Indonesian Journal of Environmental Management and Sustainability
e-ISSN:2598-6279 *p*-ISSN:2598-6260

IJEMS

Research Paper

Hydrothermal Carbonization of *Eucheuma cottonii* for Selective Adsorption of Anionic Dyes

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Abstract

The contamination of wastewater with synthetic dyes, particularly anionic dyes, poses a significant environmental challenge due to their persistence and difficulty in removal. Traditional adsorbents are often expensive or inefficient, driving the need for sustainable, eco-friendly alternatives. In response to this problem, this study explores the use of *Eucheuma cottonii*, a fast-growing and widely available macroalgae, as a raw material for producing hydrochar through hydrothermal carbonization (HTC). The goal is to develop a renewable and effective adsorbent capable of selectively removing anionic dyes from contaminated water. Hydrochar was synthesized at two different HTC temperatures, 150°C and 250°C, and its surface properties were characterized using FT-IR and BET analyses. Adsorption experiments were conducted on four anionic dyes-Congo Red (CR), Direct Yellow (DY), Methyl Orange (MO), and Direct Green (DG)-under varying pH, contact time, dye concentration, and temperature conditions. The hydrochar produced at 250°C (HC-250) demonstrated the highest surface area and pore volume, leading to superior adsorption performance, particularly for DY. Kinetic studies revealed a chemisorption-driven mechanism, while thermodynamic analysis confirmed the adsorption process to be spontaneous and endothermic, with both chemisorption and physisorption contributing to dye removal. The adsorption behavior followed the Langmuir isotherm model, indicating monolayer adsorption, with minimal interaction between adsorbed molecules. Regeneration tests confirmed that *Eucheuma cottonii* hydrochar could be reused over multiple cycles with minimal efficiency loss. Future work could optimize the HTC process by adjusting pressure, heating rates, and pre-treatment methods to improve adsorption properties. Incorporating nanomaterials or metal oxides could enhance adsorption for a wider range of pollutants, while machine learning could predict adsorption behavior under different conditions. Additionally, exploring the hydrochar's use in energy storage or as a catalyst offers promising applications. Life-cycle assessments (LCAs) and techno-economic analyses (TEAs) will be vital for assessing scalability and environmental impact, positioning *Eucheuma cottonii* hydrochar as a sustainable, multifunctional material for industrial applications.

Keywords

Eucheuma cottonii Hydrochar, Hydrothermal Carbonization, Selectivity, Anionic Dyes

Received: 26 August 2024, Accepted: 16 November 2024
https://doi.org/10.26554/ijems.2024.8.4.154-165

1. INTRODUCTION

Water pollution has become a significant environmental challenge in modern society, particularly due to the increasing discharge of synthetic dyes from various industrial processes, such as textile, plastics, and paper manufacturing (Yaseen and Scholz, 2019; Verma et al., 2022). These dyes, especially anionic dyes, are chemically stable and resistant to degradation, making them persistent in aquatic environments. This long-term presence disrupts aquatic ecosystems by reducing oxygen levels and interfering with the biological cycles of marine organisms (Palapa et al., 2019a,b). Moreover, many dyes are non-biodegradable and toxic, even in small concentrations, posing serious health risks to both aquatic life and humans (Verma et al., 2022).

Various methods have been developed to remediate dye-contaminated wastewater, including chemical, physical, and biological techniques. Methods such as photodegradation, precipitation, ion exchange, coagulation, membrane filtration, and photocatalysis have been explored extensively (**?**Hamad and Idrus, 2022). While these approaches offer certain advantages, they are often limited by high costs, operational complexity, and low efficiency in removing specific

dyes. Adsorption has emerged as one of the most effective and feasible solutions due to its simplicity, cost-effectiveness, and high efficiency (Ahmad and Kumar, 2023). However, beyond efficiency, the selectivity of adsorbents is critical in targeting specific contaminants in wastewater, as different dyes and pollutants vary in their chemical properties. Selectivity allows for the removal of targeted substances, making adsorption processes more precise and adaptable to complex wastewater conditions (Gupta and Nayak, 2020). Conventional adsorbents, such as activated carbon, are commonly used for dye removal but are expensive and difficult to regenerate, raising concerns about sustainability (Jegatheesan et al., 2020). Consequently, there is increasing interest in finding alternative adsorbents that are both sustainable and cost-effective. Biomass-derived adsorbents, particularly those from seaweeds and other organic sources, offer a promising solution due to their abundance, biodegradability, and renewability (Ahmad and Kumar, 2023; Wijaya and Yuliasari, 2023). Previous studies have demonstrated the effectiveness of several algae-based adsorbents, such as *Spirulina, Chlorella*, and *Gracilaria*, in removing pollutants from wastewater (Ahmad and Kumar, 2023). These studies highlight the potential of algae-derived materials in dye adsorption, providing a more sustainable alternative to conventional materials.

Among these biomass options, macroalgae such as *Eucheuma cottonii* (*E. cottonii*) offer a highly promising solution. *E. cottonii*, which is widely cultivated in tropical regions, especially Southeast Asia, is known for its rapid growth and high biomass yield, making it a plentiful and renewable resource for hydrochar production. Utilizing *E. cottonii* for hydrochar manufacturing addresses two key issues: it provides a sustainable alternative to traditional adsorbents, and it offers an effective method for combating environmental contamination. Additionally, *E. cottonii* thrives in saline environments, reducing the need for freshwater resources and further increasing its value as an environmentally friendly industrial material (Meinita et al., 2012).

In this study, we focus on addressing the underexplored potential of *E. cottonii* for selective adsorption of anionic dyes. While previous research has concentrated on other algae like *Spirulina*, *Chlorella*, and *Gracilaria* (Ahmad and Kumar, 2023), *E. cottonii* remains underutilized despite its rapid growth and high biomass yield (Meinita et al., 2012). Additionally, the selective removal of specific dyes from wastewater remains a critical challenge in adsorption technology. Although adsorption is efficient, the lack of selectivity for targeted contaminants limits its practical application (Gupta and Nayak, 2020). This research explores the use of hydrothermal carbonization (HTC) to produce hydrochar from *E. cottonii*, assessing its ability to act as a renewable, eco-friendly adsorbent with high selectivity for anionic dyes. By investigating the characteristics of hydrochar produced at different HTC temperatures, this study aims to close the research gap and provide valuable insights into the development of sustainable, selective adsorbents for water treatment.

2. EXPERIMENTAL SECTION

2.1 Materials and Characterizations

Macroalgae *E. cottonii* was sourced from the coastal waters of Maluku, Indonesia. The study used distilled water (H_2O), as well as dyes such as Congo Red (CR), Direct Yellow (DY), Methyl Orange (MO), and Direct Green (DG). The macroalgae were analyzed using a Shimadzu Prestige-21 FTIR spectrophotometer and BELSORP-miniX BET surface area analyzer. Dye solution absorbance was measured with a UV-visible Biobase spectrophotometer UV BK-1800PC.

2.2 Preparation of Macroalgae *E. cottonii*

E. cottonii was first thoroughly washed to remove any residual dirt and salt, with multiple washes to ensure cleanliness. The macroalgae was then rinsed with distilled water and dried in an oven at 80°C for 5 hours to eliminate moisture (Farobie et al., 2022). Once dried, the macroalgae was ground into a fine powder and sifted through a 200-mesh screen. The processed material was then characterized using FT-IR and BET techniques.

2.3 Preparation of Hydrochar *E. cottonii*

To begin, 2.5 grams of finely ground *E. cottonii* macroalgae was mixed with 50 mL of distilled water. This mixture was then homogenized by stirring with a magnetic stirrer for three minutes before being transferred into a hydrothermal autoclave. The hydrothermal treatment was performed at two different temperatures, 150°C and 250°C, for 3 hours. Afterward, the samples were dried in an oven at 80°C for 48 hours. The hydrochar samples were characterized using BET, and FT-IR techniques. Samples produced at 150°C and 250°C were labeled HC-150 and HC-250, respectively.

2.4 Selectivity and Determination of Optimal Adsorption Conditions

A test for selectivity was performed on hydrochar adsorbent made from macroalgae for anionic dyes including CR, DY, MO and DG. The adsorbent was combined with 50 mg/L of each dye in a solution of 10 mL, and absorbance readings were taken every 2 minutes from 0 to 10 minutes at wavelengths of 400-700 nm. The concentrations of dye that were not used and the concentrations that were taken in were measured with a UV-Vis spectrophotometer. The dye that showed the best selectivity was then utilized to determine the ideal pH for adsorption. A 50 mg/L solution (20 mL) was then pH adjusted from 2-10 with NaOH and HCl, combined with 0.02 grams of adsorbent, and agitated for 30 minutes prior to examination. Then, the best contact time was found by mixing the dye solution at the optimal pH for 10, 20, 35, 55, 70, and 100 minutes. The adsorption

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efficiency was assessed under different dye concentrations (ranging from 40 to 80 mg/L) and temperatures (30°C, 40°C, 50°C, and 60°C). By examining absorbance using a UV-Vis spectrophotometer and adjusting pH, time, concentration, and temperature, the ideal conditions were determined.

2.5 Regeneration Adsorbent

The regeneration process was repeated over seven cycles. After each cycle, the adsorbent, which had been desorbed using 20 mL of a selective dye solution at the optimal concentration, was reintroduced. The mixture was stirred for an optimal duration at the ideal temperature, and the remaining dye concentration in the solution was measured using a UV-Vis spectrophotometer.

3. RESULT AND DISCUSSION

3.1 Characterization of Hydrochar and *E. cottonii*

This section focuses on the characterization of hydrochar derived from *Eucheuma cottonii*, with an emphasis on evaluating its synthesis through hydrothermal carbonization (HTC). Fourier Transform Infrared (FT-IR) spectroscopy was used to analyze chemical composition and structural changes caused by the activation process, allowing the identification of functional groups on the hydrochar's surface.

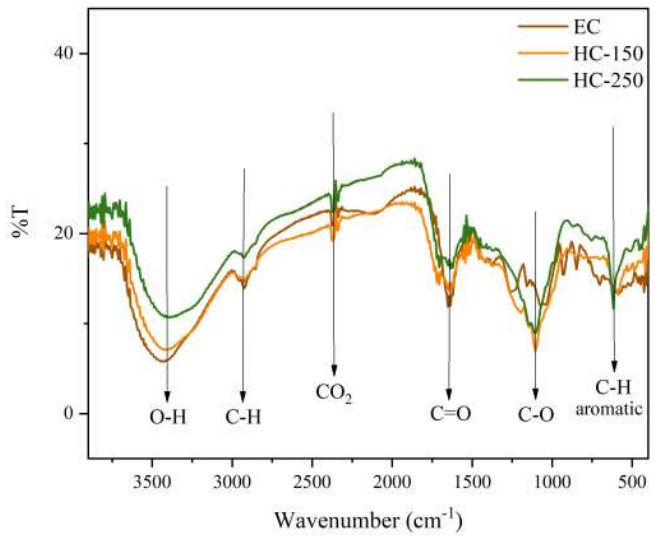


Figure 1. FT-IR Spectrum of the Materials

FT-IR results revealed significant changes in functional groups as the temperature increased during hydrochar production. A strong absorption band around 3425 cm^{-1}, attributed to O–H stretching vibrations (Ariya et al., 2023), was observed across all samples. This band is associated with hydroxyl groups present in water molecules and carbohydrates, though its intensity varied slightly between samples. Additionally, C–H stretching vibrations at 2924 cm^{-1} and 2854 cm^{-1} were detected, indicating the retention of organic material during the hydrochar production process (Ledesma et al., 2021).

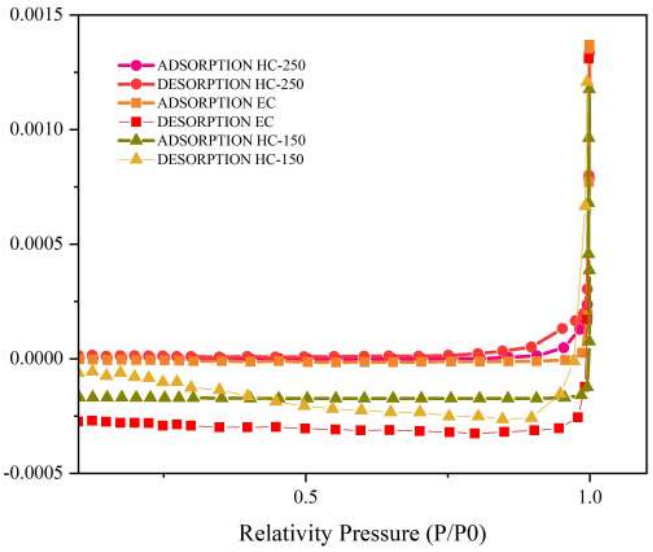


Figure 2. BET Curves of the Materials

Table 1. Surface Area, Average Pore Size and Average Pore Volume of the Materials

Materials	Surface Area (m^2/g)	Average Pore Size (nm)	Average Pore Volume (cm^3/g)
EC	1.533	136.79	0.045
HC-150	1.622	32.044	0.024
HC-250	7.478	35.177	0.17 2

The presence of carboxyl or ester functional groups was noted by a peak at 1651 cm^{-1} in the *E. cottonii* (EC) sample, which shifted slightly to 1705 cm^{-1} in hydrochar samples. This peak, associated with carbonyl (C=O) stretching, became sharper with higher temperatures, especially in HC-250, suggesting enhanced carbonization. The formation of stable carbon structures, such as C=C bonds in aromatic rings, was further confirmed by a band at 1635 cm^{-1} in the HC-250 sample (Ariya et al., 2023; Ledesma et al., 2021; Lin et al., 2021). The FT-IR spectrum shown in Figure 1.

Peaks at 2368 cm^{-1} and 2337 cm^{-1} were linked to CO_2 emissions during carbonization, while C–O stretching bands between 1100 and 1050 cm^{-1}, prominent in EC and HC-150, indicated the presence of alcohols, esters, or ethers (Ariya et al., 2023). As temperature increased, these peaks diminished, suggesting the breakdown of oxygen-containing functional groups at higher activation temperatures. The loss of oxygenated functional groups and the emergence of aromatic structures at higher temperatures aligns with findings from studies on marine algae hydrochar by Lee et al. (2022) and Shoaib et al. (2024).

The BET analysis, shown in Figure 2, and Table 1. shows

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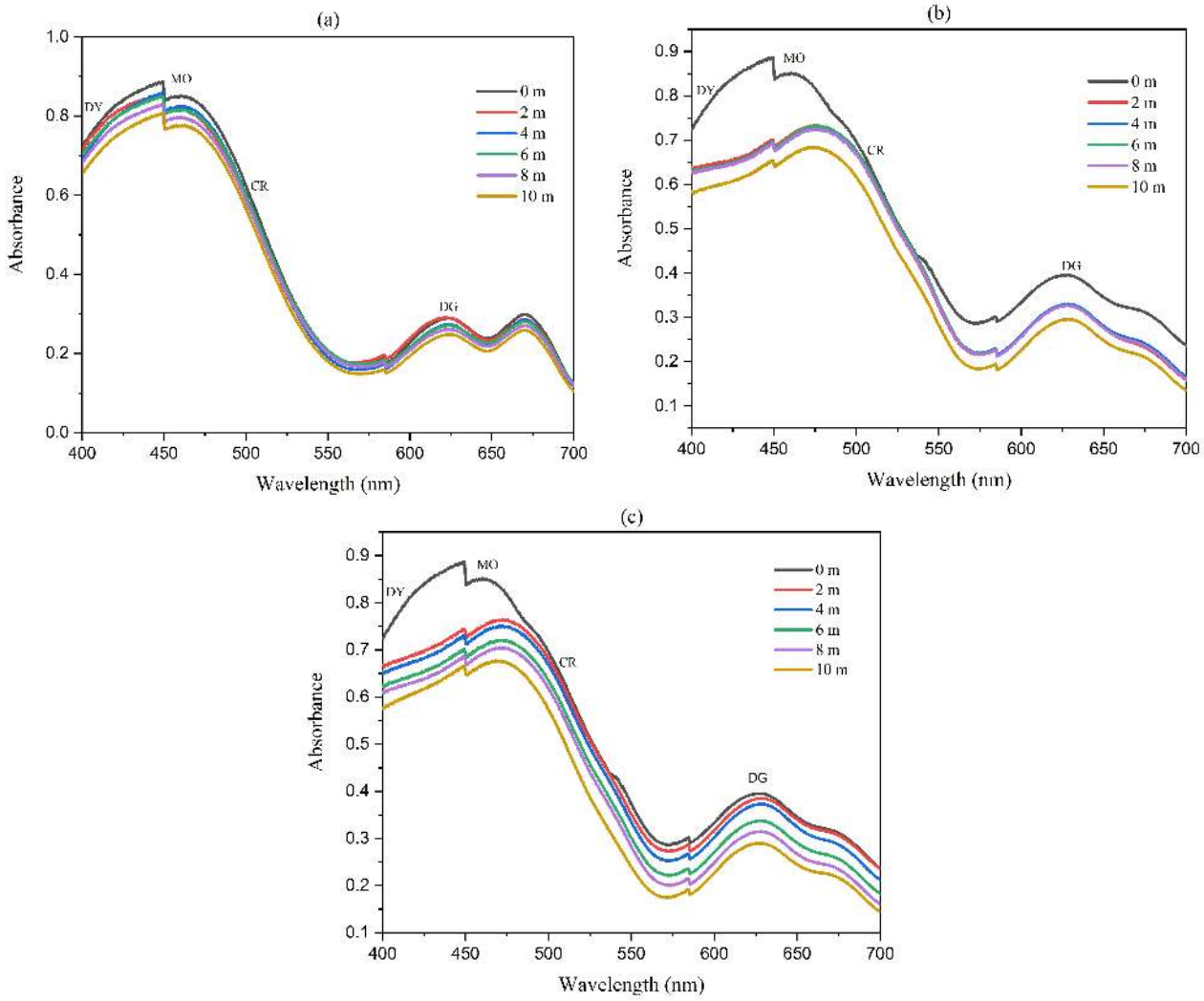


Figure 3. Adsorption Selectivity of Materials in Anionic Dyes: (a) EC (b) HC-150 (c) HC-250

Table 2. The Kinetic Parameters PFO and PSO models by EC, HC-150 and HC-250

Adsorbent	Qe_{exp} (mg/g)	Pseudo First Order			Pseudo Second Order		
		Qe_{calc} (mg/g)	k1 (min^{-1})	R^2	Qe_{calc}(mg/g)	k2 (g/mg)/min	R^2
EC	16.810	19.665	0.0302	0.854	36.630	0.0002	0.730
HC-150	17.616	14.605	0.0299	0.919	20.576	0.0024	0.971
HC-250	19.125	18.105	0.0366	0.978	22.936	0.0021	0.981

the surface area, average pore size and average pore volume of the materials. The BET analysis identified the presence of mesopores (2–50 nm) critical for adsorption through capillary condensation. Surface area increased with temperature, peaking at 7.4776 m^2/g for HC-250, indicating that higher temperatures improved surface activation and adsorption capacity. The unactivated sample had larger pore sizes (32.044 nm for HC-150 and 136.79 nm for non-activated *E. cottonii*), but after activation, HC-250 showed more controlled pores (35.177 nm), ideal for selective adsorption. The increase in pore volume at higher temperatures, especially in HC-250 (0.1718 cm^3/g), provided greater adsorption space.

Compared to other research, *E. cottonii* hydrochar showed notable improvements. Hydrochar from *Chlorella pyrenoidosa* and *Ulva reticulata* typically exhibited surface areas between 12.67 and 23 m^2/g after chemical activation (Guo et al., 2021; Anastopoulos et al., 2024), with similar trends in adsorption efficiency. The development of smaller, more uni-

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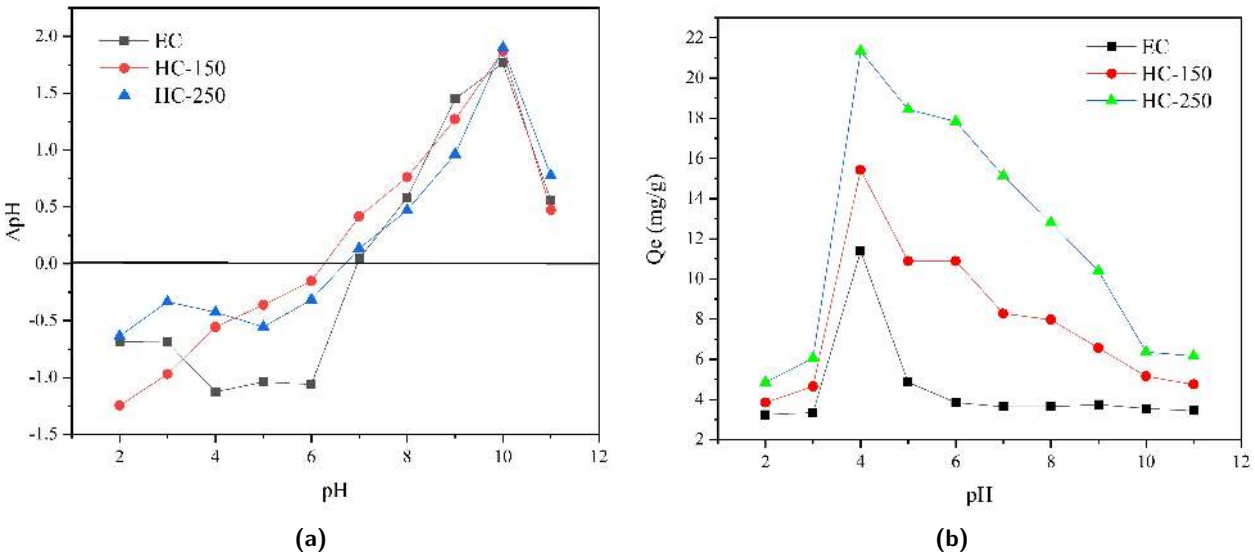


Figure 4. (a) pHpzc and (b) pH Optimum Curves

form pores and increased surface area in HC-250 highlights its potential for selective adsorption applications.

3.2 Adsorption Selectivity of *E. cottonii* Hydrochars

The selectivity of *Eucheuma cottonii*-derived hydrochar for Direct Yellow (DY) was clearly demonstrated in the adsorption experiments, where both raw *E. cottonii* and its hydrochar derivatives (HC-150 and HC-250) exhibited stronger selectivity for DY compared to other anionic dyes such as Methyl Orange (MO), Congo Red (CR), and Direct Green (DG), as shown in Figure 3.

This enhanced selectivity of raw E. *cottonii* for DY is likely due to its intrinsic functional groups, such as hydroxyl (−OH) and carboxyl (−COOH), which interact selectively with dye molecules. This observation aligns with previous research on macroalgae, which highlights that the functional groups present on the algal surface can strongly influence the adsorption of certain dyes (Zhang et al., 2020). Additionally, the molecular size and specific charge distribution of DY may further enhance its selective interaction with the algal surface, providing a competitive advantage over smaller or less charged dyes like MO, CR, and DG (Lee et al., 2022).

As for HC-150, its retention of selectivity for DY can be attributed to the development of additional functional sites during early activation while preserving some of the functional groups from the raw biomass. Lower activation temperatures, like those used for HC-150, help maintain the original biomass structure, which plays a critical role in dye selectivity (Jalilian et al., 2024). The moderate activation temperature results in an increased surface area, allowing for better interaction with DY, a finding consistent with Shoaib et al. (2024) who reported that lower activation temperatures can enhance adsorption by maintaining key surface characteristics conducive to selective dye adsorption.

HC-250, on the other hand, exhibited the highest selectivity for DY, primarily due to its significantly larger surface area and well-developed pore structure. The higher activation temperature intensifies surface interactions, creating a more porous material with unique surface properties, ideal for DY adsorption. This result aligns with the studies by Alabbad et al. (2022), which demonstrated that higher activation temperatures produce materials with enhanced porosity and surface characteristics that significantly improve dye adsorption. The overall trend observed in this study is consistent with prior research, suggesting that the structural and chemical changes that occur during hydrochar production are critical in influencing the selectivity towards anionic dyes like DY.

3.3 Effect of pHpzc and pH of Adsorption

The pH point of zero charge (pHpzc) represents the pH at which the surface of the material has no net electrical charge. This parameter is crucial in adsorption studies because it determines the surface charge behavior of the adsorbent in different pH environments. For this study, the pH pzc values were 6.57 for raw *E. cottonii* (EC), 5.99 for HC-150 and 6.50 for HC-250 This suggests that, at a pH lower than these values, the surface of the hydrochar would carry a positive charge, whereas at a pH above these values, the surface would be negatively charged.

In the context of anionic dye adsorption (such as Direct Yellow, DY), it is critical to operate under conditions where the surface charge is positive, as this enhances electrostatic attraction between the negatively charged dye molecules and the adsorbent surface. In this study, the optimal pH for DY adsorption was found to be pH 4, which is lower than

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Table 3. The Adsorption Isotherm Langmuir and Freundlich Parameter by EC, HC-150 and HC-250

Adsorbent	T (°C)	Langmuir			Freundlich		
		Q_{max}	kL	R^2	N	kF	R^2
EC	30	33.557	0.086	0.919	2.887	123.766	0.436
	40	34.602	0.093	0.953	3.202	112.590	0.469
	50	33.670	0.296	0.924	3.064	116.252	0.396
	60	33.113	0.279	0.925	3.043	116.574	0.391
HC-150	30	34.965	0.319	0.953	3.340	108.468	0.443
	40	35.461	0.339	0.956	3.321	109.421	0.474
	50	33.784	0.294	0.939	3.160	115.798	0.414
	60	33.445	0.284	0.933	3.060	116.413	0.413
HC-250	30	35.461	0.347	0.946	3.330	108.968	0.436
	40	40.323	0.614	0.978	4.108	94.624	0.561
	50	35.211	0.332	0.954	3.320	109.270	0.459
	60	34.483	0.310	0.942	3.233	111.199	0.422

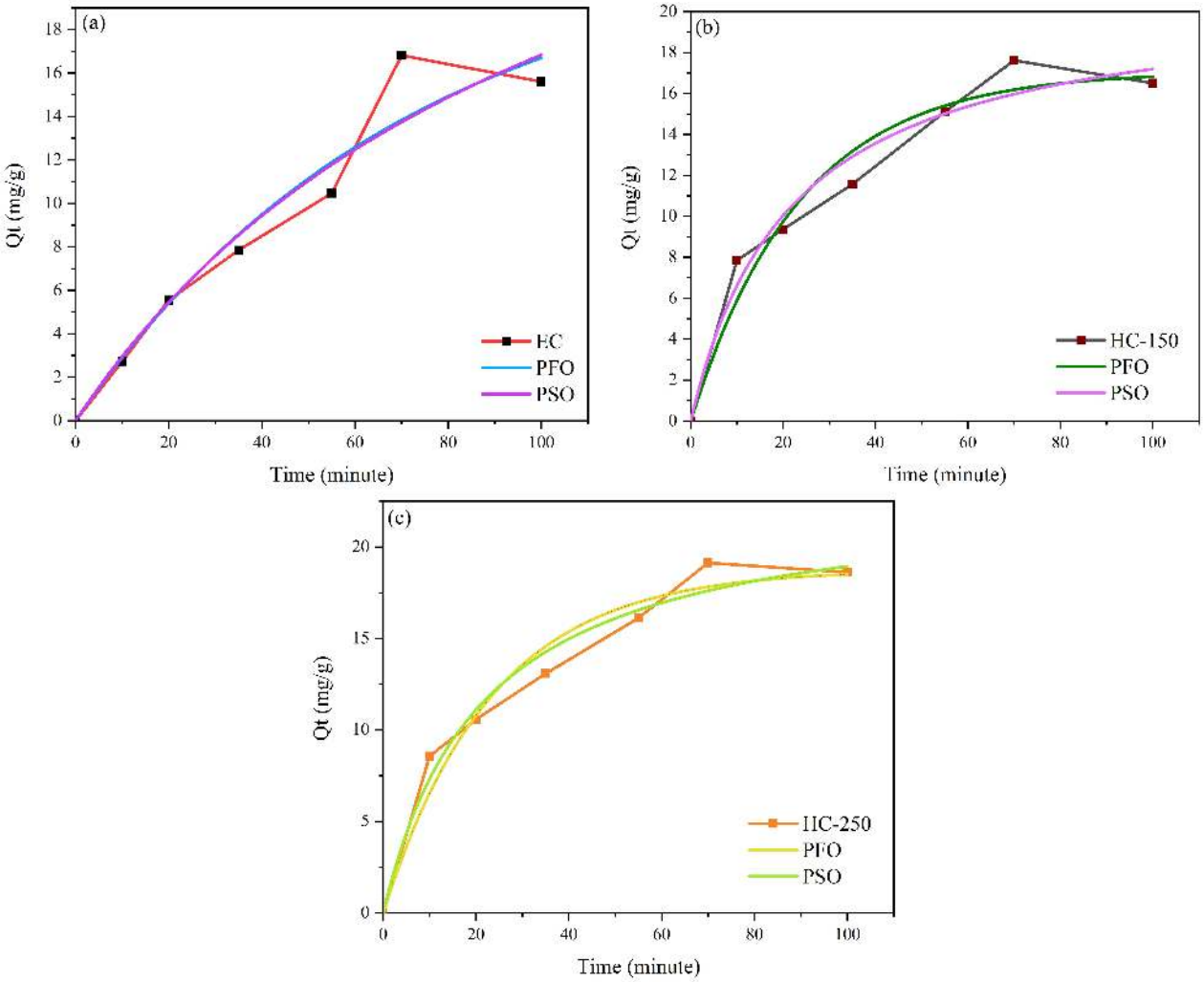


Figure 5. The Impact of Adsorption Contact Time of (a) EC, (b) HC-150 and (c) HC-250

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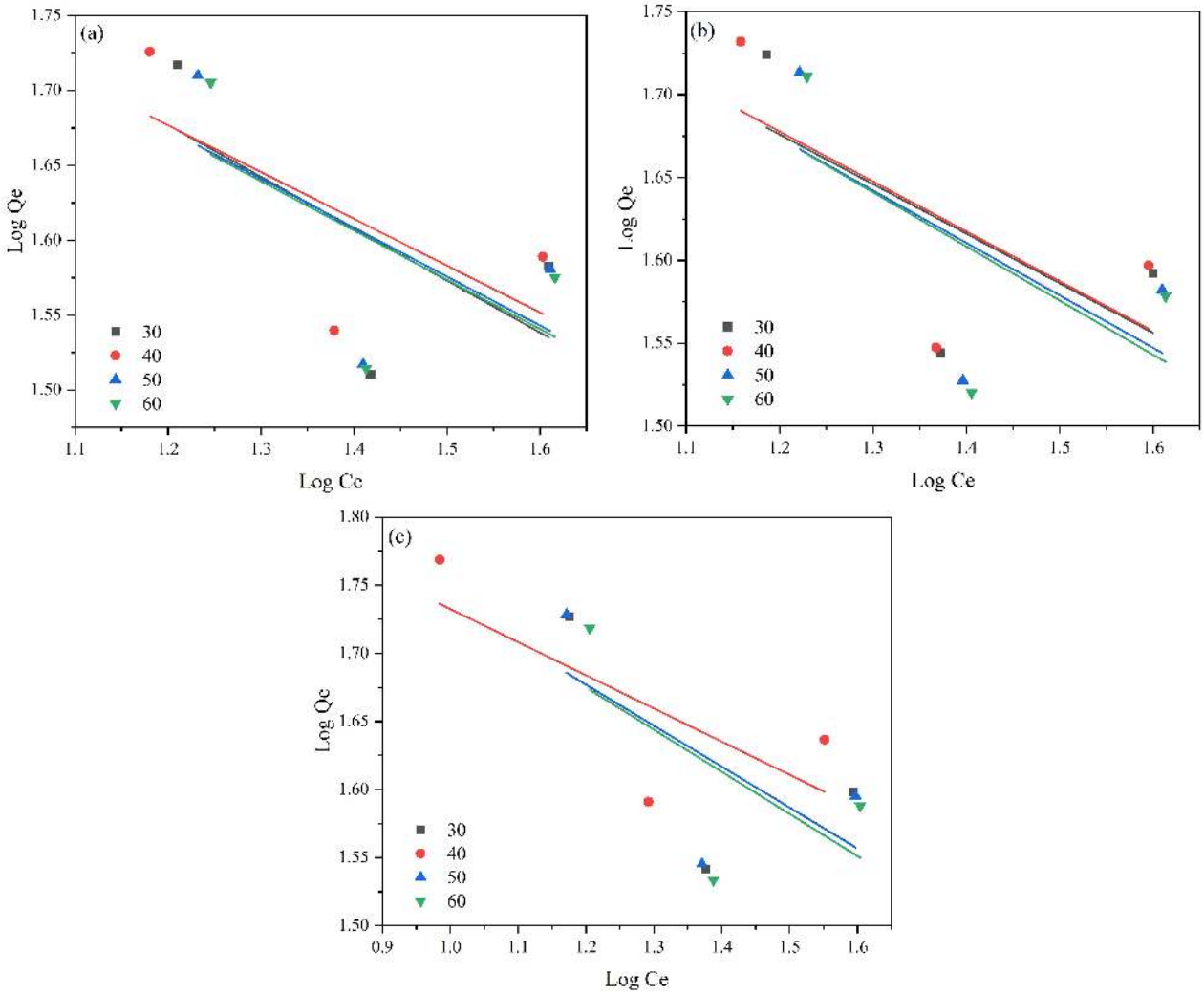


Figure 6. Freundlich Curve of Materials, (a) EC, (b) HC-150 and (c) HC-250

the pH pzc for all hydrochar samples. At this acidic pH, the hydrochar surfaces carry a positive charge, facilitating the adsorption of negatively charged dye molecules due to strong electrostatic interactions.

The result is consistent with the theory that anionic adsorbates, like DY, are more effectively attracted and adsorbed by positively charged surfaces. Electrostatic attraction is one of the key mechanisms in adsorbing ionic species, and this is enhanced when the surface charge of the adsorbent and the charge of the dye are opposite. This relationship between surface charge and dye adsorption efficiency has been well-documented in studies of hydrochar and activated carbon. For instance, research by Zhang et al. (2020) on hydrochar derived from *Spirulina* demonstrated enhanced anionic dye adsorption at pH levels below its pHpzc, which was around 5.8. Similarly, Sztancs et al. (2020) showed that Chlorella vulgaris hydrochar, with a pH pzc of 6.2, exhibited high adsorption efficiency for anionic pollutants at acidic pH levels. These studies corroborate the findings of this research, suggesting that hydrochar materials with pH pzc values in the range of 5.5 to 6.5 are highly effective in adsorbing anionic species in slightly acidic environments.

Moreover, Figure 4 illustrates the relationship between pH pzc and adsorption capacity for DY. The trend shows that as the solution pH approaches pH 4, the adsorption capacity increases significantly, highlighting the critical role of pH in optimizing adsorption efficiency. The combination of surface charge and electrostatic interaction not only drives the adsorption process but also underlines the importance of selecting the correct pH conditions when designing adsorption systems for wastewater treatment.

3.4 Effect of Adsorption Contact Time

Adsorption kinetics are critical in understanding how quickly an adsorbent can capture contaminants from a solution. To analyze the kinetics of DY adsorption onto *E. cottonii*

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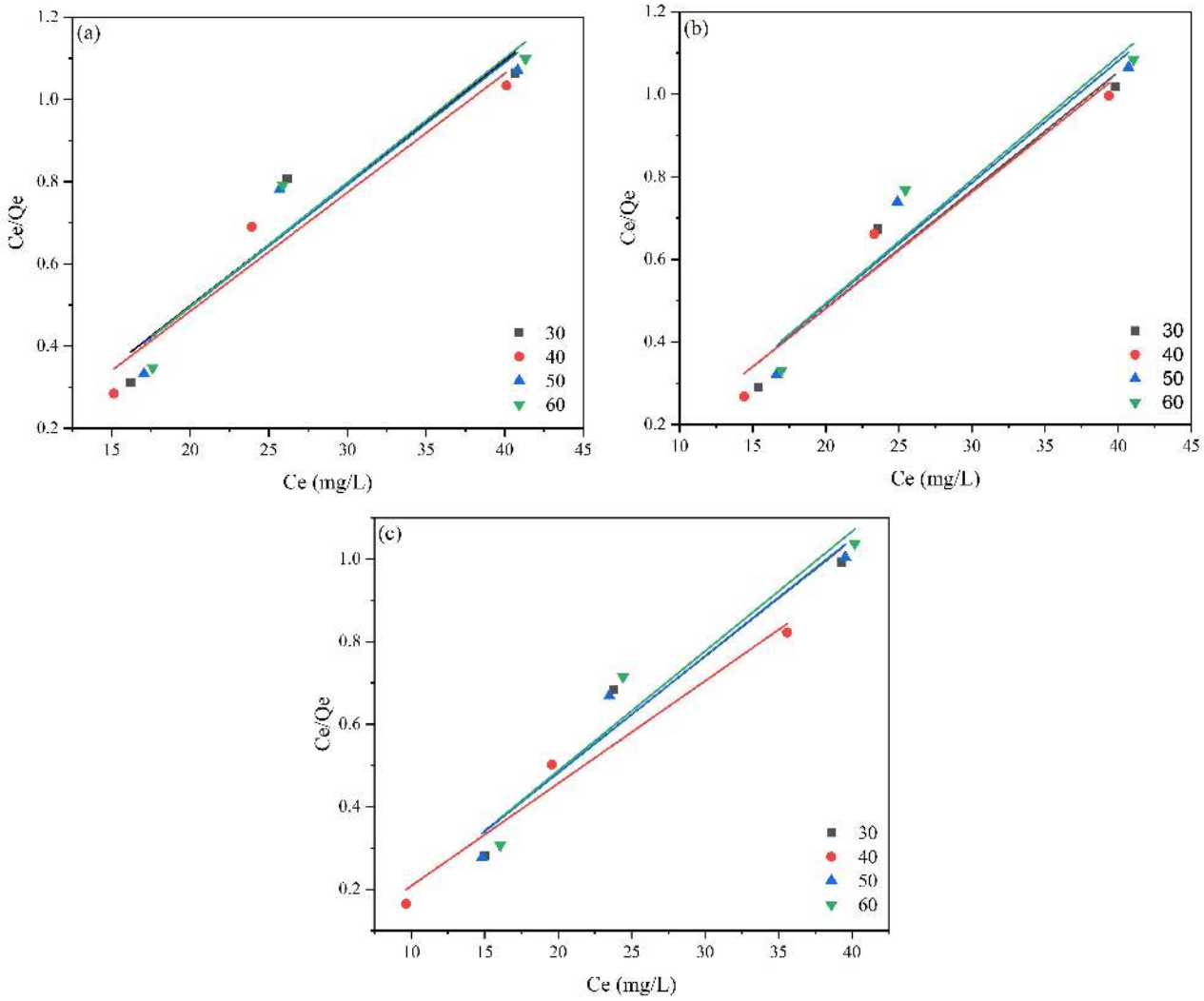


Figure 7. Langmuir Curve of Materials, (a) EC, (b) HC-150 and (c) HC-250

hydrochar, the study applied Pseudo-First-Order (PFO) and Pseudo-Second-Order (PSO) kinetic models. Table 2. shows the kinetic parameters PFO and PSO models by EC, HC-150 and HC-250 and Figure 5 shows the curve. The results showed that while both models could describe the adsorption process, the PSO model provided a better fit, especially for HC-250 with a high R^2 value of 0.981. The PSO model is typically associated with chemisorption, where the adsorption rate depends on the availability of active sites and the formation of chemical bonds between the dye molecules and the hydrochar surface. The good correlation between the experimental and calculated values for HC-250 supports the idea that chemisorption is the dominant mechanism at this temperature.

In contrast, the PFO model, which assumes that adsorption is driven by diffusion, showed weaker fits for the raw *E. cottonii* (EC) and HC-150, indicating that the adsorption in these cases was less dependent on chemical bonding and more influenced by physisorption. Physisorption involves weaker van der Waals forces and is typically faster but less stable than chemisorption. The moderate R^2 values for the PFO model suggest that physical interactions contributed to adsorption, but they were secondary to the chemisorption process.

Additionally, the presence of intraparticle diffusion implies that mass transfer within the hydrochar pores plays a role in adsorption, further supporting the coexistence of physisorption and chemisorption mechanisms. This aligns with studies by Srivastav et al. (2024), who also observed that adsorption systems involving dyes often exhibit a combination of physical and chemical interactions.

Thus, the superior performance of the PSO model for HC-250 suggests that the adsorption of DY onto hydrochar at this temperature is largely driven by chemical bonding at the

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Table 4. The Adsorption Thermodynamic Parameter by EC, HC-150 and HC-250

Adsorbent	Concentration (mg/L)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol) 30°C	40°C	50°C	60°C
EC	40	1.358	0.007	-0.627	-0.692	-0.758	-0.823
	50	0.957	0.001	0.568	0.555	0.542	0.529
	60	0.387	0.001	0.086	0.076	0.066	0.056
	70	4.021	0.003	3.066	3.034	3.003	2.971
	80	1.172	0.004	-0.113	-0.156	-0.198	-0.240
HC-150	40	1.667	0.006	-0.240	-0.303	-0.366	-0.429
	50	0.695	0.001	0.520	0.514	0.508	0.502
	60	4.390	0.010	1.251	1.147	1.044	0.940
	70	5.214	0.006	3.535	3.479	3.424	3.369
	80	2.183	0.007	0.073	0.004	-0.066	-0.135
HC-250	40	3.314	0.010	0.230	0.128	0.027	-0.075
	50	4.217	0.009	1.537	1.449	1.361	1.272
	60	3.524	0.007	1.496	1.429	1.362	1.295
	70	6.999	0.009	4.139	4.044	3.950	3.855
	80	2.771	0.008	0.307	0.226	0.145	0.063

surface, with contributions from physical forces, particularly during the initial stages of adsorption. This dual mechanism enhances the overall adsorption efficiency.

3.5 Effect of Concentration and Temperature on Adsorption

The adsorption of DY dye on hydrochars derived from *E. cottonii* (EC) with varying temperatures (HC-150 and HC-250) was studied to understand the thermodynamic and adsorption characteristics. The data obtained from the experiments, conducted at pH 4 for 70 minutes, provides insight into the adsorption process under different conditions. Table 3 shows the adsorption isotherm Langmuir and Freundlich parameter by EC, HC-150 and HC-250. The adsorption isotherms, evaluated using the Langmuir and Freundlich models, reveal detailed characteristics of the adsorption behavior. The Langmuir model, which assumes monolayer adsorption on a surface with a finite number of identical sites, shows that the maximum adsorption capacity (Q_{max}) for HC-250 at 40°C is 40.323 mg/g, with a Langmuir constant (kL) of 123.766. This indicates that HC-250 has a high capacity for dye uptake at elevated temperatures. The Freundlich model, which describes adsorption on heterogeneous surfaces, shows that the Freundlich constant (kF) and adsorption intensity (N) values in the materials fluctuate. Each material shows the same pattern, where the N and kF values increase from 30°C to 40°C and show a significant decrease at 50°C and 60°C. This indicates that the materials effectively absorb DY at 40°C. The high R^2 values for the Langmuir model suggest that the adsorption system closely follows monolayer adsorption, with minimal interaction between adsorbed molecules. This indicates a well-defined, finite adsorption capacity with homogeneous adsorption sites. Figure 6 shows Freundlich plot of materials and Figure 7 shows Langmuir plot of materials.

The thermodynamic parameters of the adsorption process of DY dye on hydrochars derived from *E. cottonii* offer valuable insights into the nature of the adsorption under varying conditions. Enthalpy change (ΔH) reflects the heat absorbed or released during the adsorption process. Positive ΔH values, such as those observed in the study, indicate that the adsorption is endothermic. This means that the process absorbs heat from the surroundings. For example, at a 70 mg/L concentration, ΔH HC-250 shows 6.999 kJ/mol. The endothermic nature suggests that higher temperatures facilitate the adsorption of the dye onto the hydrochar, likely due to the increased mobility of dye molecules and the expansion of adsorption sites on the hydrochar surface as temperature rises. This behavior aligns with many adsorption studies, where an increase in temperature enhances the interaction between the adsorbate and adsorbent (Wang and Chen, 2009).

Entropy change (ΔS) represents the degree of disorder or randomness at the adsorption interface. Positive ΔS values across different conditions suggest that the process leads to an increase in disorder. For instance, at 70 mg/L concentration, ΔS values are 0.003 kJ/mol.K for EC and 0.010 kJ/mol.K for HC-250. This increase in entropy indicates that the adsorption process involves a significant increase in the randomness of the system, likely due to the dispersion of dye molecules in the aqueous phase and their interactions with the hydrochar surface. A higher ΔS typically suggests that the dye molecules are more freely distributed in the solution after adsorption, which supports the idea of increased

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Table 5. Comparison of Adsorption Capacity, Selectivity, and Mechanisms of *Eucheuma cottonii* Hydrochar and Other Biomass-Based Adsorbents for DY Dye

Adsorbents	Adsorption Capacity (mg/g)	Selectivity	Reference
Eucheuma cottonii before treatment	34.602	Highly selective towards DY due to the presence of functional groups	This study
Eucheuma cottonii after treatment (HC-150)	35.461	Highly selective towards DY due to the presence of functional groups	This study
Eucheuma cottonii after treatment (HC-250)	40.323	Highly selective towards DY due to the presence of functional groups	This study
Ulva lactuca	15.22	Less specific towards	Wang and Chen (2009)
Chlorella pyrenoidosa	12.67	Strong preference for DY after chemical activation	Guo et al. (2021)
Ulva reticulata	8.12	Lower adsorption capacity compared to *E. cottonii*	Senthilkumar et al. (2019)
Gracilaria rhodophyta	4.7	Lower adsorption capacity compared to *E. cottonii*	Naga Babu et al. (2023)
Chitosan	Not specified	Preference for DY due to surface functional groups	Alabbad et al. (2022)
Gracilaria edulis	2.72	Lower adsorption capacity compared to *E. cottonii*	Liu and He (2021)
Ulva lactuca	-	Physisorption contributes to adsorption performance, especially at lower temperatures	Srivastav et al. (2024)

adsorption efficiency at elevated temperatures.

Gibbs free energy change (ΔG) determines the spontaneity of the adsorption process. Negative ΔG values imply that the process is spontaneous. The study shows increasingly negative ΔG values with rising temperature, such as -0.823 kJ/mol for EC at 70 mg/L and -0.075 kJ/mol for HC-250 at 40°C. This trend indicates that the spontaneity of the adsorption process improves as the temperature increases. The more negative ΔG values at higher temperatures suggest that the adsorption process becomes more thermodynamically favorable with temperature, reinforcing the endothermic nature of the process. Spontaneous adsorption at elevated temperatures is consistent with the observations that higher temperatures facilitate greater dye uptake due to increased kinetic energy and more effective interactions between the dye and the hydrochar (Sztancs et al., 2020).

In summary, the thermodynamic parameters reveal that the adsorption of DY dye on hydrochars derived from *E. cottonii* is endothermic and spontaneous. The positive ΔH values indicate that the process requires heat, while the positive ΔS values reflect increased disorder and improved adsorption efficiency with temperature. The increasingly negative ΔG values confirm that the adsorption is more favorable at higher temperatures, making the process both thermodynamically and practically advantageous for dye removal applications.

3.6 Regeneration Study of Adsorbent

The ability of an adsorbent to be regenerated and reused is essential for its practical application in environmental remediation. In this study, the regeneration performance

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of *E. cottonii* hydrochar was tested over seven adsorption-desorption cycles. HC-250 demonstrated the highest regeneration efficiency, retaining over 50% of its adsorption capacity after the first cycle, compared to lower efficiencies for EC and HC-150, which retained around 40–45%. Figure 8 shows the regeneration cycle adsorption of materials.

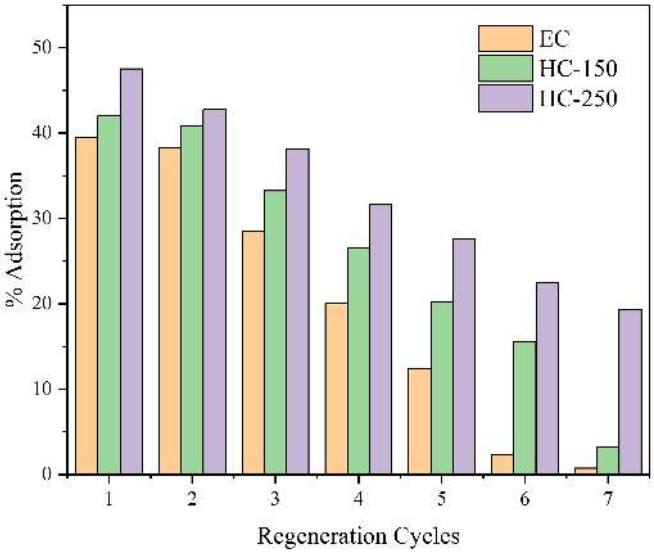


Figure 8. Regeneration Cycle Adsorption of Materials

While a natural decline in performance was observed over repeated cycles, HC-250 outperformed the other materials due to its more stable surface characteristics and better-developed pore structure, which helped maintain adsorption efficiency. By the fourth cycle, adsorption efficiency dropped significantly, but HC-250 remained the most resilient, maintaining higher adsorption capacity than EC and HC-150, which experienced a more rapid decline in performance.

The superior performance of HC-250 in multi-cycle regeneration highlights the importance of carbonization temperature in creating adsorbents with durable surface properties that can withstand repeated use. This makes HC-250 a viable candidate for applications requiring multiple adsorption-desorption cycles, emphasizing its practical potential in real-world wastewater treatment systems

3.7 Comparison with Previous Studies

To provide a clearer comparison of the adsorption performance and selectivity of *E. cottonii* hydrochar with other biomass-derived adsorbents, the following table summarizes key findings from various studies. Table 5. highlights the adsorption capacities for DY dye as well as the mechanisms and selectivity observed across different hydrochars. This comparison demonstrates the effectiveness of *E. cottonii* hydrochar, especially at higher HTC temperatures, in outperforming other macroalgal-based adsorbents.

4. CONCLUSIONS

This study has demonstrated that hydrochar derived from *Eucheuma cottonii* undergoes significant changes in its functional groups and surface properties as the hydrothermal carbonization (HTC) temperature increases. This study indicates that increasing HTC temperatures, particularly at 250°C (HC-250), significantly enhances the carbonization process, as confirmed by FT-IR analysis. The degradation of oxygen-based functional groups such as hydroxyl (O−H), aliphatic (C−H), and carbonyl (C=O) groups, coupled with the emergence of stable aromatic structures, makes HC-250 particularly suitable for adsorption applications. BET surface area analysis confirmed that increasing temperatures lead to larger surface areas and more optimized pore structures, with HC-250 achieving the highest surface area (7.478 m^2/g). This structural improvement is critical for adsorption efficiency, providing more available sites for dye uptake. pHpzc measurements further demonstrated that at pH 4, the positively charged hydrochar surface significantly enhances the adsorption of anionic dyes like Direct Yellow (DY) through electrostatic attraction. One of the notable findings is the strong selectivity of the hydrochar for Direct Yellow across all HTC temperatures, with HC-250 displaying the highest adsorption capacity and selectivity. The Langmuir isotherm model provided a better fit than the Freundlich model, suggesting adsorption occurs on monolayer adsorption, with minimal interaction between adsorbed molecules. Thermodynamic analysis revealed that the adsorption process is endothermic, with positive enthalpy values indicating that higher temperatures improve adsorption efficiency. Furthermore, the negative Gibbs free energy values confirm the spontaneity of the process, which becomes increasingly favorable at elevated temperatures.

5. ACKNOWLEDGEMENT

We extend our heartfelt gratitude to Hibah Profesi Universitas Sriwijaya, as stated in SK No. 0016/UN9/SK.LP2M.PT/2024, and to the Research Center of Inorganic Materials and Coordination Complexes for their invaluable support, which enabled the completion of our research.

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