Adsorption mechanism of basic blue-9 onto quartz mineral: kinetics, isotherms and thermodynamic

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Abstract

Adsorption of basic blue-9 (BB9) by natural quartz mineral was tested. The quartz mineral was characterized by FTIR, SEM, DRX, zeta potential and Sear’s surface area measurements. The quartz mineral contains 99.13% of SiO₂ and has a specific surface area of 0.6 m² g⁻¹. The zeta potential measurements of quartz showed a zero point charge (ZPC) at a pH of 2.12. Adsorption experiments results of basic blue-9 showed an excellent achievement after 15 min, for 100 μm sorbent particles seize, 1.0 g l⁻¹ sorbent mass, pH of 5.0, agitation speed of 200 rpm and Temperature of 60 °C. Moreover, the BB9 concentration and temperature were directly related to increase in adsorption capacity and the highest adsorption capacity of 27.78 mg g⁻¹ was achieved for 30 mg l⁻¹ at 60 °C. Langmuir isotherm and pseudo-second-order kinetics (R² > 0.99) were found to be the most appropriate models to describe the removal of metylen blue dye by quartz mineral. The apparent diffusion parametres were estimated to be between 3.24 × 10⁻⁶ and 3.67 × 10⁻⁶ cm² s⁻¹, indicating an adsorption process controlled by the external mass transfert on the quartz surface. The calculated thermodynamic parameters and Dubinin–Radushkevich adsorption free energy (Eads = 0.28 kJ mol⁻¹) showed that adsorption of BB9 on quartz was spontaneous, endothermic and a physisorption reaction. FTIR spectroscopy and semi empirical RM1 calculations established an adsorption mecanism by electrostatic attraction. The regeneration tests after four runs showed that natural quartz could be an alternative material for cationic dyes removal.

1. Introduction

The major part of the industrial activities consumes big amounts of water and produces rejected wastes with variable degrees pollution [1]. Commercial dyes are prevalent in many aspects of our life in textile, paper, printing, carpet, plastic, food and cosmetic industries [2]. Dyeing waste showed substantial toxicity with EC20 and EC50 in the range of 5–9 [3]. Close to 15% of the generated charges (7 × 10⁵ tons/year) are emitted as effluents by the textile sector [4, 5]. The mutagenic, cytogenic and toxicity of both raw and treated textile effluents limits the aquatic biodiversity and causes several risks to human health [6]. As a consequence, the chemicals must be eliminated from the aquatic environment. Several approaches, involving biological, physico-chemical, and chemical procedures, have been used to remediate dye-containing effluents [7]. Adsorption is a successful method for removing dyes from wastewater in terms of efficiency and cost when compared to other traditional remediation method [8, 9]. Because commercially available synthetic adsorbents are expensive and difficult to regenerate, the present conjuncture of wastewater treatment develops the use of natural low-cost materials for color removal like natural minerals without any modification include calcite [10–12], dolomite [13], quartz [14], silicate [15, 16], silica quartz sand [17], phosphate [18], palygorskite [19], bentonite [20], montmorillonite [21], kaolin [22], zeolite [23], natural illitic clay [24], sepiolite [25] perlite [26], diatomite [27]. However, to the present day no published study of basic blue-9 (BB9) removal by adsorption onto quartz.
mineral as natural low-cost adsorbent. To the best of our knowledge, this is the first paper that showed full experimental and theoretical study on the adsorption of the cationic basic blue-9 (BB9) dye and its mechanism onto the quartz surface.

The present study reports the application of Algerian white quartz mineral as new sorbent for the removal by adsorption of basic blue-9 dye from aqueous solutions. The main parameters affecting the adsorption process such as agitation speed, sorbent dose, and particles size, pH value, temperature and contact times, were investigated. The isotherm constants for the Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) isotherms have been calculated using the linear models. Kinetics study was carried out using the pseudo-first-order (PFO), pseudo-second-order (PSO) and intra particle diffusion (IPD) models. The adsorption mechanism of BB9 onto quartz mineral was further analyzed by the thermodynamic, spectroscopic (FTIR) and the theoretical RM1 calculation.

2. Material and methods

2.1. Materials and reagents
A mining company (FERPHOS Mining Company, Algeria) provided the quartz material (figure 1). The samples are washed and dried (110 °C for 24 h), then 50 g of quartz was crushed in a ceramic ball mill and sieved for 10 min using ASTM standard sieves to get a size fraction of 80 μm and 100 μm used for adsorption experiments.

Hydrochloric acid HCl (37%; Merck), sodium hydroxide anhydrous NaOH (reagent grade ≥98%; Merck), potassium nitrate KNO₃ (assay >99%; Chemlab) and Nitric acid HNO₃ (purity >90.0%; Merck). Basic blue-9 (BB9) (dye content ≥95%; Sigma-Aldrich) is a cationic dye with MW of 319.85 g mol⁻¹ and a formula C₁₆H₁₈N₃SCl. The concentrations of BB9 were measured by a UV–Visible spectrophotometer (Shimadzu UVmini-1240 V) at a wavelength of 664 nm. The structure of the BB9 is shown in figure 2. The solutions pH was adjusted with 0.1 M HCl and/or NaOH.

2.2. Materials characterization
The chemical composition of the quartz mineral was determined using an electron microprobe (EMP, Cameca SX-50). X-ray diffraction analysis was carried out by a Bruker AXS diffractometer (10 kV; 10 mA;
CuKα = 1.54056 Å), data were recorded from 2θ = 10 to 120°. FTIR spectra are collected on JASCO 460 spectrophotometer in the range of 400–4000 cm\(^{-1}\). The surface area was measured by Sear’s method using the following equation: 
\[ S \text{ (m}^2\text{g}^{-1}) = \frac{(V_b - V_a)}{5} \times 32 \]  
where \( V_b \) and \( V_a \) are the volumes of the basic and acidic solutions [28].

2.3. Electrokinetic measurements
The electrokinetic characteristics were determined by a Lazer Zee Meter (Pen Kem Inc.), at a voltage of 100 V and a temperature of 20 °C. Quartz particles were suspended in KNO\(_3\) solution at 10\(^{-3}\) M and agitated for 2 h and then the pH was adjusted using 0.1M HNO\(_3\) and 0.1M NaOH solutions. OHAUS (Starter 3100) pH meter was used to measure solution pH before and after the zeta potential experiments [29].

2.4. Adsorption experiments
The amount of basic blue-9 adsorbed on quartz mineral was measured in batch adsorption tests. A 1 to 5 grams of quartz mineral that are 100 μm in size was kept in 100 ml of basic blue-9 concentrations (5–30 mg l\(^{-1}\)) at different temperatures (20 °C–60 °C), pH range from 1 to 13, agitation speed (0–500 rpm) and a contact time (0 to 90 min), were used to check their effect on removal efficiency. Following equilibrium, the amount of residual dye was determined at \( \lambda_{\text{max}} \) of 664 nm using an UV–vis spectrophotometer (Shimadzu UVmini-1240 V). The adsorption capacity (mg g\(^{-1}\)) and the uptake efficiency (R %) of quartz sorbent for basic blue-9 were calculated with equations (1) and (2) [30, 31]:
\[ q_e = \frac{(C_0 - C_e)V}{m} \]  
\[ R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \]  
Where \( C_0 \) and \( C_e \) denote initial and equilibrium concentrations (mg l\(^{-1}\)), m is the sorbent dose (g), and V is the solution volume (L).

2.5. Regeneration tests
The quartz was desorbed from the loaded basic blue-9 using 40 ml of 1 M CH\(_3\)COOH solution and stirred in a shaker at 120 rpm for 8 h. Then, the adsorbent was washed with distilled water and placed in the oven at 60 °C for 12 h. After drying, it was reused for 4 cycles [1].

2.6. Theoretical calculation
The possible interactions sites in quartz sorbent and the functional groups of BB9 dye were considered through the theoretical calculation of electronic charges and electrostatic potential distribution in basic blue-9 dye using HyperChem v8 software [32]. The geometry optimization of the BB9, Mulliken atomic charges and electrostatic potential were assessed by the semi empirical RM1 method derived from the Hartree–Fock theory [33].

3. Results and discussions
The chemical composition of quartz is given by an electron microprobe (EMP, Cameca SX-50). It contained about 99.13% SiO\(_2\), 0.34% CaO, 0.31% MgO and 0.22% Fe\(_2\)O\(_3\). The specific surface area of quartz measured by Sear’s method was 0.60 m\(^2\) g\(^{-1}\), this value agrees well with that found using the BET method, in which the quartz has a specific surface area of 0.62 m\(^2\) g\(^{-1}\) for N\(_2\), 0.67 m\(^2\) g\(^{-1}\) for Kr and 0.65 m\(^2\) g\(^{-1}\) for H\(_2\)O [34]. Figure 3, shows the x-ray Miller diffraction plane of quartz. The usual characteristic peaks of the quartz sample are around 2θ = 20.88°, 2θ = 26.78° and, 2θ = 50.01° and 2θ = 55.5°, 2θ = 60.0° and 2θ = 68.7° which correspond to the Miller indices: (110), (011), (112), (013), (211) and (031), by comparison with the standard JCPDS No. 5–0490 [35]. The quartz x-ray peaks are identical to those of pure quartz [36]. No shift in the diffraction peaks were detected in the x-ray pattern of the quartz after BB9 adsorption (the DRX pattern is not reported here).

FTIR analysis was used to evaluate the adsorbed BB9 functional groups on the quartz surface. Figures 4(a), (b) shows the FTIR spectra of the quartz before and after basic blue-9 dye adsorption. For the quartz mineral before adsorption (figure 4(a)), the most important absorption bands are in the range 470 cm\(^{-1}\) to 1100 cm\(^{-1}\), which corresponds to asymmetric and symmetric stretching of Si–O–Si groups at 1080 cm\(^{-1}\) and 779 cm\(^{-1}\). However, at 470 cm\(^{-1}\) and 520 cm\(^{-1}\), the –Si–O bending modes are seen [37]. The absorption peaks at 3500 cm\(^{-1}\) and 1630 cm\(^{-1}\) correspond to the stretching of hydroxyl group –OH and the deformation of the H\(_2\)O molecules, respectively. New peaks were observed after BB9 adsorption at 1340, 1370, and 1595 cm\(^{-1}\), these peaks are assigned to –C–N–, –C  =  N, and –C  =  C– stretching in the aromatic ring of basic blue-9 (figure 4(b)) [38].
Scanning electron microscopy (SEM) is used to study the surface morphology of quartz. Morphological characteristics of quartz mineral before and after BB9 dye adsorption are given in figures 5(a), (b). SEM photographs before adsorption (figure 5(a)) revealed an irregular porous texture (blue circle) with an important evolution of surface roughness. After BB9 adsorption the changement on the surface morphology reveals a rounded black deposit confirming the adsorption of this dye onto quartz surface (figure 5(b)).

The study of the chemical behaviour of the adsorbent/adsorbate materials may help to achieve the finest results in the sorption process. Figure 6, shows the zeta potential of quartz in KNO₃ electrolyte solution. As can be seen from figure 6, the zero point charge (Z.P.C) of quartz was determined to be at pHZPC close to 2.12, as the pH increases, the zeta potential of quartz increases negatively. This result was consistent with that reported for palygorskite [19]. Accordingly; palygorskite had negative surface charges in the entire measured pH range from 2 to 12. Above the pHZPC, the zeta potential is increased and the electrostatic attraction force increases between the negatively charged quartz particles and the positively charged basic blue-9 molecules, and thus the amount of adsorption increases [19]. At pH from 7.0 to 12.0, the zeta potential is less negative and varies from $-17.31 \text{ mV}$ to $-19.59 \text{ mV}$. However, at pH $< \text{pH}_{\text{ZPC}}$, the quartz surface is positively charged, and therefore likely to repel the basic blue-9 dye cations. The following reactions ascribed the quartz surface charges in acidic and basic medium [39]:

![Figure 3. XRD pattern of the quartz adsorbent.](image)

![Figure 4. FTIR spectra of quartz: (a) before and (b) after basic blue-9 adsorption.](image)
3.1. Effect of different parameters on adsorption

3.1.1. Effect of agitation speed

The effect of agitation speed on the removal capacity was studied from 50 to 700 rpm. The experimental conditions are kept constant, concentration of basic blue-9 (30 mg l\(^{-1}\)), quartz dose (1.5 g l\(^{-1}\)), contact time (15 min) and pH of 5.0. Figure 7 represents the removal efficiency of BB9 dye onto quartz as function of the stirring speed. It was observed that adsorption give increases with increasing in agitation speed (50 rpm) up to the optimal level (200 rpm). However, further grow in speed from 250 rpm to 700 rpm decline the adsorption efficiency. The divergence between the BB9 uptake at 500 rpm and 700 rpm is insignificant. The highest removal efficiency close to 80% was obtained at 200 rpm whereas the lowest of 59.70% at 50 rpm. Similar observation occurred during the adsorption experiments of basic blue-9 on kaolin and zeolite [23]. The external diffusion process may play a significant part in the basic blue-9 dye adsorption [39]. For an agitation speed between 50 rpm and 200 rpm, a plot of \(\ln(k_f)\) versus \(\ln(\text{rpm})\) (rpm: agitation speed), is expected to be linear [39]. The external surface diffusion coefficient (\(k_f; \text{min}^{-1}\)) was described by the bellow equation (\(R^2 = 0.982\)): 

\[
k_f = 8.51 \times 10^{-3} \text{ (rpm)}^{0.21}\]
3.1.2. Effect of quartz dose

To assess the impact of quartz mass on basic blue-9 adsorption at equilibrium, variable amount of sorbent from 1.0 to 5.0 g l\(^{-1}\) were used at 20 \(^\circ\)C, contact time (15 min), \(\text{pH} = 5\), agitation speed of 200 rpm and basic blue-9 dye concentration of 30 mg l\(^{-1}\). The adsorption efficiency decreases with increasing quartz dose and particles seize (figure 8). The smallest removal efficiency was 50% at 5.0 g l\(^{-1}\) whereas a maximum of 85% was reached at 1.0 g l\(^{-1}\). Also, the particle size influences the removal rates of BB9, as the size of the adsorbent particle decreases, the amount of dye retained increases. For the same sorbent mass of 1.0 gl\(^{-1}\) we reach removal rates around 85% and 42% for particle sizes of 80 \(\mu\)m and 100 \(\mu\)m, respectively. The further increase in quartz mass has a great effects on the removal efficiency. This behaviour could be explained by the aggregation of the small quartz particles at high values of adsorbent doses, leading to the decrease in the total sorbent surface available and consequently reducing the encounter probability (dye molecule- quartz site), thus leading of poorer quality retention [13, 39, 40].

3.1.3. Effect of pH variation

The amount adsorbed of basic blue-9 by quartz mineral at various pH ranges (1 to 13) was examined using 1.0 g l\(^{-1}\) of quartz sorbent, a contact time (15 min), \(\text{pH} = 5\), agitation speed of 200 rpm and an initial dye concentration of 30 mg l\(^{-1}\). The level of pH was adjusted by using 0.1 molar HCl and NaOH solutions. Figure 9 shows the influence of solution pH on BB9 uptake. The results demonstrate a significant impact of BB9 uptake by quartz when shifting the solution pH from 1–13. The adsorbed quantity increases from pH 1.0 to 5.0 to achieve a
maximum in BB9 retention of 25.45 mg g\(^{-1}\), then decreases when the pH rises above 6.0. The highest adsorption capacity was obtained at pH = 5 and dye solution of 30 mg l\(^{-1}\). From above results, it could be deduced that quartz mineral is favor to remove cationic dyes in weak acidic solution. The same results were observed at pH close to 5 for basic blue-9 adsorption on natural clay [40], Kaolin and zeolite [23].

The variation of the amount adsorbed of BB9 onto quartz with the variation in solution pH, can be explained regarding the quartz surface charges and the chemical speciation of blue methylene dye in solution [23]. Therefore, the pH\(_{pzc}\) of the quartz mineral in agreement to the different chemical forms of basic blue-9 molecules (figure 10) [41], are the main parameters influencing the adsorption process. The pH\(_{pzc}\) value of quartz mineral is found to be at a pH of 2.12 (see figure 6). In a very acidic medium (pH\(_{ZPC}\) < 2.12), an addition of H\(^{+}\) ions lower the pH leading to the neutralization of quartz silanol groups –Si–OH to –Si–OH\(_{2}^{+}\) [39]. Consequently, the number of negative sites decreases and the number of positively charged surface sites increases. The competition between H\(^{+}\) ions and the di-charged leuco base LH\(_{2}^{2+}\) [41], for the adsorption sites and the repulsive force between the positively charged adsorbent surface (–Si–OH\(_{2}^{+}\)) and leuco base (LH\(_{2}^{2+}\)), are considered the factors responsible for the lower adsorption uptake of BB9 at a low pH. When the pH increases (pH\(_{ZPC}\) < 6) there is a decrease in H\(^{+}\) ions, so the surface charge of quartz become progressively negative and this promotes the adsorption of the positively mono-charged blue methylene dye (–Si–O\(^{-}\)H). At pH > 6, we observe a decrease in the adsorption efficiency. This can be explained by the reduction of basic blue-9 to the neutral form leuco base (L) continues and the positive charges on the amine groups –N(CH\(_{3}\))\(_{2}\) disappear. This, leads to a decrease in the intensity of the electrostatic attraction between the negatively charged quartz surface (–Si–O\(^{-}\)) and the non charged methylene blue leuco base (L). At high pH, pH \(\geq\)7, OH\(^{-}\) ions promote both the deprotonation of BB9 and the adsorbent surface to generate a negatively charged surface as –Si–O\(^{-}\) and a deprotonated form of basic blue-9 dye as (L\(^{-}\)) [41]. Due to the confront for the adsorption sites between (OH\(^{-}\) ions) and (L\(^{-}\) deprotonated molecules, in addition to the repulsive effect between the negatively charged quartz surface and BB9 molecules [(–Si–O\(^{-}\))/(L\(^{-}\))] the adsorption capacity is extremely lowered.

### 3.1.4. Effect of temperature

Temperature is an extremely significant parameter in the adsorption process. Adsorption of basic blue-9 onto quartz was considered at various temperatures ranging from 20 to 60 °C while remaining constant all experimental set conditions. Figure 11 shows increases in adsorption capacity with an increase in temperature. The highest adsorption capacity of 27.78 mg g\(^{-1}\) was recorded at 60 °C whereas the lowest of 24.66 mg g\(^{-1}\) at 20 °C. An increase in temperature may enhance the diffusion of BB9 molecules that could elevate the adsorption amount [1]. Furthermore, the results means that the BB9 are principally endothermic process, which connect that the amount of dye adsorbed increases with temperatures [40, 46].

### 3.1.5. Effect of contact time

The adsorption study of basic blue-9 dye onto quartz sorbent, involves an assessment of the effect of contact time on adsorption efficiency. For this purpose, adsorption was carried out with basic blue-9 solutions at initial concentrations from 5 to 30 mg l\(^{-1}\), quartz dose 1.0 g l\(^{-1}\), at 20 °C and time intervals ranging from 0 to 90 min.

![Figure 9. Effect of solution pH on BB9 uptake. ([BB9] = 30 mg l\(^{-1}\), T = 20 °C, quartz dose = 1.0 g l\(^{-1}\), contact time = 15 min and agitation speed = 200 rpm).](image-url)
Figure 10. Different chemical forms of basic blue-9 molecules [41].

Figure 11. Effect of temperature on BB9 adsorption capacity. ([BB9] = 30 mg l⁻¹, quartz dose = 1.0 g l⁻¹, contact time = 15 min, pH = 5, agitation speed = 200 rpm).
The plot of $q_t$ against contact time is showed in figure 12. The highest adsorption capacity of BB9 was observed within 15 min. The amount adsorbed increases with increasing BB9 dye concentrations. The quartz mineral exhibited adsorption capacities at initial dye concentrations of 5, 10, 20 and 30 mg l$^{-1}$ close to 4.40, 8.03, 17.04 and 25.46 mg g$^{-1}$, respectively. The faster adsorption kinetics is correlated to the quick diffusion of BB9 molecules onto quartz surface, to the various active sites available on the sorbent surface, to the agitation speed and the strong electrostatic interaction between the negatively charged quartz surface and the cationic basic blue-9 [1, 38–40]. When compared to other adsorbents [37–40, 44–49], the quantity of BB9 adsorbed onto quartz is not higher but as natural materials, it is abundant and cheap, so quartz can be used to remove basic blue-9 from solution.

3.2. Adsorption kinetics

The Kinetic adsorption characteristic of basic blue-9 dye onto quartz mineral was determined by the linear pseudo first order (PFO) and pseudo second order (PSO) kinetic models expressed by equations (3) and (4), respectively [30].

$$\frac{1}{q_t} = \frac{1}{q_e} + \left( \frac{K_1}{q_e} \right) \times \left( \frac{1}{t} \right)$$  \hspace{1cm} (3)

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \left( \frac{1}{q_e} \right) t$$  \hspace{1cm} (4)

Where $q_e$ and $q_t$ (mg g$^{-1}$) are the adsorption quantity at equilibrium and time $t$ (min), respectively. $K_1$ (min$^{-1}$) and $K_2$ (g mg$^{-1}$ min$^{-1}$) are the PFO and PSO rate constants, respectively. The kinetic rate constants $K_1$ and $q_e$ (equation (3)) were determined from the plots of $1/q_t$ against $1/t$. However, $K_2$ and $q_e$ (equation (4)) may be calculated by plotting $t/q_t$ against $t$.

Figures 13(a), (b) and table 1 show the results obtained from the linear regression of the kinetics data of BB9 adsorption to the pseudo first order and pseudo-second-order models.

Figure 13(a) shows the plot of the pseudo first order kinetics model. A small divergence between the experimental ($q_{e,exp}$) and calculated ($q_{e,cal}$) values of the adsorption capacities. The calculated values of the determination coefficients ($R^2$) are 0.938, 0.911, 0.938 and 0.956, respectively. The (%) error between experimental ($q_{e,exp}$) and estimated ($q_{e,cal}$) adsorption capacities are between 2.89% and 5.39%. Moreover, the rate constant $K_1$ values decreases from 0.914 min$^{-1}$ to 0.515 min$^{-1}$ when increasing the dye concentrations from 5 mg l$^{-1}$ to 30 mg l$^{-1}$. This observation suggest that adsorption of BB9 dye on quartz mineral does not obey the pseudo first order mode. The plotted curve for the pseudo second order model is shown in figure 13(b). The experimental data were better fitted to the PSO model, the values of $R^2$ were closest to 1.0 ($R^2 > 0.999$). The calculated adsorbed quantity $q_{e,cal}$ increases when increasing the initial dye concentration, while the kinetics rate constant $K_2$ decreases from 0.41 to 0.13 (g mg$^{-1}$ min$^{-1}$). In addition, the amount adsorbed ($q_{e,cal}$) agreed with the experimental adsorption data ($q_{e,exp}$), the % error vary from 0.64 to 0.91. The PSO kinetics model was better than that for the pseudo first order model (table 1). The adsorption of BB9 dye onto quartz mineral was most
likely a pseudo second order process, because it possessed the higher $R^2$ value according to the results. Similar results have been reported for various adsorbent such as: palygorskite $^{1}$, dolomite $^{13}$, kaolin $^{22}$, zeolite $^{23}$, diatomite $^{26}$, natural clay $^{40}$ and pyrophyllite $^{47}$.

The intraparticle diffusion (IPD) model in equation (5) is also used to analyze the diffusion mechanism $^{30}$.

$$q_t = K_p t^{1/2} + C$$

where $q_t$ is the adsorption capacity (mg mg$^{-1}$), $K_p$ is the intraparticle diffusion rate (g mg$^{-1}$ min$^{-1/2}$) and $C$ is a constant that provides information regarding the boundary layer.

The plot of $q_t$ against $t^{0.5}$ is used to calculate the intraparticle diffusion rate. The values of the diffusion parameter (D) are deduced from the following formula $^{30}$.

| C0 (mg l$^{-1}$) | $q_{e,exp}$ (mg g$^{-1}$) | $K_1$ (min$^{-1}$) | $q_{e,cal}$ (mg g$^{-1}$) | $R^2$ | % Error | K2 (g mg$^{-1}$ min$^{-1}$) | $q_{e,cal}$ (mg g$^{-1}$) | $R^2$ | % Error |
|-----------------|-----------------|-----------------|-----------------|-------|--------|-----------------|-----------------|-------|--------|
| 5               | 4.402           | 0.914           | 4.589           | 0.938 | 4.07   | 0.333           | 19.697         | 0.99  | 0.81   |
| 10              | 8.032           | 0.841           | 8.49            | 0.911 | 5.39   | 0.410           | 65.352         | 1.00  | 0.64   |
| 20              | 17.041          | 0.711           | 17.575          | 0.938 | 3.04   | 0.144           | 295.734        | 1.00  | 0.91   |
| 30              | 25.462          | 0.513           | 26.219          | 0.956 | 2.89   | 0.131           | 659.151        | 1.00  | 0.83   |

* % Error = $|q_{e,cal} - q_{e,exp}| / q_{e,cal}$, $q_{e,cal}$ and $q_{e,exp}$ are the experimental and calculated.
Where \( t^{1/2} \) is a half-time reaction (s) (adsorption equilibrium reaction), \( r_0 \) is the particle diameter of the adsorbent in (cm), and \( D \) is intraparticle diffusion parameter (cm\(^2\) s\(^{-1}\)).

Figure 14 presents the plots of \( q_t \) versus \( t^{1/2} \) for BB9 at different concentrations (5, 10, 20 and 30 mg l\(^{-1}\)). The values of the external diffusion constant \( K_p \), diffusion coefficients (\( D; \) cm\(^2\) s\(^{-1}\)) and \( R^2 \) coefficients are listed in Table 2.

Figure 14 shows multilinearity lines, implying that two adsorption phases are taking place. The values of intraparticle diffusion constant \( K_{p,IPD} \) and the intercept \( C; \) mg mg\(^{-1}\)) are observed to have increasing values by increasing BB9 concentrations. When comparing the values of \( C_1, C_2, C_3, C_4 \) and \( K_{p,1}, K_{p,2}, K_{p,3}, K_{p,4} \) for the concentrations range 5–30 mg l\(^{-1}\) (Table 2), we found that they follow the rule \( C_1 < C_2 < C_3 < C_4 \) and \( K_{p,4} > K_{p,3} > K_{p,2} > K_{p,1} \) indicating an individual increase in the boundary layer on the adsorption stages [26, 39].

It is observed from Table 2 that the effective diffusion coefficient \( D \) increase from \( 3.24 \times 10^{-6} \) to \( 3.67 \times 10^{-6} \) cm\(^2\) s\(^{-1}\) with change in concentrations from 5 to 30 mg l\(^{-1}\). According to Singh et al [42], a D value on the order of \( 10^{-11} \) cm\(^2\) s\(^{-1}\) is indicative of intraparticle diffusion as rate-determining step in the adsorption process. In this study, the values of diffusion coefficient obtained are in the order of \( 10^{-6} \) cm\(^2\) s\(^{-1}\), which are five orders of magnitude greater than the value quoted by Singh et al [35]. This indicates that intraparticle diffusion was not the rate-controlling step. The diffusion coefficient values of methylene blue on quartz are in the order of \( 10^{-6} \) cm\(^2\) s\(^{-1}\) with change in concentrations from 5 to 30 mg l\(^{-1}\). In the IPD model, the values of \( R^2 \) (< 0.95) were lower than in the pseudo-second-order (PSO) model. Hence, it was concluded that the intraparticle diffusion models cannot be applied as the limiting step, but other kinetic processes may be operating simultaneously [40, 42, 43].

\[
D = \frac{0.03 \times \sigma_0}{t^{1/2}} \tag{6}
\]

Table 2. IPD parameters for BB9 adsorption onto quartz.

| \( C_0 \) (mg l\(^{-1}\)) | \( K_p \) (mg g\(^{-1}\) min\(^{0.5}\)) | \( C \) | \( R^2 \) | \( D \) (cm\(^2\) s\(^{-1}\)) |
|----------------|----------------|-----|------|-------------|
| 5              | 1.849          | 0.435  | 0.971 | 3.50 \times 10^{-6} |
| 10             | 3.543          | 0.798  | 0.951 | 3.67 \times 10^{-6} |
| 20             | 5.333          | 4.688  | 0.962 | 3.24 \times 10^{-6} |
| 30             | 7.701          | 9.342  | 0.948 | 3.58 \times 10^{-6} |

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3.3. Adsorption isotherm

Adsorption isotherms are important for the analysis of adsorption data. Finding the most suitable model that can be used to describe the adsorption process is an important step. In this part, Langmuir (equation (7)) and Freundlich (equation (8)) isothermal models were used to reveal the experimental data [45].

\[
\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L}\right) \times \frac{1}{C_e}
\]

(7)

\[
\log (q_e) = \log K_F + \left(\frac{1}{n}\right) \log (C_e)
\]

(8)

Where \( q_e \) and \( C_e \) are the adsorbed amount (mg g\(^{-1}\)) and equilibrium concentration (mg l\(^{-1}\)), respectively; \( q_m \) is the highest adsorbed capacity (mg g\(^{-1}\)) and \( K_L \) (L mg\(^{-1}\)) is the Langmuir constant. \( K_F \) and \( n \); Freundlich’s uptake and intensity factors.

The Langmuir and Freundlich isotherm constants as well as the coefficients of determination were obtained using the linear method which consisted of plotting \( 1/q_e \) versus \( 1/C_e \) (equation (7)) and \( \log (q_e) \) versus \( \log (C_e) \) (equation (8)), respectively. The obtained results are presented in figure 15 and listed in table 3.

The results in figure 15(a) and table 3, shows the \( R^2 \) (0.997) values of the Langmuir model higher than that of the Freundlich model models. The predicted sorption capacity (\( q_m \)) is equal to 25.54 mg g\(^{-1}\), which is close of the experimental value, suggesting a monolayer arrangement of BB9 onto quartz surface [1, 25, 39]. In addition, the calculated Langmuir constant (\( K_L \)) is 1.17 (L mg\(^{-1}\)) and the separation factor \( R_e \) equals to 0.03 indicating a favorable adsorption process [40]. The Freundlich model in figure 15(b), with a correlation coefficient \( R^2 \) of 0.984 did not meet the requirements of the experimental data. However, the result of \( 1/n \) is equal to 0.39, indicating an effective adsorption capacity on heterogeneous surface [48]. From the values of \( R^2 \) and the (%), errors, it is apparent that the Langmuir model better described the basic blue-9 adsorption onto quartz surface. A similar result was obtained in previous investigations for natural clay [40], kaolinite [37], and dolomite [13]. The authors found that the Langmuir model described the equilibrium adsorption data well for basic blue-9 adsorption. Compared with other absorbents (see table 5), the quartz mineral have potential for removal cationic dyes from wastewater.
Dubinin–Radushkevich (D-R) isotherm (equation (9)) [46], is also used to distinguish between the nature of adsorption process (physical/chemical).

\[ \ln q_e = \ln(q_s) - \beta \varepsilon^2 \]

(9)

Where \( q_e \) the equilibrium amount of solute adsorbed (mg g\(^{-1}\)); \( q_s \) is the saturation capacity (mg g\(^{-1}\)); \( \beta \) is the activity coefficient related to mean free energy (Eads\(^{\circ}\)) of adsorption (mol\(^2\) kJ\(^{-2}\)); \( \varepsilon \) is the Polanyi potential.

In the D–R model, the adsorption average free energy Eads\(^{\circ}\) (kJ mol\(^{-1}\)) is calculated by (equation (10));

\[ E_{ads} = \left( \frac{1}{\sqrt{2\beta}} \right) \]

(10)

Figure 15(c) and table 3 displays the Dubinin–Radushkevich constants (\( q_s, \beta \) and Eads\(^{\circ}\)) resulting from the linear fitting of the ln (\( q_e \)) versus \( \varepsilon^2 \). It has been established that adsorption is physical in character if Eads\(^{\circ} < 8\) (kJ mol\(^{-1}\)) [47]. The calculated adsorption free energy is 0.28 (kJ mol\(^{-1}\)), suggesting that physisorption is the prevailing adsorption mechanism for basic blue-9 onto quartz mineral.

### Table 3. Parameters of Langmuir, Freundlich and Dubinin–Radushkevich isothermal models for BB9 adsorption onto quartz.

| Method       | \( q_{\text{max}} \) (mg g\(^{-1}\)) | \( K_L \) (L mg\(^{-1}\)) | R² | % Error* |
|--------------|-------------------------------|-----------------------------|----|----------|
| Langmuir     | 0.03357 + 0.03915.X            | 0.166                       | 0.997 | 0.32     |
| Freundlich   | 0.77499 + 0.38786.X           | 0.168                       | 0.984 |          |
| Dubinin–Radushkevich | 3.05281–6.29636.X | 8.86 × 10\(^{-4}\) | -6.296 | 0.282 | 0.939 |

* % Error = \( \frac{|q_{\text{exp}} - q_{\text{cal}}|}{q_{\text{cal}}} \times 100\% \)

### Table 4. Thermodynamic parameters of adsorption of BB9 onto quartz.

| \( \frac{1}{T} \times 10^{-3} \) | \( \Delta H \) (kJ mol\(^{-1}\)) | \( \Delta S \) (kJ mol\(^{-1}\) K\(^{-1}\)) | \( \Delta G \) (kJ mol\(^{-1}\)) |
|-------------------|----------------------|----------------------|----------------------|
| 3.41              | 2.684                | 18.495               | -6.337               |
| 3.30              | 2.800                | 18.715               | -7.285               |
| 3.19              | 3.040                | 19.031               | -8.535               |
| 3.09              | 3.185                | 19.635               | -9.867               |
| 3.00              | 3.641                | 20.095               | -9.725               |

3.4. Adsorption thermodynamic

Adsorption data of BB9 dye onto quartz at different temperatures from 20 °C to 60 °C were used to assess the thermodynamic parameters. The values of thermodynamic parameters (\( \Delta H^0 \), \( \Delta S^0 \) and \( \Delta G^0 \)) at different temperatures were calculated from the Van’t Hoff equation (11) and the Gibb’s free energy (\( \Delta G^0 \)) were calculated according to equation (12) [48].

\[ \ln(K_L) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \]

(11)

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]

(12)

Where: \( K_L = (q_s / C_s) \) is the thermodynamic equilibrium constant; \( \Delta S^0 \) is standard entropy change (J mol\(^{-1}\) K\(^{-1}\)); \( \Delta H^0 \) is enthalpy change (J mol\(^{-1}\)); \( \Delta G^0 \) is Gibbs free energy change (J mol\(^{-1}\)); R the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)); and T (°K).

Ln \( K_L \) was plotted versus (1/T), value of \( \Delta H \) was calculated from the slope and \( \Delta S^0 \) from the intercept as shown in figure 15(d) and table 4. The Value of \( \Delta H^0 \) (+18.50 kJ mol\(^{-1}\)) is positive signifying an endothermic adsorption process [40, 43]. Positive values of \( \Delta S^0 \) (+84.71 J mol\(^{-1}\) K\(^{-1}\)) confirmed the increased randomness on BB9/quartz interface during adsorption [40, 46]. The \( \Delta G \) values for the temperatures ranges (20 °C–60 °C) were obtained between -9.725 and -6.337 kJ mol\(^{-1}\), this indicated a spontaneous adsorption progression and
higher temperature favored the adsorption [43]. The negative value of $\Delta G^0$ localized in the free energy physisorption region ($-20$ and $0$ kJ mol$^{-1}$) [48], suggested a physical adsorption process.

### 3.5. Regeneration propriety

Regeneration of the adsorbent is important for industrial application. Figure 16 presents the results of removal efficiency (%) in the first five removal–regeneration cycles for quartz mineral. The results obtained, indicated that the BB9 uptake is decreased by a percentage of 13.46% after five cycles of reuse. This means that the removed basic blue-9molecules were weakly attached to the adsorption sites of quartz. It could be concluded that quartz mineral has a strong regeneration performance and can be reused as a potential adsorbent for cationic dyes contaminated water.

To assess quartz mineral as a prospective sorbent, the maximum adsorption capacity of basic blue-9dye is compared to that of other natural low cost adsorbents published in the literature. According to table 5, the quartz mineral engaged in this investigation has a satisfactory adsorption potential as compared to other reported natural material. Also, because of the natural character and geological abundance in Algeria, the quartz mineral used in this study is cheap and presents an economic advantage as low-cost adsorbent.

### 3.6. Theoretical calculation and adsorption mecanism

The possible interaction sites through semi empirical computation of electronic charge distribution and electrostatic potential was investigated. The interactions between acidic or basic silanols groups in quartz...
mineral and BB9 dye were considered. Mulliken atomic charges and 2D total charge density were calculated by the semi-empirical RM1 theoretical method and presented in figure 17. For BB9 dye, the most of the negative charges were centered in the left side of the molecule onto carbon atoms forming the double bonds in the benzene ring (–C = C–; −0.064e, −0.153e), in the carbon atoms of alkyl groups –CH3 (–C; −0.105 and −0.112 e⁻), nitrogen atoms in the alkyl amine group –N⁺H(Me)2 (–N; −0.161 e⁻) and nitrogen atoms in the middle ring (–N; −0.381 e⁻), while the positive charges were situated on the sulfur (–S; +0.330e⁻), nitrogen atoms of the alkyl amine group of the right side of BB9 –N(Me)2 (–N; +0.373 e⁻) and hydrogen atoms in all molecule (–H, +0.046, +0.038, and + 0.047 e⁻). From the calculated 2D total charge density of BB9, we conclude that the half side of the molecule with nitrogen heteroatoms (–NH), terminal alkyl (–CH₃) and alkyl amine groups –N(CH₃)₂ are the most positively charged.

The chemical reactivity of materials is better perceptive by the electric potential surface (ESP). It is useful to detect favorable interaction sites in molecules. Figure 18 illustrates the RM1 calculated 3D mapped isosurface of the electrostatic potential surrounding the BB9 molecule. The red colors indicate negative potential regions (−0.114−0 esu), followed by green colors, which denote strong positive potential regions (0−0.268). Positively charged molecules tend to interact with the sites where the electrostatic potential is strongly negative.

The physical adsorption in BB9/quartz systems occurs by electrostatic attraction. Basic blue-9 molecules will have a predisposition to orient their self preferentially to the quartz surface by the sides possessing the highest values of positive charge density: (i) orientation via the nitrogen atoms of the alkyl amine groups –N(CH₃)₂ situated in the first extremity of the molecule; (ii) orientation with the nitrogen heteroatom (–N) in the midle ring. The envisageable orientations of BB9 molecules in parallel and anti-parallel positions considering the negatively charged quartz surface (–Si–O⁻) were presented in figure 19.

4. Conclusions

Natural quartz material was studied using x-ray diffraction, FT-IR spectroscopy, particle size distribution, Zeta potential, and Sear’s surface area measurements. The sample used in this examination includes 99.13% SiO₂ and has a surface area of 0.6 (m² g⁻¹). According to zeta potential measurements, the quartz seize fraction (–80 μm +100 μm) had a zero point charge point (Z.P.C.) at pHZPC = 2.12. Quartz mineral showed a good adsorption capability to basic blue-9 dye, with a highest experimental quantity of 25.64 (mg g⁻¹) after only 15 min. The
Figure 18. RM1 calculated (3D) mapped isosurface surrounding the BB9 molecule.

Figure 19. Proposed mechanism of BB9 adsorption onto quartz surface with the molecular plane orientations parallel and anti parallel.
adsorption isotherm was suitable for the Langmuir model, indicative of a monolayer adsorption process. The adsorption kinetic fit well the pseudo second order kinetics model. The effective diffusion parameters (D_e) were particularly elevated of 10^{-6} cm^2 s^{-1}, indicating an adsorption process consisting essentially by external mass transfer on the quartz surface. The thermodynamic parameters indicated spontaneous, endothermic and physical adsorption process. Adsorption mechanism based on the theoretical RM1 calculations revealed that basic blue-9 dye can be adsorbed onto quartz surface by electrostatic interaction with two envisageable orientations parallel and anti-parallel positions. The calculated Dubinin–Radushkevich adsorption energy (E_{ads}) was 0.28 (kJ mol^{-1}), implying that the adsorption was predominantly physical in nature confirming the proposed mechanism. The regeneration tests indicated that quartz mineral has a stable reuse after four cycles, this provide a new insight into designing quartz mineral for the removal of cationic pollutants from aqueous solutions.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Silva V C, Araújo M E B, Rodrigues A M, Cartaxo J M, Menezes R R and Neves G A 2020 Adsorption behavior of acid-treated Brazilian palygorskite for cationic and anionic dyes removal from the water Sustainable 13 3954
[2] Elwakded K Z, Elgarahy A M, Elshoubyaka G A and Mohammad S H 2020 Microwave assist sorption of crystal violet and Congo red dyes onto amphoteric sorbent based on upcycled sepiolite shells J. Environ. Health Sci. Eng. 18 35–30
[3] Abbas M, Adil M, Ehtisham-ul-Haque S, Munir B, Yameen M, Ghaffar A, Shar A G, Tahir Asif M and Iqbal M 2018 Vibrio fischeri bioluminescence inhibition assay for ecotoxicity assessment: a review Sci. Total Environ. 626 1295–309
[4] Onal E S, Yaktin T, Ergüt M and Ozer A 2017 Green synthesis of iron nanoparticles by aqueous extract of eriochrome black japonica leaves as a heterogeneous fentonlike catalyst: degradation of basic red 46 Int. J. Chem. Eng. Appl. 8 327–33
[5] Zuleyha B 2022 Determination of affecting parameters on removal of methylene blue dyestuff from aqueous solutions using natural clay: Isotherm, kinetic, and thermodynamic studies J. Mol. Struct. 1250 131729
[6] Iqbal M 2016 Vicia faba bioassay for environmental toxicity monitoring: a review Chemosphere 144 785–802
[7] Ngulube T, Gumbo J R, Masindi V and Maity A 2017 An update on synthetic dyes adsorption onto clay based minerals: a state-of-art review J. Environ. Manage. 191 35–57
[8] Jiang H L, Xu M Y, Xie Z W, HaiW, Xie X L and He F A 2020 Selective adsorption of anionic dyes from aqueous solution by a novel β-cyclodextrin-based polymer J. Mol. Struct. 1203 127737
[9] Fernandes J V, Rodrigues A M, Menezes R R and Neves G D A 2020 Adsorption of anionic dye on the acid-functionalized bentonite Materials 13 3600
[10] Zhu J, Zhang P, Wang Y, Wen K, Su X, Zhu R, He H and Xi Y 2018 Effect of acid activation of palygorskite on their toluene adsorption behaviors Appl. Clay Sci. 159 60–7
[11] Wen J, Yi Y and Zeng G 2016 Effects of modified zeolite on the removal and stabilization of heavy metals in contaminated lake sediment using BCR sequential extraction J. Environ. Manage. 178 63–9
[12] Gulten A and Elif Türker A 2010 Competitive adsorption of basic dyes onto calcite in single and binary component systems Sep. Sci. Technol. 45 1471–81
[13] Yan S, Wang Q, Liu J, Huo W, Yang J and Huang Y 2019 Synthesis, characterization and adsorption properties of low-cost porous calcined dolomite microspheres for removal of dyes J. Wuhan Univ. Technol. Mater. Sci. Ed. 34 507–15
[14] Kazi S, Iqbal H H, Shahid N, Shah G M and Jameel N 2016 Removal of reactive dye Yellow 145 by adsorption using white quartz Bull. Environ. Stud. 1 39–42 (https://ojs.njtu.edu.cn/articles/2016/3875-1472490603.pdf)
[15] Chen P, Cao Z F, Wen X, Wang J, Yang F, Qiu P, Yue Y J, Liu G Y, Wang S and Zhong H 2017 A novel mesoporous silicate material (MS) preparation from dolomite and enhancing basic blue-9 removal by electronic induction J. Taiwan Inst. Chem. Eng. 80 125–36
[16] Selim K A, Yousef M A, Abd El-Rahim F H and Hassan M S 2014 Dye removal using some surface modified silicate minerals Int. J. Min. Sci. Technol. 24 183–9
[17] Jada A and Ait Akbour R 2014 Adsorption and removal of organic dye at quartz sand water interface Oil Gas Sci. Technol. - Rev. IFP Energies nouvelles. 69 405–13
[18] Barka N, Assabbane A, Nounah A, Laanah L and Ait Yhya I 2009 Removal of textile dyes from aqueous solutions by natural phosphate as a new adsorbent Desalination 235 264–75
[19] Ran Y, Dawei L, Aimin I. and Hu Y 2018 Adsorption properties and mechanisms of palygorskite for removal of various ionic dyes from water Appl. Clay Sci. 151 20–8
[20] Santos S C R, Oliveira A F M and Boaventura R A R 2016 Bentonitic clay as adsorbent for the decolourisation of dyehouse effluents J. Clean. Prod. 126 667–76
[21] Sarma G K, Sen-Gupta S and Bhattacharyya K G 2011 methylene blue adsorption on natural and modified clays Sep. Sci. Technol. 46 1602
[22] Mouni L, Belkhiri I and Bollinger J C 2018 Removal of methylene blue from aqueous solutions by adsorption on kaolin: kinetic and equilibrium studies Appl. Clay Sci. 153 38–45
[23] Rida K, Boursouf S and Hadnine S 2013 Adsorption of methylene blue from aqueous solution by kaolinite and zeolite Appl. Clay Sci. 83 99–105
[24] Ozdes D, Duran C, Senturk H B, Avan H and Bicer B 2014 Kinetics, thermodynamics, and equilibrium evaluation of adsorptive removal of methylene blue onto natural illitic clay mineral Desalin. Water Treat. 52 208–18
[25] Santos S C R and Boaventura R A R 2016 Adsorption of cationic and anionic azo dyes on sepiolite clay: equilibrium and kinetic studies in batch mode J. Environ. Chem. Eng. 4 1473–83
[26] Dogan M, Alkan M, Türkyılmaz A and Özdemir Y 2004 Kinetics and mechanism of removal of methylene blue by adsorption onto perlite J. Hazard. Mater. B. 109 141–8
[27] Touma A, Cherns S, Mansour B, Hadjar H, Ouakouak A and Hamdi B 2021 Characterization and efficient dye discoloration of Algerian diatomite from ouled djilali-mostaganem SN Appl. Sci. 3 476
[28] Sears G 1956 Determination of specific surface area of colloidal silica by titration with sodium hydroxide Anal. Chem. 28 1981–3
[29] Purohit P, SomaSunandan P and Kulkarni R 2006 Study of properties of modified silicones at solid–liquid interface: Fabric–silicone interactions J. Colloid Interface Sci. 298 987–90
[30] Ho Y S, Ng J C Y and McKay G 2000 Kinetics of pollutant sorption by biosorbents Review Sep. Purif. Rev. 29 189–232
[31] Ho Y S and McKay G 1999 Pseudo-second-order model for sorption process Biochem. 34 451–65
[32] Züleyha B 2022 Determination of affecting parameters on removal of methylene blue from aqueous solution between 293.15 and 323.15 K J. Clean. Prod. 298 1–11
[33] Leviën L, Previti C T and Weidner D J 1980 Structure and elastic properties of quartz at pressure P = 1 atm Am. Mineral. 65 920–30 (http://minsocam.org/ammin/AM65/A65_920.pdf)
[34] Omer O S, Hussein M A, Hussein B H and Mgaidi A 2018 Adsorption thermodynamics of cationic dyes (methylene blue and crystal violet) to a natural clay mineral from aqueous solution between 293.15 and 323.15 K Arab. J. Chem. 11 615–23
[35] Khan K F et al 2022 Review on methylene blue: its properties, uses, toxicity and photodegradation Water, 14 242
[36] Al-Ghouti M A, Khraisheh M A M, Ahmad M N M and Stephen A 2009 Adsorption behaviour of methylene blue onto Jordanian diatomite: a kinetic study J. Hazard. Mater. 165 589–98
[37] Zuleyha B 2022 Determination of affecting factors on removal of methylene blue dyestuff from aqueous solutions using natural clays: Isotectonic, chemical and thermodynamic studies J. Mol. Struct. 1250 131729
[38] Labidi N S 2021 Experimental determination of basic blue-9 properties: electro - chemical, electrical conductivity and optical study Algerian J. Mater. Chem. 4 33–50
[39] Singh K K, Rastogi R and Hasan S H 2005 Removal of Cr(VI) from wastewater using rice bran J. Colloid Interface Sci. 290 61–8
[40] Weihsu Z, Ke L, Hongjuan B, Xiaolan S and Runping H 2011 Enhanced cationic dyes removal from aqueous solution by oxalic acid modified rice husk J. Chem. Eng. Data 56 1882–23
[41] Amparo F P and Gregorio M 2020 Visible light spectroscopic analysis of basic blue-9 in water. What comes after dimer ACS Omega. 5 29801–15
[42] Al-Ghouti M A and Daana D A 2020 Guidelines for the use and interpretation of adsorption isotherm models: a review J. Hazard. Mater. 393 12383–405
[43] Manlin Z, Qingfeng Y, Chao L, Zenghe L and Wenxing W 2014 Layered double hydroxide carbon dots composite: high performance adsorbent for removal of anionic organic dye ACS Appl. Mater. Interfaces. 6 20225–33
[44] Li A, Deng H, Ye C and Jiang Y 2020 Fabrication and characterization of novel ZnAl- layered double hydroxide for the superadsorption of organic contaminants from wastewater ACS omega 5 15152
[45] Hajjaji W, Andrejkovićová S, Pullar R C, Tobaldi D M, Lopez- Galindo A, Jammousi F, Rocha F and Labrincha J A 2016 Effective removal of anionic and cationic dyes by kaolinite and TiO2/kaolinite composites Clay Miner. 51 19–27
[46] Miyah Y, Idress M and Zerrouq F 2015 Study and modeling of the kinetics methylene blue adsorption on the clay adsorbents (Pyrophillite, calcite) J. Mater. Environ. Sci. 6 699–712 (http://mmatemvironsci.com/Document/vol6/vol6_N3/82-JMES-1183-2014-Miyah.pdf)
[47] Labidi N S and B Mechati M 2022 Review on methylene blue: its properties, uses, toxicity and photodegradation Mater. Res. Express 9 115501