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Research Article

Production of Chemically and Microwave Activated Hazelnut Husk As An Adsorbent for Dye Contaminated Wastewaters

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Abstract

Adsorption has traditionally been evaluated as an economical and easily applicable process for treating certain wastewaters, such as ones including dyes and heavy metals. Even though adsorbent materials specifically produced for the purpose of wastewater treatment commercially exist, the production cost may create an economic burden on wastewater treatment processes. Agricultural wastes can be valorized as adsorbents in adsorption processes. The adsorption capacity of these wastes can be improved via pre-treatment methods such as chemical application and microwave irradiation. This study investigated the potential applicability of hazelnut husk as an adsorbent for methylene blue (MB) dye. To this purpose, the husk was activated by sequential chemical or water and microwave applications. Structural analysis on the produced adsorbent was performed by Fourier transform infrared spectrophotometry (FTIR) and field emission scanning electron microscopy (FE-SEM). Isotherm (Langmuir, Freundlich, Temkin and Harkins-Jura isotherms) and kinetic (pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic models) behaviours of adsorption were also evaluated. The results indicated that MB could be removed by 92-94% considering all adsorbents produced. Further isotherm and kinetic studies revealed that MB adsorption was both physically and chemically induced, and the reaction followed the pseudo-second-order kinetic model (R^2>0.99).

Keywords: Adsorption, Dye, Waste, Microwave, Hazelnut Husk, Adsorbent

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1. Introduction

The adsorption process can be defined as the concentration or deposition of solute molecules on a porous solid material, i.e. adsorbent, via intermolecular attraction forces [1]. Adsorption processes can be employed in the removal of contaminants, including dyes, phenols, other organic pollutants such as pharmaceuticals, surfactants, solvents etc. [1] and heavy metals [2]. Adsorption has been considered as a viable option for wastewater treatment processes due to its simplicity in operation, feasibility, cost-effectiveness and insensitivity for toxic compounds [3–5]. Adsorption can be preferable over biological, chemical or physical methods like membrane processes, flocculation/coagulation, advanced oxidation, extraction, biodegradation as a treatment process depending on these benefits offered [6].

Dye containing wastewater (DCWW) can be considered one of the most crucial wastewater streams to employ adsorption treatment based on the pollution potential of dyes. DCWW can originate from many industries such as textile, paper, pharmaceutical, chemical, food, tannery. The annual production of dyes has been estimated as 700,000 tons [5], which results in large volumes of DCWW generation. Legislations are regulating their discharge into water bodies. DCWW requires treatment before discharge since mutagenic and carcinogenic effects can be observed on aquatic organisms [3]. However, DCWW can also be illegally discharged from the industries, potentially contaminating water bodies [6]. Dye contamination at concentrations of 1 ppm or even lower can be detectable by the naked eye [3].

Moreover, more than 45% of organic pollution is grounded on the use of dyes [6]. Among the dyes used in industries, methylene blue (MB) is a cationic thiazine one [6] and it has a high solubility in water [5]. It is frequently used in cotton, wool and silk dying processes and as a biological staining agent [3, 5]. Paper, pulp, textile, food, plastics, mills and leather are the related industries with MB use [6]. Cationic dyes present more toxicity compared to anionic and nonionic ones [6]. Methemoglobinemia, burning sensation, mental confusion, vomiting, nausea and profuse sweating are adverse health effects that can be experienced by MB exposure [3].

Treatment of DCWW can be problematic since they may contain refractory compounds that may resist the treatment involving digestion, light, heat and oxidizing agents [3]. Therefore, adsorption has been recognized as a viable process for the treatment of such wastewater streams. Activated carbon (AC) presents a viable option considering its effective dye treatment performance. However, the high cost of AC is the main limitation that hinders its wide range of applicability in wastewater treatment. Carbonaceous, metallic and magnetic nanomaterials, biosorbents such as chitosan and its composites and the composites of β-cyclodextrin and geopolymers have also been investigated for wastewater treatment [7]. Recent studies focus on developing economically viable and environmentally friendly adsorbents for wastewater treatment purposes. Employing agricultural, household, and industrial by-products in wastewater treatment can be considered a sustainable approach. This approach contributes to waste minimization and/or its recovery or reuse while treating wastewaters [8].

Agricultural wastes have the potential to be economical and environmentally friendly adsorbents depending on their chemical composition, abundance, renewability and cheap value [3, 9]. The production of agricultural wastes is directly related to the crops of regional cultivation. Hazelnut production in Turkey has been estimated to be approximately 70% of global production [10]. Annual husk waste produced is 180-200,000 tons in Turkey, corresponding to the hazelnut production of 500-600,000 tons/year [11]. The husk is a waste with no intended use and it has no economic value [12]. The use of husk in adsorption processes can potentially provide an economic value to husk waste and reuse.

Agricultural wastes can be applied without pretreatment or after pretreatment in adsorption processes. Pretreatment is generally applied to modify and improve the number of active sites so that the adsorption capacity is increased [8]. Pretreatment options include various physical and/or chemical activation methods. Thermal pre-treatment, applications of acidic (e.g. H_2SO_4, H_3PO_4) or basic solutions (e.g. NaOH, $NaHCO_3$) or particulates (e.g. $ZnCl_2$) can be accounted as pretreatments methods [9]. Recent studies have focused on the emerging technology of microwave irradiation as a pretreatment option. Microwave irradiation prevents the formation of thermal gradients in solid materials while heating. Thermal gradient entraps volatile compounds and pyrolysis gasses which may clog the active sites for adsorption. Thus, microwave application can improve the functional groups on the adsorbent material and increase the carbon to oxygen ratio, which can also improve adsorption capacities [13]. Hazelnut husk has been previously treated with several chemicals (H_3PO_4, KCH_3COO) and heat under nitrogen flow to produce activated carbon for the removal of MB [12], cadmium (II) [14] and copper (II) [15]. Activated carbon produced from hazelnut husk was also modified with zinc chloride ($ZnCl_2$) to produce an adsorbent for MB removal [16]. Hazelnut husk was sequentially treated by H_2SO_4 and $NaHCO_3$ solutions for nickel (II) adsorption [17]. However, hazelnut husk has not been previously subjected to consecutive chemical and microwave treatments for adsorbent production, with the aim of dye removal. The dye adsorption capacity of microwave-assisted chemically activated hazelnut husk is yet to be revealed.

This study investigated the MB removal potential of husk waste after consecutive chemical or water and microwave pretreatments to valorize agricultural waste without any economic value. To this purpose, husk was first subjected to pretreatment using deionized water, sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3) and irradiated in a microwave oven. The results were promising in terms of providing an economic value to the waste as well as functionality.

2. Material and Methods

2.1. Preparation of Adsorbents

Husk was washed with tap water and dried in an oven for a day. It was grounded to obtain husk particles in the size range of 0.5-2 mm. Three setups were prepared. Deionized water, Na_2CO_3 (4 M) and K_2CO_3 (4 M) as activators were added to the husk particles to obtain a slurry in setups 1, 2 and 3, respectively. The slurry was stirred for a day at room temperature on an orbital shaker. Deionized water and chemically (Na_2CO_3, K_2CO_3) treated slurry were subjected to irradiation under a laboratory microwave oven at 500 W, 60 °C for 7 minutes. The slurry was filtered through a coarse filter. It was rinsed with distilled water and dried at 100 °C for 24 h. It was further employed in the adsorption process for MB removal. The related experimental conditions and the corresponding nomenclatures for the adsorbents are given in Table 1.

Table 1. Experimental conditions for adsorbents produced

Activator / Nomenclature	Volume of activator (mL)	Amount of husk (g)	Microwave operating conditions
Deionized water (HW)	70	10	500 W, 60 °C, 7 min
Na_2CO_3 (HNa)	60	10	500 W, 60 °C, 7 min
K_2CO_3 (HK)	60	10	500 60 °C, 7 min

2.2. Structural Analysis

The structures of husk and adsorbents were analyzed by Fourier transform infrared spectrophotometry (FTIR) and field emission scanning electron microscopy (FE-SEM). The functional groups on both husk and adsorbents were determined by FTIR analysis (Shimadzu IRPrestige 21). FTIR resolution was 1 cm^{-1} and the data were acquired for the wavelength interval between 40 and 4000 cm^{-1}. FE-SEM images were obtained using Quanta FEG 250 instruments (FEI Co., Hillsboro, OR, USA).

2.3. Adsorption Experiment

A stock MB solution of 500 mg/L concentration was prepared and diluted by 1/10 for the adsorption experiment. Adsorption experiment was conducted with 200 mL of 50 mg/L MB solution and 1 g/L adsorbent dosage. The pH of the MB solution was approximately 5.5 and the experiment was carried out at room temperature under constant stirring at 190 rpm on an orbital shaker. The total operation time was 1080 min and samples were withdrawn at times 10, 30, 60, 120, 240, 300, 360, 1020 and 1080 min. MB concentration was measured by a UV–Vis spectrophotometer under 663 nm wavelength.

2.4. Isotherm And Kinetic Analysis

Isotherm and kinetic analysis were performed on adsorption data. Four isotherm models were studied (Langmuir, Freundlich, Temkin and Harkins-Jura isotherms). Kinetic behaviours were analysed by pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models.

3. Results and Discussion

3.1. Structural Analysis Of Adsorbents

FTIR analyses were conducted to determine the surface functional groups of husk and adsorbents produced (Figure 1). The bands located at 3334 cm^{-1} and 1610 cm^{-1} can be attributed to O–H stretching vibrations originating from phenols, alcohols or adsorbed water molecules [18]. The bands at 2922 cm^{-1} and 2851 cm^{-1} can be ascribed to asymmetric C-H stretching and symmetric C-H bending absorption bands that might be present in long alkyl chain groups in the precursor [19]. The relative band at 2494 cm^{-1} can be attributed to aliphatic C–H stretching vibrations. The bands at 1731-1610 cm-1 can be related to C-O stretching from ketones, aldehydes, carboxylic or aromatic C-C stretching vibrations. The broad and very intense bands at 1300–1000 cm^{-1} can be referred to as C-O bonds such as lactones, ethers and phenols [20].

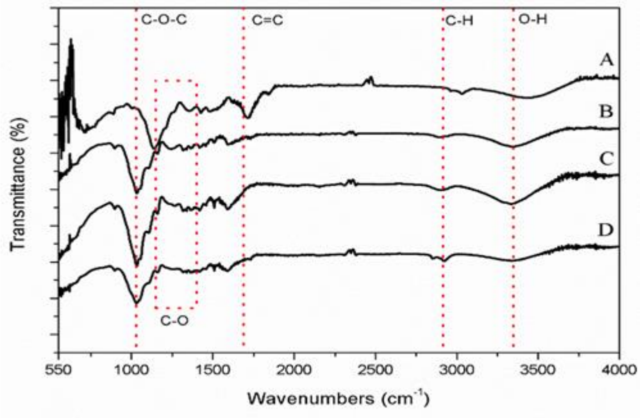

Figure 1. FTIR spectrum: (A) Husk, (B) HW, (C) HNa, (D) HK.

The bands at 1455 cm^{-1} and 1366 cm-1 are deformation peaks from CH_2 lignin and hemicelluloses; and deformation peaks from C-H cellulose and hemicellulose, respectively. The peak intensity at 3334 cm^{-1} increased due to O-H hydrogen bond interactions in adsorbent produced with water (HW) and it decreased with the use of K_2CO_3 and Na_2CO_3 in activation. The band densities in the spectrum range of 2922-2851 cm^{-1} (C-H bond region) altered considerably compared to the raw husk via activation. Weak intensities of many weak bonds in raw materials can be greatly reduced by microwave activation [19]. Moreover, the activation methods applied on adsorbents can significantly increase the number of C-C bonds as well as the abundance of oxygen and hydrogen atoms [21].

FE-SEM images (Figure 2) also indicated that the morphology of the husk was altered by activation methods applied. Husk had a relatively denser and rougher surface compared to microwave activated adsorbents treated with either water, Na_2CO_3 or K_2CO_3. The microwave treated adsorbents had a more abundant number of pores on the surface. Those pores may be formed by evaporation of the activating agent from the surface of adsorbents and leaving the space behind, which was previously occupied by activating agents [19, 22–23]. HK had many micropores, and the micropores were observed to collapse in HNa.

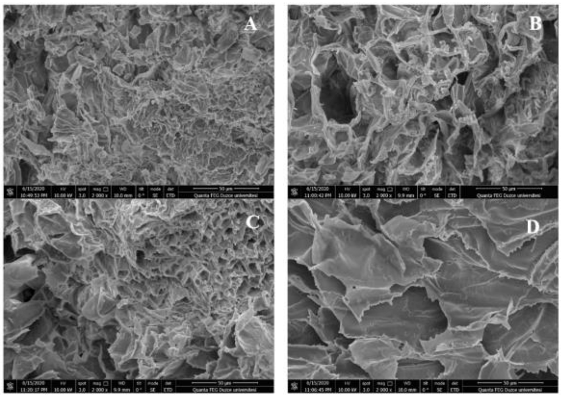

Figure 2. FE-SEM images: (A) Husk, (B) HW, (C) HNa, (D) HK.

3.2. Adsorption of MB

The total experimental period of adsorption (1080 min) ended with residual MB concentrations of 3.16, 4.14 and 3.37 mg/L, which were slightly above the measured concentration at 1020 min (Figure 3). This fact indicated that desorption of MB started between the operation periods of 1020 and 1080 min. Thus, further evaluation on the removal of MB and analysis for both kinetic and isotherm models was reported for the adsorption phase only, between operation periods of 0 and 1020 min. Water and microwave treated sample, HW, was observed to be fast-responsive to the adsorption by 68% MB removal compared to HNa (57%) and HK (55%) at the first 60 min.

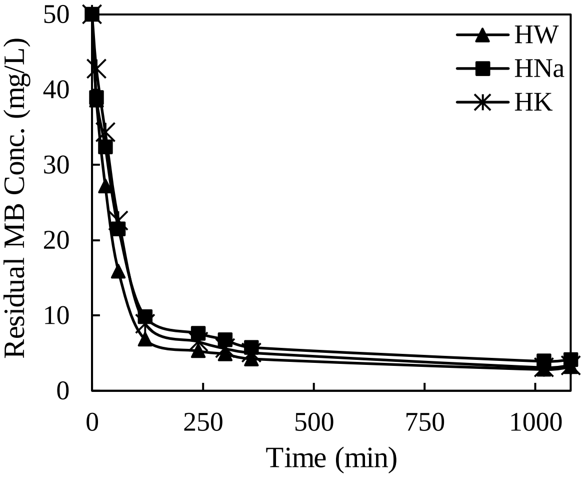

Figure 3. Retentate concentrations of MB during adsorption experiment (MB: 50 mg/L, Adsorbent: 1 g/L, pH~5.5, 20-25°C).

The removal of MB using HW, HNa and HK as adsorbents was completed by 86%, 80% and 82%, respectively, at the first 120 min of operation. MB removal was almost equilibrated at the end of the total operation period for the three adsorbents. Total MB removals obtained were 94% for HW, 92% for HNa and 94% for HK at 1020 min. The corresponding experimental adsorption capacities at equilibrium ($q_{e,exp}$) were found as 47.18 mg/g for HW, 46.09 mg/g for HNa and 46.92 mg/g for HK. The adsorption capacity of HW (47.18 mg/g) was slightly higher than HNa (46.09 mg/g) and HK (46.92 mg/g). Thus, microwave irradiation using deionized water as an activator, instead of any chemical, can also lead to comparable results. This fact may be due to the occupying of the active sites of the adsorbents by the chemicals used, namely Na^+ and K^+ ions, or the formation of the MB and salt complexes which may limit the adsorption of MB [24].

The adsorption capacities of produced adsorbents for MB removal were higher than or comparable to many adsorbents produced from agricultural wastes such as banana peel (15.9 mg/g), orange peel (13.9 mg/g) [9] and activated banana bark (40 mg/g), bagasse (38 mg/g) and pea shell charcoal (44 mg/g) reported for the removal of certain dyes [25]. The results were also compared with the studies aiming at the removal of MB (Table 2). The MB adsorption capacity of the adsorbents produced in this study was found to be comparable with those produced from the coffee husk, sugarcane bagasse, grape peel and Moroccan pozzolana at similar initial concentrations. The adsorption capacity obtained for pre-treated coffee husk at an initial MB concentration of 50 mg/L was recorded as 49.40 mg/g [20]. To point out, the adsorption capacity obtained for the coffee husk was reached after multiple treatments of the husk, such as heating, drying, pyrolyzing under pure nitrogen and again heating. All these treatment steps are energy-intensive processes. The activation of the hazelnut husk was performed by microwave irradiation for only 7 minutes, in our study. Microwave irradiation has a short heating period, less energy and chemical consumption, and accurate temperature control [26]. Hazelnut husk can be valorized via the production of activated carbon (AC) (Table 2) and the AC can potentially yield better MB removals [12, 16]. Even though AC has a unique adsorption capacity for the removal of pollutants [9], conventional thermal treatment of the husk for prolonged periods may hinder its economic advantage.

Table 2. Methylene blue adsorption capacity of various adsorbents.

Raw waste	Treatment of raw waste	Initial MB concentration	Adsorption capacity	Reference
Coffee husk	Application of 1M KOH to husk + heating at 130 °C for 2 h + drying at 105 °C for 12 h + pyrolyzing under pure nitrogen (95.995%) for 2 h + heating at 800 °C	50 mg/L	49.4 mg/g	[20]
		500 mg/L	415.7 mg/g	
Sugarcane bagasse	Mixed with $Fe(NO_3^-)_3 \cdot 9H_2O$ + microwave application for 750 W for 75 seconds	100 mg/L	18.4 mg/g	[26]
		1000 mg/L	36.0 mg/g	
Grape peel	Heated at 180 °C for 3 min in a microwave	100 mg/L	38.4 mg/g	[27]
		600 mg/L	207.6 mg/g	
Moroccan pozzolana	None		43.9 mg/g	[28]
Bean peel	Carbonization at varying temperatures between 623-923 K + KOH + microwave at 800 W and 7 min	10 mg/L	19.6 mg/g	[29]
Acorn peel		10 mg/L	17.2 mg/g	
Pistacia lentiscus		10 mg/L	17.9 mg/g	
Rice husk	NaOH		39.2 mg/g*	[30]
	Ultrasound		23.5 mg/g*	
	supercritical CO_2		18.4 mg/g*	
Hazelnut husk	H_3PO_4 + under nitrogen at 500 °C for 3 h (AC)	50 mg/L	50.0 mg/g	[12]
		400 mg/L	197.0 mg/g	
Hazelnut husk	$ZnCl_2$ + under nitrogen at 700 °C for 4 h ($ZnCl_2$-AC)	100 mg/L	194.9 mg/g	[16]
		500 mg/L	456.0 mg/g	
Hazelnut husk	deionized water application for a day + microwave at 500 W, 60 °C, 7 min	50 mg/L	47.18 mg/g	This study
Hazelnut husk	4M Na_2CO_3 application for a day + microwave at 500 W, 60 °C, 7 min	50 mg/L	46.09 mg/g	This study
Hazelnut husk	4M K_2CO_3 application for a day + microwave at 500 W, 60 °C, 7 min	50 mg/L	46.92 mg/g	This study

* Maximum adsorption capacity calculated according to the Langmuir isotherm at 25 °C.

The pH and temperature are the factors that affect the MB adsorption capacity of the adsorbent via altering the chemistry of the adsorbent and dye molecules. MB adsorption can be expected to decrease when the pH is low. The decrease in MB adsorption can be related to the protonation of MB in an acidic medium and the competing of the cations of dyes with excess hydrogen ions for active adsorption sites. Positively charged sites may decrease and negatively charged sites may increase, as the pH increases. The increase in negative charges on the adsorbent surface at high pHs creates an electrical double layer and changes the polarity of the adsorbent, which induces adsorption capacity [31]. The optimum pH of MB solution was previously recorded at 11.2-11.5 for microwave treated grape peel [27], 7 for $ZnCl_2$-AC of hazelnut husk [16] and below 5 for microwave treated bamboo charcoal [32]. Therefore, the general conclusion made on the improvement of MB adsorption in alkali environment can alter depending on the origin, and the treatment of the raw material. On the other hand, MB removal efficiencies in the pH range of 2 or 4 to 10 were regarded as insignificant [26, 33]. Additionally, keeping the original pH of the solution prevents the consumption of the chemicals used in pH regulation. Thus, the rest of the studies was conducted at the pH of initial MB solution (i.e., 5.5).

The adsorption process can be either endothermic or exothermic. Temperature increase results in an increase in the adsorption capacity of pollutants in endothermic reactions and a decrease in exothermic reactions [34]. The MB adsorption on the heat-, chemical- or microwave-treated organic wastes has been mostly stated as an endothermic process [12, 16, 26, 31-35].

3.3. Adsorption Kinetics

Kinetic study on adsorption data provides beneficial information on reaction pathways and adsorption mechanisms [35]. The data on MB removal with HW, HNa and HK adsorbents were analysed by four different kinetic models (pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich models). The related kinetic curves in linear form and the data on kinetic constants for each adsorbent material are presented in Figure 4 and Table 3, respectively.

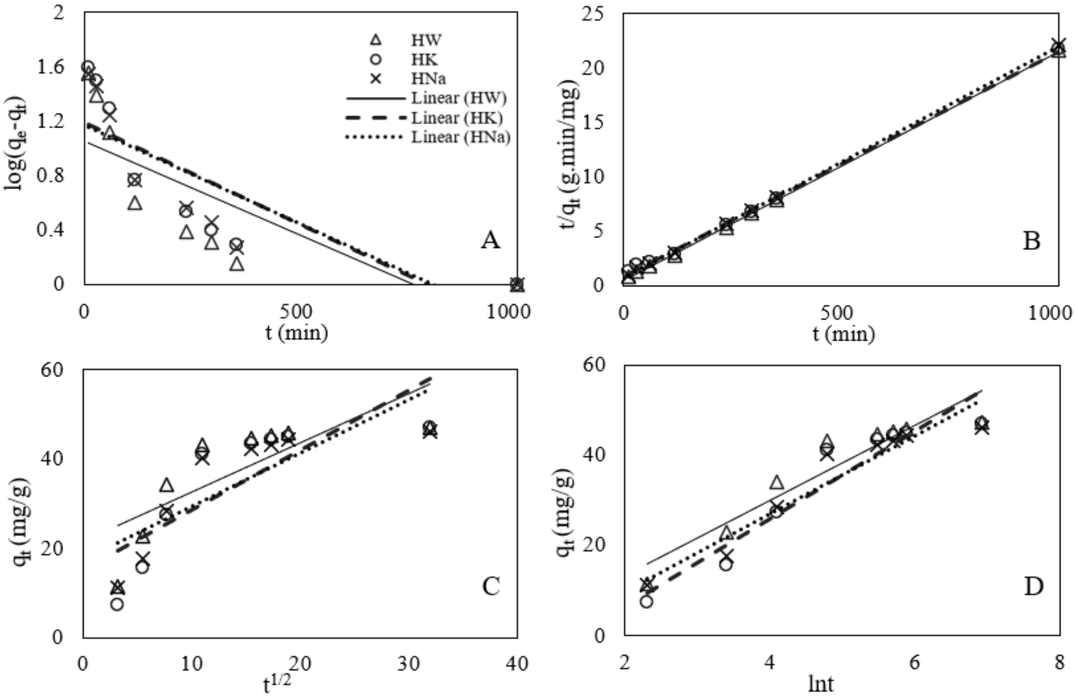

Figure 4. MB adsorption kinetics: (A) Pseudo first-order, (B) Pseudo second-order, (C) Intraparticle diffusion, (D) Elovich.

The coefficient of determination values (R^2) obtained from linearized kinetic expressions were in the range of 0.9981-0.9996 considering all adsorbents when the pseudo-second-order kinetic model was applied (Table 3). Since R^2 values were very close to 1, it can be concluded that the pseudo-second-order model can best represent the reaction mechanism of the adsorption process. This model assumes a proportionality between the occupation rate of adsorption sites and the square of the number of unoccupied sites [36]. Additionally, $q_{e,exp}$ values (47.18, 46.92 and 46.09 mg/g for HW, HK and

HNa, respectively) were very close to the calculated adsorption capacity ($q_{e,cal}$) using pseudo-second-order kinetic model (48.54, 49.50 and 47.85 mg/g for HW, HK and HNa, respectively). This fact indicated that chemisorption was the main sorption mechanism led by the exchange and share of electrons between the adsorbent and adsorbate [35, 37]. Thus, the rate of the adsorption process was mainly controlled by chemical reactions between each element in the MB adsorption system which may be driven by the number of active sites for binding [38].

Moreover, the equilibrium rate constant for pseudo-second-order reaction (k_2) ranged between 4.59-8.25x10^{-4}. Such low values of k_2 were previously reported as being indicative of a rapid adsorption process [39]. The R^2 of the linearized Elovich model was between 0.8852 and 0.9145 and was also higher than pseudo-first-order and intraparticle diffusion kinetic models (in the range of 0.5811-0.6858). The applicability of both pseudo-second-order and Elovich models is strong evidence for chemisorption of MB dye on HW, HNa and HK [40]. Pseudo-first-order and intraparticle diffusion kinetic models were found not to be applicable for the MB adsorption process on the produced adsorbents due to relatively much lower R^2 values (0.5811-0.6858 and 0.6056-0.6734, respectively).

Table 3. Kinetic models and calculated parameters

Kinetic model	**Linear equation**	**Parameters**	**HW**	**HNa**	**HK**	**Reference**
Pseudo first-order[a]	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$	$q_{e,cal}$ (mg/g)	11.26	14.84	15.51	[41]
		k_1 (1/min)	3.22x10^{-3}	3.22x10^{-3}	3.45x10^{-3}	
		R^2	0.5811	0.6858	0.6622	
Pseudo second-order[b]	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$q_{e,cal}$ (mg/g)	48.54	47.85	49.50	[41]
		k_2 (1/min)	8.25x10^{-4}	5.94 x10^{-4}	4.59 x10^{-4}	
		R^2	0.9996	0.9993	0.9981	
Intraparticle diffusion[c]	$q_t = k_p t^{\frac{1}{2}} + C$	k_p	1.11	1.19	1.34	[35]
		C	21.43	17.56	15.29	
		R^2	0.6056	0.6734	0.6575	
Elovich[d]	$q_t = \frac{1}{\beta}(\alpha\beta) + \frac{1}{\beta}\ln t$	β (g/mg)	0.12	0.11	0.10	[35]
		α (mg/g min)	3.09	7.77	13.36	
		R^2	0.8852	0.9145	0.9073	

[a] q_t, q_e and k_1 are time dependent MB adsorption capacity, adsorption capacity at equilibrium and rate constant of pseudo-first order reaction, respectively.

[b] k_2 is the equilibrium rate constant for pseudo second-order reaction.

[c] k_p and C are intraparticle diffusion and the diffusion constants, respectively.

[d] α indicates the primary adsorption extent and β indicates the adsorbent area occupied by adsorbates.

3.4. Adsorption Isotherms

Isotherm models are used to predict the affinity of adsorbate (i.e., MB dye) to the adsorbent. A correlation between the total amount of adsorbate and the retaining amount of adsorbate in solution under equilibrium conditions is being established with isotherm applications [42]. In this study, four different isotherm models were analysed for MB removal by HW, HNa and HK adsorbents. The related isotherm curves in linear form and the data on isotherm constants for each adsorbent are presented in Figure 5 and Table 4, respectively. The R^2 values obtained were between 0.8165-0.8946 for all adsorbents according to Langmuir isotherm which was higher than those of Freundlich isotherm (0.8107-0.8598). The separation factor in Langmuir (R_L) indicates whether adsorption is favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$). This factor was calculated as 0.09 for HW, 0.10 for HNa and 0.11 for HK, which were between 0 and 1. Thus, MB dye adsorption on adsorbents was found to be favourable [43–44]. The best-fitted isotherm model was Temkin isotherm with R^2 of 0.9220, 0.9413 and 0.9300 for HW, HNa and HK, respectively. Temkin isotherm assumes that the binding energies in the adsorption process are uniformly distributed. The surface coverage owing to the interactions between adsorbent and adsorbate results in a decrease in the heat of adsorption of all molecules [28]. The enthalpy of the adsorbate has a linear correlation with interactions. The factors affecting adsorption are considered as density and distribution of the active sites of both adsorbent and adsorbate in Temkin isotherm [5]. Furthermore, Temkin isotherm constant, b_t, ranged between 0.158-0.182 kj/mol considering all adsorbents produced (Table 4). Adsorption energy was previously reported to be less than 8 kJ/mol [45–46] for a typical physisorption process, and in the range of 8-16 kJ/mol for an ion-exchange process [47] according to Temkin isotherm. However, the b_t values calculated were not close to the previously defined levels, representing a complex adsorption process and may involve both chemisorption and physisorption [5, 48]. Harkins-Jura isotherm was not applicable for the MB adsorption process on HW, HNa and HK based on relatively much lower R^2 values obtained (0.4835-0.6128).

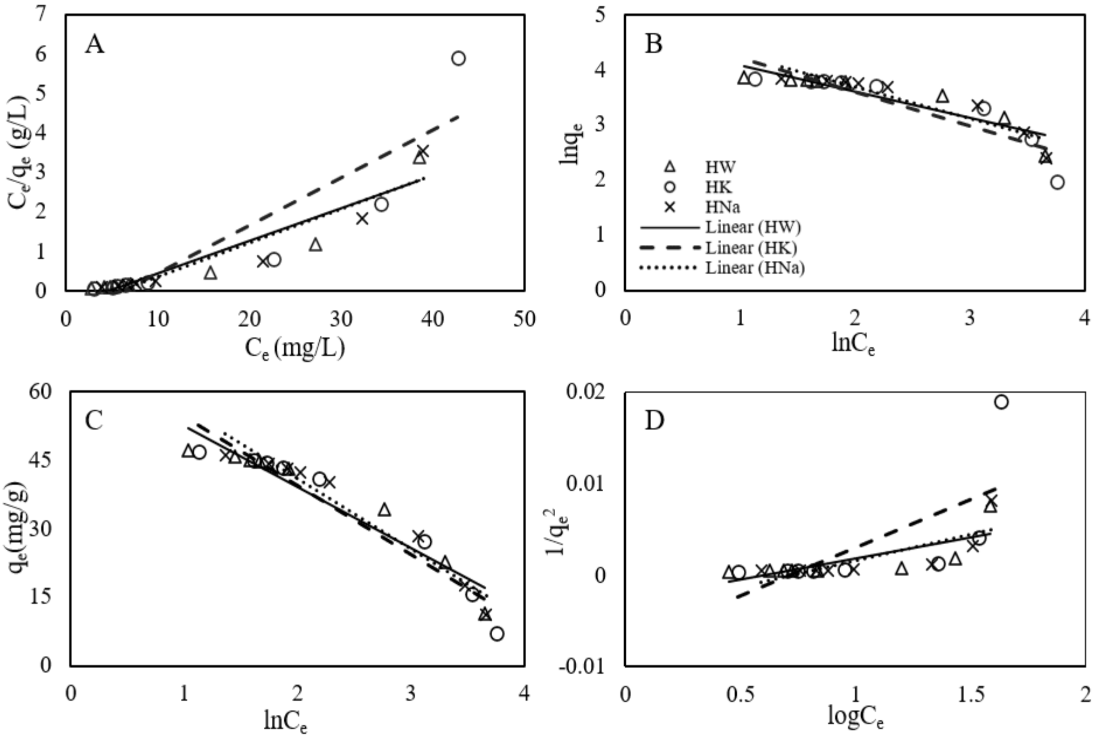

Figure 5. MB adsorption isotherms: (A) Langmuir, (B) Freundlich, (C) Temkin, (D) Harkins-Jura

Table 4. Isotherm models and calculated parameters

Isotherm	Linear equation	Parameters	HW	HNa	HK	Reference
Langmuir[a]	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	q_m (mg/g)	12.13	11.59	8.33	[43, 49]
	$R_L = \frac{1}{1+K_L C_0}$	K_L (L/mg)	0.21	0.17	0.16	
		R_L	0.09	0.10	0.11	
		R^2	0.8846	0.8946	0.8165	
Freundlich[b]	$lnq_e = lnK_f + \frac{1}{n} C_e$	K_F (mg/g)	95.40	126.06	127.59	[50]
		$1/n$	0.48	0.57	0.62	
		R^2	0.8221	0.8598	0.8107	
Temkin[c]	$q_e = \frac{RT}{b_T} lnC_{e+} \frac{RT}{b_T} lnA$	A	139.77	105.64	100.58	[28]
		b_t (kJ/mol)	0.182	0.158	0.161	
		R^2	0.9220	0.9413	0.9300	
Harkins-Jura[d]	$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H} logC_e$	B_H	0.59	0.74	1.00	[51]
		A_H	217.39	175.44	94.34	
		R^2	0.5690	0.6128	0.4835	

[a] q_m is maximum adsorption capacity, C_e is equilibrium concentration of MB, q_e is amount of MB absorbed at equilibrium, K_L is Langmuir isotherm constant. R_L is the separation factor and C_o is the initial MB concentration.

[b] K_F is Freundlich constant, n is a constant indicating adsorption intensity.

[c] R, T, A and b_t are gas constant, absolute temperature, Temkin isotherm equilibrium binding constant and Temkin isotherm constant, respectively.

[d] B_H and A_H are isotherm constants of Harkins-Jura model.

4. Conclusion

This study was conducted for the purpose of investigating the potential of hazelnut husk as an adsorbent material after being pre-treated with chemical/water and microwave applications. All adsorbent materials produced were structurally altered after pre-treatments applied either by chemical/water or microwave exposure. The MB removal was attained in the range of 92-94% resulting in an adsorption capacity of the produced adsorbents in the range of 46.09-47.18 mg/g. The isotherm and kinetic models tested revealed that the adsorption process was favourable, and chemical interactions predominantly controlled the sorption. Adsorbent materials produced showed a promising adsorption capacity for dye removal. However, process parameters are required to be further optimized to be able to valorize the husk as an adsorbent.

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