CHEMICAL ENGINEERING TRANSACTIONS

VOL. 106, 2023

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Peck Loo Kiew, Hon Huin Chin

ISBN 979-12-81206-05-2; **ISSN** 2283-9216

DOI: 10.3303/CET23106053

Chemical Regeneration of Spent Empty Fruit Bunch Biochar for Sodium Ion Adsorption

Huiyi Tan[a], Roswanira Abdul Wahab[b], Pei Ying Ong[a], Pei Sean Goh[a], Keng Yinn Wong[c], Yee Van Fan[d], Chew Tin Lee[a,*]

[a]Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310, Johor, Malaysia
[b]Department of Biosciences, Faculty of Science, Universiti Teknologi Malaysia, 81310, Johor, Malaysia
[c]Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
[d]Sustainable Process Integration Laboratory – SPIL, NETME Centre, Faculty of Mechanical Engineering, Brno University of Technology - VUT Brno, Technická 2896/2, 616 69 Brno, Czech Republic
ctlee@utm.my

Biochar is a carbonaceous porous material produced by pyrolysis under oxygen-anoxic conditions. It has been widely adopted as an adsorbent to remove various pollutants from contaminated water due to its distinctive characteristics such as high porosity and surface-to-volume ratio, abundant functional groups, etc. One of the major problems in utilising biochar as an adsorbent is the recovery and sustainable management of the spent biochar. To determine the potential and reusability of biochar for wastewater treatment, the desorption and regeneration processes to reactivate the biochar should be studied and explored. This study aims to identify the desorption characteristics of sodium ions (Na^+) on hydrothermal nitric acid pre-treated empty fruit bunch biochar (HNO_3 EFB-BC). Different desorption eluents, i.e., tap water, deionised water, hydrochloric acid (HCl), sulphuric acid (H_2SO_4), sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3). Among these eluents, HCl was chosen as the best desorbing agent for Na^+, due to the highest desorption efficiency (66.23 %), at a concentration of 0.1 M. By using HCl, the exhausted HNO_3 EFB-BC was regenerated up to six cycles. The Na^+ desorption efficiency of HNO_3 EFB-BC can be maintained as high as 69.03 % and 57.77 %, respectively, in the first two cycles. The efficiency of Na^+ desorption remained as high as 18.85 %, after six successive adsorption and desorption experiments. The results have proven the potential of HNO_3 EFB-BC as a cost-effective adsorbent for the sustainable remediation of saline solution. It also provided new insights to researchers on the desorption characteristics of HNO_3 EFB-BC and display its potential to be regenerated from other cationic pollutants. Future desorption and regeneration studies should be performed using the actual saline soil or water with a mixture of pollutants to illustrate the effects of adsorbates on the performance of the regeneration process.

1. Introduction

Freshwater is essential for the survival of all living organisms. The demand for clean and freshwater is rising due to the rapid population growth and industrial development along with the concomitant discharge of human-created pollutants into the freshwater. The discharge of huge loads of pollutants into the freshwater can cause severe ecological degradation such as the reduction in the quality and availability of freshwater, alteration in the structure and distribution of aquatic biodata, and changes in the food chain and productivity patterns, thus resulting in deleterious effects to the ecosystems and hazards to human health (Bashir et al., 2020). One of the major contributors to water pollution is the accumulation of soluble salts (Na+) in the water bodies which leads to a phenomenon known as freshwater salinisation (Nyakuma et al., 2023). The cases of water salinisation are dynamic and it is increasing globally in over 100 countries (Khondoker et al., 2023). It is urgent to reclaim saline water to realise the achievement of the sixth sustainable development goal (SDG), 'Clean water and sanitisation' for ensuring human health and well-being.

Significant research has proposed proactive and innovative methods to remediate the saline water for drinking and irrigation purposes. Among the technologies deployed to remove Na^+ from saline water, adsorption has

Paper Received: 29 May 2023; Revised: 28 July 2023; Accepted: 31 August 2023
Please cite this article as: Tan H., Wahab R.A., Ong P.Y., Goh P.S., Wong K., Fan Y.V., Lee C.T., 2023, Chemical Regeneration of Spent Empty Fruit Bunch Biochar for Sodium Ion Adsorption, Chemical Engineering Transactions, 106, 313-318 DOI:10.3303/CET23106053

received particular attention owing to its simplicity, high efficiency and environmental-friendly nature (Tan et al., 2023a). Biochar has emerged as a potential candidate for water desalinisation due to its unique physicochemical properties and ability in removing various pollutants. It is a carbon-rich material produced by pyrolysis of biomass under oxygen-deprived conditions (Jamaludin et al., 2019). Based on previous literature, biochar has been used as an adsorbent in eliminating salt ions (Tan et al., 2021), heavy metals (Tyagi, 2022), dyes (Guo et al., 2022) and herbicides (Binh and Nguyen, 2020). In terms of saline water remediation, the rice husk (Nyakuma et al., 2021), corn stalk (Nguyen et al., 2022), hemp (Awan et al., 2021) and empty fruit bunch biochar (Tan et al., 2023b) are some examples of the agricultural biomass-based biochar that have been used. One of the major practical challenges in the context of resource recovery is the sustainable management of the spent biochar. The uncontrolled disposal of the spent biochar may give rise to negative environmental consequences. There is a need to desorb the pollutants from the surface of the spent biochar to ensure safe disposal or to regenerate it for further use.

Biochar regeneration is defined as an inverse process involving the desorption of pollutants (Odega et al., 2023). It is a fundamental approach to assessing the commercial applicability of the adsorbent, especially in both batch and continuous processes. (Bayuo et al., 2020). During the desorption process, the ions accumulated on the surface of biochar can be eliminated under proper operating conditions. After desorption, the cationic pollutants could be recovered by extraction from the liquid phase, and so the biochar could be preserved. Previous literature showed that several techniques, including thermal regeneration, wet air oxidation, electrochemical process and chemical regeneration have been used to desorb the cationic pollutants (Márquez et al., 2022). Among these techniques, wet air oxidation and thermal regeneration are the most commonly used approach for wastewater treatment (Bion et al., 2018). Although these techniques are effective in desorbing cationic pollutants, their destructive manner and the involvement of high operating temperature (up to 800 °C) increases the overall operating cost (Greiner et al., 2018). In terms of the electrochemical method, the high maintenance fee has limited its applicability (López et al., 2022). Chemical regeneration is a non-thermal approach involving the use of inorganic acids or alkalis to desorb the adsorbate (Dai et al., 2019). The choice of desorbing agents is dependent on the type of adsorbent (pristine or composite), its properties and the type of cationic pollutants (Alsawy et al., 2022). This study focused on the use of a chemical regeneration approach due to its simplicity of operation and ability to preserve the biochar for several cycles (Larasati et al., 2021).

There have been increasing efforts in designing biochar with enhanced adsorption capacity towards cationic pollutants, notably Na^+. Several reviews have demonstrated the potential of biochar in saline water treatment (Awan et al., 2021). There is little study on the recovery of Na^+-loaded EFB biochar in which its potential to be regenerated for reuse is relatively unknown. This study aims to identify the desorption characteristics and regeneration of hydrothermal nitric acid pre-treated empty fruit bunch biochar (HNO_3 EFB-BC) using different desorbing agents such as tap water, deionised water, hydrochloric acid (HCl), sulphuric acid (H_2SO_4), sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3). This study could provide a better understanding of the desorption efficiency and regenerate the HNO_3 EFB-BC without much loss in the adsorption capacity after several regeneration cycles. Following the desorption and regeneration processes, the spent biochar could be managed sustainably and the secondary pollution could be minimised, thus reducing the operational and running cost of the saline water treatment process.

2. Methods

2.1 Preparation and chemical pre-treatment of EFB biochar

The EFB biochar was purchased from Usaha Strategik Sdn. Bhd (Puchong, Malaysia). The specification of the EFB biochar is as follows: pyrolysed at 300 °C in a furnace under oxygen deficit conditions for 1 h. The EFB biochar was ground using a 32,000 rpm high-speed electric fibre grinder (Hao Jie Technology Co, Ltd, Shang Hai, China) and sieved manually to 2-4 mm. The ground and sieved biochar were rinsed with deionised water to remove impurities. The rinsed biochar (EFB-BC) was dried at 75 °C for 24 h using an oven (UN110, Memmert, Schwabach, German) (Ibrahim et al., 2021) and stored at room temperature (25 °C) in an airtight container for further use. The EFB-BC was then pre-treated with 3 M HNO_3 under optimised hydrothermal conditions (120 °C, 60 min) (HNO_3 EFB-BC).

2.2 Desorption and regeneration experiments

4.96 g of HNO_3 EFB-BC was introduced into the Erlenmeyer flask containing 100 mL of 0.39 M NaCl solution (pH 7.46). After equilibration for 17.4 h under room temperature (25 °C), the suspension was centrifuged (Hettich Universal 320 R, Tuttlingen, Germany) at 1,000 rpm for 5 min to recover the biochar from the saline solution (Amin et al., 2018). The Na^+-loaded HNO_3 EFB-BC was rinsed with deionised water until pH 7 and oven dried at 75 °C for 24 h. The Na^+-loaded HNO_3 EFB-BC was then transferred into six desorption agents (100 mL), i.e., tap water, deionised water, 0.1 M HCl, 0.1 M H_2SO_4, 0.1 M NaOH and 0.1 M Na_2CO_3. The flasks containing the suspension were agitated at 150 rpm for 24 h. After agitation, the suspension was centrifuged, and the supernatant was decanted into a separate flask. The concentration of desorbed Na^+ in the supernatant was measured, and the percentage of Na^+ desorption was calculated using Eq (1) (Yusof et al., 2020).

$$Desorption\ (\%) = \frac{C_{Na-desorbed}}{C_{Na-adsorbed}} \times 100 \quad (1)$$

where $C_{Na-desorbed}$ (mg L-1) is the concentration of Na+ desorbed from the HNO3 EFB-BC into the solution and $C_{Na-adsorbed}$ is the concentration of Na+ adsorbed onto the HNO3 EFB-BC during the batch adsorption study. The regenerated HNO_3 EFB-BC was rinsed with deionised water to remove excess acids or alkalis until the pH of the rinsing water reached 6 to 7. The rinsed HNO_3 EFB-BC was dried in the oven before the subsequent adsorption and desorption experiments to determine the reusability of the prepared biochar. The processes of adsorption and regeneration were repeated for six cycles and the Na^+ desorption efficiency of HNO_3 EFB-BC for each cycle was recorded. All experiments were performed in triplicate to ensure the reproducibility and accuracy of the results obtained. Figure 1 shows the schematic diagram of the biochar desorption and regeneration studies using different desorbing agents.

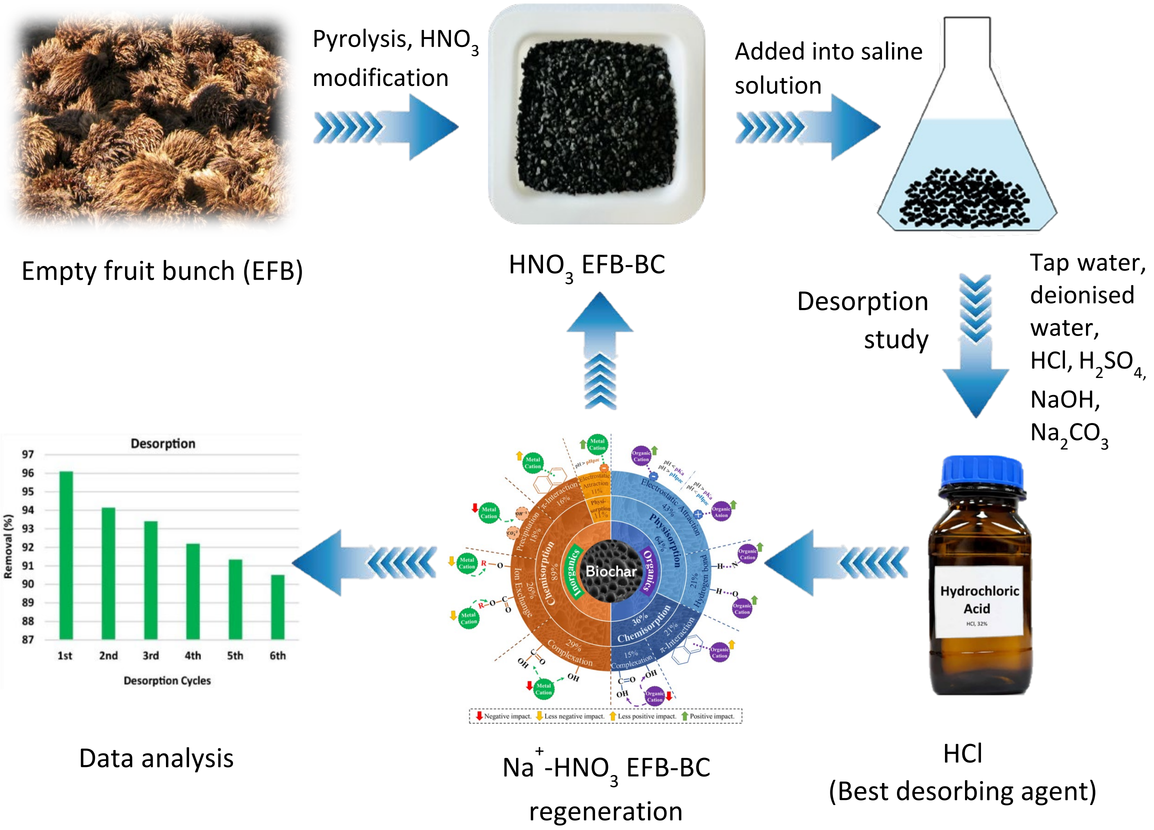

Figure 1: Schematic diagram of the biochar desorption and regeneration

3. Results and discussion

3.1 Desorption and stability of Na^+-loaded HNO_3 pre-treated EFB biochar

This section mainly presents and discusses the results obtained from the desorption and regeneration studies of HNO_3 EFB-BC. Desorption is a crucial process for recovering and separating pollutants to regenerate the exhausted bio-adsorbent. In this study, desorption experiments were conducted to determine the stability of Na^+-loaded HNO_3 EFB-BC and select the optimum desorption agent to be used in successive regeneration cycles. A total of six desorption agents, such as tap water, deionised water, HCl, H_2SO_4, NaOH and Na_2CO_3, were used to desorb the Na^+ from the biochar, and the results obtained are summarised in Table 1. When tap water (5.65 %) and deionised water (8.60 %) are employed as the desorption agents, only a very minimal amount of Na^+ was detected in the eluent, suggesting that the HNO_3 EFB-BC is stable in water. It also signifies that the adsorbed Na^+ on HNO_3 EFB-BC were not easily desorbed into the water environment under normal conditions. In contrast, the acidic desorption agent, HCl and H_2SO_4, demonstrate higher desorption percentages of 66.23 % and 52.17 % for Na^+. This might be due to the presence of oxygen-containing functional groups such as nitro, carboxylic acid, carbonyl and hydroxyl groups that made it amenable to easy desorption and regeneration with an acidic desorption agent (Bayuo et al., 2019). NaOH and Na_2CO_3 liberated 40.82 % and 23.44 % of Na^+, respectively. The acids outperformed the alkaline desorption reagents due to the minimal pore blockage, resulting from dissolving the adsorbate complexes on the biochar. Since HCl possess the highest Na^+ desorption efficiency (66.23 %), it is chosen as the desorption agent for subsequent adsorption and regeneration study. HCl is the most utilised acidic eluent to desorb cationic pollutants such as Cu^{2+}, with a desorption efficiency of around 92.8 % (Patel, 2021).

Table 1: Desorption and stability of Na^+-loaded HNO_3 EFB-BC in desorption agents

Desorption agent	Desorption Percentage (%)
Tap water	5.65 ± 0.19
Deionised water	8.60 ± 0.04
HCl	66.23 ± 0.05
H_2SO_4	52.17 ± 0.12
NaOH	40.82 ± 0.11
Na_2CO_3	23.44 ± 0.16

3.2 Regeneration and reusability of HNO_3 pre-treated EFB biochar

Regeneration is one of the key parameters in determining the potential of adsorbent for commercial application and improving the economy of the adsorption process. In this study, the reusability of HNO_3 EFB-BC was investigated by conducting six successive adsorption and desorption cycles with 0.1 M HCl solution as the desorption agent. As shown in Figure 2, the Na^+ desorption efficiency of HNO_3 EFB-BC decreased gradually with an increasing number of adsorption and desorption cycles. It was observed that the first and second cycles liberated 69.03 % and 57.77 % of Na^+ from the surface of biochar into the desorption agent. After the third cycle, the Na^+ desorption efficiency has reduced from 57.77 % to 30.96 %. This also signifies that the uptake capacity of HNO_3 EFB-BC has reduced from 69.03 % to 30.96 % after three regeneration cycles. Progression in cycles has contributed to a slight decrease in the Na^+ desorption efficiency for each cycle.

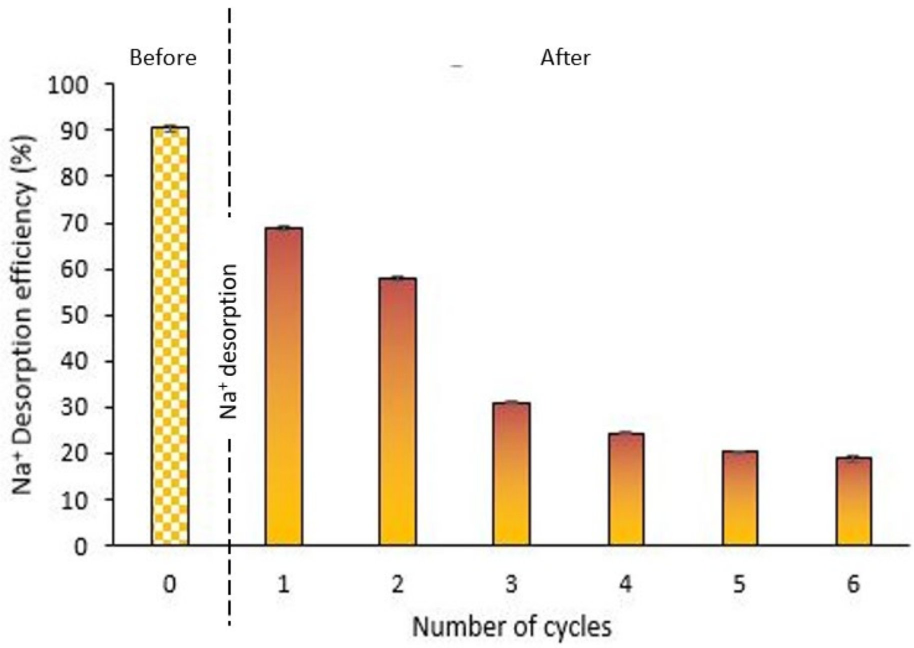

Figure 2: Na^+ Desorption efficiency of HNO_3 EFB-BC with HCl as the desorption agent in six adsorption-desorption cycles

During the process of regeneration, the biochar losses some of its active sites in each cycle owing to the strong chemical bonds in chemisorption, which negatively impacts the regeneration process (Alsawy et al., 2022). The regeneration experiments in Figure 2 show that the efficiency of Na^+ desorption remained as high as 18.85 % after six successive adsorption and desorption experiments. By using the same desorption agent (HCl), previous study revealed that the cadmium (Cd^{2+}) and chromium (Cr^{4+}) desorption efficiency of douglas fir green wood chips biochar remained only 3 % to 7 % after three regeneration cycles (Herath et al., 2021). This signifies that the HNO_3 EFB-BC could be utilised repeatedly without significant loss in its adsorption properties. Bayuo et al. (2020) also concluded that groundnut husk biochar with Cr^{4+} and Pb^{2+} desorption efficiency of 20.0 % and 26.7 % after three regeneration cycles can be recycled when used to remove Cr^{4+} and Pb^{2+} from the wastewater. In this study, the results have proven the potential of HNO_3 EFB-BC as a cost-effective adsorbent for the sustainable remediation of saline solution.

4. Conclusion

In conclusion, the desorption and regeneration studies were conducted to determine the reusability of HNO_3 EFB-BC for saline water remediation. These studies are also crucial in determining the potential of HNO_3 EFB-BC for commercial application and improving the economy of the adsorption process. Several desorbing agents, i.e., tap water, deionised water, HCl, H_2SO_4, NaOH and Na_2CO_3 were used to desorb the Na^+ from HNO_3 EFB-BC. Based on the results obtained, HCl was identified as the best desorption agent as it possessed the highest Na^+ desorption efficiency (66.23 %). The desorption efficiency of tap water, deionised water, H_2SO_4, NaOH and Na_2CO_3 for Na^+ was 5.65 %, 8.60 %, 52.17 %, 40.82 %, and 23.44 %, respectively. The reusability of HNO_3 EFB-BC was further investigated by conducting six regeneration cycles using 0.1 M HCl solution. After the sixth adsorption and desorption experiment, the regenerated HNO_3 EFB-BC could still achieve a Na^+ uptake rate of around 18.85 %, signifying its potential to be utilised repeatedly without significant loss in its adsorption properties. Future desorption and regeneration studies should be performed using the actual saline soil or water with a mixture of pollutants to illustrate the effects of adsorbates on the performance of the regeneration process. The biochar surface functionalities and morphological characteristics after each regeneration cycle should be investigated to obtain a deeper understanding of the desorption process and its behavior as an adsorbent. The mechanism of Na^+ adsorption and desorption should be further explored for designing the effective biochar adsorbent.

Acknowledgements

The authors would like to acknowledge the Ministry of Higher Education (MOHE) Malaysia, Fundamental Research Grant Scheme (FRGS) with grant no. R.J130000.7809.5F147.The authors also acknowledged the funding and support by the EU project Sustainable Process Integration Laboratory – SPIL, funded as project No. CZ.02.1.01/0.0/0.0/15_003/0000456, by Czech Republic Operational Programme Research and Development, Education, Priority 1: Strengthening capacity for quality research under a collaboration agreement with the Universiti Teknologi Malaysia - UTM, Malaysia. The UTM Zamalah Grant also funded this research by the Universiti Teknologi Malaysia, under the Vot No. of 00N04.

References

Alsawy T., Rashad E., El-Qelish M., Mohammed R. H., 2022, A comprehensive review on the chemical regeneration of biochar adsorbent for sustainable wastewater treatment, Nature Partner Journal Clean Water, 5(1), 29.

Amin M., Alazba A., Shafiq M., 2018, Removal of copper and lead using banana biochar in batch adsorption systems: isotherms and kinetic studies, Arabian Journal for Science and Engineering, 43(11), 5711-5722.

Awan S., Ippolito J. A., Ullman J., Ansari K., Cui L., Siyal A., 2021, Biochars reduce irrigation water sodium adsorption ratio, Biochar, 3(1), 77-87.

Bashir I., Lone F. A., Bhat R. A., Mir S. A., Dar Z. A., Dar S. A., 2020, Concerns and threats of contamination on aquatic ecosystems, Bioremediation and Biotechnology, 1-26.

Bayuo J., Abukari M. A., Pelig-Ba K. B., 2020, Desorption of chromium (VI) and lead (II) ions and regeneration of the exhausted adsorbent, Applied Water Science, 10(7), 1-6.

Bayuo J., Pelig-Ba K. B., Abukari M. A., 2019, Adsorptive removal of chromium (VI) from aqueous solution unto groundnut shell, Applied Water Science, 9(4), 1-11.

Binh Q. A., Nguyen H.-H., 2020, Investigation the isotherm and kinetics of adsorption mechanism of herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) on corn cob biochar, Bioresource Technology Reports, 11, 100520.

Bion N., Can F., Courtois X., Duprez D., 2018, Transition metal oxides for combustion and depollution processes, In: Védrine JC (Editor), Metal Oxides in Heterogeneous Catalysis, Elsevier, pp. 287-353.

Dai Y., Zhang N., Xing, C., Cui Q., Sun Q., 2019, The adsorption, regeneration and engineering applications of biochar for removal organic pollutants: A review, Chemosphere, 223, 12-27.

Greiner B. G., Shimabuku K. K., Summers R. S., 2018, Influence of biochar thermal regeneration on sulfamethoxazole and dissolved organic matter adsorption, Environmental Science: Water Research & Technology, 4(2), 169-174.

Guo L., Zhao L., Tang Y., Zhou J., Shi B., 2022, An iron–based biochar for persulfate activation with highly efficient and durable removal of refractory dyes, Journal of Environmental Chemical Engineering, 10(1), 106979.

Herath A., Layne C. A., Perez F., Hassan E. I. B., Pittman C. U., Mlsna T. E., 2021, KOH-activated high surface area Douglas Fir biochar for adsorbing aqueous Cr(VI), Pb(II) and Cd(II), Chemosphere, 269, 128409.

Ibrahim I., Tsubota T., Hassan M. A., Andou Y., 2021, Surface functionalization of biochar from oil palm empty fruit bunch through hydrothermal process, Processes, 9(1), 149.

Jamaludin N., Rashid S.A., Tan T., 2019, Natural biomass as carbon sources for the synthesis of photoluminescent carbon dots, Synthesis, Technology and Applications of Carbon Nanomaterials, Elsevier, pp. 109-134.

Khondoker M., Mandal S., Gurav R., Hwang S., 2023, Freshwater shortage, salinity increase, and global food production: A need for sustainable Irrigation water desalination—A scoping review, Earth, 4(2), 223-240.

Larasati A., Fowler G. D., Graham N. J. D., 2021, Insights into chemical regeneration of activated carbon for water treatment, Journal of Environmental Chemical Engineering, 9(4), 105555.

López Y. C., Ortega G. A., Reguera E., 2022, Hazardous ions decontamination: From the element to the material. Chemical Engineering Journal Advances, 11, 100297.

Márquez P., Benítez, A., Chica A. F., Martín M. A., Caballero A., 2022, Evaluating the thermal regeneration process of massively generated granular activated carbons for their reuse in wastewater treatments plants, Journal of Cleaner Production, 366, 132685.

Nguyen B. T., Dai Dinh G., Dong H. P., Le L. B., 2022, Sodium adsorption isotherm and characterization of biochars produced from various agricultural biomass wastes, Journal of Cleaner Production, 131250.

Nyakuma B. B., Wong S., Mong G. R., Utume L. N., Oladokun O., Wong K. Y., Ivase T. J. P., Abdullah T. A. T., 2021, Bibliometric analysis of the research landscape on rice husks gasification (1995–2019), Environmental Science and Pollution Research, 28(36), 49467-49490.

Nyakuma B. B., Wong S. L., Oladokun O., Bello, A. A., Hambali H. U., Abdullah T. A. T., Wong K. Y., 2023, Review of the fuel properties, characterisation techniques, and pre-treatment technologies for oil palm empty fruit bunches, Biomass Conversion and Biorefinery, 13(1), 471-497.

Odega C. A., Ayodele O. O., Ogutuga S. O., Anguruwa G. T., Adekunle A. E., Fakorede C. O., 2023, Potential application and regeneration of bamboo biochar for wastewater treatment: A review, Advances in Bamboo Science, 2, 100012.

Patel H., 2021, Review on solvent desorption study from exhausted adsorbent. Journal of Saudi Chemical Society, 25(8), 101302.

Tan H., Ong P. Y., Klemeš J. J., Bong, C. P. C., Li, C., Gao Y., Lee C. T., 2021, Mitigation of soil salinity using biochar derived from lignocellulosic biomass, Chemical Engineering Transactions, 83, 235-240.

Tan H., Wahab R. A., Ong P. Y., Goh, P. S., Wong K. Y., Klemeš J. J., Lee C. T., 2023a, Functionalisation of Biowaste-derived Biochar via Accelerated Hydrothermal-assisted Pre-treatment for Enhanced Sodium Ion Adsorption, Biomass Conversion and Biorefinery, 1-18.

Tan H., Ong P. Y., Wahab R. A., Goh P. S., Wong K. Y., Klemeš J. J., Fan Y. V., Yaakob H., Lee C. T., 2023b, Mechanistic insight and optimisation of hydrothermally pre-treated biowaste-derived biochar for saline water treatment, Journal of Cleaner Production, 138465.

Tyagi U., 2022, Enhanced adsorption of metal ions onto Vetiveria zizanioides biochar via batch and fixed bed studies, Bioresource Technology, 345, 126475.

Yusof M. S. M., Othman M. H. D., Wahab R. A., Jumbri K., Razak F. I. A., Kurniawan T. A., Samah, R. A., Mustafa A., Rahman M. A., Jaafar J., 2020, Arsenic adsorption mechanism on palm oil fuel ash (POFA) powder suspension, Journal of Hazardous Materials, 383, 121214.