Isotherm, kinetic and thermodynamic studies of methylene blue adsorption using *Leucaena leucocephala*

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**ABSTRACT**

In recent years, great focused has been placed on the development of low-cost adsorbents to be used for applications regarding treatment of wastewater. In this study, *Leucaena leucocephala* peel (LLP) was used for adsorption of methylene blue from aqueous solutions. The experiments were conducted at seven concentrations (15, 30, 45, 60, 75, 90, 105 mg L⁻¹) and three temperatures (298, 308, 318 K). The obtained data were applied to adsorption isotherm, kinetic and thermodynamic calculations. The results showed that Freundlich isotherm was more appropriate compared to Langmuir and Temkin isotherms. The kinetic results indicated that the process fitted pseudo second order model with higher R² values compared to pseudo first order and intra-particle diffusion models. Gibbs free energy, enthalpy and entropy values were calculated for 298 K as 2.776 kJ mol⁻¹, 6.262 kJ mol⁻¹ and 11.699 J mol⁻¹, respectively.

**Keywords:** Adsorption, isotherm, kinetic, *Leucaena leucocephala*, methylene blue, thermodynamic

1. **INTRODUCTION**

Dyes are used in variety of manufacturing such as textile, plastics, pharmaceutical, paper, printing, rubber, leather, paint, cosmetic, food and pulp [1-3]. Recently, worldwide attention has been brought to the fact that dyes, the toxic effects of which threaten the lives of humans, animals and the environment, are directly discharged into the environment [4]. Various methods have been designed to treat dye wastewater, such as adsorption [5-10], oxidation [11-12], membrane separation [13-14], electrochemical techniques [15-16] and ion exchange [17]. However, none of these methods have been successful in completely removing dyes from wastewater and all have limitations including high cost, secondary pollutant generation and poor removal efficiency. Among the different methods, adsorption has been determined as effective, low-cost and simplest process for wastewater treatment [18-20].

Activated carbon is widely used and it is the most effective adsorbent in the treatment of dyes in wastewater. However, the manufacturing and regeneration costs of activated carbon are high which is remain a major drawback [21-23]. Studies in the literature have used various low-cost adsorbents such as Barbados shells [24], palm kernel fiber [25], cacti [26], sawdust [27], Eichhioria crassipes roots [28]. But the adsorption capacity of such adsorbents is generally quite low and it has become important to discover more cost effective, eco-friendly, efficient, renewable and abundant materials to be used as adsorbents.

Adsorption onto biochars made from land-plant residues including sawdust, weeds, corn straws, and hickory wood, has been determined as high efficient and eco-friendly option to removal dyes from wastewater [29]. Some studies have evaluated for remove capacity of dye through interactions between the dye molecule and functional groups on the surface of these adsorbents. As most land-plant residues are discarded as waste, their use as low-cost and eco-friendly adsorbents is a promising alternative.

The aim of this study was to investigate dye removal ability of *Leucaena leucocephala* peels (LLP) as a cost effective adsorbent on MB in aqueous solutions containing. MB was selected as the adsorbate as it has been found to adversely affect human health by causing different diseases [30]. Within the scope of
this research, isotherm, kinetic and thermodynamic studies of the MB adsorption onto LLP was conducted.

2. MATERIALS AND METHOD

2.1. Materials

In this study, methylene blue was used as the adsorbate which formula is \( C_6H_18N_3SCl.3H_2O \) (MW 319.85 g mol\(^{-1}\)). Methylene Blue (MB), sulfuric acid (\( H_2SO_4 \)) and sodium hydroxide (NaOH) pellets (99 %) were purchased from Merck. The stock solution 1000 mg L\(^{-1}\) by dissolving the exact amount of MB in distilled water. The concentrations of MB solutions used for experiments were prepared by diluting the stock dye solution.

2.2 Adsorbent (Leucaena leucocephala) preparation

The Leucaena leucocephala peels (LLP), which were used as the adsorbent in the experiments, they were collected from the Robinia pseudoacacia trees that were grown on the grounds of Van Yüzüncü Yıl University, Turkey. The collected LLP were washed with distilled water and dried at 75 °C until steady weight was achieved. The dried adsorbent was then ground in a mill and divided into different size groups using a set of sieves. Samples with a particle size between 1.50 mm and 2 mm were used in experiments.

2.3 Adsorption experiments

In the batch experiments, which were carried out in a temperature-controlled water bath, 3 g of adsorbent was treated with 500 mL of the dye solution. The experiments were carried out at seven concentrations (15, 30, 45, 60, 75, 90, 105 mg L\(^{-1}\)) and three temperatures (298, 308, 318 K). MB concentration in the dye solution determined over 320 min while the pH was gradually adjusted by adding \( H_2SO_4 \) or NaOH solutions (0.1 M). All these experiments were carried out at pH 5.5. All experiments were performed in triplicate at the same conditions and average values were used to represent for results with all the calculated data. After adsorption experiments, the concentration of MB in the solution was determined with spectrophotometer (PG Instruments, T80 model) at 660 nm wavelength. The MB concentrations were determined with a calibration curve and adsorption capacity of LLP at equilibrium was determined with Eq. (1):

\[
q_e = \frac{C_0 - C_e}{m} V
\]

where \( V \) is solution volume (L), \( C_0 \) and \( C_e \) are initial and equilibrium concentrations of dye (mg L\(^{-1}\)) and \( m \) is adsorbent mass (g). The data obtained from experiments were tested by conducting isotherm, kinetic and thermodynamic studies. The amount of adsorption at any time \( t \), \( q_t \) (mg g\(^{-1}\)), was calculated by Eq. (2):

\[
q_t = \frac{C_0 - C_e}{m} V
\]

3. RESULTS & DISCUSSION

3.1. Isotherm modelling studies

In the present study, the obtained data were analyzed using Langmuir, Freundlich and Temkin models. The parameters of these models were calculated by linear form of isotherm equations. The amount of MB adsorbed per unit of LLP mass and the equilibrium concentrations in the aqueous solutions for all three temperatures are presented in Fig 1. It was determined that removal efficiency increased with increase in the initial MB concentrations. LLP adsorption capacity of MB concentration ranging from 15 to 105 mg L\(^{-1}\) was determined as 4.785 to 36.235 mg g\(^{-1}\) for 298 K, 5.425 to 39.025 mg g\(^{-1}\) for 308 K and 5.545 to 40.745 mg g\(^{-1}\) for 318 K.

![Fig 1. Adsorption isotherms for MB on the LLP at the three temperatures](image-url)
Langmuir isotherm assumes monolayer coverage of the MB dye onto homogeneous adsorbent surface. Linear representation of Langmuir adsorption isotherm equation is given below:

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}
\]

where \( q_m \) (mg g\(^{-1}\)) is maximum adsorption capacity and \( K_L \) (L g\(^{-1}\)) is Langmuir constant that can be determined from the plot of \( C_e/q_e \) versus \( C_e \). Langmuir isotherm results of the MB adsorption onto LLP for three temperatures are given in Fig 2.

Freundlich isotherm assumes multilayer coverage of MB dye onto the heterogeneous adsorbent surface. Linear representation of Freundlich isotherm equation is presented below:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}
\]

where \( K_F \) is Freundlich constant and \( n \) is heterogeneity factor. \( K_F \) and \( n \) constants are determined by plotting \( \ln q_e \) to \( \ln C_e \). Freundlich isotherm results of MB adsorption onto LLP for three temperatures are presented in Fig 3.

![Fig 2. Langmuir adsorption isotherm for MB adsorption onto LLP](image)

Temkin isotherm assumes decrease of adsorption heat in the layer of adsorbents that occurs due to enhancement of surface coverage of adsorbents.

\[
q_e = B \ln(K_F C_e) \tag{5}
\]

where \( B = RT/b_r \), \( T \) is absolute temperature (K), \( R \) is universal constant (J mol\(^{-1}\) K\(^{-1}\)) and \( K_F \) is constant (L g\(^{-1}\)). It was determined that the increase in isotherm constants increased with increase in temperature of adsorption temperature. \( B \) values were increased which indicated that adsorption was endothermic. Temkin isotherm results of the MB adsorption onto LLP for three temperatures are given in Fig 4.

Table 1 clearly shows that three isotherm constants determined in this study are in comparable ranges with the values in previous studies. According to Langmuir isotherm calculations \( q_m \) and \( K_L \) values were increased with the increase of temperature which signified strong bonding between adsorbate and adsorbent. \( K_F \) and \( n \) values were increased with the rise of temperature based on the Freundlich isotherm calculations. \( K_F \) and \( b_r \) values were increased with the
increase of temperature according to Temkin isotherm calculations. $R^2$ values of the Freundlich model were determined to be higher than those of the other models for removal of MB using LLP.

Fig 4. Temkin adsorption isotherm for MB adsorption onto LLP

Table 1. Adsorption isotherm model parameters of MB adsorption onto LLP

| Temp | Langmuir | Freundlich | Temkin |
|------|----------|------------|--------|
|      | $K_d$ (L·g$^{-1}$) | $q_m$ (mg·g$^{-1}$) | $R^2$ | $n$ | $K_F$ (L·g$^{-1}$) | $R^2$ | $K_T$ (L·g$^{-1}$) | $b_T$ (J·mol$^{-1}$) | $R^2$ |
| 298 K | 0.0635 | 41.667 | 0.5559 | 0.8451 | 0.3106 | 0.9805 | 0.1898 | 273.6378 | 0.8847 |
| 308 K | 0.0811 | 74.943 | 0.4969 | 0.9472 | 0.5763 | 0.9879 | 0.2557 | 284.2975 | 0.8791 |
| 318 K | 0.1002 | 101.111 | 0.5241 | 0.9805 | 0.6455 | 0.9947 | 0.2795 | 296.1466 | 0.9032 |

3.2. Thermodynamic studies

The thermodynamic parameters, Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) were significant on the adsorption of MB onto LLP. These parameters were calculated using the equations given below:

$$K_d = C_{ads}/C_e$$

$$\Delta G^\circ = -RT\ln K_d$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

where $K_d$ is the equilibrium constant. The $\Delta H^\circ$ and $\Delta S^\circ$ parameters were determined from plot natural logarithm of $K_d$ versus $1/T$ given in Fig 5. The thermodynamic parameters of MB adsorption onto LLP are listed in Table 2. The $\Delta G^\circ$ values of this removal process were determined as -1359.6 J·mol$^{-1}$ for 298 K, -1476.6 J·mol$^{-1}$ for 308 K and -1593.6 J·mol$^{-1}$ for 318 K. The $\Delta H^\circ$ and $\Delta S^\circ$ values of removal process of MB onto LLP were found to be 2126.687 J·mol$^{-1}$ and 11.699 J·mol$^{-1}$·K$^{-1}$, respectively. The negative $\Delta G^\circ$ values were indicated that adsorption was physisorption, which is the showed that feasibility and spontaneous nature of this process. The absolute values of $\Delta G^\circ$ were decreased as the temperature increased, which shows that this separation process was constructive at low temperatures. The positive $\Delta H^\circ$ and $\Delta S^\circ$ values were demonstrated that process endothermic and the enhanced randomness at the solid–solute interface with affinity of LLP for MB. The low enthalpy values were explained that interaction produces noncovalent bonding between dyes and adsorbents [31].

Fig 5. Van’t Hoff plot for adsorption of MB onto LLP
Table 2. Thermodynamic parameters of adsorption of MB onto LLP

| Temp (K) | \( \Delta G^0 \) (kJ mol\(^{-1}\)) | \( \Delta H^0 \) (kJ mol\(^{-1}\)) | \( \Delta S^0 \) (J mol\(^{-1}\) K\(^{-1}\)) | \( R^2 \) |
|----------|---------------------------------|---------------------------------|---------------------------------|-----------|
| 298      | -1.3596                         |                                 |                                 |           |
| 308      | -1.4766                         | 2126.687                       | 11.699                          | 0.9905    |
| 318      | -1.5936                         |                                 |                                 |           |

Table 3. PFO, PSO and IPD kinetic model parameters of MB adsorption onto LLP

| Kinetic Model | Temp (K) | Kinetic coefficients | 15 (mg L\(^{-1}\)) | 30 (mg L\(^{-1}\)) | 45 (mg L\(^{-1}\)) | 60 (mg L\(^{-1}\)) | 75 (mg L\(^{-1}\)) | 90 (mg L\(^{-1}\)) | 105 (mg L\(^{-1}\)) |
|---------------|----------|----------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| PFO kinetic model | 298      | \( k_0 \) (min\(^{-1}\)) | 0.0251              | 0.0225              | 0.0276              | 0.0335              | 0.0353              | 0.0361              | 0.0379              |
|               |          | \( q_e \) (mg g\(^{-1}\)) | 2.5857              | 7.1821              | 8.5968              | 18.610              | 25.498              | 23.609              | 28.9277             |
|               |          | \( R^2 \)              | 0.9832              | 0.9441              | 0.9437              | 0.9341              | 0.9459              | 0.9269              | 0.9674              |
| PSO kinetic model | 308      | \( k_0 \) (min\(^{-1}\)) | 0.0261              | 0.0277              | 0.0286              | 0.0313              | 0.0327              | 0.0345              | 0.0352              |
|               |          | \( q_e \) (mg g\(^{-1}\)) | 2.9544              | 4.5979              | 7.9050              | 11.4489             | 12.7866             | 15.9921             | 23.4062             |
|               |          | \( R^2 \)              | 0.9000              | 0.9112              | 0.9188              | 0.9108              | 0.8963              | 0.8786              | 0.9038              |
| IPD kinetic model | 318      | \( k_0 \) (min\(^{-1}\)) | 0.0257              | 0.0311              | 0.0322              | 0.0361              | 0.0369              | 0.0384              | 0.0397              |
|               |          | \( q_e \) (mg g\(^{-1}\)) | 2.7442              | 6.9019              | 12.8212             | 15.5585             | 13.2381             | 16.7617             | 23.1478             |
|               |          | \( R^2 \)              | 0.9261              | 0.9314              | 0.9398              | 0.9318              | 0.9399              | 0.9226              | 0.9521              |

3.3. Adsorption kinetics studies

In this study, the MB adsorption kinetics were calculated using PFO, PSO and IPD kinetic models. The well-suited model was selected based on the regression coefficient \( R^2 \) values. These models were investigated in accordance with the experimental data obtained at varied temperatures and MB concentrations.

The PFO kinetic model is depend on the concentration of solution and solid adsorption capacity.

This model was firstly developed for characterization of liquid-solid adsorption systems depending on adsorption capacity of solid. PFO is applied to study adsorption in liquid-solid systems which have unoccupied adsorptive sites [32]. The PFO kinetic model is given in the equation below:
\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  
(10)

where \(k_1\) (min\(^{-1}\)) is rate constant of PFO kinetic model. To achieve constants with this model, plots were drawn of \(\ln(q_e - q_t)\) against \(t\).

The PSO kinetic model, which is explained using bond formation between the adsorptive site and solute molecule [33]. The PSO kinetic model is given in the equation below:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_0} + \frac{t}{q_0}
\]  
(11)

where \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) is rate constant of PSO kinetic model. The values of \(k_2\) and \(q_0\) are identified from plot of \(t/q_t\) versus \(t\) in accordance with Equation (10).

The IPD model equation, which was proposed by Weber and Morris, is obtained by testing the possibility of IPD as the rate limiting step [34]. The IPD kinetic model is given in the equation below:

\[
q_t = k_{ipd}^{0.5} + C
\]  
(12)

where \(k_{ipd}\) (mg g\(^{-1}\) min\(^{1/2}\)) is IPD kinetic rate constant and \(C\) is boundary thickness. A plot of \(q_t\) against \(t\) at different MB concentrations gave two phases of linear plot. The PFO, PSO and IPD model parameters are given in Table 3.

The experimental results showed that the \(R^2\) coefficients were close to 1.0 which explained that this process fits the PSO kinetic model. Generally, in most dye adsorption systems the kinetic data is better represented by PSO model. In this study, the experimental and calculated \(q_t\) values for 318 K are higher than those for 298 K and 308 K. When the kinetic constants were compared, it was determined that the constant values were closer to both temperatures and concentrations for the PSO model. This result showed that the MG adsorption kinetics onto LLP confirmed the PSO model.

4. CONCLUSIONS

In this study LLP were used as an adsorbent for removal of MB, a widely used dye, from aqueous solutions. Batch experiments were carried out at seven concentrations and three temperatures. LLP adsorption capacity of MB concentration ranging from 15 to 105 mg L\(^{-1}\) was determined as 4.785 to 36.235 mg g\(^{-1}\) for 298 K, 5.425 to 39.025 mg g\(^{-1}\) for 308 K and 5.545 to 40.745 mg g\(^{-1}\) for 318 K. In the isotherm model studies, experimental results showed that Freundlich isothermal model was more suitable than the other two isotherms. These isotherm coefficients increased as the temperature increased and \(R^2\) values of Freundlich model were determined to be higher than those of the other two models for removal of MB using LLP. The monolayer adsorption capacity (\(q_m\)) of LLP was determined as 41.667 mg g\(^{-1}\) for 298 K, 74.943 for 308 K and 101.111 mg g\(^{-1}\) for 318 K. This indicated that process was of an endothermic nature. The experimental data were applied to PFO, PSO and IPD kinetic models. Kinetic studies displayed that adsorption of MB process conformed the PSO model. All kinetic model coefficients increased as the temperature increased and \(R^2\) values of PSO model were higher than the other two models for removal of MB using LLP. \(\Delta G^o\) values of MB adsorption onto LLP were calculated as -1359.6 J mol\(^{-1}\) for 298 K, -1476.6 J mol\(^{-1}\) for 308 K and -1593.6 J mol\(^{-1}\) for 318 K. \(\Delta H^o\) and \(\Delta S^o\) values of MB adsorption onto LLP were determined to be 21.26.87 J mol\(^{-1}\) and 11.69 J mol\(^{-1}\), respectively. The experimental data showed that LLP, which is the waste of Robinia pseudoacacia trees, may be an alternative material to removal of dyes from wastewater.

REFERENCES

[1]. S. Asad, M. A. Amoozegar, A. A. Pourbabeaee, M. N. Sarbolouki and S. M. M. Dastgheib, “Decolorization of textile azo dyes by newly isolated halophilic and halotolerant bacteria,” Bioresource Technology, Vol. 98 (11), pp. 2082-2088, 2007.

[2]. R. L. Singh, P. K. Singh and R. P. Singh, “Enzymatic decolorization and degradation of azo dyes – a review,” International Biodeterioration & Biodegradation, Vol. 104, pp. 21-31, 2015.

[3]. C. Srikantan, G. K. Suraishkumar and S. Srivastava, “Effect of light on the kinetics and equilibrium of the textile dye (Reactive red 120) adsorption by helianthus annuus hairy roots,” Bioresource Technology, Vol. 257, pp. 84-91, 2018.

[4]. Y. Liu, Y. Liu, R. Qu, C. Ji and C. Sun, “Comparison of adsorption properties for anionic dye by metal organic frameworks with different metal ions,” Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 586, pp. 1-7, 2020.

[5]. M. A., Ahmad, N., Ahmad, N. and O. S. Bello, “Modified durian seed as adsorbent for the removal of methyl red dye from aqueous solutions,” Applied Water Science, Vol. 5, pp. 407-423, 2015.

[6]. A. A. Spagnoli, D. A. Giannakoudakis and S. Bashkova, “Adsorption of methylene blue on cashew nut shell based carbons activated with zinc chloride: the role of surface and structural parameters,” Journal of Molecular Liquids, Vol. 229, pp. 465-471, 2017.

[7]. R. Subramaniam and S. K. Ponnusamy, “Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: optimization by response surface methodology,” Water Resources and Industry, Vol. 11, pp. 64-70, 2015.

[8]. M. T. Yagub, T. K. Sen, S. Afrzae and H. M. Ang, “Dye and its removal from aqueous solution by adsorption: a review,” Advances Colloid and Interface Science, Vol. 209, pp. 172-184, 2014.

[9]. M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad, “Adsorption of methylene blue on low-cost adsorbents: a review,” Journal of Hazardous Materials, Vol. 177(1-3), pp. 70–80, 2010.

[10]. M. A. M. Saleh, D. K. Mahmoud, W. A. W. A. Karim and A. Idris, “Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review,” Desalination, Vol. 280(1-3), pp.1-13, 2011.
[11]. Y.-G. Kang, H. Yoon, C.-S. Lee, E.-J. Kim and Y.-S. Chang, “Advanced oxidation and adsorptive bubble separation of dyes using MnO2-coated Fe3O4 nanocomposite,” Water Research, Vol. 151, pp. 413-422, 2019.

[12]. A. Muniyasamy, G. Sivaporul, A. Gopinath, R. Lakshmanan, A. Altaee, A. Achary and P. V. Chellam, “Process development for the degradation of textile azo dyes (mono-, di-, poly- ) by advanced oxidation process - ozonation: experimental & partial derivative modelling approach,” Journal of Environmental Management, Vol. 265, pp. 1-10, 2020.

[13]. Y. Lu, Y. Fang, X. Xiao, S. Qi, C. Huan, Y. Zhan, H. Cheng and G. Xu, “Petal-like molybdenum disulfide loaded nanofibers membrane with super hydrophilic property for dye adsorption,” Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 553, pp. 210-217, 2018.

[14]. Y. Ma, P. Qi, J. Ju, Q. Wang, L. Hao, R. Wang and K. Sui, Y. Tan, “Gelatin/alginate composite nanofiber membranes for effective and even adsorption of cationic dyes,” Composites Part B: Engineering, Vol. 162, pp. 671-677, 2019.

[15]. L. A. Pereira, A. B. Couto, D. A. L. Almeida and N. G. Ferreira, “Singular properties of boron-doped diamond/carbon fiber composite as anode in Brilliant Green dye electrochemical degradation,” Diamond and Related Materials, Vol. 103, pp. 1-7, 2020.

[16]. N. P. Shetti, S. J. Malode, R. S. Malladi, S. L. Nargund, S. S. Shulda and T. M. Aminabhavi, “Electrochemical detection and degradation of textile dye Congo red at graphene oxide modified electrode,” Microchemical Journal, Vol. 146, pp. 387-392, 2019.

[17]. J. Joseph, R. C. Radhakrishnan, J. K. Johnson, S. P. Joy and J. Thomas, “Ion-exchange mediated removal of cationic dye-stuffs from water using ammonium phosphomolybdate,” Materials Chemistry and Physics, Vol. 242, pp. 1-8, 2020.

[18]. H. N. Bhatti, Y. Safa, S. M. Yakout, O. H. Shair, M. Iqbal and A. Nazir, “Efficient removal of dyes using carboxymethyl cellulose/ alginate/polyvinyl alcohol/ rice husk composite: Adsorption/desorption, kinetics and recyling studies,” International Journal of Biological Macromolecules, Vol. 150, pp. 861-870, 2020.

[19]. C. Puri and G. Sumana, “Highly effective adsorption of crystal violet dye from contaminated water using graphene oxide intercalated montmorillonite nanocomposite,” Applied Clay Science, Vol. 166, pp. 102-112, 2018.

[20]. E. Alver, A. Ü. Metin and F. Brouers, “Methylene blue adsorption on magnetic alginate/rice husk bio-composite,” International Journal of Biological Macromolecules, Vol. 154, pp. 104-113, 2020.

[21]. F. Dhaouadi, L. Sellaui, G. L. Dotto, A. Bonilla-Petriciolet, A. Eto and A. B. Lamine, “Adsorption of methylene blue on comminuted raw avocado seeds: Interpretation of the effect of salts via physical monolayer model,” Journal of Molecular Liquids, Vol. 305, pp. 1-8, 2020.

[22]. A. H. Jawad, R. Razuan, J. N. Appaturi and L. D. Wilson, “Adsorption and mechanism study for methylene blue dye removal with carbonized watermelon (Citrullus lanatus) rind prepared via one-step liquid phase H2SO4 activation,” Surfaces and Interfaces, Vol. 16, pp. 76-84, 2019.

[23]. D. S. Tong, C. W. Wu, M. O. Adebajo, G. C. Jin, W. H. Yu, S. F. Ji and C. H. Zhou, “Adsorption of methylene blue from aqueous solution onto porous cellulose-derived carbon/ montmorillonite nanocomposites,” Applied Clay Science, Vol. 161, pp. 256-264, 2018.

[24]. S. Idris, Y. A. Iyaka, M. N. Ndamtsa, E. B. Mohammed and M. T. Umar, “Evaluation of kinetic models of copper and lead uptake from dye wastewater by activated pride of barbados shell,” American Journal of Chemistry, Vol. 1, pp. 47–51, 2012.

[25]. Y. Ho and A. Ofomaja, “Pseudo-second-order model for lead ion sorption from aqueous solutions onto palm kernel fiber,” Journal of Hazardous Materials, Vol. 129, pp. 137–142, 2006.

[26]. F. B. Rehah and S. M. Siddeeg, “Cactus an eco-friendly material for wastewater treatment: a review,” Journal of Materials and Environmental Science, Vol. 8, pp. 1770–1792, 2017.

[27]. H. A. Al-Husseiny, “Adsorption of methylene blue dye using low cost adsorbent of sawdust: batch and continues studies,” Journal of University of Babylon, Vol. 22(2), pp. 296-310, 2014.

[28]. W. C. Wanyonyi, J. M. Onyari and P. M. Shiundu, “Adsorption of Congo red dye from aqueous solutions using roots of Eichhornia crassipes: kinetic and equilibrium studies,” Energy Procedia, Vol. 50, pp. 862–869, 2014.

[29]. M. J. Ahmed, P. U. Okoye, E. H. Hummadi and B. H. Hameed, “High-performance porous biochar from the pyrolysis of natural and renewable seaweed (Gelidiella acerosa) and its application for the adsorption of methylene blue,” Bioresource Technology, Vol. 278, pp. 159-164, 2019.

[30]. L. M. Pandey, “Enhanced adsorption capacity of designed bentonite and alginate beads for the effective removal of methylene blue,” Applied Clay Science, Vol. 169, pp. 102-111, 2019.

[31]. I. Ghosh, S. Kar, T. Chatterjee, N. Bar and S. K. Das, “Removal of methylene blue from aqueous solution using Lathyrus sativus husk: Adsorption study, MPR and ANN modeling,” Process Safety and Environmental Protection, Vol. 149, pp. 345-361, 2021.

[32]. S. Langergren and B. K. Svenska, “Zur theorie der sogenannten adsorption geloester stoffe,” Veterinskapsakad Handlingar, Vol. 24, pp. 1-39, 1898.

[33]. Y. S. Ho and G. Mclay, “Kinetic models for the sorption of dye from aqueous solution by wood,” Process Safety and Environmental Protection, Vol. 76, pp. 183-191, 1998.

[34]. W. J. Weber and J. C. Morris, “Kinetics of adsorption on carbon from solution,” Journal of the Sanitary Engineering Division, Vol. 89, pp. 31-60, 1963.