Uluslararası İleri Doğa
Bilimleri ve Mühendislik
Araştırmaları Dergisi
Sayı 8, S. 71-81, 9, 2024
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Araştırma Makalesi

IJANSER
https://as-proceeding.com/index.php/ijanser
ISSN:2980-0811

International Journal of Advanced
Natural Sciences and Engineering
Researches
Volume 8, pp. 71-81, 9, 2024
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Research Article

Comparative Isotherm and Kinetic Analysis of Acid Violet 7 (AV7) and Methylene Blue (MB) Adsorption onto MOF-5

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(Received: 22 September 2024, Accepted: 02 October 2024)

(6th International Conference on Applied Engineering and Natural Sciences ICAENS 2024, 25-26 September 2024)

ATIF/REFERENCE: Shafti, D. M., Dahlan, I. & Din, A. T. M. (2024). Comparative Isotherm and Kinetic Analysis of Acid Violet 7 (AV7) and Methylene Blue (MB) Adsorption onto MOF-5, *International Journal of Advanced Natural Sciences and Engineering Researches*, 8(9), 71-81.

Abstract – One of the most critical issues in the field of wastewater contamination is the occurrence of colored compounds, including dyes. Synthetic dyes, including acid violet 7 (AV7) and methylene blue (MB), have been employed in a variety of applications. In this study, the adsorption of AV7 and MB dyes was compared using an adsorbent prepared from MOF-5. The adsorption isotherm and kinetics were employed for the respective analysis of AV7 and MB dyes. The adsorption isotherm and kinetics were best described by the Henry and Freundlich isotherm and the elovich and pseudo-second-order kinetic models, respectively, for AV7 and MB. The BET (Brunauer-Emmett-Teller) analysis was employed to ascertain the specific area and pore volume of MOF-5. The findings of this study demonstrate that MOF-5 adsorbents are effective at removing AV7 and MB from aqueous media.

Keywords – MOF, Dye, Pollutants, Adsorption, Removal, Isotherm, Kinetics

I. INTRODUCTION

Dyes are extensively used in various industries such as printing ink, textiles, cosmetics, paper, leather, and ceramics [1, 2]. As reported by [1], it is expected that approximately 15% of the dye will be lost during processing and subsequently released into wastewater. As reported by [3], dye pollutants significantly affect groundwater and environmental pollution. Synthetic dyes are a significant group of water pollutants that pose a threat to public health and the environment. They can even promote the growth of algae [4, 7] because most of them are hazardous and may cause cancer. The rapid expansion of several industries, including coking, plastics, synthetic fibers, dyes, and petrochemicals, has led to a significant increase in the volume of wastewater containing refractory organic contaminants. Its complex composition, high concentration, low biodegradability, and biotoxicity pose significant risks to both human health and the environment [9, 10, 11, 12]. Synthetic dyes are a significant class of water contaminants that attract algae owing to their harmful and potentially carcinogenic properties [4, 7]. The acidic color violet is harmful to humans and other animals because of its adverse effects on the skin, eyes, and respiratory system, as well as its ability to modify the structure of genes and cause gene mutations. The dumping of dye waste into rivers can damage ecosystems, pollute water, cause eutrophication, and disturb aquatic life. Watercolor is one of the most noticeable indicators of contamination. Some of the challenges associated with dye waste treatment include a slow sorption capacity and multi-step adsorbent synthesis.

Acid violet (AV7) and methylene blue (MB) are among the most frequently utilized water-soluble cationic dyes. Acid Violet-7 (AV-7) is an azo dye commonly used in various industries such as food, leather, paper, soap, wool, silk, polyamide fiber, leather, medicine, and cosmetics. The substance is non-volatile and highly soluble in water, with a reddish-purple color. AV-7 dye is more difficult to degrade and genotoxic than other azo dyes due to its structure, which includes aromatic rings, and amino and sulfonic groups [13]. Methylene blue (MB) (3,7-bis(dimethylamino) phenothiazine chloride tetra methylthionine chloride) is one of the synthetic dyes that is applied in large quantities as a colourant for papers, in wool, silk, and cotton and is classified as a cationic dye [8]. In addition to dye-containing wastewater, industrial activity generates a large amount of ash as a by-product of burning solid fuels, such as rice husks and coal fly ash.

Various physicochemical, chemical, and physical methods have been developed to remove dyes from aqueous solutions, including membranes, adsorption techniques, and catalyst-assisted color oxidation. Fruit peels, bio-coagulants, and cellulose-based bio-adsorbents are examples of materials that have been employed as adsorbents for color removal. Metal-organic frameworks (MOFs) are a new class of crystalline, porous materials that can hold both inorganic and organic molecules. Yaghi made this discovery in 1999. According to [14], MOF-5, also known as IRMOF-1, has a cubic structure composed of $Zn_4O(BDC)_3$, which is a metal-organic framework. The constituents of MOF-type materials are impressive [15,16] because of their exceptional porosity, large surface area, ease of adjusting the pore size and shape (microporous and mesoporous structures), as well as their potential for adsorption, storage, and separation [17, 18, 19, 20, 21]. With a surface-to-volume ratio of 2200 m^2/cm^3, MOF-5 has one of the highest ratios among the MOFs. MOFs are utilized to adsorb hazardous pollutants from both liquid and vapor phases. MOF-5 is a unique cubic network that joins the ZnO_4 units with 1,4-benzene dicarboxylate linkers. The interaction between the inorganic Zn_4O molecule of MOF-5 and the bidentate ligand benzene-1,4-dicarboxylate produces a three-dimensional structure [22].

However, pristine MOF adsorbents are unstable and exhibit low adsorption capabilities. Therefore, MOF adsorbents have been developed in combination with other active species. Attempts have been made to use waste siliceous materials such as rice husk ash (RHA) and coal fly ash (CFA) for incorporation into MOFs, which may have significant potential to enhance some of their properties and partially solve the waste material disposal problem. This study aimed to investigate the effectiveness and efficiency of MOF-5 and its modification for removing AV7 and MB dyes from aqueous solutions. Furthermore, the kinetics and isotherms adsorption were examined.

II. MATERIALS AND METHOD

II.I Raw materials

` Sigma provided the acid violet and methylene blue dyes, zinc (II) nitrate hexahydrate, 1,4-benzaldicarboxylic acid, and N, N-dimethylformamide (DMF). The rice husk (RH) and the burnt rice husk (labeled as RHA-Ind) were obtained from Kilang Beras Co. Titi Serong Sdn Bhd, Parit Buntar, Perak.

II.II Synthesize of MOF-5

The process was initiated by using a combination of 1,4-benzaldicarboxylic acid and zinc (II) nitrate hexahydrate. The subsequent stage involved the addition of 100 mL N, N-dimethylformamide (DMF), 0.2 g of 1,4-benzaldicarboxylic acid, and zinc (II) nitrate (1 g), followed by the completion of the process. Finally, to aid the adsorption process, the beaker was covered with an aluminum foil. After that, heat the samples in an autoclave at 110°C for 30 minutes. After the completion of the procedure, the samples were cooled to room temperature. Once cooled, the material was centrifuged in multiple tubes, to ensure that the volume of each tube was 50 mL. The mixture was centrifuged at 4000 rpm for 10 minutes was performed to separate the particles. Finally, the sample was filtered through a paper filter and placed in an oven (80°C) for 24 hours.

II.III Batch adsorption studies

The batch adsorption experiments were performed using an IKA KS 4000 I control incubator shaker. Preliminary tests were conducted for pristine and modified MOF-5 to determine the adsorption efficiency. All experiments were conducted in 250 mL conical flasks covered with aluminum foil, with varying amounts of adsorbent, mixing time, pH level, shaking rate, initial dye concentration, and solution temperature. Approximately 100 mL of the AV7 or MB dye solution was used. Following each batch of adsorption, the adsorbents were separated by centrifugation at 4000 rpm for 10 minutes. The remaining solution was analysed using a UV-Vis spectrophotometer, and the concentration of residual AV7 or MB was calculated using the calibration curve equation. Blank experiments were conducted to ensure that no dye was adsorbed onto the beakers or adsorbent, and only water was used to prevent leaching. All adsorption tests were performed in triplicate, and the data were analysed using average values. The amount of AV7 dye adsorbed (q_e) and the AV7 and MB removal efficiencies were calculated using Eqs. (1) and (2), respectively.

$$q_e = \frac{(c_0 - c_e)}{m} \times V \qquad (1)$$

$$\text{Removal (\%)} = \frac{c_0 - c_e}{c_0} \times 100 \qquad (2)$$

where q_e is the amount of dye adsorbed (mg/g), m is the mass of the adsorbent (g), V is the volume of the solution (L), and C_0 and C_e are the initial and equilibrium concentrations of AV7 and MB dye (mg/L), respectively.

II.IV Adsorption isotherm

Adsorption isotherm models are commonly used to study adsorption processes. This study used the Elovich, Henry, Redlich-Peterson, and Jossens isotherms models for the MOF-5 equilibrium data. The coefficient of determination (R^2) was used to evaluate the application of the isotherm models to adsorption treatment.

II.IV.I Elovich Isotherm

The Elovich adsorption isotherm is founded upon kinetic principles and takes into account the phenomenon of multilayer adsorption. It postulates that the number of adsorption sites increases exponentially with the progression of adsorption. Mathematically, this is expressed as [23], where K_E represents the Elovich constant. The linearized form is given by Eqs. (7) and (8). The plot of ln q_e/C_e versus q_e, which yields a straight line with a slope of $-1/q_o$ and an intercept of ln K_E q_o.

$$\frac{q_e}{q_o} = K_E C_e e^{-\left(\frac{q_e}{q_o}\right)} \qquad (7)$$

$$\ln \frac{q_e}{C_e} = \ln\ K_E q_o - \frac{q_e}{q_o} \qquad (8)$$

II.IV.II Henry’s Isotherm

This is the most straightforward adsorption isotherm, in which the quantity of surface adsorbate is directly proportional to the partial pressure of the adsorptive gas [5]. The isotherm model, which demonstrates that all adsorbate molecules are isolated from their closest neighbours, provides an accurate description of the adsorption process at very low concentrations [6]. The following linear Eq.(9) represents the relationship between the equilibrium adsorbate concentrations in the liquid and adsorbed phases:

$$q_e = K_{HE}C_e \qquad (9)$$

In this context, C_e represents the equilibrium concentration of the adsorbate on the adsorbent, K_{HE} is Henry's adsorption constant, and q_e is the quantity of the adsorbate at equilibrium (mg/g).

II.IV. III Redlich-Peterson Isotherm

The Freundlich and Langmuir isotherms are combined to form the Redlich-Peterson isotherm, which is a further extension of the Langmuir isotherm. One advantage of the equation is that it approaches the Henry area at infinite dilution and is derived from the Langmuir isotherm [31]. This empirical isotherm model comprises three parameters. The Redlich-Peterson isotherm incorporates the ideas set forth in the Freundlich and Langmuir equations. As a consequence, the adsorption process integrates the two and diverges from the predicted behavior of the optimal monolayer adsorption model [32]. The nonlinear form of the Redlich-Peterson Isotherm is given by Eq. (10).

$$q_e = \frac{AC_e}{1+BC_e^{\beta}} \qquad (10)$$

As β represents an exponent that ranges from 0 to 1. A is the Redlich-Peterson isotherm constant, expressed as (L/g), while B is also a constant, expressed as (L/mg). The equilibrium liquid-phase concentration of the adsorbent, represented by C_e (mg/L)), and the equilibrium adsorbate loading of the adsorbent, represented by q (mg/g), are defined. At high adsorbate liquid-phase concentrations, the model reduces to the Freundlich Eq. (11).

$$q_e = \frac{A}{B}C_e^{1-\beta} \qquad (11)$$

In the Freundlich isotherm model, the following relationships are represented: $A/B = K_F$ and $(1 - \beta) = 1/n$. The Langmuir equation, which is associated with the energy of adsorption, is reduced to b = B (Langmuir adsorption constant, or L/mg) when β = 1. A is represented by the equation bq_{ml}, where q_{ml} is the maximal Langmuir adsorption capacity of the adsorbent (mg/g),when β is equal to zero. The Eq. (12) simplifies to Henry's isotherm model, with the Henry constant represented by 1/(1+b). The linear form of the Redlich-Peterson isotherm is given by Eq. (12) [30]:

$$\ln\frac{C_e}{q_e} = \beta\ln\,C_e - \ln\,A \qquad (12)$$

The Redlich-Peterson constants can be determined by plotting of ln (C_e/q_e) versus ln C_e. In this plot, β and A represented the slope and the intercept, respectively [28,32,33,34,35]. The versatility of this isotherm model allows its application to both homogeneous and heterogeneous systems. The model is linear in the numerator and exponential in the denominator, representing adsorption equilibrium over a wide range of adsorbate concentrations [36, 37].

II.IV.IV Jossens Isotherm

The Jossens isotherm model is based on the assumption that the energy distribution of adsorbate-adsorbent interactions at adsorption sites provides the foundation for its theoretical framework. This model offers a straightforward equation for predicting the equilibrium state of a system [38]. In this model, the term "heterogeneous surface" denotes the fact that the interactions between the adsorbent and the adsorbate are not uniform. To illustrate, the Jossen isotherm can be represented as Eq. (13).

$$C_e = \frac{q_e}{H}\exp\left(Fq_e^{p}\right) \qquad (13)$$

As F and H represent the Jossens isotherm constant, and equivalent to Henry's constant, P is the Jossens isotherm constant, which provides insight into the adsorbent regardless of temperature and type. In the case of low capacity, the equation reduces to Henry's law. However, following a reorganization of Eq. (14) [39],

$$\ln\left(\frac{C_e}{q_e}\right) = -\ln(H) + Fq_e^p \qquad (14)$$

In order to ascertain the values of H and F, it is possible to employ either the least-squares fitting technique or a plot of ln (C_e/q_e) vs. q_e.

II. V Adsorption Kinetics

II.V.I Elovich Kinetic Model

In the context of chemically adsorption processes occurring on surfaces with heterogeneous energy distributions, the Elovich equation may be applicable [24]. In the case of low surface coverage, the effect of adsorbed species on the rate of reaction is relatively insignificant [26]. Furthermore, the adsorption energy increases in a linear fashion with surface coverage, as described by the Arrhenius equation [27]. The initial rate and extent of adsorption can be described by parameters, which can be used to assess the chemisorption process. The lineal form of the Elovich kinetic model is given by Eq.(18).

$$q_t = \frac{1}{\beta}\text{In}(\alpha\beta) + \frac{1}{\beta}\text{In}(t) \qquad (18)$$

The constants α and β represent Elovic constants for the initial adsorption rate (mg/g.hr) and the degree of surface coverage and the activation energy for chemisorption (g/mg), respectively.

II.V.II Liquid Film Diffusion Kinetic Model (LFD)

The rate-limiting step represents a crucial element in the corroboration of the adsorption mechanism. The adsorption process is governed by a solute transfer process, which may be represented by external mass transfer, intraparticle diffusion, or both. Accordingly, the liquid film diffusion model, as represented by the Boyd kinetic expression [29], was employed. In order to quantify the magnitude of mass transfer, the term containing the fractional capacity ($\ln(1-q_t/q_e)$) was plotted against time, and the slope of the resulting curve was calculated to be the film diffusion rate constant (k_{lf}, 1/hr). The linear form of the liquid film diffusion kinetic model is given by Eq. (19) [29].

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -K_{lf}t \qquad (19)$$

II.VI Characterization of adsorbents

A single analytical tool was employed to assess the selected MOF-5 adsorbents for the aforementioned adsorption testing. Furthermore, the specific surface area of the adsorbents was quantified utilizing a surface area and porosity analyzer, in accordance with the BET (Brunauer-Emmett-Teller) method (Micromeritics ASAP 2020).

III. RESULTS

III.I Adsorption Isotherms

The relationship between the amount of adsorbent and the concentration of the liquid phase can be determined using the Langmuir, Freundlich, Temkin, Elovich, Henry, Redlich-Peterson, and Jossens isotherms. The constant values and coefficients of determination for each isotherm are listed in Table 1.

Table 1. Adsorption isotherms constants

Dyes	Isotherm Types	Constant	Value
AV7	**Elovich**	q_0 (mg/g)	-3.66
		K_e (L/mg)	-0.0055
		K_eq_0	0.02
		R^2	0.969
	Henry	K_{HE}	-0.4
		R^2	1
	Redlich-Peterson	β	5.7185
		A (L/g)	-20.195
		R^2	0.955
	Jossens	F	-0.2732
		H	0.0202
		P	0.8305
		R^2	0.969
MB	**Langmuir**	Q_m (mg/g)	13.23
		K_L (L/mg)	0.25
		R^2	0.9738
	Freundlich	Q_e (mg/g)	4.39
		K_F (L/mg)	2.77
		R^2	0.9674

III.II Adsorption Kinetics

Kinetic studies were used to determine the potential rate-controlling step and adsorption mechanism. Adsorption kinetics are governed by a number of processes, including those of reaction and diffusion [43]. The kinetic types (pseudo-first order, pseudo-second order, intraparticle diffusion, Elovich, and Bangham model) and constants for AV7 and MB are listed in Table 2.

Table 2. Adsorption Kinetics constants

Dyes	Kinetics Types	Constant	Value
AV7	**Liquid film diffusion**	K_{lf} (hr^{-1})	0.6464
		R^2	0.9558
	Elovich	β (g/mg)	0.7872
		α (mg/g·hr)	9.095
		R^2	0.9755
MB	**Pseudo-first-order**	Q_m (mg/g)	13.21
		K_1 (1/hr)	0.00005
		R^2	0.9201
	Pseudo-Second-order	Q_e (mg/g)	5.65
		K_2 (1/hr)	0.0021
		R^2	0.9864
	Intraparticle diffusion model	k_{id} (mg/g·$hr^{1/2}$)	0.2073
		R^2	0.9709
	Bangham model	K_B	0.098
		R^2	0.9726

IV. DISCUSSION

IV.I Adsorption Isotherms

The constant values and coefficients of determination for each isotherm are listed in Table 1. An in-depth review of the data revealed that Henry, with the highest R^2 value of 1, provides a better fit to the experimental data. The coefficient of determination (R^2) values obtained for the Elovich, Redlich-Peterson and Jossens isotherms are 0.969, 0.955, and 0.969 respectively. This result suggests that the adsorption equilibrium data were not adequately described by the Langmuir and Freundlich, Temkin, Elovich, Redlich-Peterson and Jossens isotherm models. The Henry isotherm model demonstrated the most accurate representation of the adsorption behaviour of AV7, as evidenced by the highest coefficient of determination presented in Table 1. The Henry isotherm constant was -0.4. These values are considered to be significant in promoting the surface binding of AV7 dye molecules onto the high-energy sites of MOF-5. Table 1 presents the isotherm model constants and the coefficient of determination (R^2) for the adsorption of MB dye onto modified MOF-5. However, the MB dye adsorption process of the modified MOF-5 adsorbent is not well explained by the Langmuir isotherm model, as indicated by the K_L value of 0.25, which is relatively high and indicates a strong interaction between the adsorbate and the adsorbent surface, suggesting a favourable adsorption process. As an indication that the Freundlich isotherm can adequately explain the adsorption mechanism, the Freundlich constant had a larger value compared to the Langmuir constant. Accordingly, the adsorption of MB on MOF-5/CNC supported by CA could follow a process involving multilayer coverage on a heterogeneous surface. Comparable results, showing a better agreement with the Freundlich isotherm, were obtained for MB removal using cellulose-based adsorbents [40,41,42,43]. The results indicated a significant interaction between AV7 and MB dyes molecules and the surface of MOF-5 adsorbent, owing to the uniform distribution of binding energies in the latter.

IV.II Adsorption Kinetics

Kinetic parameters play an essential role in the modelling of adsorption processes and the exploration of the fundamental mechanisms underlying these processes. The applicability of the pseudo-first-order, pseudo-second-order, intraparticle diffusion, liquid film diffusion, elovich, and Bangham models were evaluated for AV7 and MB respectively. The kinetic data for the AV7 dye on the modified MOF-5 adsorbent were found to be best fit by the liquid film diffusion, and Elovich models, respectively. The constant values and coefficients of determination for each kinetic model are presented in Table 2. Following a comprehensive analysis of the data, it was determined that the elovich model provided a superior fit to the data set ($R^2 = 0.9755$). The adsorption data were fitted to the linearized pseudo-first-order kinetic model, which proved to be inapplicable over the entire contact time for MB. The calculated q_e was determined to be 13.21 mg/g. In the majority of cases, the first-order model is applicable to the initial phase of the adsorption process, but not to the remainder of the contact time [45,46]. The experimental data exhibited a favourable fit over the entire adsorption range for the pseudo-second-order kinetic model. The calculated q_e from the pseudo-second-order model was determined to be 5.65 mg/g, which was closer to the experimentally obtained q_e (4.29 mg/g). Chemical interactions dominate the adsorption process, which may be explained by pseudo-second-order kinetics for the adsorption reaction [47, 48]. The kinetic parameters and coefficient of determination (R^2) values are listed in Table 2. The adsorption process can occur via a number of different pathways, including external diffusion, intraparticle diffusion and pore diffusion [48]. The rate of the adsorption process is typically influenced by both intraparticle and pore diffusion. The process of aligning experimental data with the parameters of diffusion models. The Weber–Morris plot (q_t vs $t^{0.5}$) yielded a linear relationship with an coefficient of determination (R^2) value exceeding 0.9, suggesting that intraparticle diffusion may be a potential pathway for AV7 and MB adsorption. The intercept of the Weber–Morris plot has been identified as a potential indicator of the thickness of the boundary layer, with a larger intercept potentially indicating a larger boundary layer [43,49]. In this model, the linear fit must pass through the origin, indicating that intraparticle diffusion is not the sole controlling mechanism and that the adsorption process is a combination of multiple mechanisms [43,48]. The Bangham model was employed to ascertain the potential for pore diffusion to act as the rate-limiting step. The plot was found to be linear with a coefficient of determination (R^2) value greater than 0.9, indicating that pore diffusion is the dominant mechanism governing the adsorption process for AV7 and MB. These results indicate that the adsorption kinetics are fitted to elovich and pseudo-second-order model, which is based on a chemical interaction between the adsorbent and adsorbate for AV7 and MB dyes [44].

IV.III Characterization

IV.II.I BET (Brunauer-Emmett-Teller)

The modified MOF-5(MOF-5/RHA-1000/1.75:2) had large specific surface area 33.43 m^2/g for AV7 than the adsorbent film of MB 19.87 m^2/g. In addition, the adsorbent film of MB had large pore volume 0.27 cm^3 /g compared to the modified MOF-5 (MOF-5/RHA-1000/1.75:2) 0.18 cm^3 /g for AV7. The BET analysis showed that the AV7 and MB dyes follow the type III and I isotherm adsorption respectively. The Type III Isotherm is defined by a gradual increase in adsorption at low relative pressures, which is then followed by a sharp increase at higher pressures. This type of isotherm is frequently observed in non-porous or weakly porous materials, where the interactions between the adsorbate and the adsorbent are relatively weak. This type of isotherm does not exhibit a sharp increase at low relative pressures, indicating that microporous adsorption is either minimal or absent. Instead, the adsorption increases gradually at higher pressures without reaching a clear plateau, suggesting the presence of multilayer adsorption [50]. Furthermore, the type I isotherms are those where the pore size is not significantly larger than the molecular diameter of the sorbate molecules. This isotherm shows that the extent of adsorption increases with pressure until it reaches saturation, at which point no further adsorption occurs and the monolayer is formed.

V. CONCLUSION

` The present study examined the efficacy of MOF-5 adsorbents for the removal of AV7 and MB dyes from aqueous media, with a particular focus on the adsorption isotherms and kinetics. The adsorption isotherm and kinetics were employed for the respective analysis of the AV7 and MB dyes. The adsorption isotherm and kinetics were best described by the Henry and Freundlich isotherm and the elovich and pseudo-second-order kinetic models, respectively, for AV7 and MB. The comparative results demonstrated that the adsorption isotherms and kinetics for the AV7 and MB dyes, respectively. The BET (Brunauer-Emmett-Teller) analysis revealed the specific area and pore volume of MOF-5. The findings of the present study suggest that MOF-5 has notable potential for the remediation of polluted water sources by removing AV7 and MB dyes.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support from the Ministry of Higher Education Malaysia for the Fundamental Research Grant Scheme (FRGS) with Project Code: FRGS/1/2019/TK02/USM/02/2 and University Sains Malaysia.

REFERENCES

[1] Junejo, Y., Sirajuddin, Baykal, A., Safdar, M., & Balouch, A. (2024). A Novel Green Synthesis and Characterization of Ag NPs with its Ultra-Rapid Catalytic Reduction of Methyl Green Dye. Appl. Surf. Sci, 290, 499- 503. https://doi.org/10.1016/j.apsusc.2013.11.106.

[2] Zarei-Chaleshtori, M., Correa, V., López, N., Ramos, M., Edalatpour, R., Rondeau, N., & Chianelli, R.R.(2014).Synthesis and Evaluation of Porous Semiconductor Hexanoates Nanotubes for Photolysis of Organic Dyes in Wastewater. Catalysts, 4, 346- 354, 2014. https://doi.org/10.3390/catal4040346.

[3] Mallampati, R., Li, X., Adin, A., & Valiyaveettil S. (2015). Fruit Peels as Efficient Renewable Adsorbents for Removal of Dissolved Heavy Metals and Dyes from Waterc ACS Sustain. Chem. Eng, 3, 1117 1124, 2015. https://doi.org/10.1021/acssuschemeng.5b00207.

[4] Chi, Y., Geng, W., Zhao, L., Yan, X., Yuan, Q., Li, N., & Li X. (2012). Comprehensive study of mesoporous carbon functionalized with carboxylate groups and magnetic nanoparticles as a promising adsorbent. J. Colloid Interface Sci, 369, 366- 372. https://doi.org/10.1016/j.jcis.2011.12.051.

[5] Fost, S. D., & Aly, M. O. (1981). Adsorption Processes for Water Treatment. Betterworth Publications, Stoneharm, Massachusetts, Mass, USA.

[6] Ruthven, D. M. (1984). Principle of Adsorption and Adsorption Processes. JohnWilley and Sons, New Jersey, NJ, USA.

[7] Tuttolomondo, M.V., Alvarez, G.S., Desimone, M.F., & Diaz L.E. (2014). Removal of azo dyes from water by sol–gel immobilized Pseudomonas sp. J.Environ.Chem.Eng.,2,131–136. https://doi.org/10.1016/j.jece.2013.12.003.

[8] Khodaie, M., Ghasemi, N., Moradi, B., & Rahimi, M. (2013). Removal of methylene blue from wastewater by adsorption onto znclactivated corn husk carbon equilibrium studies. J. Chem.,1- 6. https://doi.org/10.1155/2013/383985.

[9] Babuponnusami, A., & Muthukumar K. (2014). A review on Fenton and improvements to the Fenton process for wastewater treatment. J. Environ. Chem. Eng., 2, 557- 572, 2014. https://doi.org/10.1016/j.jece.2013.10.011.

[10] Peng, Q., Cong, H.L., & Yu B. (2018). Preparation of Polymeric Janus Microparticles with Hierarchically Porous Structure and Enhanced Anisotropy. J. Colloid Interface Sci., 522, 144–150. https://doi.org/10.1016/j.jcis.2018.03.066.

[11] Yuan, H., Yu, B., Cong, H.L., Chi, M., Cheng, Y.Z., & Lv, C.X. (2018). Preparation of hierarchical highly ordered porous films of brominated poly (phenylene oxide) and hydrophilic SiO_2/C membrane via breath figure method. Mater, pp,1,11. https://doi.org/10.3390/ma11040481.

[12] Yu, B., Li, Z., Cong, H.L., Li, G.L., Peng, Q.H., & Yang, C.F. (2017). Synthesis and application of sulfonated Polystyrene, ferrosoferric oxide and diazo resin nanocomposite microspheres for highly selective removal of dyes. In: G Gibson, G Nguyen, M Sebastiani, S Xu, E Bourses (eds.), Volume 135. Mater. Des., Elsevier, 333- 342. https://doi.org/10.1016/j.matdes.2017.09.039.

[13] Gonzalez-casamachin, D. A., Rosa, J. R., Lucio-Ortiz, C.J., Rio, D. D. H. D., Martínez-Vargas, D., Flores-Escamilla, G. A., Dávila Guzmán N.E., Ovando-Medina V. M., & Moctezuma-Velazquez, E.(2019).Visible-light photocatalytic degradation of acid violet 7 dye in a continuous annular reactor using ZnO/PPy photocatalyst: synthesis, characterization, mass transfer effect evaluation and kinetic analysis. Chem. Eng. J., 373, 325–337, 2019. http://dx.doi.org/10.1016/j.cej. 2019.05.032.

[14] Rosi, N.L., Eckert, J., Eddaoudi, M., Vodak, D.T., Kim, J., O'Keefe, M., &Yaghi O. M. (2003). Hydrogen storage in microporous metal- organic frameworks. Science, 300, (5622). https://doi.org/10.1126/science.1083440.

[15] Li, J.-R., Sculley, J., & Zhou, H.-C. (2012). Metal-Organic Frameworks for Separations. Chem. Rev., 112, 869–932. https://doi.org/10.1021/cr200190s.

[16] Voorde, B.V.de, Bueken, B., Denayer, J., & De-Vos, D. (2014). Adsorptive Separation on Metal–Organic Frameworks in the Liquid Phase. Chem. Soc., 43, 5766,5788. https://doi.org/10.1039/C4CS00006D.

[17] Ahmed, I., Khan, N.A., Hasan, Z., & Jhung, S.H. (2013). Adsorptive denitrogenation of model fuels with a porous metal-organic framework (MOF) MIL-101 impregnated with phosphotungstic acid: effect of acid site inclusion. J. Hazard. Mater., 250, 251, 37,44.https://doi.org/10.1016/j.jhazmat.2013.01.024.

[18] Barea, E., Montoro, C., & Navarro, J. A. R. (2014). Toxic Gas Removal Metal–Organic Frameworks for the Capture and Degradation of Toxic Gases and Vapours. Chem. Soc. 43, 5419-5430. https://doi.org/10.1039/C3CS60475F.

[19] Furukawa, H., Cordova, K., O'Keeffe, M., & Yaghi, O. (2013). The Chemistry and Applications of Metal- Organic Frameworks. Science, 341 (6149): 974. https://doi.org/10.1126/science.1230444

[20] Hasan, Z., & Jhung, S. H. (2015). Removal of Hazardous Organics from Water Using Metal-OrganicFrameworks (MOFs): Plausible Mechanisms for Selective Adsorptions," J. Hazard. Mater., 283, 329-339. https://doi.org/10.1016/j.jhazmat.2014.09.046.

[21] Hasan, Z., Tong, M., Jung, B. K., Ahmed, I., Zhong, C., & Jhung, S. H. (2014). Adsorption of Pyridine over Amino-Functionalized Metal–Organic Frameworks: Attraction Via Hydrogen Bonding Versus Base Base Repulsion. J. Phys. Chem. C, 118, 21049- 21056. https://doi.org/10.1021/jp507074x.

[22] Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M., & Yaghi, O. M. (2002). Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. Science, 295, 469- 472. https://doi.org/10.1126/science.1067208.

[23] Elovich, S. Y., & Larionov, O. G. (1962). Theory of Adsorption from Solutions of Non Electrolytes on Solid (I) Equation Adsorption from Solutions and the Analysis of Its Simplest Form, (II) Verification of the Equation of Adsorption Isotherm from Solutions. Russ. Chem. Bull, 11, 191–197. https://doi.org/10.1007/BF00908016.

[24] Aharoni, C., & Tompkins, F. (1970). Kinetics of adsorption and desorption and the Elovich equation. Adv. Catal., Volume 21, pp. 1–49. https://doi.org/10.1016/S0360-0564(08)60563-5.

[25] Nandi B.K., Goswami A., & Purkait M.K. (2009). Adsorption characteristics of brilliant green dye on kaolin. J. Hazard. Mater., vol. 161, no. 1, pp. 387- 395, 2009. http://dx.doi.org/10.1016/j.jhazmat.2008.03.110 .

[26] Ferreira, A., Mota, A., Oliveira, A., Rodrigues, F., Pacífico, S., Da Silva, J., Abagaro, B., Saraiva, G., De Castro, A., & Teixeira, R. (2019). Equilibrium and kinetic modelling of adsorption: Evaluating the performance of an adsorbent in softening water for irrigation and animal consumption. Rev. Virtual Quim, 11, 1752–1766. https://doi.org/10.1088/1755-1315/1024/1/012022

[27] Largitte, L., & Pasquier, R. (2016). A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. Chem. Eng. Res. Des., 109, 495–504. https://doi.org/10.1016/j.cherd.2016.02.006.

[28] Rania, F., & Yousef, N. S. (2015). Equilibrium and Kinetics studies of adsorption of copper (II) on natural Biosorbent. Int. J. Chem. Eng. Appl., vol. 6, no. 5.

[29] Boyd, G.E., Adamson, A.W., Myers, L.S. (1947). The exchange adsorption of ions from aqueous solutions by organic zeolites, II, Kinetics. J. Am. Chem. Soc., 69(11):2836-2848. https://doi.org/10.1021/ja01203a066.

[30] Kiseler, A. V. C. (1958). Vapour adsorption in the formation of adsorbate Mollecule Complexes on the surface. Kolloid Zhur, vol. 20, pp. 338–348.

[31] Davoundinejad, M., & Gharbanian, S. A. (2013). Modelling of adsorption isotherm of benzoic compounds onto GAC and introducing three new isotherm models using new concept of adsorption effective surface (AEC). Academic Journals, vol. 18, no. 46, pp. 2263–2275. https://doi.org/10.5897/SRE10.643.

[32] Brouers, F., & Al-Musawi, T. J. (2015). On the optimal use of isotherm models for the characterization of biosorption lead onto algae. J. Mol. Liq, vol. 212, pp. 46- 51. https://doi.org/10.1016/j.molliq.2015.08.054.

[33] Wu, F.-C., Liu, B.-L., Wu, K.-T., & Tseng, R.-L. (2010). A new linear form analysis of Redlich-Peterson isotherm equation for the adsorptions of dyes. Chem. Eng. J, vol. 162, no. 1, pp. 21–27. https://doi.org/10.1016/j.cej.2010.03.006.

[34] Chan, L. S., Cheung, W. H., Allen, S. J., & McKay, G. (2012). Error analysis of adsorption isotherm models for acid dyes onto bamboo derived activated carbon. Chin. J. Chem. Eng, vol. 20, no. 3, pp. 535–542. https://doi.org/10.1016/S1004-9541(11)60216-4.

[35] Ng, J. C. Y., Cheung, W. H., & McKay, G. (2002). Equilibrium studies of the sorption of Cu (II) ions onto chitosan. J. Colloid Interface Sci., vol. 255, no. 1, pp. 64–74. https://doi.org/10.1006/jcis.2002.8664.

[36] Gimbert, F., Morin-Crini, N., Renault, F., Badot, P.-M., & Crini, G. (2008). Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: error analysis. J. Hazard. Mater., vol. 157, no. 1, pp. 34- 46. https://doi.org/10.1016/j.jhazmat.2007.12.072.

[37] Sips, R. (1948). On the structure of a catalyst surface. J. CHEM. PHYS., vol. 16, no. 5, pp. 490–495. https://doi.org/10.1063/1.1746922.

[38] Dilekoglu, M. F. (2016). Use of generic algorithm optimzation Techniques in the adsorption of phenol on Banana and grapetruit peels. J. Chem. Soc. Pak, vol. 38, no. 6.

[39] Juang, R., Wu, F., & Tseng R. (1996). Adsorption isotherms of phenolic compounds from aqueous solutions onto activated carbon fibers. J. Chem. Eng. Data, vol. 41, no. 3, pp. 487–492. https://doi.org/10.1021/je950238g.

[40] Melese, H., & Tsade, H. (2024). Cellulose based adsorbent for cationic methylene blue dye removal. Discovery Appl. Sci., 6, 46. https://doi.org/10.1007/s42452-024-05653-3.

[41] Amrutha Jeppu, G., Girish, C.-R., Baakrishna, P., & Mayer, K. (2023). Multi-component Adsorption Isotherms: Review and Modeling Studies. Environ. Process,10, 38. https://doi.org/10.1007/s40710-023-00631-0.

[42] Khatri, M., Ahmed, M.-E., Al-Juboori, R.-A., Khanzada, N.-K., & Hilal, N. (2024). Reusable environmentally friendly electrospun cellulose acetate/cellulose nanocrystals nanofibers for methylene blue removal. J. Environ. Chem. Eng.,12, No. 111788. https://doi.org/10.1016/j.jece.2023.111788.

[43] Wang, J., & Guo, X. (2022). Rethinking of the intraparticle diffusion adsorption kinetics model: Interpretation, solving methods and applications. Chemosphere, 309, No. 136732. https://doi.org/10.1016/j.chemosphere.2022.136732.

[44] Zaidi, N.A.H.M., Lim, L.B.L. Usman, A. (2019). Enhancing adsorption of malachite green dye using base modified Artocarpus odoratissimus leaves as adsorbents. Environ. Technol. Innov., 13, pp.211-223. http://dx.doi.org/10.1016/j.eti.2018.12.002.

[45] Şendal, K., Özgür, M.-U., & Gülen, J. (203). Biosynthesis of ZnO photocatalyst and its application in photo catalytic degradation of methylene blue dyestuff. J. Disper. Sci. Technol., 2023, 44, 2734−2747. https://doi.org/10.1080/01932691.2022.2125005.

[46] Gülen, J., Akın, B., & Özgür, M. (2016). Ultrasonic-assisted adsorption of methylene blue on sumac leaves. Desalin. Water Treat., 57, 9286. https://doi.org/10.1080/19443994.2015.1029002.

[47] Gülen, J., & İskeçeli, M. (2017). Removal of methylene blue by using porous carbon adsorbent prepared from carbonized chestnut shell. Mater. Test., 59, 188- 194. https://doi.org/10.3139/120.110984.

[48] Mekuria, D., Diro, A., Melak, F., & Asere, T.-G. (2022). Adsorptive Removal of Methylene Blue Dye Using Biowaste Materials: Barley Bran and Enset Midrib Leaf. J. Chem., 1. https://doi.org/10.1155/2022/4849758.

[49] Gülen, J., & Zorbay, F. (2017). Methylene Blue Adsorption on a Low Cost Adsorbent Carbonized Peanut Shell. Water Environ. Res., 89, 805. https://doi.org/10.2175/106143017X14902968254836.

[50] Klobes, P., Meyer, K., & Munro, R.G. (2006). Porosity and Specific Surface Area Measurements for Solid Materials. Natl Inst. Stand. Technol., Spec. Publ., 960- 17. https://tsapps.nist.gov/publication/get_pdf.cfm?pub_id=854263.