be reused because its surface functional groups area was occupied *via* chemical adsorption (Wilamas *et al*., 2022). Thus, the combination with AC or EB filter media could enhance manganese removal efficiency.

The cost of the commercial grade of AC, MnG and $KMnO_4$ ranges from 95-120, 200-250 and 180 - 250 Baht /kg. The EB cost is 7.5 Baht/kg, while MEB cost is 8.13 Baht/kg. Thus, in comparison to MnG, EB should be developed further by using a smaller amount. In addition, use of these local materials can reduce the cost of water treatment for the community.

The literature-reported adsorption capacities (q) of Mn(II) onto EB and MEB were compared with those of other filter media, and the results are displayed in Table 3. According to the table, although EB and MEB could remove manganese, their efficiency was dependent on operating conditions.

Table 2 Parameters of Thomas and Yoon-Nelson models under column adsorption process.

Filter media	M (g)	Q(mL/min)	Thomas Model			Yoon-Nelson Model			
			k_{Th} mL/min. mg	q_0 mg/g	R^2	k_{YN} (min^{-1})	t_{exp} (min)	τ (min)	R^2
AC	10	34.72	0.830	2.3383	0.9613	0.0005	1140	1205	0.8334
EB	10	34.72	0.968	1.8124	0.8717	0.0005	1020	1149	0.8197
MEB	10	34.72	4.426	0.7692	0.9709	0.0032	240	306	0.9709
MnG	40	34.72	2.490	0.6470	0.9029	0.0019	660	918	0.7960

Table 3 Comparison of Mn(II) adsorption capacity with other filter media.

Media	Experimental Conditions				Thomas model			Removal efficiency	Reference
	Type of water	pH	Flow rate mL/min	Initial Mn mg/L	K_{th} mL/min. mg	q_0 mg/g	R^2		
Palm waste-derived biochar	synthetic groundwater	6	5	5	0.16	3.61	0.86	73.20%	(Fseha & Yildiz, 2022).
Tea leaves-derived char (nano-biosorbents)	synthetic water solutions	7.9	10	5	0.0010	70.4	0.98	78.13%	(Akbari Zadeh *et al.*, 2022)
Rice straw-derived char (nano-biosorbents)	synthetic water solutions	7.9	10	5	0.0011	203.58	0.9	92.01%	(Akbari Zadeh *et al.*, 2022)
EB	groundwater	6.78	3.47	0.723	0.968	1.812	0.8717	63.67%	This study
MEB	groundwater	6.78	3.47	0.723	4.426	0.769	0.9709	58.72%	This study

Conclusions

This study evaluated the efficiency of fixed-bed adsorption columns using EB and MEB as filter media to remove manganese from actual groundwater. The results revealed that EB and MEB can be used as filter media. The manganese removal efficiency in EB and MEB were 63.67% and 58.72%, respectively, with the Mn concentration within the acceptable range at 0.3 mg/L. Both types of filters were equivalent to AC (88.01%) and MnG (68.27%). In addition, application with groundwater having different concentrations of manganese needs to be studied on a case-by-case basis.

Acknowledgements

The authors are grateful to thank the School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi for partially support the financial fund, and the Faculty of Science, Ubon Ratchathani for supporting the laboratory in conducting research.

References

Akbari Zadeh, M., Daghbandan, A., & Abbasi Souraki, B. (2022). Removal of iron and manganese from groundwater sources using nano-biosorbents. *Chemical and Biological Technologies in Agriculture*, *9*(1), 1-14.

Alvarez-Bastida, C., Martínez-Miranda, V., Solache-Ríos, M., Linares-Hernández, I., Teutli-Sequeira, A., & Vázquez-Mejía, G. (2018). Drinking water characterization and removal of manganese. Removal of manganese from water. *Journal of Environmental Chemical Engineering*, *6*(2), 2119-2125.

Ayoob, S., & Gupta, A. K. (2007). Sorptive response profile of an adsorbent in the defluoridation of drinking water. *Chemical Engineering Journal*, *133* (1-3), 273-281.

Benis, K. Z., Damuchali, A. M., Soltan, J., & McPhedran, K. N. (2020). Treatment of aqueous arsenic-A review of biochar modification methods. *Science of The Total Environment*, *739*, 139750.

Chen, J., Yiacoumi, S., & Blaydes, T. G. (1996). Equilibrium and kinetic studies of copper adsorption by activated carbon. *Separations Technology*, *6*(2), 133-146.

Chen, S., Yue, Q., Gao, B., Li, Q., Xu, X., & Fu, K. (2012). Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: a fixed-bed column study. *Bioresource Technology*, *113*, 114-120.

Department of Groundwater Resources. (2022). *Annual report on the situation of water and groundwater* 2021, http://www.dgr.go.th/ th/public-service/329

Ferrara, A. P. (1980). Controlling bed losses of granular activated carbon through proper filter operation. *Journal-American Water Works Association*, *72*(1), 60-63.

Fseha, Y. H., & Yildiz, I. (2022). Manganese and nitrate removal from groundwater using date palm biochar: Application for drinking water. *Environmental Advances*, *8*, 100237.

Gabelman, A. (2017). Adsorption basics: part 1. *Chemical Engineering Progress*, *113*(7), 48-53.

Guppy, L., Uyttendaele, P., Villholth, K. G., & Smakhtin, V. U. (2018). *Groundwater and sustainable development goals: Analysis of interlinkages*.

Hargette, A. C., & Knocke, W. R. (2001). Assessment of fate of manganese in oxide-coated filtration systems. *Journal of Environmental Engineering*, *127*(12), 1132-1138.

Henry, J. G., & Heinke, G. (1989). Environmental Science and Engineering Prentice Hall. *Eaglewood Cliffs, NJ07632*, 78-243.

Idrees, M., Batool, S., Ullah, H., Hussain, Q., Al-Wabel, M. I., Ahmad, M., Ok, Y. S., & Kong, J. (2018). Adsorption and thermodynamic mechanisms of manganese removal from aqueous media by biowaste-derived biochars. *Journal of Molecular Liquids*, *266*, 373-380.

Kim, H., Ko, R. A., Lee, S., & Chon, K. (2020). Removal efficiencies of manganese and iron using pristine and phosphoric acid pre-treated biochars made from banana peels. *Water*, *12*(4), 1173.

Knocke, W. R., Occiano, S., & Hungate, R. (1990). *Removal of soluble manganese from water by oxide-coated filter media*. AWWA Research Foundation and the American Water Works Association

Lefkowitz, J. P., Rouff, A. A., & Elzinga, E. J. (2013). Influence of pH on the reductive transformation of birnessite by aqueous Mn (II). *Environmental science & technology*, *47*(18), 10364-10371.

Letterman, R. D., Amirtharajah, A., & O'Meilia, C. R. (1999). Water Quality and Treatment, Letterman, RD (Ed). *Coagulation and Flocculation*.

Menard, V., & Demopoulos, G. P. (2007). Gas transfer kinetics and redox potential considerations in oxidative precipitation of manganese from an industrial zinc sulphate solution with $SO2/O_2$. *Hydrometallurgy*, *89*(3-4), 357-368.

Omri, A., & Benzina, M. (2012). Removal of manganese (II) ions from aqueous solutions by adsorption on activated carbon derived a new precursor: Ziziphus spina-christi seeds. *Alexandria Engineering Journal*, *51*(4), 343-350.

Patil, D. S., Chavan, S. M., & Oubagaranadin, J. U. K. (2016). A review of technologies for manganese removal from wastewaters. *Journal of Environmental Chemical Engineering, 4*(1), 468-487.

Rahman, M. F., Mahmud, M. J., Sadmani, A. A., Chowdhury, A. I., Anderson, W. B., Bodruzzaman, A. B., & Huq, S. (2021). Previously unrecognized potential threat to children from manganese in groundwater in rohingya refugee camps in Cox's Bazar, Bangladesh. *Chemosphere*, *266*, 129128.

Saha, S., Reza, A. H. M., & Roy, M. K. (2019). Hydrochemical evaluation of groundwater quality of the Tista floodplain, Rangpur, Bangladesh. *Applied Water Science*, *9*(8), 1-12.

Schullehner, J., Thygesen, M., Kristiansen, S. M., Hansen, B., Pedersen, C. B., & Dalsgaard, S. (2020). Exposure to manganese in drinking water during childhood and association with attention-deficit hyperactivity disorder: a nationwide cohort study. *Environmental health perspectives*, *128*(9), 097004.

Singh, B., Walia, B. S. and Arora, R. 2018. Eucalyptus wood charcoal as Biosorbent for removal of lead (II) ions from aqueous solution. *IJRAR- International Journal of Research and Analytical Reviews,5*(4), 993-998.

Taffarel, S. R., & Rubio, J. (2009). On the removal of Mn^{2+} ions by adsorption onto natural and activated Chilean zeolites. *Minerals Engineering*, *22*(4), 336-343.

Tay, A. K., Islam, R., Riley, A., Welton-Mitchell, C., Duchesne, B., Waters, V., & Ventevogel, P. (2018). Culture, context and mental health of Rohingya refugees: A review for staff in mental health and psychosocial support programmes for Rohingya refugees. *Geneva: United Nations High Commissioner for Refugees (UNHCR)*.

Venkatesan, G., Senthilnathan, U., & Rajam, S. (2014). Cadmium removal from aqueous solutions using hybrid eucalyptus wood based activated carbon: adsorption batch studies. *Clean Technologies and Environmental Policy, 16*(1), 195-200.

Vesselinov, V. V., Alexandrov, B. S., & O'Malley, D. (2018). Contaminant source identification using semi-supervised machine learning. *Journal of Contaminant Hydrology, 212*, 134-142.

Wang, F. Y., Wang, H., & Ma, J. W. (2010). Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent—Bamboo charcoal. *Journal of Hazardous Materials*, *177*(1-3), 300-306.

Wilamas. A, Vinitnantharat. S, & Pinisakul. A. (2022). Manganese Adsorption from Groundwater by Eucalyptus Biochar. *Science and Technology Journal Ubon Ratchathani University*, *24*(3), 1-10.

Xuwen, H. E., Huimin, Y. A. N. G., & Yong, H. E. (2010). Treatment of mine water high in Fe and Mn by modified manganese sand. *Mining Science and Technology (China)*, *20*(4), 571-575.

Yavuz, Ö., Altunkaynak, Y., & Güzel, F. (2003). Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. *Water Research, 37*(4), 948-952.

Yin, C. Y., Aroua, M. K., & Daud, W. M. A. W. (2007). Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. *Separation and Purification technology*, *52*(3), 403-415.