



International Journal of Phytoremediation

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/bijp20

Adsorption of Reactive Red 195 from aqueous medium using Lotus (Nelumbo nucifera) leaf powder chemically modified with dimethylamine: characterization, isotherms, kinetics, thermodynamics, and mechanism assessment

Venkata Subbaiah Munagapati, Hsin-Yu Wen, Jet-Chau Wen, Anjani R.K Gollakota, Chi-Min Shu, Kun-Yi Andrew Lin & Jhy-Horng Wen

To cite this article: Venkata Subbaiah Munagapati, Hsin-Yu Wen, Jet-Chau Wen, Anjani R.K. Gollakota, Chi-Min Shu, Kun-Yi Andrew Lin & Jhy-Horng Wen (2021): Adsorption of Reactive Red 195 from aqueous medium using Lotus (*Nelumbo nucifera*) leaf powder chemically modified with dimethylamine: characterization, isotherms, kinetics, thermodynamics, and mechanism assessment, International Journal of Phytoremediation, DOI: 10.1080/15226514.2021.1929060

To link to this article: <u>https://doi.org/10.1080/15226514.2021.1929060</u>



Published online: 31 May 2021.



Submit your article to this journal 🕑



View related articles





Check for updates

Adsorption of Reactive Red 195 from aqueous medium using Lotus (*Nelumbo nucifera*) leaf powder chemically modified with dimethylamine: characterization, isotherms, kinetics, thermodynamics, and mechanism assessment

Venkata Subbaiah Munagapati^a, Hsin-Yu Wen^b, Jet-Chau Wen^{a,c}, Anjani R.K Gollakota^c, Chi-Min Shu^c, Kun-Yi Andrew Lin^d, and Jhy-Horng Wen^e

^aResearch Center for Soil & Water Resources and Natural Disaster Prevention (SWAN), National Yunlin University of Science and Technology, Douliou, Taiwan; ^bDepartment of Pathology, West China Hospital, Sichuan University, Chengdu, PR China; ^cDepartment of Safety, Health, and Environmental Engineering, National Yunlin University of Science and Technology, Douliou, Taiwan; ^d Department of Environmental Engineering, National Chung Hsing University, Taichung, Taiwan; ^eDepartment of Electrical Engineering, Tunghai University, Taichung, Taiwan

ABSTRACT

Lotus leaf powder (LLP) was chemically modified with dimethylamine (DMA) to achieve a tertiary amine type powder, named DMA-LLP, and used as an adsorbent for the removal of Reactive Red 195 (RR 195) from the aqueous medium. DMA-LLP was characterized using field emission-scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX), Brunauer-Emmett-Teller (BET), point of zero charge (pH_{PZC}), and fourier transform infrared (FTIR) spectroscopy. The kinetic data exhibited a good correlation coefficient ($R^2 > 0.9916$) for the pseudo-second-order model. To evaluate the equilibrium data at different temperatures, the non-linear Langmuir and Freundlich isothermal models were used. The Langmuir model best described the equilibrium data ($R^2 > 0.9931$). The maximum adsorption uptake from the Langmuir model, q_{maxi} was 131.5 mg/g (pH = 2.0, C_o = 300 mg/L, dosage = 0.03 g/30 mL, and T = 298 K). The pH_{PZC} of DMA-LLP was found to be 5.5. The obtained thermodynamic parameters demonstrated the spontaneous and endothermic nature of the adsorption. The regeneration findings indicate that DMA-LLP could be used up to five times, with maximum removal of 72% achieved after the fifth cycle. Thus, we conclude that the DMA-LLP was an efficient adsorbent for removing RR 195 from the aqueous environment.

NOVELTY STATEMENT

In the modern era, dyes are inevitable and their surging usage leads to colossal contamination of aqueous streams, thereby threatening both the land and aquatic species. One among such dye is anionic Reactive Red 195 (RR 195), and traceable even at minute concentrations of aqueous streams, posing a severe threat to living species. Moreover, RR 195 is highly recalcitrant offering resistance to biodegradation due to the presence of an azo (-N=N-) group within its structure. Thus, there is a definite need to address the issue of eliminating RR 195 from industrial wastewater effluents. In lieu of this, the primitive objective of this study is to test the effectiveness of the natural adsorbent lotus leaf (*Nelumbo nucifera*) for the selective sorption of RR 195 from the aqueous stream. Although ample literature is available on the direct utilization of lotus leaf as adsorbent, yet no study was performed on the chemical modification (dimethylamine) of the aforementioned adsorbent. Hence, an attempt has been made in this direction to add a new sorbent into the adsorbents database.

KEYWORDS

Adsorption; Reactive Red 195; Lotus leaf; kinetics; isotherms

CONTACT Jet-Chau Wen 🐼 wenjc@yuntech.edu.tw 🝙 Research Centre for Soil & Water Resources and Natural Disaster Prevention (SWAN), National Yunlin University of Science & Technology, Douliou, Taiwan; Department of Safety, Health, and Environmental Engineering, National Yunlin University of Science and Technology, Douliou, Taiwan.



Introduction

Rapid industrialization and increased agricultural activities resulted in a substantial decline in the water quality that has affected both surface and ground waters (Xu et al. 2020). One of the global severe environmental concerns is the presence of numerous hazardous dyes (like methyl orange, congo red, methylene blue, eosin yellow, etc.) in wastewater released from various industries (Anitha et al. 2016; Albadarin et al. 2017; Zubair et al. 2018; Ahmed et al. 2020). Dyes are classified as nonionic (dispersed dyes), cationic (all basic dyes), and anionic (reactive, direct, and acid dyes). They play a significant role in textile, leather, plastics, pulp and paper mills, food processing, dyeing, pharmaceuticals, inkjet printing, and paint industries for coloring the final products. About 30% of synthetic dyes that are produced are used by the textile industry. Within the textile industry, cotton fiber dyeing occupies the predominant proportion. More than half of the cotton fibers that the produced are dyed with reactive dyes. It was reported that most of the reactive dyes were lost during textile dyeing leading to large amounts of effluent wastewater that is mostly contaminated with various dyes (Cardoso et al. 2012), which will adversely impact the aquatic environment by hindering sunlight penetration consequently photosynthesis of aqueous flora (Cardoso, Lima, Calvete, et al. 2011b, Cardoso, Lima, Pinto, et al. 2011a). Besides, these dyes cause various aberrations, such as allergic dermatitis, skin irritation, and even cause cancer in humans due to mutations (Alves de Lima et al. 2007; Brookstein 2009; Carneiro et al. 2010). To overcome this issue, reactive dyes should be sufficiently eliminated from the industrial effluents before being discharged into aquatic systems. However, due to their complex aromatic molecular structure, stability, and non-biodegradable nature it is rather challenging to treat these reactive dye effluents (Cardoso et al. 2012). Reactive Red 195, a watersoluble anionic dye is posing risks on the ecosystem as well as human health. Due to the presence of an azo (-N = N-)group within its structure, RR 195 is resistant to undergo natural biodegradation. Consequently, the elimination of RR 195 from industrial wastewater effluents is the need of the hour.

Previous studies suggested various physicochemical or biological techniques to deal with this issue. These methods include reverse osmosis (Uzal et al. 2010), ion exchange (Raghu and Ahmed Basha 2007), electrochemical (Mu et al. 2009), advanced oxidation process (Nidheesh et al. 2018), coagulation/flocculation (Moghaddam et al. 2010), photodegradation (Khan et al. 2017; Naushad et al. 2019; Hassani et al. 2020; Sharma et al. 2020; Yashni et al. 2020), membrane filtration (Qi et al. 2019), adsorption (Munagapati et al. 2019), etc. have been used for the removal of dyes from aqueous media. Among these methods, adsorption has been proven to be the most potential one due to its simplicity of design, flexibility, ability to separate a wide range of chemical compounds, high adaptability, cheapness, high efficiency, and reusability. However, selecting an appropriate adsorbent is challenging. For example, activated carbon and silica gel are the most preferred adsorbents due to their potent adsorption capacity. But their high cost and related problems restrict their usage limits. Therefore, the scientific community is in the process of developing newer adsorbents from natural materials and domestic, agricultural, and industrial wastes. Previous studies were shown several adsorbents from natural origin. For example leaves (Guerrero-Coronilla et al. 2015; Peydayesh and Rahbar-Kelishami 2015; Devi et al. 2020), wheat bran (Çiçek et al. 2007), barks (Ahmad 2009; Asif Tahir et al. 2016), fruit peels (Munagapati et al. 2018; Stavrinou et al. 2018), sawdust (Wang et al. 2014), moringa oleifera seed (Celekli et al. 2019), nutshells (Sartape et al. 2017; Şentürk and Alzein 2020), and other similar inexpensive materials. However, adsorbents made from a single source of a compound may suffer from specificity and usage limitations. There are a growing interest and scope in developing newer adsorbents that are chemically modified, which would work efficiently than their unmodified precursors. Recently, a variety of chemicals such as citric acid (Ghosh and Bandyopadhyay 2017), sodium hydroxide (Jain and Gogate 2017), phosphoric acid (Ahmaruzzaman et al. 2015), ammonia and lauric acid (Yang and Hong 2018), sulfuric acid (Krishna Murthy et al. 2019), tetradecyltrimethyl ammonium bromide (Mahmoud et al. 2016), polyethyleneimine (Wong et al. 2019), were shown to be successfully used to modify the sorption capacity of waste materials based biosorbents.

Nevertheless, it is notable to mention that the choice of a modifying chemical agent depends on certain factors. They are the nature of starting material, the overall cost of the process, the nature of polluting adsorbate, and ultimately the adsorption capacity under the adopted set of conditions.

A common aquatic species, *Nelumbo nucifera* (Lotus), is an ornamental plant and also a farm product. During the usage of this plant for various purposes, usually the lotus leaves are discarded. But these leaves are considered to be a cheap, abundant, renewable, and eco-friendly resource. It is known that both leaves and plumules of lotus showed medicinal properties that have been used in traditional medicine to treat hemoptysis, obesity, diarrhea, hyperlipidemia, metrorrhagia, insomnia, nervous disorders, high fevers with restlessness, and cardiovascular diseases such as hypertension and arrhythmia (Chen *et al.* 2019). These leaves are known to contain rich plant fibers, proteins, and components with various functional groups. Lotus leaf can be used as an excellent adsorbent to remove pollutants from an aqueous medium (Han *et al.* 2011, 2014).

A literature survey showed that researchers had not used DMA-LLP as a biosorbent for the removal of RR 195 from the aqueous phase. The present study is aimed to (i) DMA-LLP applied efficient removal of RR 195; (ii) characterize the DMA-LLP using FE-SEM, EDX, BET, pH_{PZC} , and FTIR; (iii) investigate the factors affecting the adsorption process; (iv) study the isotherms, kinetics, and thermodynamics of the sorption process; (v) evaluate the regeneration of DMA-LLP; (vi) explore the possible reaction mechanism for the removal of RR 195 onto DMA-LLP.

Materials and methods

Materials

All of the other reagents used were AR grade in the current study. 1000 mg/L of the RR 195 stock solution was prepared by dissolving a suitable volume of RR 195 in deionized (DI) water. Diluting the stock solution was used to prepare working solutions varying from 100 to 1000 mg/L of RR 195.

Preparation of LLP

The Lotus leaves (LL) were collected locally from the campus of YUNTECH, Douliu, Taiwan. The gathered leaves were cleaned with tap water to remove the dust and other impurities and eventually washed with DI water. The rinsed leaves were then cut into small pieces and air-dried for one week at room temperature and then for 24 h at 343 K in a hot-air oven. The dried leaves were ground to a powdered form and 20–40 mesh fractions were then sieved. The powder was dried for 24 h at 343 K after thorough washing with DI water. The dried powder was boiled in double DI water until the water becomes colorless by repeatedly replacing it. This indicates the removal of water-soluble color compounds in the powdered sample. The washed and the boiled powder was oven dried for 24 h at 343 K. The obtained biomass was named LLP.

Preparation of DMA-LLP

The DMA-LLP was prepared as follows. 5.0 g of the LLP was mixed with a mixture of 5.0 g of $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ (paraformaldehyde) and 100 mL of HCl solution and was stirred for 15 h at 348 K. The formed product (chlorinated) was cleaned with DI water and kept in a hot air oven for 4 h at 333 K. After cooling, added 50 mL of 50% (CH₃)₂NH (dimethylamine) solution and 10 mL of 37% HCHO (formaldehyde) solution and continuously stirred for 4 h with 353 K temperature. The product was filtered and first washed with a base, NaOH (0.1 M) next with acid, HCl (0.1 M) and finally washed with NaCl (0.1 M) solution. Finally, the resulting product was obtained after drying in a hot air oven at 333 K for 6 h and sieved to 45 (0.35 mm) mesh size. The reaction occurs as follows:



Characterization

By using FE-SEM (JEOL, JSM-7800F, Japan), the surface morphology of the DMA-LLP was elucidated before and after RR 195 adsorption. The instrument was combined with an EDX analyzer that was used in examining the elemental composition of the DMA-LLP. The FTIR (Nicolet IS10, Thermo Scientific, USA) was used to determine the surface functional groups of the DMA-LLP before and after RR 195 adsorption. The samples were incorporated in KBr pellets and the spectrum was obtained in the range of 4000-400 cm⁻¹. The textural characteristics of DMA-LLP were obtained from the conventional analysis of N₂ adsorption/desorption (Micromeritics ASAP 2060, USA) isotherms measured at 77.35 K. The pH_{PZC} of the DMA-LLP was determined according to the method described in the literature (Stavrinou et al. 2018). 30 mL of NaCl (0.01 M) solution was transferred to a series of 50 mL polypropylene tubes in this process. By adding either NaOH or HCl (0.1 M), the pH_i (initial pH) solution was adjusted from 2.0 to 12.0 for each tube. Then 0.03 g of DMA-LLP was added to each tube and the tubes were placed for 24 h in an orbital shaker at a constant temperature. The suspensions were filtered and the solutions were noted by pH_f (final pH). In addition, by plotting a graph of $pH = pH_i - pH_f$ against pH_i , the pH_{PZC} values are evaluated by crossing the line $\Delta pH = 0$.

Batch adsorption experiments

A batch method was examined for the adsorption of RR 195 on the DMA-LLP. An amount of 0.03 g of the DMA-LLP was added with a volume of dye solution (30 mL) and stirred for a period of time at 200 rpm. The initial pH solution (2.0-12.0) was measured by a digital pH (Mettler

4 🕒 V. S. MUNAGAPATI ET AL.

Toledo, USA) meter and properly adjusted using NaOH (or) HCl 0.1 M solution. At the end of each experiment, the adsorbent was separated from the solution after shaking for a certain period of time by centrifugation at 3000 rpm for 10 min. The estimation of the adsorbed amount of dye concentration was calculated at the wavelength of 534 nm using a UV-Visible spectrophotometer (CT-2200, Taiwan) after proper dilutions. Each experimental test was carried out in duplicate and for data interpretation, the mean value was dosage taken. Contact time (0-420 min), adsorbent (0.03-0.1 g/30 mL),initial concentration of dye (100-1000 mg/L), and temperature (298-328 K) were evaluated. In all cases, the adsorbed amount of RR 195 dye at equilibrium, q_e (mg/g), was calculated using the following Eq. (1):

$$q_e = \frac{(C_o - C_e)V}{M} \tag{1}$$

Desorption and regeneration studies

Four eluents of different nature have been investigated for desorption studies. For this, one alkaline (NaOH 0.1 M), one salt (NaCl 0.1 M), one acidic (H_2SO_4 0.1 M), and DI water have been used as desorbing eluents. Initially, the adsorption process has been carried out using the following procedure: 0.03 g of DMA-LLP was added to the solution containing 30 mL of 300 mg/L of RR 195 for 150 min under 200 rpm at 298 K. After 150 min, the loaded adsorbent was separated from the adsorbate solution and again agitated with the eluents at the same experimental conditions, for desorption study. The desorption efficiency of RR 195 was determined using the following equation:

$$Desorption efficiency = \frac{Amount of RR195 desorbed}{Amount of RR195 adsorbed} \times 100 \quad (2)$$

After each cycle, the adsorbent was washed and soaked with DI water and filtered. After filtration, the solid residue was again used for the next cycle. This process has been successfully carried out for five adsorption-desorption cycles.

Statistical analysis

The data obtained from a model is generally evaluated by a non-linear Chi-square (χ^2) statistical tool. This is the ratio between the sums of square differences of the data calculated from isotherm models and experimental data. The value of χ^2 will be a lower number if the calculated data closer to the experimental data and a higher number if the estimated data differ from the experimental data. Therefore, to validate the best-fit isotherm for adsorption of RR 195 on the DMA-LLP, it is also appropriate to evaluate the data set using the χ^2 test. The expression of χ^2 can be defined as follows:

$$\chi^{2} = \sum_{i=1}^{n} \left(\frac{(q_{e} - q_{e,m})^{2}}{q_{e,m}} \right)$$
(3)



Figure 1. FTIR spectra: (a) unloaded DMA-LLP and (b) RR 195-loaded DMA-LLP.

Results and discussion

Characterization

In a band range of $400-4000 \text{ cm}^{-1}$, FTIR analysis was used to evaluate the functional groups present on the adsorbent surface. Figure 1 displays the FTIR spectrum of DMA-LLP before and after adsorption of RR 195. The band around 3365 cm^{-1} could be assigned to -NH stretching vibrations. Two strong bands at 2926 and 2878 cm⁻¹ were assigned for C-H stretching of the alkyl groups, respectively. The bands at 1614 and 1417 cm⁻¹ were attributed to the C=C and C-O stretching vibrations of the carboxyl group. The band at 1335 cm^{-1} may be attributed to -C-H bending of the alkyl group. The bands at 1150 and 1105 cm⁻¹ can be ascribed to -OH bending and C-O stretching vibrations. The band at 1061 cm^{-1} was assigned to C-OH stretching vibration. The bands at 775 and 647 cm^{-1} corresponded to -C-H bending and -S=O stretching vibrations (Figure 1a). The observed that some bands are shifted, and few additional new bands (1542, 1374, and 1244 cm⁻¹) are also detected after adsorption of RR 195 (Figure 1b). The observed difference in the spectrum shows the possibility of those functional groups on the DMA-LLP surface involving the RR 195 adsorption process. FTIR band positions (before and after adsorption of RR 195) and functional groups are presented in Table 1.

The surface morphology and the elemental composition of the adsorbent are found out from the FE-SEM/EDX analysis. Figure 2 illustrates the FE-SEM images and their respective EDX spectra of DMA-LLP before and after RR 195 adsorption, respectively. Before adsorption Figure 2a, it can be observed that the surface of DMA-LLP has aggregated particles with uniform distribution. After adsorption (Figure 2b), the surface of DMA-LLP was entirely covered by RR 195, confirming the adsorption of RR 195 onto DMA-LLP. The EDX analysis of DMA-LLP revealed the presence of C, O, Na, and Cl (Figure 2c), but after RR 195 adsorption, two new peaks of S and Ca elements appeared (Figure 2d). Additionally, the changes in the values of elemental weight % confirm the successful adsorption of RR 195 on the surface of DMA-LLP.

| | | Frequency (cm ⁻¹) | | | |
|---------|-------------------|-------------------------------|-------------|---|--|
| IR peak | Before adsorption | After adsorption | Differences | Vibration assignment | |
| 1 | 3365 | 3391 | -26 | Bonded –NH groups | |
| 2 | 2926 | 2918 | 8 | $-CH_2$ stretching | |
| 3 | 2878 | 2850 | 28 | -C-H stretching | |
| 4 | 1614 | 1650 | -36 | –C=O stretching (ketones and aldehydes) | |
| 5 | _ | 1542 | - | C-O (or) C=C stretching | |
| 6 | 1417 | 1444 | -27 | C–O stretching | |
| 7 | _ | 1374 | - | -O-H and -C-H bending | |
| 8 | 1335 | 1318 | 17 | -C-H bending | |
| 9 | _ | 1244 | - | -O-H bending | |
| 10 | 1150 | 1158 | -8 | –O–H bending and C–O stretching | |
| 11 | 1105 | 1108 | -3 | C–O stretching | |
| 12 | 1061 | 1042 | 19 | C-OH stretching | |
| 13 | 775 | 779 | -4 | -C-H bending | |
| 14 | 647 | 621 | 26 | -S = O stretching | |

Table 1. FTIR bands of the DMA-LLP before and after adsorption of RR 195.



Figure 2. (a, b) FESEM images for DMA-LLP before and after adsorption of RR 195 and (c, d) EDX images of DMA-LLP before and after adsorption of RR 195.

The surface area plays a crucial role in adsorption as it leads to more number of active sites to the adsorbent. The BET surface area (S_{BET}), pore volume (V_P), and pore diameter (D_P) of the DMA-LLP were determined by using BET (Brunauer-Emmett-Teller) and BJH (Barret-Joyner-Halenda) methods. Figure 3a displays the N₂ adsorption-desorption isotherms obtained at 77.35 K. The observed isotherm can be classified as an IV-type isotherm (according to the IUPAC classification) with the H₃-type hysteresis loop, which indicates that the mesoporous structure. The DMA-LLP adsorbent permits easy diffusion of dye molecules through its mesoporous structure for efficient adsorption. The S_{BET} , V_{P} , and D_{P} of DMA-LLP were obtained from the analysis $4.6 \text{ m}^2/\text{g}$, 0.0067 cc/g, and 2.145 nm. Figure 3b depicts the D_{P} plot of DMA-LLP. As can be observed that the sharp peak of D_{P} was located at 2.15 nm, and D_{P} is mainly in the range of 2.1–8.3 nm, suggesting that the DMA-LLP is a mesoporous (with the diameter of 2-50 nm) nature.

Effect of pH

One of the significant factors affecting the uptake of adsorption is the pH of the solution. It regulates the degree of ionization that influences the surface charge of the adsorbent.



Figure 3. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution curve of DMA-LLP calculated with the BJH model.

In the pH range of 2.0 to 12.0 at 298 K, the initial solution pH effect on RR 195 adsorption on DMA-LLP was achieved. As is visible in Figure 4a, DMA-LLP adsorption uptake decreased from 59.6 to 2.5 mg/g when the pH varied from 2.0 to 12.0. The highest RR 195 uptake of adsorption (59.6 mg/g) was observed at pH 2.0. It is also possible to use the pH_{PZC} study to clarify the effect of pH on RR 195 adsorption. The pH_{PZC} of the DMA-LLP was found to be 5.5, as shown in Figure 4b. These results reveal that the DMA-LLP surface can be acquired a negative charge at $pH > pH_{PZC}$ and a positive charge at $pH < pH_{PZC}$. The degree of ionization is high for Reactive dyes in aqueous solutions and forms colored anions due to -SO₃⁻ (sulfonate) functional groups in their structures. The RR 195 dye has five -SO₃⁻ groups, and they readily dissociate and gain negative charges in the aquatic environment. In the present study, the higher uptakes obtained at a very acidic pH may be due to the strong electrostatic attractions between RR 195 dye anions (negative charge) and the surface of the adsorbent, DMA-LLP (positive charge). As the pH of the solution rises significantly above pHPZC, the number of positively charged sites decreases and the number of negatively charged sites raises. The negative charge on the adsorbent surface is generally not favored for the dye anions because of electrostatic repulsion. A similar tendency of the pH



Figure 4. Effect of (a) pH (c) contact time (d) adsorbent dosage on the adsorption of RR 195 onto DMA-LLP, and (b) point of zero charge of DMA-LLP of different pHs.

| | | | Pseudo-first-order model | | | Ps | Pseudo-second-order model | | |
|-----------|-----------------|-------------------------------------|-----------------------------------|-------------------------------|----------------|--------------------------------|------------------------------|----------------|--|
| Adsorbent | Conc. (mg/L) | <i>q_{e, exp}</i> (mg/g) | <i>q_{e1, cal}</i> (mg/g) | <i>k</i> ₁ (1/min) | R ² | 9 _{e2, cal} (mg/g) | k ₂ (g/mg min) | R ² | |
| DMA-LLP | 100 | 29.6 | 24.9 | 0.0399 | 0.9807 | 30.4 | 0.0008 | 0.9924 | |
| | 300 | 60.5 | 53.1 | 0.0406 | 0.9772 | 61.7 | 0.0012 | 0.9916 | |
| | 500 | 86.8 | 81.8 | 0.0494 | 0.9646 | 85.9 | 0.0019 | 0.9949 | |

Table 2. Kinetic parameters for the adsorption of RR 195 onto DMA-LLP.

solution of the RR 195 adsorption was observed and discussed in the literature for various types of adsorbents (Çiçek *et al.* 2007; Belessi *et al.* 2009; Aksakal and Ucun 2010; Kamranifar *et al.* 2018). In subsequent adsorption experiments, the pH of the RR 195 solution was maintained at 2.0.

Contact time

Another factor that highly affects the efficiency of the adsorption process is the contact time between the adsorbent and adsorbate molecules. The effect of contact time on the adsorption of RR 195 onto the DMA-LLP was examined using various initial dye concentrations (100, 300, and 500 mg/L) at 298 K and pH of 2.0. It can be observed from Figure 4c that the adsorption uptake of RR 195 on the DMA-LLP increased as the contact time increased up to 150 min for all initial dye concentrations. The saturation of active sites on the surface of the DMA-LLP is probably after 150 min. Because after 150 min, the adsorption rate becomes slow. The rate of the initial stage of adsorption is high may be due to the availability of a large number of vacant surface sites on the adsorbent surface. After a certain period of time, the vacant sites were filled up by dye molecules that leading to generate a repulsive force in the bulk phase between the adsorbent surface and adsorbate (Mahmoud et al. 2016). The adsorption efficiency at equilibrium for an initial dye concentration of 100, 300, and 500 mg/L was 29.6, 60.5, and 86.8 mg/g. The equilibrium was attained at 150 min for all initial dye concentrations. Thus, 150 min was selected as the equilibrium time for further adsorption experiments in the present study.

Effect of adsorbent dosage

The adsorbent dosage is a dominant factor influencing the adsorption process because adsorption mainly depends on the surface area and the availability of active sorption sites on the adsorbent. Figure 4d displays the effect of DMA-LLP dosage on the adsorption of RR 195 at 298 K. It was noticed that the figure the adsorption efficiency of RR 195 remarkably decreased from 62.6 to 12.3 mg/g with an increase of DMA-LLP dosage from 0.03 to 0.1 g/30 mL.

With the rising dose of adsorbent, the efficiency of adsorption is diminished. Based on overlapping or aggregation of the adsorption sites by adsorbent particles, this may be clarified. This hinders the overall area of the surface, contributing to reduced adsorption at higher doses of the adsorbent. The rise in adsorbent dose contributes to saturation of active sites on the adsorbent surface at a constant dye concentration and volume, and the decrease in contact between particulate aggregates may be the explanation for decreased adsorption efficiency because aggregation will have a direct effect on reducing the adsorbent's total surface area and therefore making it difficult to disperse via pores (Asif Tahir *et al.* 2016). Thus, the amount of RR 195 adsorbed per unit mass of DMA-LLP was reduced at a higher DMA-LLP dosage. Therefore, in all the following subsequent adsorption experiments, the optimum DMA-LLP dosage was fixed at 0.03 g/30 mL.

Adsorption kinetics

Kinetics is a must for adsorption studies because it can predict the rate of removal of a pollutant from aqueous solutions. This also helps to better understand the mechanism of the reaction. The kinetic experiments were carried out using three different initial concentrations of 100, 300, and 500 mg/L to evaluate the impact of initial dye concentrations on kinetic behavior. The non-linearized forms of pseudofirst-order (PFO) and pseudo-second-order (PSO) kinetic equations can be described as the following equations:

$$q_t = q_{e1}(1 - \exp(-k_1 t)) \tag{4}$$

$$q_t = \frac{q_{e2}^2 k_2 t}{1 + q_{e2} k_2 t} \tag{5}$$

The estimated constants and R^2 values for the PFO and PSO non-linear kinetic models at several initial concentrations are tabulated in Table 2. From Table 2, the lower R^2 and the difference between $q_{e, exp}$ (experimental) and $q_{e2, cal}$ (calculated) values indicate that the PFO model was not well fitted to describe the adsorption of RR 195 onto DMA-LLP. On the other side, the R^2 values of the PSO model are greater than those of the PFO model for all initial concentrations of RR 195. Moreover, the PSO $q_{e, exp}$ (experimental) values were agreed satisfactory with the $q_{e2, cal}$ (calculated) values. Therefore, these results indicate that the adsorption of RR 195 on DMA-LLP was better represented in the PSO kinetic model. Figure 5 displays the non-linear plots of the kinetic models PFO and PSO for the adsorption of RR 195 to DMA-LLP.

Adsorption isotherms

In general, adsorption isotherms are known to understand the interaction of adsorptive molecules with adsorbents and the distribution of these molecules between the solid and liquid phases in the equilibrium state. Optimization of the adsorbent is therefore necessary for the selective removal



Figure 5. Kinetic models for the adsorption of RR 195 onto DMA-LLP at different concentrations: (a) 100 mg/L, (b) 300 mg/L, and (c) 500 mg/L.

| Table 3. | Description | of | adsorption | process | based | on | R_L | values |
|----------|-------------|----|------------|---------|-------|----|-------|--------|
|----------|-------------|----|------------|---------|-------|----|-------|--------|

| Nature of adsorption process | R_L , Separation factor |
|------------------------------|---------------------------|
| Favorable | $0 < R_L < 1$ |
| Unfavorable | $R_{L} > 1$ |
| Linear | $R_L = 1$ |
| Irreversible | $R_L = 0$ |
| | |

 Table 4. Langmuir and Freundlich isotherm constants for the adsorption of RR 195 onto DMA-LLP at different temperatures.

| | | Langmui | Freundlich | | | | | |
|-----------|-----------------------------|--------------|----------------|----------|-----------------------------|-------|----------------|----------|
| Temp. (K) | <i>q_m</i> (mg/g) | K_L (L/mg) | R ² | χ^2 | <i>K_f</i> (mg/g) | n | R ² | χ^2 |
| 298 | 131.5 | 0.0094 | 0.9956 | 28.8 | 10.1 | 2.556 | 0.9471 | 143.2 |
| 308 | 143.4 | 0.0106 | 0.9931 | 54.6 | 11.3 | 2.561 | 0.9335 | 153.6 |
| 318 | 151.6 | 0.0124 | 0.9969 | 21.5 | 11.6 | 2.581 | 0.9455 | 128.7 |
| 328 | 163.7 | 0.0131 | 0.9985 | 18.9 | 12.5 | 2.594 | 0.9513 | 119.3 |

from the environment of pollutants. Non-linearized equilibrium models of Langmuir and Freundlich were used for experimental data at different temperatures in order to assess the sorption efficiency of DMA-LLP for RR 195.

Langmuir isotherm is based on the assumption of energetically equivalent solid surface pores and forms only a monolayer of solute on the homogeneous surface of a single-solute system.

The Langmuir (non-linear form) model can be described as:

$$q_e = \frac{q_{\max}K_L C_e}{1 + K_L C_e} \tag{6}$$

With the rise in temperature from 298 to 328 K, the value of q_{max} rose from 131.5 to 163.7 mg/g. This indicated that the adsorption of RR 195 onto DMA-LLP was endothermic. K_L , a measure of the binding energy of RR 195 to DMA-LLP, was found to increase from 0.0094 to 0.0131 L/mg when the temperature was raised from 298 to 328 K. The value of K_L , being highest at 328 K, indicated that RR 195 binding was better with the surface of DMA-LLP at a higher temperature.

The R_L (separation factor) is the essential characteristic of the Langmuir isotherm defined in the following Eq. (7):

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{7}$$

The R_L values, as shown in Table 3, give an idea of the nature of the process of adsorption. The calculated R_L values in the present study were found to be 0.248, 0.229, 0.205, and 0.196 at 298, 308, 318, and 328 K, respectively. These R_L values indicate that the adsorption of RR 195 onto the DMA-LLP was favorable.

Freundlich model stresses over the mechanism having different adsorption energies with multilayer active



Figure 6. Adsorption isotherms for the adsorption of RR 195 onto DMA-LLP at different temperatures: (a) 298 K, (b) 308 K, (c) 318 K, and (d) 328 K.

| Adsorbent | q _{max} (mg/g) | рН | Reference |
|---|-------------------------|-----|---------------------------------|
| Wheat bran | 116.3 | 1.5 | Çiçek <i>et al.</i> (2007) |
| Modified switchgrass biochar | 27.02 | 5.0 | Mahmoud et al. (2016) |
| Barberry stem powder | 27.2 | 3.0 | Kamranifar <i>et al.</i> (2018) |
| Barberry ash | 8.8 | 3.0 | Kamranifar <i>et al.</i> (2018) |
| Pinus sylvestris Linneo | 8.425 | 1.0 | Aksakal and Ucun (2010) |
| Nanoparticles TiO ₂ | 87 | 3.0 | Belessi <i>et al.</i> (2009) |
| Clinoptilolite | 3.186 | - | Sismanoglu et al. (2010) |
| Soybean leaves modified with acetic acid | 12.0 | - | Mahanna and Azab (2020) |
| Modified palygorskite | 34 | - | Xue et al. (2010) |
| Grafted carboxymethyl cellulose Nanosized gel | 8.16 | - | Radwan et al. (2018) |
| Chitosan coacervated particles | 82.1 | 4.0 | Pérez-Calderón et al. (2018) |
| Dehydrated beet pulp carbon | 58 | 1.0 | Dursun and Tepe (2011) |
| Dimethylamine modified lotus leaf powder | 131.5 | 2.0 | Present study |

Table 5. Comparison of maximum monolayer adsorption capacity of different reported adsorbents for RR 195.

sites. The Freundlich (non-linear form) model can be expressed as:

$$q_e = K_f C_e^{1/n} \tag{8}$$

The values of K_L were increased with rising temperature, which displayed that the intensity of adsorption was improved at higher temperatures. The values of *n* obtained expressed the favorability of the adsorption process. The *n* values in the present study were > 1; it indicated that RR 195 was favorably adsorbed on the surface of DMA-LLP (Table 4).

The non-linear isothermal plots of Langmuir and Freundlich for RR 195 adsorption on DMA-LLP at various

ambient temperatures are shown in Figure 6. The constant parameters calculated from Langmuir and Freundlich models based on experimental data and their R^2 , as well as χ^2 values, are given in Table 4. According to the lowest χ^2 and the highest values of R^2 , RR 195 adsorption onto DMA-LLP was best described by the Langmuir model.

Comparison with other adsorbents

To evaluated the RR 195 removal performance of DMA-LLP, the maximum monolayer adsorption capacity of DMA-LLP for RR 195 was compared with the variously reported biosorbents are listed in Table 5. It is clear from the table



Figure 7. (a) Effect of temperature on the adsorption of RR 195 onto DMA-LLP and (b) Van't Hoff plot for the adsorption of RR 195 onto DMA-LLP.

 Table 6. Thermodynamic parameters for the adsorption of RR 195 onto DMA-LLP at different temperatures.

| | ΔG^{ads} | ΔH^{ads} | ΔS^{ads} |
|-----------|------------------|------------------|------------------|
| Temp. (K) | (kJ/mol) | (kJ/mol) | (kJ/mol K) |
| 298 | -2.5642 | | |
| 308 | -3.5389 | 22.5 | 0.084 |
| 318 | -4.3614 | | |
| 328 | -5.0892 | | |

that the adsorption efficiency of the RR 195 dye molecule on DMA-LLP was very high when compared with different reported adsorbents. However, the DMA-LLP shows excellent adsorption efficiency for RR 195 from the aqueous solution, which approves that the new adsorbent has the potential for eliminating dye from the aqueous environment.

Effect of temperature

Another significant parameter that governs the efficiency of the sorption process is temperature. The effect of temperature was examined at four different temperatures at a constant initial dye concentration of 300 mg/L and pH of 2.0.



Figure 8. (a) Desorption of DMA-LLP using different eluents and (b) adsorption/desorption cycles of DMA-LLP using 0.1 M NaOH as eluent.

Figure 7a displays the effect of temperature on the adsorption uptake of DMA-LLP for the removal of RR 195. It's clear that the removal of RR 195 was increased with the temperature rise, which suggested that the adsorption of RR 195 onto DMA-LLP was endothermic. The viscosity of the solution gets decreased when the temperature is increased that enhances the rate of across phase boundary crossing of adsorbate molecules into the inner pores of the solid adsorbent; hence the adsorptive capability of the adsorbent increases (Thirunavukkarasu *et al.* 2018).

Thermodynamic studies

The thermodynamic study was performed to investigate the nature of the sorption process. Present work, the adsorption of RR 195 onto DMA-LLP was carried out in the temperature range of 298–328 K, and the thermodynamic parameters, including change in Gibb's free energy (ΔG^{ads}), change in enthalpy (ΔH^{ads}), and change in entropy (ΔS^{ads}) were calculated using the following Eqs. (9-12).

$$\Delta G^{ads} = -RT\ln K_c \tag{9}$$

$$K_c = \frac{C_{Ae}}{C_e} \tag{10}$$

$$\Delta G^{ads} = \Delta H^{ads} - T\Delta S^{ads} \tag{11}$$



A = Adsorbent

Figure 9. Adsorption mechanism of RR 195 onto DMA-LLP.

$$\ln K_c = -\frac{\Delta G^{ads}}{RT} = -\frac{\Delta H^{ads}}{RT} + \frac{\Delta S^{ads}}{R}$$
(12)

The calculated thermodynamic parameters and constants were listed in Table 6. The values of ΔH^{ads} and ΔS^{ads} can be calculated by the intercept and slope of the curve of $ln K_c$ against 1/T, as displayed in Figure 7b. The negative ΔG^{ads} values obtained at all temperatures suggest that the adsorption reaction was feasible and spontaneous ($\Delta G^{ads} < 0$). Moreover, the ΔG^{ads} value decrease with a temperature rise indicates that the RR 195 adsorption was more favorable at higher temperatures (Razmi et al. 2019). Usually, the values of ΔG^{ads} between -20.0 and 0.0 kJ/mol corresponds to physisorption; however, G^{ads} value between -400.0 and -80.0 kJ/mol corresponds to chemisorption (Konicki et al. 2018). The values of ΔG^{ads} obtained in the current study are between -20.0 and 0.0 kJ/mol, indicating that the dye adsorbed onto the surface of DMA-LLP through a physisorption mechanism. The positive value of ΔH^{ads} indicates the favorable condition that is endothermic ($\Delta H^{ads} > 0$) nature of the adsorption process that implies a strong bonding between the dye and the adsorbent (Pereira et al. 2018). The positive value of ΔS^{ads} reveals the rise of randomness ($\Delta S^{ads} > 0$) at the solid-liquid interface during the adsorption of RR 195 on the active sites of the DMA-LLP and its affinity toward the dye (Kaur *et al.* 2015).

Desorption and regeneration studies

It is essential to allow the reuse of adsorbents to make every adsorption operation more economical. For that desorption and regeneration of biosorbent is one of the significant aspects of the adsorption process. The desorption study of RR 195 from DMA-LLP was carried out using 0.1 M solution of various eluents NaOH/NaCl/H₂SO₄ and DI water in the same conditions. Figure 8a displays the comparison between the different desorption efficiencies. NaOH (0.1 M) showed the highest desorption efficiency of 94%, while the use of NaCl (0.1 M), H₂SO₄ (0.1 M), and DI water resulted in low desorption efficiency 58%, 31%, and 18%, respectively. Therefore, in the present study, NaOH (0.1 M) solution was selected as the most suitable desorbing eluent to remove the adsorbed RR 195 molecules on the DMA-LLP surface. After desorption, the regeneration studies were carried out with NaOH (0.1 M) for five cycles (adsorption/ desorption) that were done using the same adsorbent, and the results were displayed in Figure 8b. It was seen that the adsorption efficiency of RR 195 was found to be 81% in the first cycle and the subsequent cycles; the adsorption efficiency reduced slightly and reached 72% in the fifth cycle. The desorption efficiency of RR 195 can still reach 83% after the fifth cycle. The gradual reduction in the dye adsorption efficiency was due to the persistence of engaged adsorption reactive sites of the DMA-LLP. Based on these results, the DMA-LLP is an excellent reusable adsorbent, which can be successfully used to remove RR 195 from practical wastewater treatment.

Adsorption mechanism

It has been reported that the $pH < pH_{PZC}$ represents the tendency of the adsorbent surface is positively charged and can attract anions from the dye solution, whereas $pH > pH_{PZC}$ facilitates the repulsion (Banerjee and Chattopadhyaya 2017). In the present study, the selected RR 195 dye molecules are anionic possessing excess negative charges due to the presence of five sulfonate $(-SO_3^{-})$ groups and readily dissociates in the aqueous medium. Thus, the adsorption mechanism is more inclined toward the electrostatic interactions between the positively charged DMA-LLP $(pH < pH_{PZC})$ and the negatively charged RR 195. This is due to the strong adsorption affinity of DMA-LLP toward the dye is probably due to its small particle size, pore volume, and surface area coupled with electrostatic interactions involved, shown in Figure 9. Further, the DMA-LLP adsorption uptake was considerably higher than its counterparts, and the details are listed in Table 5.

Conclusions

DMA-LLP has been effectively applied in the present paper as a biosorbent for the removal of RR 195 from aqueous media. The effect of solution pH (2.0-12.0), amount of dosage (0.03-0.1 g/30 mL), initial RR 195 concentration (100-1000 mg/L), temperature (298-328 K), contact time (0-420 min), and also isotherms, kinetics, thermodynamics, and regeneration studies were performed. FE-SEM, EDX, FTIR, pH_{PZC} , and BET analysis have characterized the DMA-LLP. FT-IR and FESEM analysis indicated the presence of numerous pores and several functional groups on the surface of the DMA-LLP. Based on BET results, the S_{BET} of DMA-LLP is $4.6 \text{ m}^2/\text{g}$, a V_P of 0.0067 cc/g, and the D_P is 2.145 nm. The V_P calculated via BJH theory indicates that the morphology structure of DMA-LLP was mesoporous. The q_{max} (maximum monolayer adsorption capacity) of RR 195 was 131.5 mg/g at optimum pH 2.0, equilibrium time 150 min, temperature 298 K, amount of biosorbent dosage 0.03 g, and initial RR 195 concentration 300 mg/L. The pH_{PZC} of the DMA-LLP was found to be 5.5. Using PFO

and PSO models, kinetic adsorption experiments were examined. The results revealed that the PSO model in the experimental data was best described. Langmuir and Freundlich isothermal models analyzed the equilibrium data and were well-fitted with the Langmuir model. The adsorption efficiency increased (131.5–163.7 mg/g) with rising temperatures (298-328 K), which indicated that the adsorption of RR 195 onto DMA-LLP was endothermic in nature. The electrostatic interactions were considered to be the main force contributing to the RR 195 adsorption of DMA-LLP. The calculated thermodynamic parameters revealed that the adsorption of RR 195 onto DMA-LLP was spontaneous and endothermic. The reusability of DMA-LLP showed that after even five cycles, the adsorption efficiency was 72%, which indicated that DMA-LLP is a probable renewable adsorbent. Because of these results, it can be concluding that the DMA-LLP could be employed as a cheap, eco-friendly, and efficient biosorbent for the removal of RR 195 from wastewaters.

Nomenclature

| C_e | equilibrium concentration of RR 195 (mg/L) |
|-----------------------------------|---|
| C_o | initial concentration of RR 195 (mg/L) |
| C_{Ae} | solid phase concentration at equilibrium (mg/L) |
| Cal | calculated |
| Exp | experimental |
| k_1^{-} | rate constant of PFO (1/min) |
| k_2 | rate constant of PSO (g/mg min) |
| K _c | distribution constant |
| K_f | Freundlich constant (mg/g) |
| κ _L | Langmuir constant (L/mg) |
| Μ | mass of adsorbent (g) |
| п | number of samples $(\chi^2 \text{ analysis})$ |
| 1/n | Freundlich constant |
| q _e | amount of RR 195 adsorbed measured at equilibrium |
| | (mg/g) |
| q _e | theoretical data (χ^2 analysis) |
| q _{e,m} | experimental data (χ^2 analysis) |
| q _{e1} , q _{e2} | amount of dye adsorbed at equilibrium (mg/g) |
| q_t | amount of dye adsorbed at time t (mg/g) |
| q _{max} | maximum amount of RR 195 adsorbed (mg/g) |
| R | universal gas constant (8.314 kJ/mol K) |
| Т | temperature (K) |
| V | liquid phase volume (L) |

Funding

The authors would like to acknowledge the research support from MOST 106-2625-M-224-002, MOST 106-2915-I-224-501, MOST 107-2625-M-224-002, and MOST 108-2625-M-224-005, by the Ministry of Science and Technology (MOST), Taiwan.

References

- Ahmad R. 2009. Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP). J Hazard Mater. 171:767–773. doi:10.1016/j.jhazmat.2009.06.060.
- Ahmaruzzaman M, Ahmed MJK, Begum S. 2015. Remediation of Eriochrome Black T-contaminated aqueous solutions utilizing H₃PO₄-modified berry leaves as a non-conventional adsorbent. Desalin Water Treat. 56(6):1507–1519. doi:10.1080/19443994.2014. 950995.
- Ahmed DN, Naji LA, Faisal AAH, Al-Ansari N, Naushad M. 2020. Waste foundry sand/MgFe-layered double hydroxides composite

material for efficient removal of congo red dye from aqueous solution. Sci Rep. 10:2042. doi:10.1038/s41598-020-58866-y.

- Aksakal O, Ucun H. 2010. Equilibrium, kinetic and thermodynamic studies of the biosorption of textile dye (Reactive Red 195) onto *Pinus sylvestris* L. J Hazard Mater. 181:666–672. doi:10.1016/j.jhazmat.2010.05.064.
- Albadarin AB, Collins MN, Naushad M, Shirazian S, Walker G, Mangwandi C. 2017. Activated lignin-chitosan extruded blends for efficient adsorption of methylene blue. Chem Eng J. 307:264–272. doi:10.1016/j.cej.2016.08.089.
- Alves de Lima RO, Bazo AP, Salvadori DMF, Rech CM, de Palma Oliveira D, de Aragão Umbuzeiro G. 2007. Mutagenic and carcinogenic potential of a textile azo dye processing plant effluent that impacts a drinking water source. Mutat Res - Genet Toxicol Environ Mutagen. 626(1-2):53-60. doi:10.1016/j.mrgentox.2006.08. 002.
- Anitha T, Senthil Kumar P, Sathish Kumar K. 2016. Synthesis of nanosized chitosan blended polyvinyl alcohol for the removal of eosin yellow dye from aqueous solution. J Water Process Eng. 13:127–136. doi:10.1016/j.jwpe.2016.08.003.
- Asif Tahir M, Bhatti HN, Iqbal M. 2016. Solar Red and Brittle Blue direct dyes adsorption onto Eucalyptus angophoroides bark: equilibrium, kinetics and thermodynamic studies. J Environ Chem Eng. 4(2):2431–2439. doi:10.1016/j.jece.2016.04.020.
- Banerjee S, Chattopadhyaya MC. 2017. Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. Arab J Chem. 10:S1629–S1638. doi: 10.1016/j.arabjc.2013.06.005.
- Belessi V, Romanos G, Boukos N, Lambropoulou D, Trapalis C. 2009. Removal of Reactive Red 195 from aqueous solutions by adsorption on the surface of TiO₂ nanoparticles. J Hazard Mater. 170:836–844. doi:10.1016/j.jhazmat.2009.05.045.
- Brookstein DS. 2009. Factors associated with textile pattern dermatitis caused by contact allergy to dyes, finishes, foams, and preservatives. Dermatol Clin. 27:309–322. doi:10.1016/j.det.2009.05.001.
- Cardoso NF, Lima EC, Calvete T, Pinto IS, Amavisca CV, Fernandes THM, Pinto RB, Alencar WS. 2011a. Application of aqai stalks as biosorbents for the removal of the dyes reactive black 5 and reactive orange 16 from aqueous solution. J Chem Eng Data. 56(5): 1857–1868. doi:10.1021/je100866c.
- Cardoso NF, Lima EC, Pinto IS, Amavisca CV, Royer B, Pinto RB, Alencar WS, Pereira SFP. 2011b. Application of cupuassu shell as biosorbent for the removal of textile dyes from aqueous solution. J Environ Manage. 92:1237–1247. doi:10.1016/j.jenvman.2010.12.010.
- Cardoso NF, Lima EC, Royer B, Bach MV, Dotto GL, Pinto LAA, Calvete T. 2012. Comparison of Spirulina platensis microalgae and commercial activated carbon as adsorbents for the removal of Reactive Red 120 dye from aqueous effluents. J Hazard Mater. 241–242:146–153. doi:10.1016/j.jhazmat.2012.09.026.
- Carneiro PA, Umbuzeiro GA, Oliveira DP, Zanoni MVB. 2010. Assessment of water contamination caused by a mutagenic textile effluent/dyehouse effluent bearing disperse dyes. J Hazard Mater. 174:694–699. doi:10.1016/j.jhazmat.2009.09.106.
- Çelekli A, Al-Nuaimi AI, Bozkurt H. 2019. Adsorption kinetic and isotherms of Reactive Red 120 on Moringa oleifera seed as an ecofriendly process. J Mol Struct. 1195:168–178. doi:10.1016/j.molstruc. 2019.05.106.
- Chen G, Zhu M, Guo M. 2019. Research advances in traditional and modern use of Nelumbo nucifera: phytochemicals, health promoting activities and beyond. Crit Rev Food Sci Nutr. 59:S189–S209. doi:10. 1080/10408398.2018.1553846.
- Çiçek F, Ozer D, Ozer A, Ozer A. 2007. Low cost removal of reactive dyes using wheat bran. J Hazard Mater. 146(1-2):408-416. doi:10. 1016/j.jhazmat.2006.12.037.
- Devi VS, Sudhakar B, Prasad K, Jeremiah Sunadh P, Krishna M. 2020. Adsorption of Congo red from aqueous solution onto Antigonon leptopus leaf powder: equilibrium and kinetic modeling. Mater Today Proc. 26:3197–3206. doi:10.1016/j.matpr.2020.02.715.

- Dursun AY, Tepe O. 2011. Removal of Chemazol Reactive Red 195 from aqueous solution by dehydrated beet pulp carbon. J Hazard Mater. 194:303-311. doi:10.1016/j.jhazmat.2011.07.105.
- Ghosh SK, Bandyopadhyay A. 2017. Adsorption of methylene blue onto citric acid treated carbonized bamboo leaves powder: Equilibrium, kinetics, thermodynamics analyses. J Mol Liq. 248: 413–424. doi:10.1016/j.molliq.2017.10.086.
- Guerrero-Coronilla I, Morales-Barrera L, Cristiani-Urbina E. 2015. Kinetic, isotherm and thermodynamic studies of amaranth dye biosorption from aqueous solution onto water hyacinth leaves. J Environ Manage. 152:99–108. doi:10.1016/j.jenvman.2015.01.026.
- Han X, Wang W, Ma X. 2011. Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf. Chem Eng J. 171(1): 1–8. doi:10.1016/j.cej.2011.02.067.
- Han X, Yuan J, Ma X. 2014. Adsorption of malachite green from aqueous solutions onto lotus leaf: Equilibrium, kinetic, and thermodynamic studies. Desalin Water Treat. 52(28–30):5563–5574. doi:10. 1080/19443994.2013.813102.
- Hassani A, Faraji M, Eghbali P. 2020. Facile fabrication of mpg-C₃N₄/ Ag/ZnO nanowires/Zn photocatalyst plates for photodegradation of dye pollutant. J Photochem Photobiol A. 400:112665. doi:10.1016/j. jphotochem.2020.112665.
- Jain SN, Gogate PR. 2017. Acid Blue 113 removal from aqueous solution using novel biosorbent based on NaOH treated and surfactant modified fallen leaves of *Prunus dulcis*. J Environ Chem Eng. 5(4): 3384–3394. doi:10.1016/j.jece.2017.06.047.
- Kamranifar M, Khodadadi M, Samiei V, Dehdashti B, Noori Sepehr M, Rafati L, Nasseh N. 2018. Comparison the removal of reactive red 195 dye using powder and ash of barberry stem as a low cost adsorbent from aqueous solutions: isotherm and kinetic study. J Mol Liq. 255:572–577. doi:10.1016/j.molliq.2018.01.188.
- Kaur S, Rani S, Mahajan RK, Asif M, Gupta VK. 2015. Synthesis and adsorption properties of mesoporous material for the removal of dye safranin: kinetics, equilibrium, and thermodynamics. J Ind Eng Chem. 22:19–27. doi:10.1016/j.jiec.2014.06.019.
- Khan ZUH, Khan A, Chen Y, Khan AU, Shah NS, Muhammad N, Murtaza B, Tahir K, Khan FU, Wan P. 2017. Photo catalytic applications of gold nanoparticles synthesized by green route and electrochemical degradation of phenolic azo dyes using AuNPs/GC as modified paste electrode. J Alloys Compd. 725:869–876. doi:10.1016/ j.jallcom.2017.07.222.
- Konicki W, Hełminiak A, Arabczyk W, Mijowska E. 2018. Adsorption of cationic dyes onto Fe@graphite core-shell magnetic nanocomposite: equilibrium, kinetics and thermodynamics. Chem Eng Res Des. 129:259–270. doi:10.1016/j.cherd.2017.11.004.
- Krishna Murthy TP, Gowrishankar BS, Chandra Prabha MN, Kruthi M, Hari Krishna R. 2019. Studies on batch adsorptive removal of malachite green from synthetic wastewater using acid treated coffee husk: equilibrium, kinetics and thermodynamic studies. Microchem J. 146:192–201. doi:10.1016/j.microc.2018.12.067.
- Mahanna H, Azab M. 2020. Adsorption of Reactive Red 195 dye from industrial wastewater by dried soybean leaves modified with acetic acid. DWT. 178:312–321. doi:10.5004/dwt.2020.24960.
- Mahmoud HR, Ibrahim SM, El-Molla SA. 2016. Textile dye removal from aqueous solutions using cheap MgO nanomaterials: adsorption kinetics, isotherm studies and thermodynamics. Adv Powder Technol. 27(1):223–231. doi:10.1016/j.apt.2015.12.006.
- Mahmoud ME, Nabil GM, El-Mallah NM, Bassiouny HI, Kumar S, Abdel-Fattah TM. 2016. Kinetics, isotherm, and thermodynamic studies of the adsorption of reactive red 195 A dye from water by modified Switchgrass Biochar adsorbent. J Ind Eng Chem. 37: 156–167. doi:10.1016/j.jiec.2016.03.020.
- Moghaddam SS, Moghaddam MRA, Arami M. 2010. Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology. J Hazard Mater. 175:651–657. doi:10.1016/j.jhazmat.2009.10.058.
- Mu Y, Rabaey K, Rozendal RA, Yuan Z, Keller J. 2009. Decolorization of azo dyes in bioelectrochemical systems. Environ Sci Technol. 43: 5137–5143. doi:10.1021/es900057f.

- Munagapati VS, Wen JC, Pan CL, Gutha Y, Wen JH. 2019. Enhanced adsorption performance of Reactive Red 120 azo dye from aqueous solution using quaternary amine modified orange peel powder. J Mol Liq. 285:375–385. doi:10.1016/j.molliq.2019.04.081.
- Munagapati VS, Yarramuthi V, Kim Y, Lee KM, Kim DS. 2018. Removal of anionic dyes (Reactive Black 5 and Congo Red) from aqueous solutions using Banana Peel Powder as an adsorbent. Ecotoxicol Environ Saf. 148:601–607. doi:10.1016/j.ecoenv.2017.10. 075.
- Naushad M, Sharma G, Alothman ZA. 2019. Photodegradation of toxic dye using gum Arabic-crosslinked-poly (acrylamide)/Ni(OH)₂/ FeOOH nanocomposites hydrogel. J Clean Prod. 241:118263. doi:10. 1016/j.jclepro.2019.118263.
- Nidheesh PV, Zhou M, Oturan MA. 2018. An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes. Chemosphere. 197:210–227. doi:10.1016/j.chemosphere. 2017.12.195.
- Pereira IC, Carvalho KQ, Passig FH, Ferreira RC, Rizzo-Domingues RCP, Hoppen MI, Macioski G, Nagalli A, Perretto F. 2018. Thermal and thermal-acid treated sewage sludge for the removal of dye reactive Red 120: characteristics, kinetics, isotherms, thermodynamics and response surface methodology design. J Environ Chem Eng. 6(6):7233–7246. doi:10.1016/j.jece.2018.10.060.
- Pérez-Calderón J, Santos MV, Zaritzky N. 2018. Reactive RED 195 dye removal using chitosan coacervated particles as bio-sorbent: analysis of kinetics, equilibrium and adsorption mechanisms. J Environ Chem Eng. 6(5):6749–6760. doi:10.1016/j.jece.2018.10.039.
- Peydayesh M, Rahbar-Kelishami A. 2015. Adsorption of methylene blue onto Platanus orientalis leaf powder: kinetic, equilibrium and thermodynamic studies. J Ind Eng Chem. 21:1014–1019. doi:10. 1016/j.jiec.2014.05.010.
- Qi Y, Zhu L, Shen X, Sotto A, Gao C, Shen J. 2019. Polythyleneiminemodified original positive charged nanofiltration membrane: removal of heavy metal ions and dyes. Sep Purif Technol. 222: 117–124. doi:10.1016/j.seppur.2019.03.083.
- Radwan EK, Kafafy H, El-Wakeel ST, Shaheen TI, Gad-Allah TA, El-Kalliny AS, El-Naggar ME. 2018. Remediation of Cd(II) and reactive red 195 dye in wastewater by nanosized gels of grafted carboxymethyl cellulose. Cellulose. 25(11):6645–6660. doi:10.1007/s10570-018-2003-0.
- Raghu S, Ahmed Basha C. 2007. Chemical or electrochemical techniques, followed by ion exchange, for recycle of textile dye wastewater. J Hazard Mater. 149:324–330. doi:10.1016/j.jhazmat.2007.03.087.
- Razmi FA, Ngadi N, Wong S, Inuwa IM, Opotu LA. 2019. Kinetics, thermodynamics, isotherm and regeneration analysis of chitosan modified pandan adsorbent. J Clean Prod. 231:98–109. doi:10.1016/j. jclepro.2019.05.228.
- Sartape AS, Mandhare AM, Jadhav VV, Raut PD, Anuse MA, Kolekar SS. 2017. Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. Arab J Chem. 10:S3229–S3238. doi:10. 1016/j.arabjc.2013.12.019.

- Şentürk İ, Alzein M. 2020. Adsorptive removal of basic blue 41 using pistachio shell adsorbent - performance in batch and column system. Sustain Chem Pharm. 16:100254. doi:10.1016/j.scp.2020.100254.
- Sharma G, Kumar A, Sharma S, Naushad M, Dhiman P, Vo DVN, Stadler FJ. 2020. Fe₃O₄/ZnO/Si₃N₄ nanocomposite based photocatalyst for the degradation of dyes from aqueous solution. Mater Lett. 278:128359. doi:10.1016/j.matlet.2020.128359.
- Sismanoglu T, Kismir Y, Karakus S. 2010. Single and binary adsorption of reactive dyes from aqueous solutions onto clinoptilolite. J Hazard Mater. 184:164–169. doi:10.1016/j.jhazmat.2010.08.019.
- Stavrinou A, Aggelopoulos CA, Tsakiroglou CD. 2018. Exploring the adsorption mechanisms of cationic and anionic dyes onto agricultural waste peels of banana, cucumber and potato: Adsorption kinetics and equilibrium isotherms as a tool. J Environ Chem Eng. 6(6): 6958–6970. doi:10.1016/j.jece.2018.10.063.
- Thirunavukkarasu A, Muthukumaran K, Nithya R. 2018. Adsorption of acid yellow 36 onto green nanoceria and amine functionalized green nanoceria: comparative studies on kinetics, isotherm, thermodynamics, and diffusion analysis. J Taiwan Inst Chem Eng. 93:211–225. doi:10.1016/j.jtice.2018.07.006.
- Uzal N, Yilmaz L, Yetis U. 2010. Nanofiltration and reverse osmosis for reuse of indigo dye rinsing waters. Sep Sci Technol. 45(3): 331–338. doi:10.1080/01496390903484818.
- Wang H, Yuan X, Zeng G, Leng L, Peng X, Liao K, Peng L, Xiao Z. 2014. Removal of malachite green dye from wastewater by different organic acid-modified natural adsorbent: kinetics, equilibriums, mechanisms, practical application, and disposal of dye-loaded adsorbent. Environ Sci Pollut Res. 21:11552–11564. doi:10.1007/ s11356-014-3025-2.
- Wong S, Tumari HH, Ngadi N, Mohamed NB, Hassan O, Mat R, Saidina Amin NA. 2019. Adsorption of anionic dyes on spent tea leaves modified with polyethyleneimine (PEI-STL). J Clean Prod. 206:394–406. doi:10.1016/j.jclepro.2018.09.201.
- Xu MY, Jiang HL, Xie ZW, Li ZT, Xu D, He FA. 2020. Highly efficient selective adsorption of anionic dyes by modified β -cyclodextrin polymers. J Taiwan Inst Chem Eng. 108:114–128. doi:10.1016/j.jtice. 2020.01.005.
- Xue A, Zhou S, Zhao Y, Lu X, Han P. 2010. Adsorption of reactive dyes from aqueous solution by silylated palygorskite. Appl Clay Sci. 48(4):638–640. doi:10.1016/j.clay.2010.03.011.
- Yang JX, Hong GB. 2018. Adsorption behavior of modified *Glossogyne* tenuifolia leaves as a potential biosorbent for the removal of dyes. J Mol Liq. 252:289–295. doi:10.1016/j.molliq.2017.12.142.
- Yashni G, Al-Gheethi A, Mohamed R, Arifin SNH, Salleh SNAM. 2020. Photodegradation of basic red 51 in hair dye greywater by zinc oxide nanoparticles using central composite design. Reac Kinet Mech Cat. 130(1):567–588. doi:10.1007/s11144-020-01792-x.
- Zubair M, Jarrah N, Ihsanullah, Khalid A, Manzar MS, Kazeem TS, Al-Harthi MA. 2018. Starch-NiFe-layered double hydroxide composites: efficient removal of methyl orange from aqueous phase. J Mol Liq. 249:254–264. doi:10.1016/j.molliq.2017.11.022.