

Adsorption of Methylene Blue from Aqueous Solution onto a Low-Cost Natural Jordanian Tripoli

Atef S. ALzaydien

Department of Chemistry, Mutah University, P.O. Box 7, Jordan

Abstract: Problem statement: It is well documented that lead is one of contaminants of industrial wastewaters and its pollution exists in the wastewater of many industries. As a result, recent research has focused on the development of cost effective alternatives using various natural sources and industrial wastes. In this setting, the use of low-cost agricultural materials, waste and residues for recovering heavy metals from contaminated industrial effluent has emerged as a potential alternative method to high cost adsorbents. In the present study, adsorption of lead(II) ions onto Orange Peel (OP), a typical agricultural byproduct, was investigated systematically with the variation in the parameters of pH, sorbent dosage, contact time and the initial concentration of adsorbate. Langmuir and Freundlich isotherms were used to analyze the equilibrium data. Kinetic and thermodynamic parameters were also calculated to describe the adsorption mechanism. **Approach:** The Orange Peel (OP) was obtained from a local market in the south of Jordan. The orange peel was cut into small pieces using scissors. Then OP was dried at 100°C for 24 h using hot air oven. Qualitative analyses of the main functional groups involved in metal adsorption were performed using a Fourier transformed infrared spectrometer (Perkin-Elmer FTIR 1605, Uberlingen, Germany). Biosorption experiments were carried out in a thermostatic shaker at 180 rpm and at an ambient temperature (20±2°C) using 250 mL shaking flasks containing 100 mL of different concentrations and initial pH values of Pb(II) solutions, prepared from reagent grade salt Pb(NO₃)₂ (Merck). The initial pH values of the solutions were previously adjusted with 0.1 M HNO₃ or NaOH and measured using a hand held pH meters (315i/SET). The sorbent (0.2-1.0 g) was added to each flask and then the flasks were sealed up to prevent change of volume of the solution during the experiments. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and filtered through a Whatman filter paper. The filtrate was analyzed by AAS (Perkin Elmer Analyst 300). **Results:** Four kinetic models are the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion equations, were selected to interpret the adsorption data. Kinetic parameters such as the rate constants, equilibrium adsorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. The linear Langmuir and Freundlich models were applied to describe equilibrium isotherms and both models fitted well. The monolayer adsorption capacity was found as 21.1 mg g⁻¹ at pH 6 and 20°C. The dimensionless separation factor (R_L) has shown that orange peel can be used for removal of Pb(II) from aqueous solutions. The negative free energy of adsorption indicated that the adsorption of lead (II) ions onto orange peel was feasible and spontaneous. **Conclusion:** The sorption capacity of the orange peel is comparable to the other available adsorbents and it is quite cheaper.

Key words: Pb(II), orange peel, kinetics, adsorption isotherm, diffusion

INTRODUCTION

Dyes and pigments are widely used, mostly in the textiles, paper, plastics, leather, food and cosmetic industry to color products. Organic dyes are an integral part of many industrial effluents and demand an appropriate method to dispose them off. Most commercial dyes are chemically stable and are difficult to be removed from wastewater^[1]. At present, more

than 10,000 dyes have been effectively commercialized^[2].

The release of colored wastewater from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man through the food chain.

Various techniques like precipitation, ion exchange, chemical oxidation and adsorption have been

used for the removal of toxic pollutant from wastewater^[3-5]. Over the years, a number of workers have used different waste materials. They have studied the feasibility of using low cost materials, such as waste orange peel^[6], banana pith^[7], cotton waste, rice husk^[8], bentonite clay^[9], neem leaf powder,^[10] powdered activated sludge, perlite^[11], bamboo dust, coconut shell, groundnut shell, rice husk and straw, duck weed^[12], sewage sludge^[13], sawdust carbon^[14] and gram husk^[15], coal bottom ash^[16-18], bagasse fly ash^[19], blast furnace slag^[20], deoiled soya^[21,22], red mud^[23] and sawdust^[24] as adsorbents for removal of various dyes from wastewaters.

Methylene Blue (MB) is selected as a model compound for evaluating the potential of tripoli to remove dye from wastewaters. MB is a thiazine (cationic) dye, which is most commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools and so on. Although MB is not considered to be a very toxic dye, it can reveal very harmful effects on living things. After inhalation, symptoms such as difficulties in breathing, vomiting, diarrhea and nausea can occur in humans^[10].

Tripoli is a clay mineral, contains more than 92% SiO₂, available in large quantities in the southern part of Jordan. Commercial tripoli is available with 98 or 99% of silica and minor amounts of alumina and iron oxide, it's color may be white or brownish yellow or reddish depending upon the percentage of iron oxide^[25]. Chemical composition of tripoli from other sources is mentioned^[26].

In this study, Jordanian low-cost locally available tripoli was studied for its potential use as an adsorbent for removal of a cationic dye (methylene blue, MB) from aqueous solution. Factors affecting adsorption, such as, initial dye concentration, pH, contact time and adsorbent dose, were evaluated. The equilibrium of adsorption was modeled by using the Langmuir and Freundlich isotherm models, the kinetic parameters and intraparticle diffusion were also then determined for the methylene blue-tripoli system. Results of this study will be useful for future scale up using this clay material as a low-cost adsorbent for the removal of cationic dyes.

MATERIALS AND METHODS

Adsorbent: The raw tripoli samples were kindly supplied by the Authority of Natural Resources (Jordan, Amman). The fraction of the particles between 63-150 μm was used for adsorption study.

The chemical compositions of the raw tripoli were estimated by XRF (Philips Magix PW 2424). X-Ray Diffraction spectroscopy (XRD) analysis was carried

out with PANalytical X-ray, Philips Analytical. A dried sample of the produced material was ground using an agate mortar and pestle and tested at 40 kV and 40 mA.

Fourier transform infrared spectrophotometry (FT-IR) analysis was conducted for the produced samples by mixing a pre-dried sample of 3.0 mg with blank KBr and pressed hydraulically at 10 tons m⁻² to obtain a thin transparent disk, then analyzed using 8400S Shimadzu spectrophotometer.

The zero point charge (pH_{ZPC}) for the adsorbent was determined by introducing 1.0 g of tripoli into six 100 mL Erlenmeyer flasks containing 100 mL of 0.1 M potassium nitrate solution. Initial pH values of the six solutions were adjusted to 2, 4, 6, 8, 10 and 12 by either adding few drops of nitric acid or potassium hydroxide. The solution mixtures were allowed to equilibrate in an isothermal shaker (25±1°C) for 24 h. Then the suspension in each sample was filtered and the final pH was measured again. The procedure was repeated by varying the mass of tripoli introduced into the solution from 0.1-1.0 g. The value of pH_{ZPC} can be determined from the curve that cuts the pH₀ line of the plot Δ pH versus pH₀.

The Cation Exchange Capacity (CEC) of tripoli was estimated using The copper bis-ethylenediamine complex method^[27]. A quantity of 50 mL of 1 M CuCl₂ solution was mixed with 102 mL of 1 M ethylenediamine solution to allow the formation of the [Cu(en)₂]²⁺ complex. A slight excess of the amine ensures complete formation of the complex. The solution is diluted with water to 1 L to give a 0.05 M solution of the complex. A quantity of 0.5 g of dry adsorbent was mixed with 5 ml of the complex solution in a 100 mL flask and diluted with distilled water to 25 mL and the mixture was agitated for 30 min in a thermostatic water bath shaker and centrifuged. The concentration of the complex remaining in the supernatant was determined by mixing 5 mL of it with 5 mL of 0.1 M HCl to destroy the [Cu(en)₂]²⁺ complex, followed by adding 0.5 g KI mL⁻¹ and then titrating iodometrically with 0.02 M Na₂S₂O₃ in the presence of starch as an indicator. The CEC was calculated from the formula:

$$CEC (\text{meq } 100 \text{ g}^{-1}) = MSV (x - y)/1000 \text{ m} \quad (1)$$

Where:

M = The molar mass of the complex

S = Concentration of the thio solution

V = Volume (mL) of the complex taken for iodometric titration

m = Mass of adsorbent taken (g)

- x = Volume (mL) of thio required for blank titration (without the adsorbent)
 y = Volume (mL) of thio required for the titration (with the adsorbent)

The specific surface area of tripoli was estimated using Sears' method^[28] by agitating 1.5 g of the tripoli sample in 100 mL of diluted hydrochloric acid of a pH = 3. Then a 30 g of sodium chloride was added with stirring and the volume was made up to 150 mL with deionized water. The solution was titrated with 0.10 N NaOH and the volume, V, needed to raise the pH from 4-9 was then recorded. The surface area according to this method was calculated by the following equation:

$$S \text{ (m}^2 \text{ g}^{-1}\text{)} = 32 V - 25 \quad (2)$$

where, V is the volume of sodium hydroxide required to raise the pH of the sample from 4-9. This volume was measured in replicate and the average value was taken for the surface area calculation.

Preparation of MB solutions: All chemicals used in this study were of analytical-grade. Methylene Blue (MB), the basic dye used as the model sorbate in the present study is a monovalent cationic dye. It is classified as CI Basic blue 9, CI solvent blue 8, CI 52015. It has a molecular formula $C_{16}H_{18}N_3ClS$ and molecular weight of 319.85. Its molecule structure is shown in Fig. 1.

The MB used was of analytical grade so it was used without further purification. A stock solution of 1000 mg L^{-1} was prepared by dissolving an appropriate quantity of MB in a liter of deionized water. The working solutions were prepared by diluting the stock solution with deionized water to give the appropriate concentration of the working solutions.

Adsorption studies: The adsorption of MB on the native tripoli were investigated in a batch system. All adsorption experiments were conducted using 250 mL flasks, 100 mL of MB solution and weighted tripoli were added. The mixture was shaken in thermostated water bath at temperature of the experiment for different contact time at 160 rpm. The samples were withdrawn from the shaker at predetermined time intervals and adsorbent was separated from the solution by centrifugation at 4500 rpm for 10 min.

All experiments were performed in duplicate at least and mean values were presented with a maximum deviation of 5% in all the cases studied.

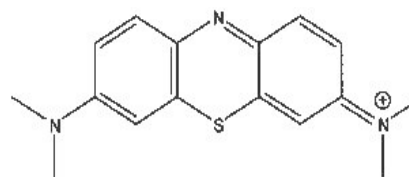


Fig. 1: Molecular structure of MB

Blank samples were run under similar experimental conditions but in the absence of adsorbent. It was not detected chemical precipitation and losses of MB to the containers wall.

Effect of pH on adsorption: The influence of the initial solution pH on the adsorption extent of MB onto tripoli was investigated in the pH range of 2-10 (which was adjusted with HCl or NaOH at the beginning of the experiment and not controlled afterwards) at a constant temperature of 25°C. The initial concentration of MB in the solution was in the range 50-300 mg L^{-1} and the amount of tripoli is 5.0 g dried weight per liter. The pH was measured using a 3151 MWT pH meter (MWT GmbH, Germany).

Equilibrium studies: Adsorption equilibrium studies were carried out by adding 0.5 g of tripoli in a series of 250 mL flasks containing 100 mL of MB solution of different dye concentrations at temperature of 25°C.

Kinetic studies: The experiments of adsorption kinetics were carried out in stirred batch mode. For each experiment, 0.1 L of the MB dye solution at specified concentrations was continuously stirred at 160 rpm with 0.5 g of tripoli at 25°C. Samples were withdrawn at appropriate time intervals and then centrifuged at 4000 rpm for 15 min and the absorbance of the supernatant was measured.

Analysis: The concentration of the residual dye was measured using UV/visible spectrometer at a λ_{max} corresponding to the maximum absorption for the dye solution ($\lambda_{max} = 661 \text{ nm}$) by withdrawing samples at fixed time intervals, centrifuged and the supernatant was analyzed for residual MB.

Dye uptake: The amount of dye adsorbed onto unit weight of adsorbent, $Q_e \text{ (mg g}^{-1}\text{)}$, was calculated from the mass balance equation given by:

$$Q_e = (C_0 - C_e)V \text{ m}^{-1} \quad (3)$$

Where:

C_0 = The initial dye concentration in liquid phase (mg L^{-1})

Ce = The liquid phase dye concentration at equilibrium (mg L⁻¹)
 V = The volume of dye solution used (L)
 M = The mass of adsorbent used (g)

Theory:

Isotherm models: The most common sorption models were used to fit the experimental data. These are Langmuir and Freundlich^[29,30]. The Langmuir model which assumes that equilibrium is attained when a monolayer of the adsorbate molecules saturates the adsorbent. The linear form of Langmuir model is given as:

$$C_e/Q_e = 1/K_L + a_L C_e / K_L \quad (4)$$

Where:

Ce = The equilibrium concentration of the adsorbate (mg L⁻¹)
 Qe = The amount of adsorbed per unit mass of adsorbent (mg g⁻¹)
 K_L (L mg⁻¹) = A constant related to the affinity between the adsorbent and the adsorbate
 K_L/a_L = The theoretical monolayer saturation capacity, Q_o

The values of Q_o and K_L can be determined by plotting Ce /Qe versus Ce.

The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless factor called separation factor (R_L, also called equilibrium parameter) which is defined by the following equation^[31]:

$$R_L = 1 / (1 + a_L C_0) \quad (5)$$

Where:

C₀ (mg L⁻¹) = The initial adsorbate concentration
 a_L (L mg⁻¹) = The Langmuir constant related to the energy of adsorption

The value of R_L indicates the shape of the isotherm to be either unfavorable (R_L>1), linear (R_L = 1), favorable (0 < R_L < 1) or irreversible (R_L = 0).

The second model is the Freundlich model. It often represents an initial surface adsorption followed by a condensation effect resulting from extremely strong solute-solute interaction. The linear form of this model takes the form:

$$\log Q_e = \log K_F + (1/n) \log C_e \quad (6)$$

Where:

K_F [(L mg⁻¹)^{1/n}] and n = Freundlich constants
 K_F = Correlated to the maximum adsorption capacity
 N = An indication of how favorable the adsorption process. The values of K_F and n can be obtained by plotting logQe versus logCe

Kinetic modeling: Two kinetic models are used to fit the experimental data. The rate of pseudo-second-order reaction is dependent on the amount of solute adsorbed on the surface of adsorbent and the amount adsorbed at equilibrium. The pseudo-second order model can be represented in the following form^[32,33]:

$$dQ_t / dt = k_2 (Q_e - Q_t)^2 \quad (7)$$

where, k₂ is the rate constant of pseudo-second-order model (g molL⁻¹ min). After integrating Eq. 12 for boundary conditions Q_t = 0 at t = 0 and Q_t = Q_t at t = t, the following form of equation can be obtained:

$$t/Q_t = 1/k_2 Q_e^2 + t / Q_e \quad (8)$$

The pseudo-second-order rate constant (k₂) and the equilibrium adsorption capacity (Qe) can be determined experimentally from the slope and intercept of the plot of t/Q_t versus t.

Half-adsorption time, t_{1/2}, is defined as the time required for the adsorption to take up half as much tripoli as its equilibrium value. This time is often used as a measure of the adsorption rate:

$$t_{1/2} = 1/k_2 Q_e \quad (9)$$

The nature of the rate-limiting step in a batch system can also be assessed from the properties of the solute and adsorbent. Weber and Morris^[34] stated that if intra-particle diffusion is the rate-controlling factor, uptake of the adsorbate varies with the square root of time. The root time dependence, known also as a Weber and Morris^[34] plot, may be expressed by Eq. 10:

$$Q_t = k_i t^{1/2} + C \quad (10)$$

where, k_i is an intra-particle diffusion rate parameter. According to Eq. 17, a plot of Q_t versus t^{0.5} should be a straight line with a slope k_i and intercept C when adsorption mechanism follows the intra-particle diffusion process. Values of intercept give an idea about the thickness of boundary layer, i.e., the larger the intercept the greater is the boundary layer effect^[35].

Thermodynamic parameters: The free energy of adsorption was evaluated from Langmuir isotherms using following equations^[36]:

$$\Delta G^\circ = -RT \ln K_L \quad (11)$$

Where:

T = The temperature
 R = Gas constant
 K_L = Langmuir constant

RESULTS

Characterization of tripoli: The chemical composition of the natural tripoli obtained by X-Ray Florescence (XRF) is 93.5% SiO₂, 2.39% Al₂O₃, 0.1% Na₂O, 0.08% Fe₂O₃, 0.07% CaO, 0.08% K₂O and 0.08% MgO. The major peak that appears in the XRD spectra for the natural tripoli that appears at 2θ of 26.7 is characteristic of SiO₂. Some of the other peaks that appear at 2θ of 36.5, 39.4, 45.86, 50.3 and 59.9 are also characteristic of quartz and other silicon oxide-containing phases.

A FT-IR spectrum of tripoli showed a wide band with maximum peak at 3439.3 cm⁻¹. This band can be assigned to the O-H stretching mode of hydroxyl groups and adsorbed water. The Si-O coordination bands at 1163.15, 1072.49 and cm⁻¹ are observed as a result of the Si-O vibrations. The peaks at 798.58 and 696.35 cm⁻¹ were attributed to Al-OH deformation and Al-O deformation. The bands at 626.90 and 518.88 cm⁻¹ represent the bending vibrations of Si-O-Si.

The specific surface area and Cation Exchange Capacity (CEC) of tripoli were 46.5 m² g⁻¹ and 1.85 meq g⁻¹, respectively. The value of pH_{ZPC} of tripoli was determined to be 1.8. the zero point of charge (pHzpc) should be less than 2.0. For pure silica oxide pHzpc value is 2.0^[37]. It is speculated that the causes of lower pHzpc value of tripoli particles is attributed to high silica oxide content versus to that of alumina, ferric and calcium oxides.

Effect of initial MB concentration: Effect of initial MB concentration on adsorption of MB by tripoli is shown in Fig. 2. The percent removal of MB decreased from 97-33% as the initial MB concentration increased from 50-250 mg L⁻¹.

Effect of pH on dye uptake: The removal of MB as a function of hydrogen ion concentration was examined at pH 2-10. The removal efficiency was found to be highly dependent on hydrogen ion concentration of

solution. The effect of pH on adsorption efficiency is shown in Fig. 3. The high adsorption yield was obtained at pH 8-10. The maximum adsorption efficiency was 97% at pH 8 and this pH value was selected as optimum pH for further studies.

Effect of adsorbent concentration on dye removal: Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions.

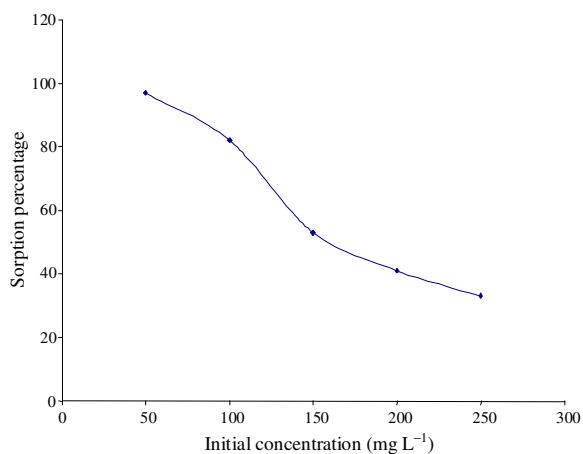


Fig. 2: Variation in adsorption of MB onto tripoli as a function of initial MB concentration, T = 25°C, pH = 8.0

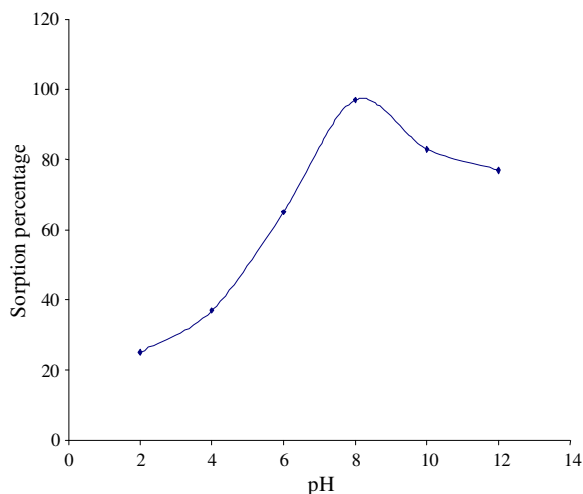


Fig. 3: Variation in adsorption of MB onto Tripoli as a function of pH initial MB concentration = 100 mg L⁻¹, T = 25°C

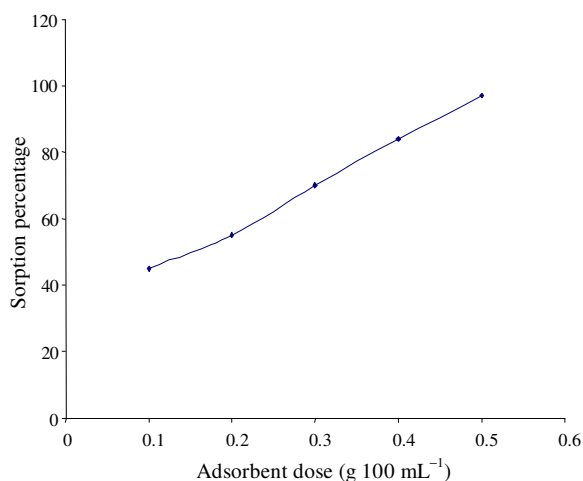


Fig. 4: Variation in adsorption of MB onto tripoli as a function of tripoli dose initial MB concentration = 100 mg L⁻¹, T = 25°C, pH = 8.0

Table 1: Summary of the Langmuir and Freundlich isotherm constants, separation factor (R_L) and linear (R²) regression coefficients

| Model | Parameters |
|------------|--|
| Langmuir | Q _{max} = 16.6 (mg g ⁻¹) K _L = 26.7 (L g ⁻¹) a _L = 1.6 (L mg ⁻¹) R _L = 0.0024-0.0123 R ² = 0.9999 |
| Freundlich | K _F = 9.98 (L g ⁻¹), n _F = 9.04 R ² = 0.8746 |

The results of the experiments with varying adsorbent concentrations are shown in Fig. 4. With increase in the adsorbent concentration, from 0.1-0.5 g 100 mL⁻¹, the amount of adsorbed MB removal increases from 45-97%. It is evident that the optimum amount of Tripoli for further adsorption experiments was selected as 0.5 g 100 mL⁻¹ and the removal of MB was found to be 97.2%.

Adsorption isotherms: The equilibrium data for the sorption of MB sorption on tripoli over the entire concentration range were fitted to the Langmuir isotherm. A linear plot was obtained when Ce/Qe was plotted against Ce over the entire concentration range (Fig. 5). The Langmuir model parameters and the statistical fits of the sorption data to this equation are shown in Table 1. Jaynes and Boyd^[44] proposed that the adsorption conforms to the Langmuir model when the value of the correlation coefficient (R² = 0.9999) is greater than 0.89. The R² values shown in Table 1 are greater than 0.89, indicating that the isotherms are consistent with Langmuir model.

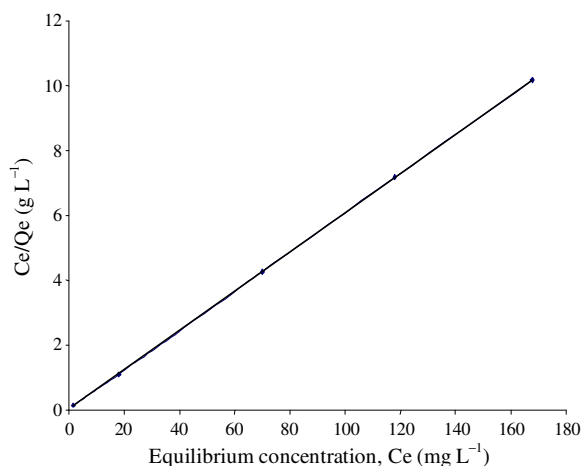


Fig. 5: Langmuir plots for the adsorption of MB onto tripoli

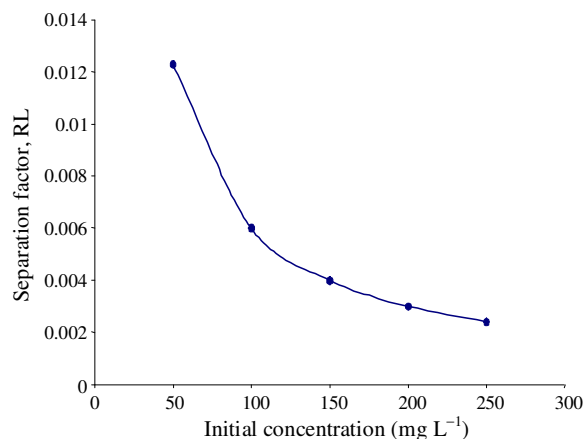


Fig. 6: Plot of separation factor versus initial MB concentration

Table 2: Comparison of adsorption capacities of various adsorbents for methylene blue

| Adsorbent | Q ₀ (mg g ⁻¹) | Temperature (°C) | Reference |
|--|--------------------------------------|------------------|------------|
| Sludge ash | 1.60 | 24 | [45] |
| Fly ash treated with HNO ₃ | 7.10 | 30 | [46] |
| <i>Caulerpa racemosa</i> var. <i>cylindracea</i> | 3.40 | 27 | [47] |
| Banana peel | 20.80 | 30 | [30] |
| Orange peel | 18.60 | 30 | [30] |
| Neem (<i>Azadirachta indica</i>) leaf powder | 8.76 | 27 | [10] |
| Sulphuric acid treated <i>Parthenium</i> (SWC) | 39.68 | 26 | [48] |
| Natural tripoli | 16.62 | 25 | This study |

Figure 6 shows the variation of separation factor (R_L) with initial MB concentration. The results that the R_L values were in the range of 0-1 indicate that the sorption of MB onto tripoli is favorable.

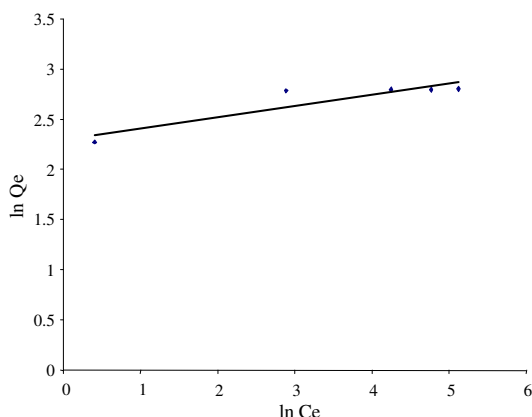


Fig. 7: Freundlich isotherm for MB uptake by tripoli

Figure 7 shows the linear plot of Freundlich isotherm of MB sorption on tripoli. Compared with the correlation coefficient value of the linear plot of Langmuir isotherm, that of Freundlich model was found less satisfactory ($R^2 = 0.8746$).

Adsorption kinetics: The chemical kinetic describes reaction pathways, along times to reach the equilibrium whereas chemical equilibrium gives no information about pathways and reaction rates. Therefore, a number of adsorption processes for pollutants have been studied in an attempt to find a suitable explanation for mechanisms and kinetics for sorting out environment solution.

Figure 8 shows influence of contact time on MB sorption on tripoli. It can be seen that sorption efficiency of MB increases with the increase of shaking time up to 120 min. Maximum sorption efficiency was attained as 97% at 25°C. Therefore, 120 min was selected as optimum shaking time for all further experiments.

In order to investigate the mechanism of adsorption various kinetic models have been suggested. In recent years, adsorption mechanisms involving kinetics-based models have been reported. In this study, some of these models were investigated to find the best fitted model for the experimental data obtained.

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Figure 9 shows the curve-fitting plot of the pseudo second-order equation and the parameters obtained for this model are shown in Table 3. The curve-fitting plots of t/Q_t versus t give a straight line, confirming the applicability of the pseudo second-order equation.

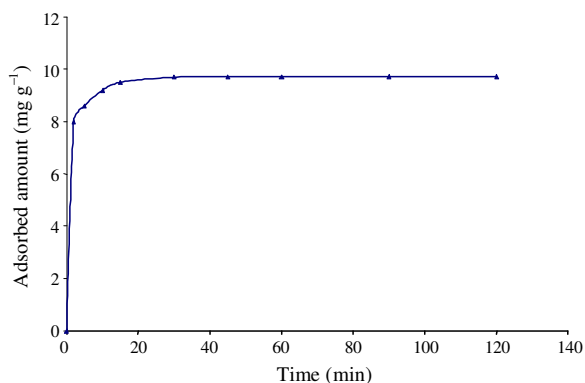


Fig. 8: Plot of the amount of MB adsorbed versus time, initial MB concentration = 100 mg L⁻¹, T = 25°C, pH = 8.0

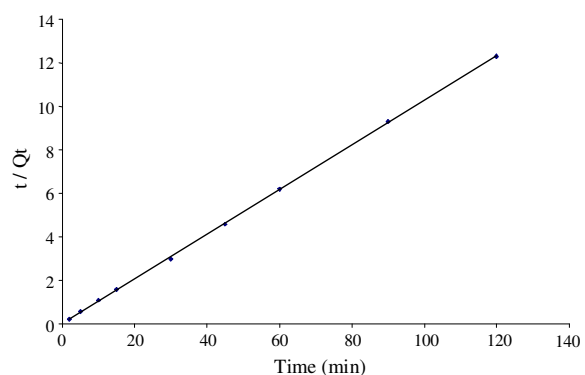


Fig. 9: Pseudo-second-order kinetic plot for the adsorption of MB onto tripoli initial MB concentration = 50 mg L⁻¹, tripoli dose 0.5 g, pH 8.0, at 25°C

Table 3: Kinetic parameters for the adsorption of MB on tripoli (pH 8.0, 25°C, initial MB concentration is 50 mg L⁻¹)

| | Models coefficients | R ² |
|--------------------------|--|----------------|
| Pseudo-second order | Qe = 9.76 mg g ⁻¹ k ₂ = 0.026 g mg ⁻¹ min ⁻¹ t _{1/2} = 4.15 min | 0.9987 |
| Intra-particle diffusion | k _i = 0.823 mg g ⁻¹ min ^{-1/2} | 0.9291 |

The correlation coefficients for the linear plots of t/Q_t against t for the second-order equation were observed to be close to 1 for the contact time of 120 min. The theoretical q_e values for the MB-tripoli system was also very close to the experimental q_e values in the case of pseudo second-order equation.

If the intra-particle diffusion is involved in the adsorption processes, then the plot of the square root of time versus the uptake (Q_t) would result in a linear relationship and the intraparticle diffusion would be controlling step if this line passed through the origin.

When the plots do not pass through the origin, this indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate controlling step, but also other processes may control the rate of adsorption^[52]. Such plots may present a multi-linearity, indicating that two or more steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes the gradual adsorption stage, where intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution^[553,54].

Gibbs free energy change: The free energy change (ΔG) for adsorption at 25°C was calculated using the Eq. 11. The calculated ΔG value were found to be -8.14 kJ mol⁻¹. The negative value of free energy change indicated the spontaneous nature of sorption and confirmed affinity of natural Jordanian tripoli for the MB basic dye.

DISCUSSION

Effect of initial MB concentration: The adsorption yield showed a decreasing trend as the initial MB concentration was increased. At lower concentrations, all MB present in the adsorption medium could interact with the binding sites on the surface of adsorbent so higher adsorption yields were obtained. At higher concentrations, lower adsorption yields were observed because of the saturation of the adsorption sites. Similar results were obtained for adsorption of MB by dehydrated wheat bran carbon^[38].

Effect of pH on dye uptake: The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity, influencing not only the surface charge of the adsorbent, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the adsorbent, but also the solution dye chemistry. It is commonly known fact that the anions are favorably adsorbed by the adsorbent at lower pH values due to presence of H⁺ ions. At high pH values, cations are adsorbed due to the negatively charged surface sites of tripoli.

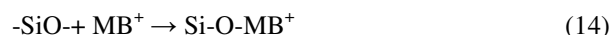
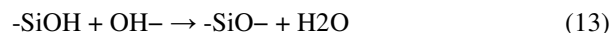
Any oxide surface creates a charge (positive or negative) on its surface. This charge is proportional to the pH of the solution which surrounds the oxide

particles. A convenient index of the propensity of a surface to become either positively or negatively charged as a function of pH is the value of the pH required to give zero net surface charge^[39]. The pH_{zpc} of tripoli is 1.8. At pH values above pH_{zpc} the clay had net negative charge and would, therefore, be prone to electro-statically attract cat-ions. MB is cationic basic dye as denoted by the presence of the positive nitrogen ions in its structure.

The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH values (pH < 2), the low adsorption observation was explained due to increase in positive charge (protons) density on the surface sites and thus, electrostatic repulsion occurred between the MB⁺ molecules and the edge groups with positive charge (Si OH²⁺) on the surface as follows:



At higher (pH > 2), the surface of tripoli clay becomes negatively charged and electrostatic repulsion decreases with raising pH due to reduction of positive charge density on the sorption edges thus resulting in an increase metal adsorption. This mechanism can be shown as follows:



A similar theory was proposed by several earlier workers for metal adsorption on different adsorbents^[40-42].

Effect of adsorbent concentration on dye removal: The variation in adsorption capacities between the various adsorbent dosages could be related to the type of surface group responsible for the adsorption of metal ions from solution. With increasing adsorbent dosage more surface area is available for the adsorption due to increase in active sites on the adsorbent and its availability for adsorption, making easier penetration of MB molecules to the adsorption sites and that increasing this number had also no effect after equilibrium was reached. Similar dependence was observed for adsorption of methylene blue onto bamboo-based activated carbon^[43].

Adsorption isotherms: The greater conformity of MB-tripoli to the Langmuir model suggests the surface sorption mechanism. The maximum sorption capacity of MB-tripoli (Q_0) and the Langmuir equilibrium constant (K_L) calculated from the slope and the intercept of the

linear plot were 16.6 mg g^{-1} and 26.7 L g^{-1} at 25°C , respectively. The value of The monolayer saturation capacity of tripoli, Q_0 , was comparable to the adsorption capacities of some other adsorbent materials for MB (Table 2). A direct comparison of literature data obtained using different adsorbents may not be appropriate since experimental conditions are not systematically the same.

Freundlich constant (K_F) and the heterogeneity factor ($1/n$) calculated from the slope and the intercept of the linear plot were 9.98 mg g^{-1} and 0.1106 , respectively. The value of $1/n$ smaller than 1 points out the favorable sorption conditions^[49,50].

The Langmuir and Freundlich isotherm constants, separation factor (R_L) and linear (R^2) regression coefficients are shown in Table 1.

Adsorption kinetics: It is clear from the accuracy of the model that the adsorption kinetic of the MB is described by a pseudo second-order chemical reaction and that this reaction is significant in the rate-controlling step. Physical adsorption and chemisorptions may be indistinguishable in certain situations and in some cases a degree of both types of bonding can be present, as with covalent bonds between two atoms having some degree of ionic character and vice versa. Although MB is considered to be organic compound, basic dye ionizes in solution to form positive ion. The structure of tripoli is metal oxides-based and the surface of metal oxides in contact with water is negatively charged at studied pH range, so it is likely that a chemical reaction may be taking place, which appears to be the main rate-determining factor in the adsorption process. In the adsorption of MB onto tripoli, the cationic dye carry charge opposite to that of the adsorbent, aiding the adsorption process. The mechanism of adsorption can also be described as chemisorptions, involving valency forces through sharing or the exchange of electrons between adsorbent and adsorbate as covalent forces. Allen *et al.*^[51] tested the application of pseudo first-and second-order equations for the description of the adsorption kinetics of three basic dyes onto kudzu, finding the pseudo second-order equation to be more suitable and stating that the chemical reaction was important and significant in the rate-controlling step^[35].

Figure 10 shows the amount of dye adsorbed versus $t^{1/2}$ for intraparticle transport of MB by tripoli. The results showed that the pots presented a multilinearity, which indicated that two or more steps occurred in the process.

As shown in Fig. 10, the external surface adsorption (stage 1). Stage 1 is the fastest and completed before 5 min and then the stage of intraparticle diffusion control (stage 2) is attained and continues from 5-35 min.

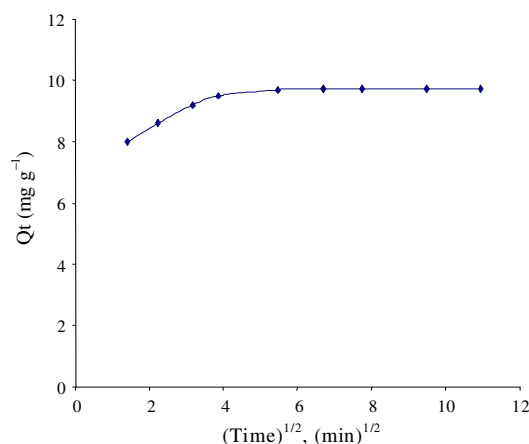


Fig. 10: Intraparticle diffusion kinetics for adsorption of MB onto tripoli: Initial concentration 50 mg L^{-1} , tripoli dose 0.5 g , pH 8.0 , at 25°C

Finally, final equilibrium adsorption (stage 3) starts after 35 min. The slope of the first linear portion (stage 2) characterizes the rate parameter corresponding to the intraparticle diffusion, whereas the intercept of this portion is proportional to the boundary layer thickness. The R^2 value for this diffusion model is 0.92 (Table 3). This indicates that the adsorption of MB onto tripoli can be followed by an intraparticle diffusion about 35 min. However, the lines do not pass through the origin (the plots have intercept of 7.8 mg g^{-1}), indicating that intraparticle diffusion is involved in the adsorption process but it is not the only rate limiting mechanism and that some other mechanisms also play an important role. Surface adsorption and intraparticle diffusion were likely to take place simultaneously, both the processes controlling the kinetics of dye-adsorbent interaction.

Gibbs free energy change: The negative value of free energy change indicated the spontaneous nature of sorption and confirmed affinity of natural Jordanian tripoli for the MB basic dye.

CONCLUSION

- The present study shows that the natural Jordanian tripoli, an abundant low-cost clay, can be used as sorbent for the removal of methylene blue dye from aqueous solutions
- The amount of dye sorbed was found to vary with initial pH, tripoli dose, methylene blue concentration and contact time
- The sorption equilibrium data were found to fit the Longmuir isotherm, indicating monolayer adsorption on a homogenous surface

- The value of The monolayer saturation capacity of tripoli was comparable to the adsorption capacities of some other adsorbent materials for MB dye
- Pseudo-second-order and intra-particle diffusion models model can be used to predict the adsorption kinetics
- The negative value of free energy change indicated the spontaneous nature of sorption and confirmed affinity of natural Jordanian tripoli for the MB basic dye

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