Environmental Research and Technology
https://dergipark.org.tr/en/pub/ert
DOI: https://doi.org/10.35208/ert.1561633

Environmental Research & Technology

Research Article

Economic performance assessment of malt dust derived biochar application for groundwater treatment: A circular economy approach

Pelin SOYERTAŞ YAPICIOĞLU [1]

[1] *Harran University Environmental Engineering Department, 63050 Sanliurfa, Türkiye*

ARTICLE INFO

Article history
Received: 04 October 2024
Revised: 27 November 2024
Accepted: 12 December 2024

Key words:
Biochar, energy costs, groundwater, nitrate, reduction

ABSTRACT

This paper mainly aimed to determine the energy cost reduction for groundwater treatment using the economic and innovative biochar adsorption process. From this point of view, malt dust which is a by-product of brewery industry was utilized as the agro-industrial raw material for the biochar production, in this study. Slow pyrolysis was performed under three different temperatures which are 250 (M1), 300 (M2) and 500 °C (M3) to produce the biochar. This unique biochar was used for the groundwater treatment as an innovative and effective water treatment technique. The groundwater was sampled from three observation points which were Uğraklı, Yaygılı and Bolatlar resources located at the Harran Plain before and post-irrigation. An economic performance assessment was carried out to benchmark the conventional and biochar adsorption processes. A new energy cost indicator (ECI) was developed based on nitrate (NO_3^-) removal. Averagely 91.69% of removal efficiency of NO_3^- was reported using three types of malt dust derived biochar. Approximately, 65.87% of reduction on energy costs was obtained using biochar adsorption process.

Cite this article as: Yapıcıoğlu P. Economic performance assessment of malt dust derived biochar application for groundwater treatment: A circular economy approach. Environ Res Tec 2025;8(4) 802-808.

INTRODUCTION

European Union (EU) Blue Deal has handled with the protection and remediation of vulnerable freshwater resources such as groundwater [1]. There are several groundwater remediation techniques [2]. Biochar application is one of these treatment techniques for the groundwater remediation [3, 4, 5]. Also, biochar application is considered as an efficient and cost-effective groundwater treatment technique [4]. Nitrate is one of the main groundwater pollutants should be disposed immediately [2]. There are several nitrate removal techniques in recent years [2]. Biochar adsorption process has been widely used for the nitrate removal from groundwater in recent years due to its stable structure, effective adsorption capacity and being economical [6, 7].

Biochar which is a carbonaceous by-product of the thermochemical processes of different bio-wastes which could adsorb the emerging pollutants [6, 7, 8, 9]. Biochar could easily adsorb the nitrate from groundwater [2]. Biochar can be produced from several feedstocks which are waste or raw materials [10, 11, 12]. Also, waste reduction and recycling are one of the major topics which have contributed to the circular economy for several environmental applications according to the EU Green Deal [13, 14]. EU Green Deal has recommended waste minimization and development of zero-waste policies for the industrial plants to achieve the circular economy targets [13, 14].

From this point of view, malt dust which is a by-product of brewery industry was used as the agro-industrial raw material for the biochar production, in this study. Also, nitrate adsorption was investigated onto the biochar. This study also recommended a waste reduction technology for brewery in-

***Corresponding author.**
*E-mail address: pyapicioglu@harran.edu.tr

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dustries to recycle the wastes. In this context, this paper represented a techno-economic performance assessment using biochar application for groundwater treatment in terms of c removal. A new energy cost indicator (ECI) was developed based on NO_3^- removal. This study majorly aimed to define the energy cost reduction for groundwater treatment using the innovative biochar adsorption process. This study also recommended a waste reduction technology for brewery industries to recycle the wastes. This study is original that malt dust derived biochar application was firstly applied as groundwater treatment technique to remove the NO_3^-. In the literature, Fseha et al. (2022) investigated nitrate removal from groundwater using date palm waste derived biochar [15]. In another study, Geng et al. (2022) used bamboo chopstick biochar electrode in order to remove nitrate from groundwater [16]. Wang et al. (2022) investigated nitrate removal biochar-assisted aluminum-substituted mineral [17]. Another study by Han et al. (2021) was conducted on removal of nitrate from groundwater using biochar derived from sawdust and iron oxide [18]. Xia et al. (2024) researched the nitrate removal from groundwater using biochar-based zero valent iron [19]. Liu et al. (2022) removed nitrate from groundwater using biochar-based iron composites [20].

MATERIALS AND METHODS

Experimental Procedure and Adsorption Process

The groundwater sampling points were Uğraklı, Yaygılı and Bolatlar resources located at the Harran Plain before and post-irrigation. These periods were selected to determine the effect of irrigation on the techno-economic performance. Impregnation (fertilization) was not applied at these sampling periods. Only farmers normally irrigated the areas the sampling points. NO_3^- analyses were performed according to standard methods using Aquamerck© nitrate kit [21]. The coagulation-flocculation process was applied as the conventional treatment method. The coagulant was alum (Al2(SO4)3) and the dose of alum was 20 mL/L.

An adsorption column was used which volume was 1 liter. In this study, a new NO_3^- adsorption calculation model was developed based on general adsorption theory by Metcalf and Eddy, (2014) (Eq.1.) [22]. The mixture of three types of biochar were added in the amount of 9 grams, totally into the adsorption column. 3 grams of each biochar was added. The optimum amount was decided according to the adsorption assays for the maximum NO_3^- removal performance from groundwater.

$$q_e = \frac{(N_0 - N_e)\,G}{B} \quad (1)$$

N0: NO_3^- concentration (mM) before treatment with biochar

N_e: NO_3^- concentration (mM) after treatment with biochar

G: Groundwater volume (L)

B: Biochar (adsorbent) dose (g)

q_e: the quantity of NO_3^- onto the biochar (mmol/g)

Biochar Production Process and Characterization Analyses

Biochar was produced using malt dust which was ensured from a brewery industry in Turkey. A fluidized bed reactor was used for the slow pyrolysis at 250, 300 and 500 °C (M1, M2 and M3), respectively. Malt dust is a solid and large by-product of the brewery industries. Firstly, the raw material was grinded for the homogenous texture. The operating conditions of pyrolysis were 10°C/minute of heating rate, 30 minutes of steam residence time and 2 hours of heating time. Argon was used as the refrigerant gas and its flow rate was 5 NL/min. X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectrometry (FTIR), and BET (Brunauer, Emmett, and Teller) analyses were applied to define the characterization and the major properties of the biochar. Structures of biochar were investigated using a scanning electron microscope (Zeiss Evo 50). Biochar was degassed in vacuum at 120°C for 6 h. Specific surface areas and pore size distributions were predicted using BET. XRD analyses were applied using Rigaku Ultima III for the record of crystalline textures at an X-Ray diffractometer. The FTIR analyses was applied by IRTracer-100shimadzo. The characterization analyses were performed at 25°C.

Techno-Economic Performance Assessment

An economic performance assessment was performed to benchmark the conventional and biochar adsorption processes. A new energy cost indicator (ECI) was developed based on nitrate (NO_3^-) removal. Then, energy costs (EC) were accounted using a new approach which was derived in this study.

ECI was developed based on a model recommended by Castellet-Viciano et al. (2018) [23]. The basic estimation model of ECI for full-scale wastewater treatment plants was given in Eq. 2. [23,24]. The new developed tool (ECI) was shown in Eq. 3.

$$EC = AV^{b} e^{(\Sigma\, ajxj)} \quad (2)$$

Where,

EC: Energy cost of the wastewater treatment plants

V: Volume of wastewater treated per year

xj: Kinds of independents in the treatment process

A, b, and α: Coefficients of the sensitivity analysis

$$ECI = 1989\ 10^{6} V^{0.754} e^{(-15.25RNO3 + 0.65Z)} \quad (3)$$

In Eq. 3., V describes the volume of water treated per year, RNO3 means to the nitrate removal ratio (%) and Z defines the performance indicator. The calculation tool of Z was given in Eq. 4. [24]. In Eq. 4., q and Q mean to the design water flow and operational water flow of a treatment system.

$$Z = \frac{(q - Q)}{Q} * 100 \quad (4)$$

Then, a new EC (€/m³ water) tool was developed based on ECI, energy consumption (c) (kWh/m³) and Ω (specific cost per 1 kWh energy of the system (€/kWh) (Eq.5.). In Turkey, Ω was assumed as 1.3958 Turkish lira /kWh [25].

$$EC = ECI \ x \ c \ x \ \Omega \tag{5}$$

RESULTS AND DISCUSSIONS

Nitrate Removal Using Biochar Adsorption Process

The results revealed that malt dust derived biochar could adsorb the NO_3^- in groundwater. Figure 1 showed the removal efficiencies related to each biochar for three sampling points. Averagely 91.69% of NO_3^- removal efficiency was reported using three types of malt dust derived biochar. The most efficient biochar was M1 which was produced at the lowest pyrolysis temperature. In Bolatlar, 98.5 % of NO_3^- removal efficiency was observed before irrigation using M1. The nitrate concentrations of each process were given in detail in Table 1. Irrigation had significant effect on NO_3^- concentrations for all processes. The concentrations were lower at post-irrigation periods. The dilution could be formed in the result of irrigation. The dilution could lead to the lower concentrations. Irrigation is considered to have a positive effect on nitrate removal. There are several studies related to dilution and groundwater pollution reduction in these areas [4, 26, 27]. Peak changes in water quality parameters occur in minimum and maximum before and post- irrigation periods [26]. There are many studies in the literature showing the positive and diluting effects of irrigation on water quality parameters [4, 26, 27]. In this study, based on this perspective, the periods were preferred as before and post- irrigation.

Fseha et al. (2022) reported 94.94% of NO_3^- removal using date palm waste derived biochar [15]. In this study, higher NO_3^- removal amounts were reported before irrigation (up to 98.5 %). It could be considered that malt dust derived biochar was more effective. The nitrate removal efficiency reached 75.8% using bamboo chopstick biochar electrode in the study by Geng et al. (2022) [16]. It could be said that only biochar was more effective to remove nitrate than electrode system. Wang et al. (2022) reported that biochar addition improved the NO_3^- removal from groundwater using aluminum-substituted goethite [17]. Han et al. (2021) reported that approximately 71% of nitrate was mitigated using biochar derived from saw dust and iron oxide [18]. It could be considered that only malt dust derived biochar was more effective rather than saw dust derived biochar assisted by iron oxide. Xia et al. (2024) researched the 93.37 ± 0.33% of nitrate removal from groundwater using biochar-based zero valent iron [19]. Liu et al. (2022) reported 97.29% to 89.04% of nitrate removal from groundwater using biochar-based iron composites [20].

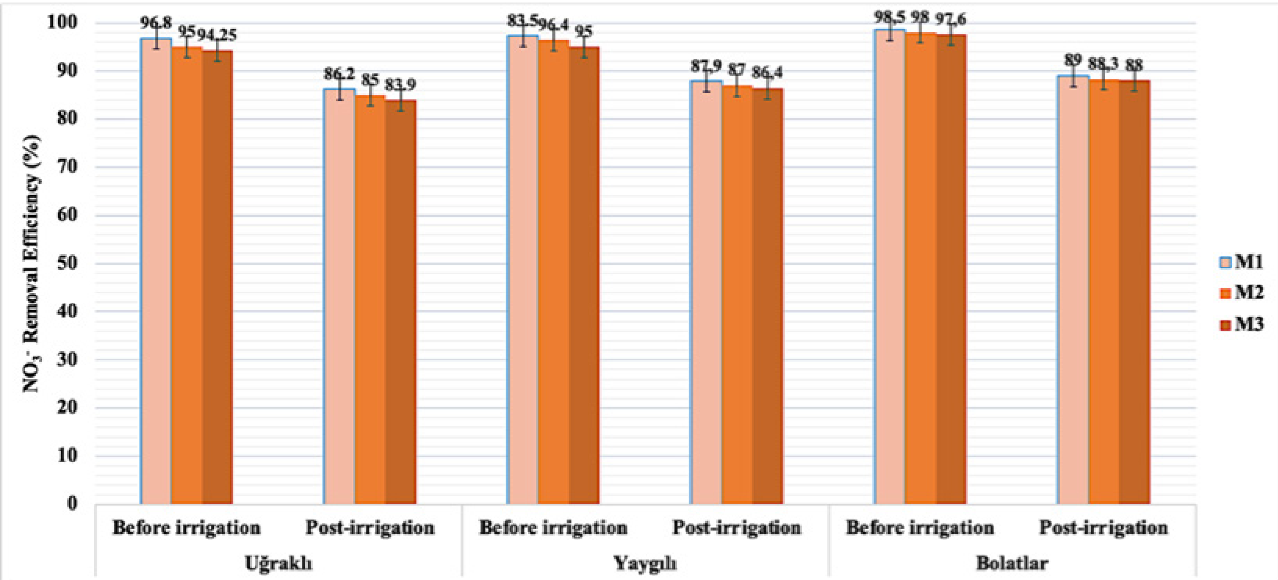

Figure 1. NO_3^- removal efficiencies (%) in terms of each biochar

Table 1. NO_3^- concentrations related to each process

			NO_3^- concentration (mg/L)			
Resource	**Period**	**Raw water**	**Coagulation-Flocculation Process**	**M1**	**M2**	**M3**
Yaygılı	Before irrigation	95	24.7	2.565	3.42	4.75
	Post-irrigation	51	16.32	6.171	6.63	6.936
Bolatlar	Before irrigation	535	139.1	8.025	10.7	12.84
	Post-irrigation	115	36.8	12.65	13.455	13.8
Uğraklı	Before irrigation	121	31.46	3.872	6.05	6.9575
	Post-irrigation	35	11.2	4.83	5.25	5.635

Results of Biochar Tests and Nitrate Adsorption

The nitrate adsorption results were given in detail in Table 2. The maximum nitrate capacity related to M1 which was produced at the lowest pyrolysis temperature. The lowest adsorption capacity related to M3 which was generated at the highest pyrolysis temperature.

Table 2. Results of NO_3^- adsorption

NO_3^- Adsorption	**M1**	**M2**	**M3**
qe (mmol/g)	5.84	5.78	5.70

Fseha et al. (2022) investigated the nitrate removal from groundwater using date palm biochar [15]. They reported higher adsorption capacity and removal efficiency (qe: 4.18 mg/g, 94.94%) [15]. Another study by Tan et al. (2020) was performed. They found that 2.1 mg/g NO_3^- adsorption [28]. In this study, higher efficiencies and adsorption amounts were reported. Bakly et al. reported lower NO_3^- adsorption capacity using Macadamia nutshell derived biochar (0.11 mg/g) [29]. Hafshejani et al. (2016) investigated the nitrate by modified sugarcane bagasse biochar [30]. They reported 28.21 mg/g of NO_3^- adsorption capacity [30]. The adsorption results overlapped with SEM, XRD, FTIR and BET analyses results. When the morphology and surface structures of biochar are investigated, porosity is reduced by the increase of temperature. When surface analysis is performed, it is seen that biochar has a flatter structure at the highest temperature. As can be seen from SEM analyses (Figure 2), it is predicted that biochar produced at lowest temperature is more efficient considering the porosity. All biochar has fibrous, prismatic, and spherical forms. Also, the shapes of the pores are irregular.

Table 3. BET analyses result of biochar

NO_3^- Adsorption	**BET Surface Area (m^2/g)**	**Langmuir Surface Area (m^2/g)**	**Total Pore Volume (cm^3/g)**
M1	14.995	26.099	0.359
M2	13.999	24.28	0.29
M3	12.999	22.95	0.219

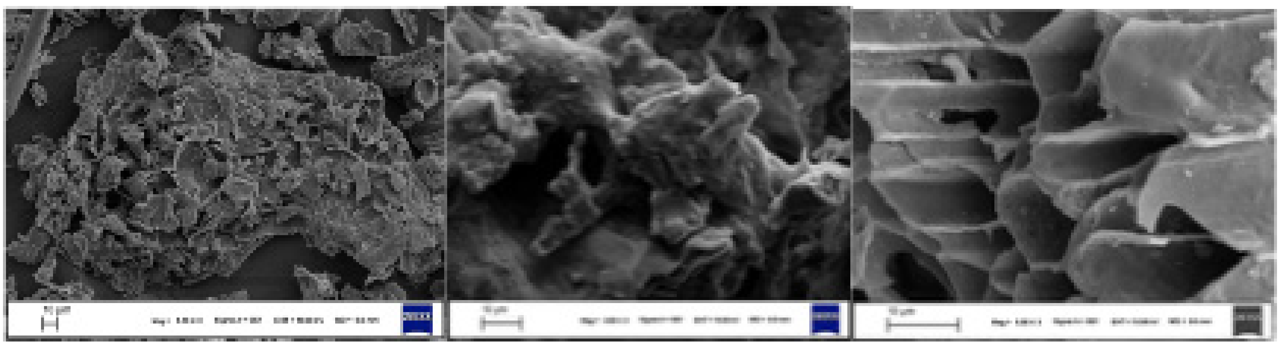

Figure 2. SEM images of biochar

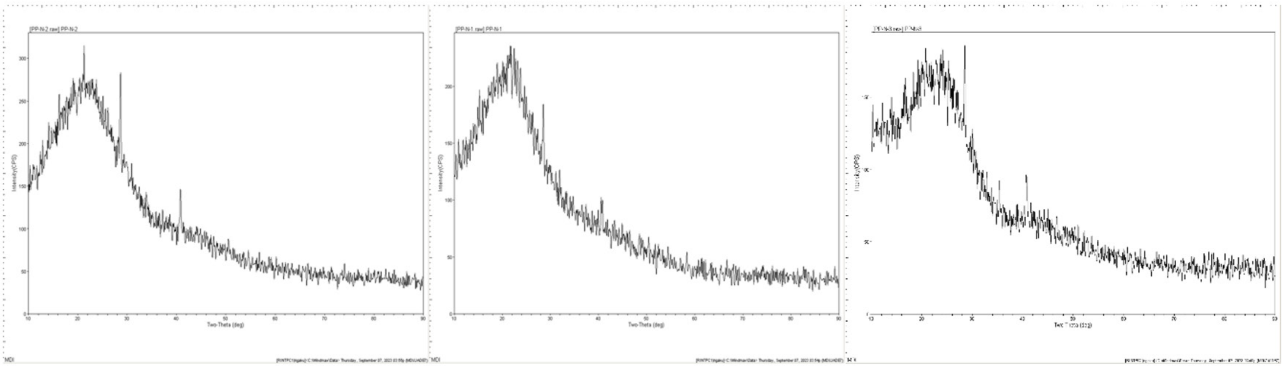

Figure 3. XRD graphics of biochar

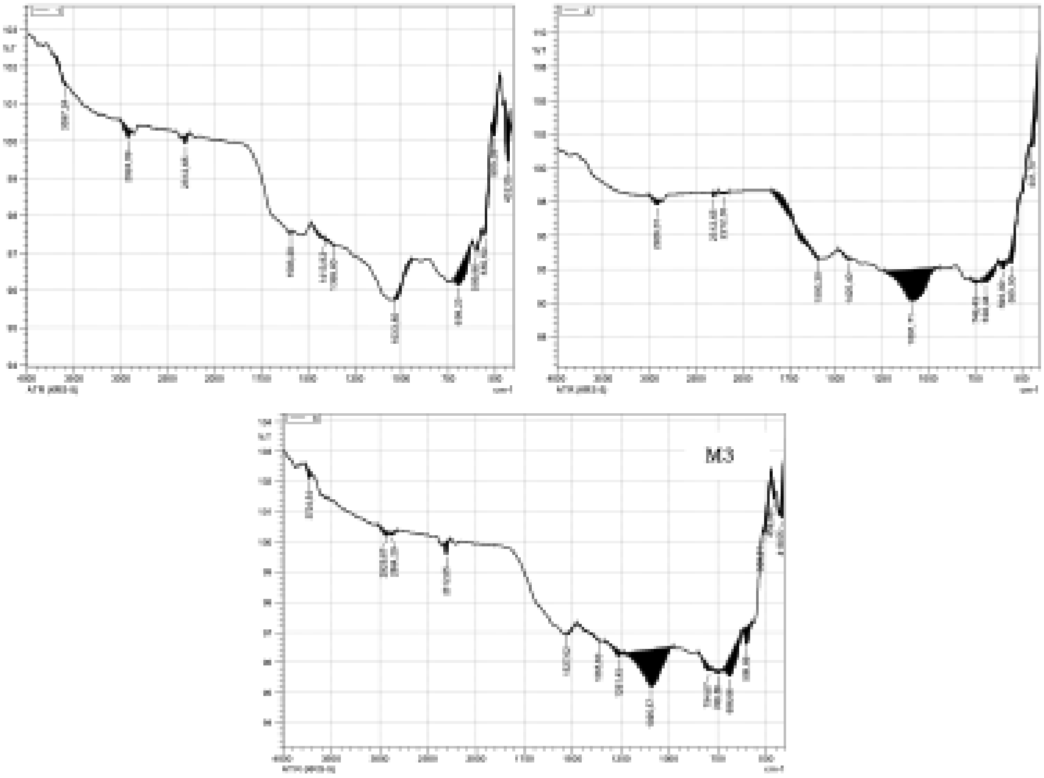

Figure 4. FTIR analyses results of biochar

Figure 3 showed the XRD analyses of biochar. According to the XRD spectrum, it could be said that amorphous structure was observed in all 3 samples. Also, FTIR analyses (Figure 4) were applied. According to FTIR analyses, three types of biochar contain alkaline functional groups. Malt dust derived biochar has higher buffering capacity due to alkaline functional groups. Due to alkaline functional groups, nitrate could be captured by malt dust derived biochar. According to the BET analyses (Table 3), the greatest surface area belonged to M1. The adsorption results were verified by BET analyses.

Results of Economic Performance Assessment

Figure 5 represented the energy costs and energy cost indictor values. According to the results, the highest energy costs related to conventional treatment with the value of 1256.22 €/m^3 water. The lowest energy costs corresponded to M1 (349.02 €/m^3 water). Approximately, 65.87% of reduction on energy costs was obtained using biochar adsorption process.

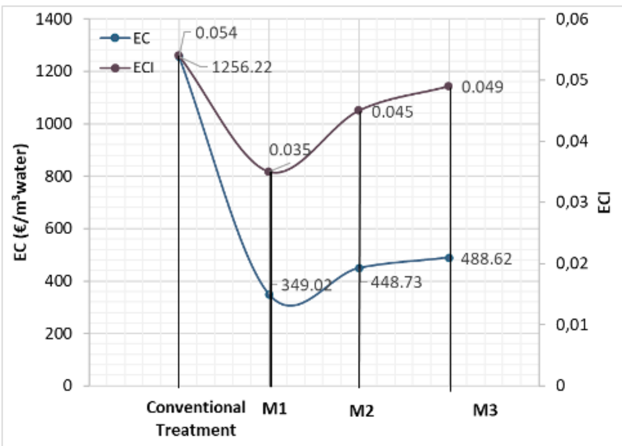

Figure 5. Energy costs based on NO_3^- removal related to processes

There were restricted studies related to this topic. Samson et al. (2018) investigated the effect of groundwater flow on cost minimization [31]. This study concentrated on groundwater treatment. Mirzaei et al. (2019) focused on agricultural production and energy costs [32]. Marchioni et al. (2023) performed a costs-benefit analysis for the use of Shallow Groundwater [33]. Apart from these studies, this study recommended the biochar application to reduce the energy costs. Brookfield et al. (2024) estimated the groundwater pumping for irrigation in terms of energy costs [34].

CONCLUSION

According to the experimental study, the most effective and eco-environmentally friendly biochar was M1 which was the biochar generated at the lowest pyrolysis temperature. This study confirmed that malt dust derived biochar is an efficient and low-cost adsorbent for NO_3^- removal from groundwater. Further research should be increased in this field. Averagely 91.69% of NO_3^- removal efficiency was reported using three types of malt dust derived biochar. Approximately, 65.87% of reduction on energy costs was obtained using biochar adsorption process.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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