Efficient dye discoloration of modified Lamiaceae leaves

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Abstract

The powder of Lamiaceae Leaves was modified by Zinc Chloride (ZnCl₂). The Chemical Modified Lamiaceae Leaves Powder (CMLLP) was characterized by BET surface analyzer, FTIR, SEM and Theydan and Ahmed method. It was found that this adsorbent has pHZPC of 6.2, surface area of 104.78 m²g⁻¹, pore volume of 0.00464 cc/g and average pore diameter of 2647.813 Å. This sorbent was used as a cheap adsorbent for the extraction of Methylene Blue (MB) from contaminated solutions. The effect of temperature, pH of solution, time of contact and MB primary concentration were also investigated. All of these variables have positive impacts on this adsorption. The data obtained from the isotherm’s experiments, were analysed using three models. The obtained results confirmed that model of Langmuir was the most efficient. The capacities of this adsorption were found to be 333.33, 384.62, 434.78 and 476.19 mg g⁻¹ at 25, 35, 45 and 60 °C, correspondingly. Three models of kinetic were applied to determine the constants of this adsorption kinetics. It was observed that the kinetic results follow the 2nd order more than the other two kinetic models. Moreover, thermodynamic constants were determined, which showed that this adsorption is an exothermic and spontaneous process.

1. Introduction

Currently, one of the most important and high priority concerns is the pollution of underground and surface waters caused by dyes. This contamination is generally discharged in wastewaters from industrial, agricultural and pharmaceutical sector [1]. As well as, the disposal of the MB-contaminated water, generated from the coloring processes of silk, cotton and wool, to the environment represents other forms of contamination [2]. It was stated by Senthilkumaar et al [3] and Deng et al [4] that dealing with, or consuming water polluted by MB can cause cyanosis, skin irritation, tachycardia, dyspnea, vomiting, diarrhea, methemoglobinemia, convulsions and nausea.

Therefore, some methodologies such as solvent extraction [5], coagulation [6], flocculation [7] and photo catalytic degradation by nanoparticles (NPs) of metallic oxides [8–10] have been applied for MB elimination from aqueous solutions. However, the high cost, excessive sludge production, technical constraints, difficulties of disposal and handling, all represent the main drawbacks of these techniques.

Adsorption by activated carbon (granular, powder and fiber) was considered as the most promising low cost and high efficiency method that can be employed for the removal of pollutants from water. This id due to its ease of operation, ability to uptake any pollutant at any amounts, etc [11]. For instance, it was reported by Al-Aoh et al [12] and Alabdullatif et al [13] that commercial activated carbon and activated carbon fibre prepared from coconut husks have superior adsorption capacity and rate towards MB. Therefore, an adsorption technique was selected in this work for the purification of synthesized wastewaters from MB.
The main disadvantages of the activated carbon used in the adsorption processes are the great efforts and high costs are required for its production from raw materials. Therefore, various attempts have been performed to examine the efficiency of some metallic oxides nano-particles (NP) for the adsorption of hazardous dyes. For example, the adsorption efficiency of CuO and NiO (NP) for methyl orange [14] and MB [15] have been studied. Moreover, the adsorption performance of bromophenol blue (BB) by NiO (NP) was investigated [16].

Presently, water and wastewater treatments using metallic oxide NP as effective adsorbents have become an undesirable method. This is due to the low yield and high cost which are usually associated with production of these types of adsorbents. Thus, substrates of spent mushroom [17], leaf powder of mango [18], stalks of sorghum [19], hulls of rice [20], stalks of crofton weed [21], calcined powder of corn cob [22], shells of walnut [23], etc were applied as inexpensive adsorbents for the decontamination of aqueous solutions from MB.

Salvia officinalis (Lamiaceae) is the scientific name for sage herb that has pharmacological properties and significant biological activity [24]. Sage herb is usually used for the production of volatile oils in large amounts due. This is to the high concentrations of those oils present in the plant [24]. This oil has a significant importance in pharmaceutical, perfumery, pesticide, cosmetic, flavouring and fragrance industries [25]. Sage (Salvia officinalis, Lamiaceae) is cultivated in different countries and used as a folk medicine against perspiration, rheumatism, sexual debility, nervous and mental diseases, chronic bronchitis and fevers [26].

Despite the various studies that have been carried out previously to investigate the efficiency of several adsorbents for MB adsorption, no effort has been done yet to use the leaves powder of Lamiaceae, as a new adsorbent for the elimination of hazardous pollutants from waters. Thus, the main object of this research is to modify the Lamiaceae leaves powder by ZnCl2. Then the adsorption performance of MB by the Chemical Modified Lamiaceae Leaves Powder (CMLLP) will be studied. Parameters of adsorption (isotherms, kinetics, thermodynamics) as well as factors affecting the adsorption rate and capacity will also be investigated in this research.

2. Methodology

2.1. Adsorbent modification

The dried leaves of Lamiaceae were supplied by a local market, Tabuk city, Kingdom of Saudi Arabia and was crushed to powder by using a mortar. The required weight (130 g) of this powder was mixed with a given volume (500 ml) of 30% w/w of ZnCl2. Then the mixture was put in 1000 ml a round-bottom flask and refluxed at boiling temperature for 2 h. The suspension was left open to the air for cooling and then filtered off using filter paper. After filtration, the residual solid was boiled in a glass beaker with 500 ml of 1M HCl for 1 h to remove ZnCl2 from the sample. The mixture was also filtered and the filter cake was repeatedly washed with distilled water until the sample became free from any amount of HCl. The clean powder was dried for 24 h in an oven at 140 °C, the dried powder was sieved to obtain adsorbent particles that ranged from 150 to 212 μm in size.

2.2. Characterization of adsorbent

The pH of solution at which the net charge of the CMLLP surface (pH_ZPC) is zero was estimated using Theydan and Ahmed method [27]. The technique of Brunauer, Emmett and Teller (BET) surface analyser (NOVA-2200 Ver. 6.11) using N2 was carried out at the required conditions (758.58 mm Hg, 77.35 K) to evaluate the density, porosity and surface area of the adsorbent used in this work. The morphology of the adsorbent surface and the surface functional groups were identified by using Microscopy of Scanning Electron (SEM) and Spectroscopy of Fourier Transform Infrared (FTIR) (Nicolet iS5 of Thermo Scientific FT-1IR), respectively.

2.3. Batch adsorption experiments

To avoid the photo-degradation of MB, batch experiments for MB adsorption by CMLLP were conducted in the dark system by using closed thermal shaker incubators and 30 ml amber bottles. In these experiments, a fixed mass (20 mg) of adsorbent was contacted with 15 ml MB solutions of different primary concentrations (130–1400 mg l−1) at four different temperatures (25, 35, 45, 60 °C). The mixtures were shaken at the original pH and 200 rpm for 12 h. The concentrations of MB at equilibrium in the residual were measured at λ_{max} of 618 nm by means of 6800 UV and Visible spectrophotometer (Jenway, Staffordshire, UK). The equilibrium adsorption amounts were calculated by equation (1).

$$q_e = \frac{(G_i - C_e) \times V}{W}$$

$q_e$: number of milligrams of MB adsorbed by one gram of CMLLP at equilibrium, $C_i$: initial strength of MB solution (mg/l), $C_e$ (mg/l): final strength of MB solution at equilibrium, $W$: mass of CMLLP (g).
The results of the above-mentioned experiments were used to investigate the effects of the temperature and adsorbate initial concentration. The obtained data of these experiments were also analyzed by the isotherm models demonstrated in Table 1 to determine the parameter of these adsorption isotherms.

Moreover, the factor of dimensionless \( R_L \) was calculated by using equation (2) to investigate the essential characteristics of Langmuir isotherm model.

\[
R_L = \frac{1}{1 + \frac{C_i}{K_L}}
\]

\( K_L \): constant of Langmuir which associated to the similarity of adsorption sites and the net enthalpy of adsorption, \( q_e \) refers to MB adsorbed at equilibrium, \( q_{\text{max}} \): maximum capacity of adsorption, and \( C_i \): the highest primary concentration of MB (mg/l).
Thermodynamic parameters ($\Delta H^\circ$, $\Delta S^\circ$, $\Delta G^\circ$) related to adsorption of 600, 700 and 800 mg l$^{-1}$ of these adsorbate solutions were determined by using equations (3) and (4).

\[
\ln K_C = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{3}
\]

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{4}
\]

$R$: universal gas constant, $T$: solution temperature, $\Delta S^\circ$, $\Delta H^\circ$ and $\Delta G^\circ$: standard changes for enthalpy, entropy and free energy, respectively.

Similar batch experiments were performed in dark system for adsorption of 130, 200 and 300 mg l$^{-1}$ of MB solutions at various periods of time ranging from 5 min to 960 min. The amount of MB adsorbed at each time was calculate by applying equation (5).

\[
q_t = \frac{(C_i - C_t) V}{W} \tag{5}
\]

$q_t$: number of milligrams of MB adsorbed by one gram of CMLLP at a time $t$, $C_i$ and $C_t$: MB primary concentration and concentration of MB at time $t$, correspondingly, $V$: solution volume, $W$: adsorbent mass.

The calculated values of $q_t$ (mg/g) were plotted against the agitation time ($t$) to explore the impact of adsorption contact time. The results of these experiments were analyzed by the linear forms of three kinetics models summarized in table 2 to examine the parameter of adsorption kinetics.

Adsorption of a given volume (15 ml) of 700 mg l$^{-1}$ of this adsorbate solutions with several values of pH that ranged from 1 to 11 was also conducted to explore the impact of pH on MB adsorption by CMLLP.

3. Results and discussion

3.1. CMLLP Characterization

Physical and chemical techniques like surface analyzer BET, scanning electron microscopy (SEM), spectroscopy of FT-IR and Theydan and Ahmed method [27] has been applied in this research to identify the physical and chemical adsorptive properties of CMLLP before adsorption.

3.1.1. Surface morphology of CMLLP

The image of SEM (figure 1) demonstrates the microstructure of CMLLP, before being applied, as a new adsorbent in this work. This image illustrates that this adsorbent has various gaps and macropores which are positively effective in the adsorption process; through which MB cations easily diffuse across the micropores to the active adsorption sites.

3.1.2. Porosity and Surface area of CMLLP

The pores’ properties and surface area of the adsorbent are significant factors that affect the efficiency of the adsorbent. Thus, the BET surface analyzer technique was applied to identify the surface properties of CMLLP.
used as an adsorbent in this study. The results of this technique proved that CMLLP has a larger surface area of 104.78 m²g⁻¹, total pore volume and average pore diameter of 0.00464 cc g⁻¹, 2647.813 Å, respectively. The high surface area along with the suitable properties of the pores of this adsorbent represent the reasonable explanation for its significant adsorption efficiency towards MB.

3.1.3. Results of FTIR spectroscopy
The selectivity and efficiency of the adsorbent depend on its functional groups of surfaces. Therefore, the CNLLP was scanned by spectroscopy of FT-IR, and the obtained spectrum was illustrated in figure 2. Three main absorption bands can be clearly seen in this figure at the regions of 2930, 1700 and 1030 cm⁻¹. These absorption peaks refer back to the stretching of C–H, ketones and vibrations of the ring, respectively [28, 29].

3.1.4. The pHZPC of CMLLP
The type and amount of the adsorbate that will be adsorbed by any adsorbent material is affected by number and type of the electric charges on the adsorbent surface. Therefore, Theydan and Ahmed’s method was used in this work to determine the values of pH at which the net electrical charge on CMLLP surface will be zero (pHZPC = 0). Then, the results achieved in this part are shown in figure 3 which proves that 6.2 is the pHZPC of the CMLLP. Therefore, it will be known whether CMLLP surface is a negatively or a positively charged. Since,
CMLLP surface will have a negative or positive charge when the pH value of MB solution is higher or less than 6.2, correspondingly.

### 3.2. Adsorption results

#### 3.2.1. Experimental factors affection the adsorption

The results related to the impacts of the dye’s primary concentration and temperature on this adsorption are established in figure 4. As shown in this figure, the adsorption amount is increased by raising the concentration of this dye from 130 to 800 mg l$^{-1}$. This was due to the elevation of the adsorption dynamic force, which decreases the resistance of mass movement at the interface $^{[30, 31]}$. Whereas, over 800 mg l$^{-1}$, values of $q_e$ become constant because there are no vacant sites on the surface of CMLLP to adsorb extra dye molecules. Additionally, figure 4 illustrates that this adsorption is positively affected by temperature, because elevating the temperature has improved the dynamic energy of adsorbate particles and reduced the viscosity of solution $^{[32]}$. It was found that the adsorption quantities of MnO$_4^-$ by the modified sage leaves powder $^{[33]}$ increased by raising the temperature.

The results related to the shaking time effect on the adsorption of 130, 200 and 300 mg l$^{-1}$ of MB solutions by a fixed mass of CMLLP (0.02 g) are shown in figure 5. The adsorption amounts suddenly increased in the range of (0–30 min) because at this period time, most of the adsorption active sites were unoccupied. While adsorption slightly increased as the time of agitation rose from 30 to 300 min, most of the adsorption sites were filled up by adsorbate molecules. Furthermore, equilibrium obtained after 300 min, confirms that there is no empty active site for additional adsorption after 300 min $^{[33]}$.

The degree of adsorbate ionization and the adsorbent surface charge are significantly affected by the pH of adsorbate solutions $^{[34]}$. Where, the adsorbate in the solution will be in the molecular or ionic form when pH is less than or higher than its pKa, correspondingly, whereas, the charge on the adsorbent surface will be negative, zero or positive if the solution pH is higher than, equal to or less than the adsorbent pH$_{ZPC}$, respectively $^{[34]}$. 

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*Figure 6. Solution pH impact on MB adsorption by CMLLP.*

*Figure 7. Isotherm models of Langmuir for MB adsorption by CMLLP.*
Therefore, the impact of pH on the adsorption of MB (pKa = 3.8) by CMLLP (pH_{ZPC} = 6.2) was examined in this work as shown in figure 6. A slight increment in q_e values can be detected (figure 6) when the pH increased from 1 to 6.2. This is because the repulsion force between MB cations and the positively charged surface of CMLLP is lowered by the increasing pH in the range of (1–6.2). Whereas, the strident increase in values of q_e obtained after 6.2 is related to the attraction force between cations of MB and the negatively charged surface of this adsorbent [12].

3.2.2. Isotherms of adsorption

Figures 7–9 represent the Langmuir, Freundlich and Temkin isotherms. According to the isotherm constants and parameters presented in table 3, it can be noticed that the Langmuir equations is more suitable than the Freundlich and Temkin equations for the adsorption system studied in this work. This assumes homogenous distribution of active sites and monolayer adsorption. Moreover, all values of 1/n and R_L (table 3) are less than the unity, indicating that the conditions applied in the isotherm experiments (original pH, 20 mg of CMLLP, temperatures of 25, 35, 45, 60 °C, adsorbate initial concentrations ranged from 130 to 1400 mg/l and 12 h
Figure 11. 2nd order kinetic model for MB adsorption by CMLLP.

Figure 12. Diffusion of intra-particle kinetic model for MB adsorption by CMLLP.

Table 3. Isotherm parameters and separation factors for MB adsorption by CMLLP.

| Isotherm model | Temperature | q_{max} (mg/g) | K_L (l/mg) | R^2 | K_D (mg/g)/(l/mg) | 1/n | n | R^2 | K_T (l/mg) | B_1 | R^2 |
|---------------|-------------|----------------|-------------|-----|------------------|-----|----|-----|--------------|-----|-----|
| Langmuir      | 25 °C       | 333.33         | 0.0097      | 0.069 | 0.993            | 31.118 | 0.348 | 2.874 | 0.993 | 31.118 | 0.348 | 2.874 |
|               | 35 °C       | 384.62         | 0.0145      | 0.047 | 0.995            | 43.013 | 0.331 | 3.021 | 0.995 | 43.013 | 0.331 | 3.021 |
|               | 45 °C       | 434.78         | 0.0186      | 0.037 | 0.996            | 54.976 | 0.324 | 3.086 | 0.996 | 54.976 | 0.324 | 3.086 |
|               | 60 °C       | 476.19         | 0.0296      | 0.024 | 0.998            | 74.754 | 0.301 | 3.322 | 0.995 | 74.754 | 0.301 | 3.322 |

Table 4. Parameters of the 1st and 2nd order kinetic models for MB adsorption by CMLLP.

| Kinetic model | Ci (mg/l) | q_{exp} (mg/g) | q_{calc} (mg/g) | K_1 (h^{-1}) | R^2 | q_{calc} (mg/g) | K_2 (g/mgh) | R^2 | Rate |
|---------------|-----------|----------------|-----------------|--------------|-----|-----------------|--------------|-----|------|
| 1st order     | 130       | 85.35          | 22.11           | 0.006        | 0.881 | 86.21           | 0.0011       | 0.999 | 0.091 |
|               | 200       | 111.94         | 32.38           | 0.005        | 0.902 | 113.64          | 0.0006       | 0.999 | 0.070 |
|               | 300       | 141.76         | 70.99           | 0.006        | 0.973 | 144.93          | 0.0002       | 0.999 | 0.038 |
Similar outcomes were reported for adsorption of MnO₄⁻ by the modified sage leaves powder [33]. Table 3 also demonstrates that CMLLP has significant adsorption capacities (333.33, 384.62, 434.78 and 476.19 mg g⁻¹) towards MB at 25, 35, 45 and 60 °C, correspondingly. This confims that CMLLP will meet supplementary attention in the purification of polluted wastewater.

3.2.3. Kinetic parameters

The graphs of the kinetic models in their linear forms (table 2) are illustrated in figure 10 (1st order), figure 11 (2nd order) and figure 12 (Intraparticle-diffusion). The values related to the kinetic parameters of these three models were computed from the intercepts and slopes of the curves of these three figures. Parameters of the 1st and 2nd order models were listed in table 4, while, that of intraparticle-diffusion model were recorded in table 5. The curves of the 1st order model (figure 10) are less linear than that of the 2nd order (figure 11) and the correlation coefficient values of the 2nd order model (table 4) are higher than that of the 1st order. Moreover, the experimental values of qₑ are completely similar to values of qₑ evaluated by applying the 2nd order model and strongly differ from the values of qₑ computed using 1st order (table 4). All of those observations completely confirm that the data of the kinetic experiments for this adsorption can only be analyzed well by applying the model of 2nd order. This proves that MB molecules were chemically adsorbed on the surface of CMLLP through sharing, transfer or exchange of electrons [36, 37].

The curves in the case of intraparticle diffusion models (figure 12) are not linear in the range of the whole-time used in this work, not pass through the original point and divided into two linear regions. Additionally,
parameter C (table 5) has high values ranging from 37.52 to 61.82 and from 83.71 to 133.8 in the case of regions 1 and 2, respectively. These observations prove that the external diffusion contributed in the mechanism of this adsorption but was not the limiting step for the adsorption rate \[34, 38\].

### 3.2.4. Thermodynamic studies

The values of $\Delta S^\circ$ and $\Delta H^\circ$ were designed respectively from the intercepts and slopes of the curves represented in figure 13. Then these two parameters' values were used for calculation $\Delta G^\circ$ values by applying equation (4). All the values obtained in this part, were tabulated in table 6. The positive values of $\Delta S^\circ$ prove that the randomness at the border between the MB solution and the CMLLP surface decreased through the process of adsorption, while the $\Delta H^\circ$ positive values (table 6) confirm that MB adsorption by CMLLP is an endothermic process.

The values of $\Delta G^\circ$ are negative and increased as the temperature rose (table 6), which confirms that the adsorption of this dye by CMLLP is a spontaneous process and that the most important factor affecting this adsorption is the temperature, respectively \[15\].

### 4. Adsorption efficiency of MB by low-cost adsorbents

The adsorption efficiency of CMLLP and some low-cost adsorbent towards MB have been listed in table 7. This table confirms that CMLLP is the most effective compared to the other cheap adsorbents. This proves that the adsorbent used in this study will be of great relevance in the case of water decontamination.

### 5. Conclusions

ZnCl$_2$ was used as a chemical agent for modification the powder of Lamiaceae leaves. BET surface analyzer, FTIR, SEM and Theydan and Ahmed method were used for characterization the modified sample. It was found that this adsorbent has pH$_{ZPC}$ of 6.2, surface area of 104.78 m$^2$g$^{-1}$, pore volume of 0.00464 cc g$^{-1}$ and average pore diameter of 2647.813 Å. Then, the modified sample was used as a new and cheap adsorbent for purification of synthesized wastewaters from MB. Adsorption results confirmed that this adsorption was positively affected by all the experimental variables, experimental data fit well the Langmuir and model of 2nd order equations. MB adsorption is endothermic and spontaneous process. CMLLP adsorption capacities were 333.33, 384.62, 434.78 and 476.19 mg g$^{-1}$ at 25, 35, 45 and 60 °C, respectively. The findings suggest that the studied Lamiaceae leaves may be successfully used as promising low-cost adsorbent for removing dyes from wastewaters.
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