

Zinc chloride-activated Denim waste carbon for methylene blue removal

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Abstract. The aim of this work was to evaluate the adsorptive properties of denim-based activated carbon for methylene blue removal from water. The adsorbent was prepared through ZnCl₂ activation and characterized for specific area, surface chemistry and morphology. The batch adsorption was carried out at different dye concentrations, contact times and solution temperatures. The activated carbon, AC-ZnCl₂, yields a high surface area of 1323 m²/g with adsorption capacity of 326 mg/g. The adsorption data were well-fitted into Langmuir and pseudo-second-order kinetic models. The adsorption is endothermic and spontaneous at high temperature. Also, the kinetic and thermodynamic studies show that the adsorption is governed by physical and chemical adsorption.

Keywords: activated carbon; adsorption; denim waste; ZnCl₂ activation; methylene blue.

1. Introduction

Textile industry has a substantial impact on the nation's economic growth. However, the industry uses a lot of water, which leads to enormous wastewater discharge rate and high level of contaminants. Industrial dyestuffs, which comprise the main population of organic compounds, are the prime contributors to the worsening of environmental pollution [1]. Because of their intricate aromatic structure and xenobiotic properties, dyes are highly visible in water even at very low concentration, and they are more difficult to biodegrade than other organic compounds [2]. Undeniably, the discharge of dye effluent to the natural streams and rivers poses not only aesthetic issue but also ecological problems because dyes are toxic to aquatic creatures and detrimental to human health [3].

Adsorption is an effective approach for removal of soluble organic pollutants from water. The process has many advantages, i.e., high removal efficiency, low cost, and easy to operate [4, 5]. More importantly, it has been used in various industrial applications [6]. Adsorption is described as the deposition of solutes on the surface of solid bodies, which is mostly attributable to surface forces [7]. As an absorbable solute solution, also known as an adsorbate, it interacts with a porous solid where the liquid-solid intermolecular forces of attraction cause the solute to collect at the solid surface. Factors affecting the adsorption efficiency include initial concentration of adsorbate, contact time, temperature, ionic strength, adsorbent dosage and pH value [8].

The suitable adsorbent, which has good adsorption performance and low cost should be considered as part

of the process economics. Activated carbon has been widely used as adsorbent for industrial wastewater treatment. It is a carbonaceous substance that has an amorphous structure, a high degree of porous texture, and a wide pore volume that gives rise to internal surface area [9]. Since carbon-based waste resources are abundant and inexpensive, they could become promising feedstocks of activated carbon.

Denim waste is a significant source of textile waste and is becoming an increasing environmental concern as the production of jeans nowadays is enormous because of high demand from consumers. The global market size of denim jeans is over 70 billion dollars today, and it continues to escalate with 2% annual growth rate [10]. Consequently, about 2.16 million tons of jeans waste are generated annually with only 35–50 % is reuse or recycle in Western Europe [11]. Therefore, denim waste could be useful in generating activated carbon for wastewater treatment which simultaneously encourages environmental conservation as well as contributing to circular economy.

Denim waste has been studied as potential adsorbent for removal of several water pollutants. Denim fiber-based adsorbent yields a specific surface of 9 m²/g and adsorption capacities of 9.83, 2.71, and 2.69 mg/g for lead, cadmium, and zinc, respectively [12]. Besides, activated carbon that bears a 1582 m²/g surface area exhibits a capacity of 292 mg/g Remazol Brilliant Blue R [13]. However, dedicated work to assess the adsorptive properties of denim waste-based activated carbons is still limited in literature. To narrow down the research gap, this work features the conversion of denim waste into activated carbon by zinc chloride. The

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adsorption studies were carried out to scrutinize the performance of activated carbon in methylene blue removal at different concentrations, contact times and temperatures. The results were analyzed and discussed.

2. Experimental

2.1. Materials

Denim fabric waste was obtained from a recycled factory. Zinc chloride (ZnCl_2) was supplied by R&M Chemicals. Methylene blue was purchased from Quality Reagent Chemicals (QRcC).

2.2. Methods

Denim waste was cut to a uniform size of 1.5×1.0 cm. The sample was impregnated with zinc chloride solution at weight ratio (ZnCl_2 powder : denim waste) of 1.5. Then, the mixture was stirred for 30 min and oven-dried for impregnation. The activation was performed in a muffle furnace at 550°C for 1.5 h. The resultant activated carbon was washed using distilled water to a constant pH. The same steps were repeated, but in the absence of zinc chloride, to produce denim char. The adsorbents were designated as AC- ZnCl_2 and char, respectively.

The activated carbon was characterized for textural properties by N_2 gas adsorption at 77 K using a BET Micromeritics TriStar II 3020. The surface morphology was obtained by a TM3000 (Hitachi Japan). The presence of surface functional groups from FTIR spectra was determined using a Spectrum One (Perkin Elmer, USA).

The adsorption was performed by varying concentration, contact time, and temperature. The control solution in the absence of adsorbent was prepared to represent the initial concentration. A 30 mg of activated carbon was brought into contact with 30 mL of methylene blue solution in a Beatson bottle. The concentration was varied from 2.5 mg/L to 600 mg/L. The mixture was allowed to equilibrate at room temperature for 96 h, and the concentration was measured using UV-vis spectrophotometer. The capacity at equilibrium, Q_e was calculated as:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_e and C_0 (mg/L) are the equilibrium and initial concentrations of dye, respectively, m (g) is the mass of adsorbent and V (L) is the solution volume.

The effect of contact time on adsorption was conducted at concentrations of 12 mg/L and 17.5 mg/L. The concentration was measured at pre-set time intervals. The adsorption capacity at time, Q_t (mg/g) was calculated as:

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_t (mg/L) is the concentration of dye at time, t .

The adsorption thermodynamics was performed at temperatures of 25°C and 50°C for higher dye concentrations of 330 mg/L, 400 mg/L, 500 mg/L, and 600 mg/L. The mixture was placed in a temperature-controlled water bath.

3. Results and discussion

3.1. Characteristics of adsorbents

Table 1 shows the textural properties of AC- ZnCl_2 . The activated carbon yields a high surface area of $1323 \text{ m}^2/\text{g}$ and total pore volume of $0.927 \text{ cm}^3/\text{g}$ upon zinc chloride activation. During activation at high temperature, the swell of cellulose molecular structure allows ZnCl_2 to disrupt the lateral bonds and widen the inter- and intra-voids, thus increasing the surface area [14, 15]. Also, the activation causes the pores to enlarge, which is micropores merge into mesopores, leading to high mesoporosity (94.2 %). The good textural characteristics of the activated carbon typically reflect the high removal performance for methylene blue.

Table 1. Textural properties of AC- ZnCl_2 .

BET surface area (m^2/g)	1323
Total pore volume (cm^3/g)	0.927
Micropore volume (cm^3/g)	0.0535
Mesopore volume (cm^3/g)	0.874
Pore width (nm)	2.80

Figure 1 shows the FTIR spectra of char and AC- ZnCl_2 . Generally, the peaks for AC- ZnCl_2 are more simplified compared to char, due to extensive liberation of functional groups during activation process. The functional groups are thermally unstable and readily released when denim is carbonized at high temperature. For AC- ZnCl_2 , the small peak at 1950 cm^{-1} corresponds to carbonyl $\text{C}=\text{O}$ and $\text{C}=\text{C}=\text{O}$ stretching vibrations [13]. The peak at 1840 cm^{-1} is the characteristic of $\text{C}=\text{O}$ stretching vibration of anhydride [16]. The wide peak in the range of $1700\text{-}1400 \text{ cm}^{-1}$ could be ascribed to $\text{C}=\text{C}$ aromatic ring and $\text{C}-\text{O}$ stretching vibration. The small peak at 1365 cm^{-1} indicates the $\text{O}-\text{H}$ and $\text{C}-\text{H}$ bends of carboxylic acid, alcohol and alkene compound. The peak at 1200 cm^{-1} is attributed to $\text{C}-\text{O}$ stretch of carboxylic acids. The peak in the range of $1000\text{-}650 \text{ cm}^{-1}$ in the fingerprint region indicates cellulosic $\text{C}=\text{C}$ bend and $\text{C}-\text{O}-\text{C}$ stretch of alkene and alcohol [13, 16].

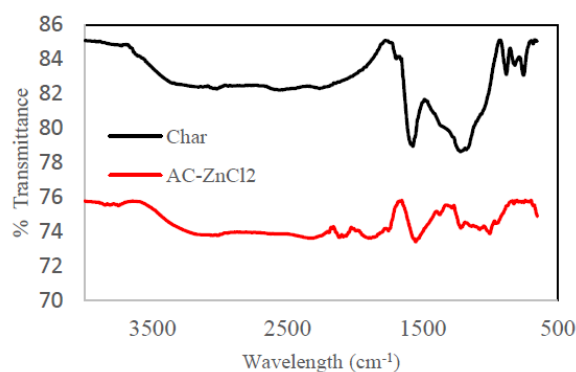


Figure 1. FTIR spectra of char and AC- ZnCl_2 .

Figure 2 shows the SEM image of AC- ZnCl_2 . The presence of small cavities, crevices, pores and rough surface indicates the interconnected porous network within the surface [16]. Generally, the activation process removes surface impurities, which contribute to the pore formation. Deep pores were observed, with non-uniform distribution of pore size. The surface is highly mesoporous with 94.2 % mesoporosity (5.72 %

microporosity). The tiny white particles randomly scattered on the carbon surface are presumably ash (zinc oxide) that was formed at high temperature during the activation process [17].

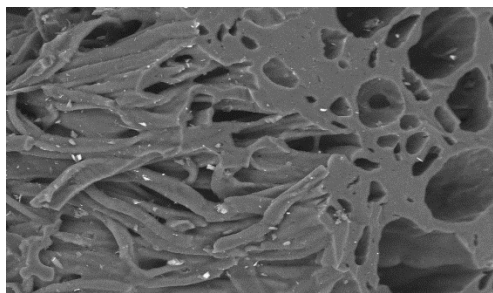


Figure 2. SEM image of AC-ZnCl₂

3.2. Equilibrium adsorption

Adsorption isotherm represents the equilibrium capacity and concentration of dye adsorbed at a given concentration in the solution. Figure 3 shows the equilibrium curve of dye removal by adsorbents and the fitting of isotherm models. The concentration gradient of dye solution provides the mass transfer driving force and affects the adsorption capacity at equilibrium. The magnitude of capacity increased to 326 mg/g as the concentration increases from 5 to 500 mg/L. The high capacity at higher initial concentration is essentially driven by large specific area of AC-ZnCl₂ (1323 m²/g) that provides more contact for interactions between carbon surface and methylene blue molecules. Besides, the mesoporous activated carbon that has a 94.2 % mesoporosity with average pore width of 2.80 nm contributes to extensive lodging of dye molecules. Nonetheless, the capacity decreased slightly to 311 mg/g at $C_o = 600$ mg/L. It indicates that the available sites for adsorption have been fully occupied and attain the surface saturation state. Hence, there is a probable desorption taking place as concentration is further increased. Consequently, the capacity reaches a plateau, and increasing dye concentration will only decrease the removal percentage.

On the other hand, the capacity of char increased to a maximum value of 20 mg/g. This may due to its under-developed surface texture when compared to activated carbon. Consequently, the binding sites become insufficient to hold methylene blue molecules when the concentration increases. The equilibrium of methylene blue adsorption by char and AC-ZnCl₂ obeys the Langmuir model with R^2 of 0.711 and 0.953, respectively. The applicability of this model implies that the adsorption is monolayer coverage of molecules onto homogeneous adsorbent surface. Yet, the fact that the char only exhibits the low adsorption capacity could result in insufficient increase along the equilibrium concentration, so rendering the relatively low regression coefficient. Moreover, the affinity, b for AC-ZnCl₂ (0.133 L/mg) is higher than that of char, suggesting a greater strength between activated carbon surface and dye molecules. Table 2 shows the constants of isotherm models for methylene blue adsorption by denim adsorbents.

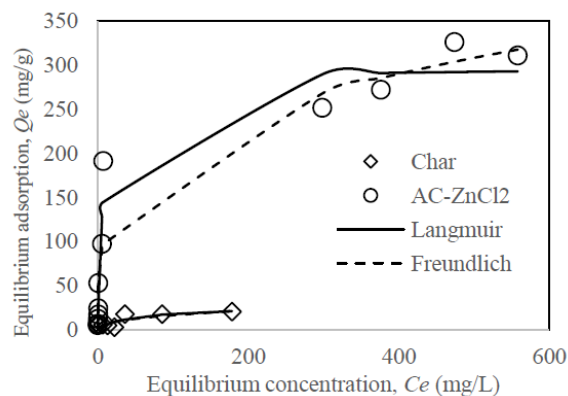


Figure 3. Fitting of isotherm models for adsorption of methylene blue onto adsorbents.

Table 2. Isotherm constants for methylene blue adsorption by denim-based adsorbents.

Adsorbent	Char	AC-ZnCl ₂
Q_{exp} (mg/g)	20.0	326
<i>Langmuir</i>		
Q_m (mg/g)	26.3	297
b (L/mg)	0.0213	0.133
SSE	135	8779
R^2	0.711	0.953
<i>Freundlich</i>		
K_f (mg/g)(L/mg) ^{1/n}	2.54	56.7
1/n	0.406	0.272
SSE	0.650	14236
R^2	0.650	0.924

3.3. Adsorption kinetics

The contact time between the adsorbent and adsorbate governs the extent of an adsorption process and provides information on the adsorption kinetics. Figure 4 shows the rate of methylene blue adsorption by denim adsorbents at different concentrations and the fitting of kinetic models. The adsorption capacities of char and AC-ZnCl₂ increased with increasing contact time, suggesting that the adsorption process is highly time-dependent. Rapid adsorption occurs at initial contact time (with up to 78.8 and 24.0 % dye removal percentage obtained within 4.5 h for AC-ZnCl₂ and char, respectively) followed by a much slower and gradual uptake to a point of equilibrium. Besides the surface area, the presence of surface functional groups on the adsorbent surface greatly contributes to the fast adsorption and high removal of methylene blue. Overall, the adsorption process requires 27.5 hours contacting period to achieve equilibrium for both concentrations.

Table 3 summarizes the constants of kinetic models for methylene blue adsorption by adsorbents. The pseudo-second order model, with $R^2 \rightarrow 1$, is more appropriate to describe the kinetics data. Thus, the adsorption rate of methylene blue is likely governed by chemisorption via sharing and exchange of electrons between dye molecules and functional groups on carbon surface [18, 19].

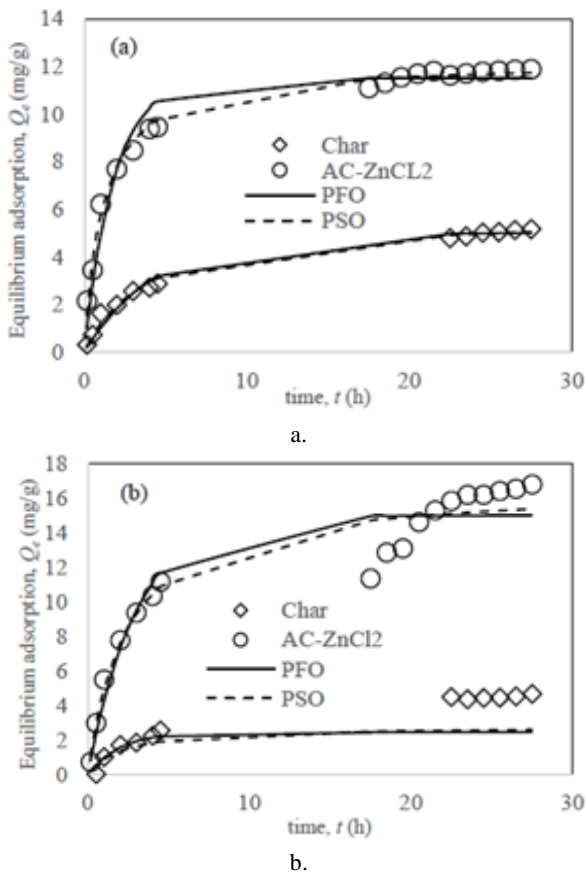


Figure 4. Fitting of kinetic models for methylene blue adsorption by denim adsorbents at (a) 12 and (b) 17.5 mg/L.

Table 3. Isotherm constants for methylene blue adsorption by denim adsorbents.

Adsorbent	Char		AC-ZnCl ₂	
C_0 (mg/L)	12	17.5	12	17.5
$Q_{e,exp}$ (mg/g)	5.17	4.68	11.9	16.8
<i>Pseudo-first Order</i>				
Q_e (mg/g)	5.00	2.47	11.5	15.0
k_1 (h ⁻¹)	0.226	0.520	0.547	0.334
SSE	0.759	55.5	6.98	35.2
R ²	0.985	0.863	0.970	0.915
<i>Pseudo-second Order</i>				
Q_e (mg/g)	5.75	2.80	12.2	16.7
k_2 (g/mg.h)	0.0451	0.174	0.0714	0.0250
SSE	0.369	54.9	1.24	26.0
R ²	0.991	0.968	0.993	0.936
<i>Intraparticle Diffusion</i>				
k_d (mg/g.h)	0.901	0.514	1.58	2.63
C (mg/g)	0.566	0.266	4.32	2.83
SSE	1.15	52.8	23.6	41.3
R ²	0.970	0.960	0.849	0.899

Meanwhile, AC-ZnCl₂ shows a low k_2 value of 0.0250 g/mg.h at higher concentration, indicating a slower adsorption. A stronger active sites competition and molecular repulsion occurred at high dye concentration, thus decreasing k_2 . Based on the plots of intraparticle diffusion (figures are not shown), all lines did not intersect at origin. Therefore, the rate limiting

step is not dominated by intraparticle diffusion alone, but could also involve film diffusion [20, 21].

3.4. Adsorption thermodynamics

The effect of solution temperature on adsorption capacity was carried out at different concentrations. Figure 5 depicts the effect of temperature on methylene blue adsorption by AC-ZnCl₂. The adsorption capacity increased with concentration and temperature. At higher temperature, the viscosity of the dye solution decreased and consequently, the diffusion rate of dye molecules increased across the external boundary layer and in the internal pores for higher adsorption capacity [22]. Also, the change in solution temperature affects the adsorption capacity of adsorbate; a higher temperature promotes disaggregation of dye molecules, which helps in the diffusion of methylene blue [23]. In addition, dye molecules acquire sufficient energy to move around and penetrate deeper into the pores of adsorbent [24].

Table 4 shows the thermodynamic parameters for methylene blue adsorption by AC-ZnCl₂. The positive value of enthalpy change, ΔH° indicates that the adsorption is endothermic process, whereby the heat is released during the process.

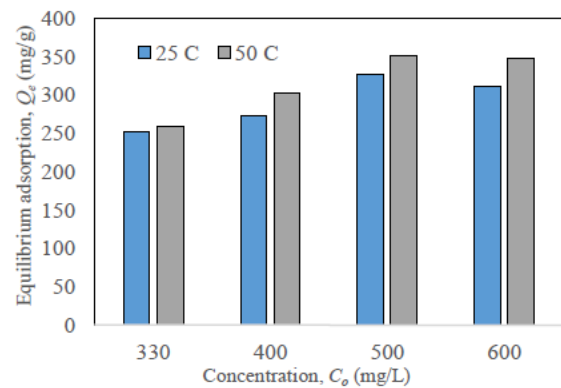


Figure 5. Effect of temperature on methylene blue adsorption by AC-ZnCl₂.

Table 4. Thermodynamic parameters for methylene blue adsorption by AC-ZnCl₂.

C_0	K_d	T (K)	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/mol.K)
330	3.22	298	-2895	3930	22.89
	3.64	323	-3467		
400	2.13	298	-1872	12300	47.53
	3.12	323	-3060		
500	1.87	298	-1558	7472	30.29
	2.37	323	-2315		
600	1.08	298	-180	7944	27.25
	1.38	323	-861		

More energy is released due to greater interaction between dye molecules and adsorbent surface at higher temperature, leading to negative ΔH° [25]. The positive or high value of entropy change, ΔS° represents the more randomness or disorder of energy during adsorption process. Thus, the ΔS° result implies that the higher concentration reduces the energy distribution and randomness of dye molecules. The negative Gibbs free energy, ΔG° describes the spontaneity and feasibility of

adsorption. Results from Table 4 show that ΔH° and ΔG° values are less than 84 kJ/mol and 20 kJ/mol, respectively, indicating that physisorption is dominant for the process [26].

4. Conclusions

Denim waste was converted into adsorbents for methylene blue adsorption. The activation using zinc chloride yields AC-ZnCl₂ with surface area of 1323 m²/g and adsorption capacity of 326 mg/g, outweighs the char with adsorption capacity of 20 mg/g. The performance of activated carbon in dye adsorption is attributed to its mesoporous structure and surface functional groups. The adsorption capacity increased with increasing concentration to a point of surface saturation, contact time to a point of equilibrium, and solution temperature. The adsorption of methylene blue by AC-ZnCl₂ is endothermic, feasible and spontaneous in nature. It can be concluded that denim waste is a potential precursor of activated carbon that is effective in removing methylene blue dye from water.

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Conflict of interest

Authors declare no conflict of interest.

References

- [1]. L. Mamy, D. Patureau, E. Barriuso, C. Bedos, F. Bessac, X. Louchart, F. Martin-laurent, C. Miege, P. Benoit, Prediction of the fate of organic compounds in the environment from their molecular properties: A review, *Critical Reviews in Environmental Science and Technology* 45 (2015) 1277–1377. Doi: 10.1080/10643389.2014.955627
- [2]. J. Sharma, S. Sharma, V. Soni, Classification and impact of synthetic textile dyes on aquatic flora: A review, *Regional Studies in Marine Science* 45 (2021) 101802. Doi: 10.1016/j.rsma.2021.101802
- [3]. V.B. Mane, S. Benkar, S. Bhavsar, A. Bandhankar, Removal of dye from wastewater using agricultural waste as low cost adsorbent, *Journal of Emerging Technologies and Innovative Research* 7 (2020) 404-414.
- [4]. N.A.A. Qasem, R.H. Mohammed, D.U. Lawal, Removal of heavy metal ions from wastewater: a comprehensive and critical review, *npj Clean Water* 4 (2021) 36. Doi: 10.1038/s41545-021-00127-0
- [5]. H. Yu, J. Zang, C. Guo, B. Li, B. Li, X. Zhang, T. Chen, Research progress on adsorption and separation of petroleum hydrocarbon molecules by porous materials, *Separations* 10 (2023) 17. Doi: 10.3390/separations10010017
- [6]. D.B. Broughton, C.G. Gerhold, Continuous sorption process employing fixed bed of sorbent and moving inlets and outlets, U.S. Patent No. 2,985,589, Washington DC, 1961.
- [7]. M. Alaqarbeh, adsorption phenomena: Definition, mechanisms, and adsorption types: Short review, *RHAZES: Green and Applied Chemistry* 13 (2021) 43-51. Doi: 10.48419/IMIST.PRSM/rhazes-v13.28283
- [8]. X. Chen, M.F. Hossain, C. Duan, J. Lu, Y.F. Tsang, M.S. Islam, Y. Zhou, Isotherm models for adsorption of heavy metals from water- A review, *Chemosphere* 307 (2022) 135545. Doi: 10.1016/j.chemosphere.2022.135545
- [9]. J. Saleem, U. Shahid, M. Hijab, H. Mackey, G. McKay, Production and applications of activated carbons as adsorbents from olive stones, *Biomass Conversion and Biorefinery* 9 (2019) 775–802. Doi: 10.1007/s13399-019-00473-7
- [10]. S.U. Aki, C. Candan, B. Nergis, N.S. Onder, Understanding denim recycling: A quantitative study with lifecycle assessment methodology, *Waste in Textile and Leather Sectors* (2020) 1–26. Doi: 10.5772/intechopen.92793
- [11]. A. Luiken, G. Bouwhuis, Recovery and recycling of denim waste, *Denim* (2015) 527-540. Doi: 10.1016/B978-0-85709-843-6.00018-4
- [12]. D.I. Mendoza-Castillo, C.K. Rojas-Mayorga, I.P. Garcia-Martinez, M.A. Perez-Cruz, V. Hernandez-Montoya, A. Bonilla-Petriciolet, M.A. Montes-Moran, Removal of heavy metals and arsenic from aqueous solution using textile wastes from denim industry, *International Journal of Environmental Science and Technology* 12 (2015) 1657–1668. Doi: 10.1007/s13762-014-0553-8
- [13]. T.L. Silva, A.L. Cazetta, P.S.C. Souza, T. Zhang, T. Asefa, V.C. Almeida, Mesoporous activated carbon fibers synthesized from denim fabric waste: efficient adsorbents for removal of textile dye from aqueous solutions, *Journal of Cleaner Production* 171 (2018) 482–490. Doi: 10.1016/j.jclepro.2017.10.034
- [14]. C. Saka, BET, TG–DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with ZnCl₂, *Journal of Analytical and Applied Pyrolysis* 95 (2012) 21–24. Doi: 10.1016/j.jaap.2011.12.020
- [15]. J. Donald, Y. Ohtsuka, C. Xu, Effects of activation agents and intrinsic minerals on pore development in activated carbons derived from a Canadian peat, *Materials Letters* 65 (2011) 744–747. Doi: 10.1016/j.matlet.2010.11.049
- [16]. S. Oumabady, P. Sebastian, S.P.B. Kamaludeen, M. Ramasamy, P. Kalaiselvi, E. Parameswari, Preparation and characterization of optimized hydrochar from paper board mill sludge, *Scientific Reports* 10 (2020) 773. Doi: 10.1038/s41598-019-57163-7
- [17]. C. Anyika, N.A.M. Asri, Z.A. Majid, A. Yahya, J. Jaafar, Synthesis and characterization of magnetic activated carbon developed from palm kernel shells, *Nanotechnology for Environmental Engineering* 2 (2017) 16. Doi: 10.1007/s41204-017-0027-6

- [18]. R. Wolski, A. Bazan-Wozniak, R. Pietrzak, Adsorption of methyl red and methylene blue on carbon bioadsorbents obtained from biogas plant waste materials, *Molecules* 28 (2023) 6712. Doi: 10.3390/molecules28186712
- [19]. T. Somsiripan, C. Sangwichien, Enhancement of adsorption capacity of Methylene blue, Malachite green, and Rhodamine B onto KOH activated carbon derived from oil palm empty fruit bunches, *Arabian Journal of Chemistry* 16 (2023) 105270. Doi: 10.1016/j.arabjc.2023.105270
- [20]. A. Pholosi, E.B. Naidoo, A.E. Ofomaja, Intraparticle diffusion of Cr(VI) through biomass and magnetite coated biomass: A comparative kinetic and diffusion study, *South African Journal of Chemical Engineering* 32 (2020) 39-55. Doi: 10.1016/j.sajce.2020.01.005
- [21]. J. Chang, Z. Shen, X. Hu, E. Schulman, C. Cui, Q. Guo, H. Tian, Adsorption of tetracycline by shrimp shell waste from aqueous solutions: Adsorption isotherm, kinetics modeling, and mechanism, *ACS Omega* 5 (2020) 3467-3477. Doi: 10.1021/acsomega.9b03781
- [22]. F. Amran, M.A.A. Zaini, Sodium hydroxide-activated Casuarina empty fruit: Isotherm, kinetics and thermodynamics of methylene blue and Congo red adsorption, *Environmental Technology & Innovation* 23 (2021) 101727. Doi: 10.1016/j.eti.2021.101727.
- [23]. S. Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu, Removal of dyes from aqueous solution using fly ash and red mud, *Water Research* 39 (2005) 129-138. Doi: 10.1016/j.watres.2004.09.011
- [24]. F. Amran, M.A.A. Zaini, Valorization of Casuarina empty fruit-based activated carbons for dyes removal – Activators, isotherm, kinetics and thermodynamics, *Surfaces and Interfaces* 25 (2021) 101277. Doi: 10.1016/j.surfin.2021.101277.
- [25]. V. Bernal, L. Giraldo, J.C. Moreno-Pirajan, Adsorption of pharmaceutical aromatic pollutants on heat-treated activated carbons: Effect of carbonaceous structure and the adsorbent–adsorbate interactions, *ACS Omega* 5 (2020) 15247-15256. Doi: 10.1021/acsomega.0c01288
- [26]. L. Alcaraz, A.L. Fernandez, F.A. Lopez, Preparation and characterization of activated carbons from winemaking wastes and their adsorption of methylene blue, *Adsorption Science & Technology* 36 (2018) 1135-1331. Doi: 10.1177/0263617418770295

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