Fast adsorptive removal of direct blue-53 dye on rare-earth doped Lanthanum aluminate nanoparticles: equilibrium and kinetic studies

S Pratibha¹, N Dhananjaya¹, C R Manjunatha² and Anjana Narayana¹
¹ Centre for advanced research on material sciences, Department of Physics, BMS Institute of Technology and Management, Bangalore-560064 and affiliated to Visvesvaraya Technological University, Belagavi, Karnataka, India
² Department of Chemistry, MS Ramaiah Institute of Technology, Bangalore, and affiliated to Visvesvaraya Technological University, Belagavi, Karnataka, India
³ Department of Mathematics, CMR University, Bangalore, India
E-mail: ndhananjayas@bmsit.in
Keywords: LaAlO₃, direct blue-53, BET, adsorption isotherms and kinetics
Supplementary material for this article is available online

Abstract
The nanocrystalline LaAlO₃: Sm³⁺: Bi³⁺ composites are synthesized using sugar as fuel through the solution combustion process. Prepared composites were well categorized by Powder X-ray Diffraction (PXRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), UV-Visible spectroscopy, Fourier Infrared Transform (FTIR) spectroscopy, Brunauer-Emmett-Teller (BET) analysis. The average size of the crystallites as estimated using Scherrer equation is in the range 30–46 nm agreeing with TEM results. The SEM images show the spherical agglomerated nanoparticles. The nominal composition of dopant and co-dopant ions present inside the host lattice is confirmed with EDX patterns. The adsorption of Direct Blue-53 (DB-53) dye has been investigated. The influence of adsorbent load, the concentration of dye, pH and time on adsorption of Direct Blue-53 dye was studied. The statistical error computation and nonlinear curve fitting of experimental isotherm and kinetic data are carried out using Excel solver-2019 (Microsoft office-2019 USA). The kinetic studies indicate that the adsorption process follows pseudo first-order kinetics and isotherm studies suggest that the Dubinin-Radushkevich (D-R) isotherm model is well fitted and is in good agreement with experimental data. The adsorbent is admirable and promising in the adsorption capacity and is beneficial in the elimination of toxic and non-biodegradable organic pollutants in water.

1. Introduction
In past decades, numerous industries like textile, cosmetics, refineries, leather, plastic and paper release inorganic and organic compounds as effluents to the aquatic biosystem leading to an increase in environmental pollution. This industrial wastewater comprises several hazardous aromatic compounds, chlorinated compounds, heavy metals, insecticides and petroleum hydrocarbons that lead to a rise in pH, odor, color, and chemical oxygen demand (COD) [1]. One of these major pollutants is Direct Blue-53 (DB-53) dye. It is a water-soluble anionic azo dye, which occurs as an impurity in industrial sewage. Furthermore, it is utilized to color leather, paper, cosmetics, rayon, and to some amount in nylon industries. In medical physiology, it is used to determine the water content in the blood plasma. But, it has many adverse health effects as it might be carcinogenic, neurotoxic and cytotoxic in higher usage. Hence removal of this dye from community wellbeing and ecological aspects is noteworthy. Quite a lot of researches have been undergone for diverse conservative water treatment such as membrane separation [2], electrochemical methods [3], adsorption [4], oxidation processes with various reagents, flotation, nanofiltration, ozonation and biological treatments [5] coagulation [6], photocatalysis [7], etc. To eliminate different pollutants, the adsorption phenomenon is the best and economical process. Many adsorbents such as graphene [8], graphene oxide composites [9], activated carbons...
metal-organic frameworks [11], carbon nanotubes [12] and amorphous iron nanoparticles [13] were successfully applied to remove dyes from aqueous solution. On the other hand, some adsorbents have high costs and low adsorption performance. Therefore, new researches are necessary for the development of new adsorbent materials.

ABO₃ structured perovskite oxide semiconductors are proven to be promising adsorbent and an extensive variety of elemental compositions can be produced in the form of crystalline structures. This ABO₃ perovskite structure includes the rare earth elements at A site and transition metals at B site [4]. Since the lanthanum (La) based materials have higher carbonaceous oxidation activity, the La³⁺ ion is preferred for the A site in the ABO₃ structure. Palas et al investigated the removal of Reactive Black, a textile azo dye, by catalytic wet air oxidation in the presence of LaNiO₃ perovskite catalyst from the aqueous solutions [14]. Gugulothu et al investigated the removal of anionic dyes using the superior adsorption capacity of strontium titanate and Titania composites [1]. Bradha et al. reported the photocatalytic oxidation of Congo red dye using La₁₋ₓAxTiO₃₋δ (A = Ba, Sr, Ca) nano perovskites [15]. In the present work, we attempted to prepare LaAlO₃ (LA), LaAlO₃:Sm³⁺ (LAS), and LaAlO₃:Sm³⁺:Bi³⁺ (LASB) nanoparticles by conventional solution combustion synthesis technique using sugar as a fuel for fast adsorptive removal of Direct Blue-53 (DB-53) dye. Adsorption isotherms and kinetic studies were carried out and different adsorption models were utilized to reveal the possible adsorption mechanism. The synthesized compound’s phases were confirmed by various analytical methods like XRD, SEM, TEM, and functional groups were validated using FTIR analysis.

2. Experimental section

2.1. Materials

The lanthanum oxide [La₂O₃], samarium oxide [Sm₂O₃], aluminium nitrate [Al(NO₃)₃·9H₂O], bismuth nitrate [Bi(NO₃)₃·5H₂O] are used as oxidizers and sucrose (C₁₂H₂₂O₁₁) is used as fuel for combustion synthesis. DB-53 dye is used for the adsorption studies and its chemical structure is as shown in figure 1. All chemicals and dye were procured from Sigma Aldrich and SD fine chemicals Ltd.

2.2. Synthesis technique

LA, LAS and LASB nanoparticles were synthesized by solution combustion method using stoichiometric quantities (keeping the unit ratio between fuel and oxidizer) of lanthanum oxide, samarium oxide, aluminium nitrate, bismuth nitrate, and sugar as fuel. To prepare LA, the lanthanum oxide is transformed into nitrate by treating with 1:1 HNO₃ in a cylindrical Petri dish of approximately 300 ml capacity. The gel is formed by keeping it on a hot sand plate for ~5 min. Later, to this gel stoichiometric amounts of aluminium nitrate, bismuth nitrate, and sugar are added along with 30 ml of distilled water to prepare an aqueous solution. This reaction mixture is kept for magnetic stirring for 5–10 min and then kept in a muffle furnace preheated at 500°C ± 10°C. The thermally dehydrated foam is formed by boiling and frothing of the reaction mixture. The entire process takes place in less time.
The phase purity and crystallinity of the obtained nanoparticles were inspected by powder x-ray diffraction (panalytical X’Pert Pro Powder diffractometer) using a wavelength of 1.5418 Å (Cu Kα radiation) with a nickel filter. The diffracted intensities were recorded from 2θ = 10° to 80° angles. The Hitachi 3000 scanning electron microscope is used to study the surface morphology along with EDXS attachments (Zeiss). Jeol 200CX Transmission electron microscope is used for the Transmission electron microscopy studies. Shimadzu UV-Visible spectrometer is used for recording absorption spectra. Perkin Elmer Spectrometer (Spectrum 1000) Frontier is used to record the Fourier transform infrared spectra using KBr as a reference at a resolution of 4 cm⁻¹ ranging from 350 cm⁻¹ to 4000 cm⁻¹. Belsorp-max surface area analyzer (Japan) was utilized in the determination of specific surface area and pore volumes of the nanoparticles.

### 2.3. Characterization

The mixture of catalyst and dye solution was kept for magnetic stirring in the reactor for 30 min than 5 min The product is crushed well using the pestle and mortar. A similar procedure is followed to prepare the LAS and LASB nanoparticles, where the samarium nitrate and bismuth nitrates are added along with aluminium nitrate. The obtained powders were calcined at 900 °C for 2 h.

### 2.4. Adsorption studies

A sequence of adsorption trials was performed to study the adsorption process and its rate. In general, the order of adsorption is time-dependent as there could be a shift from second order to first order with aging. After long hours, since the equilibrium may attain there could be no further change in the concentration of the dye, which indicates the zero-order shift. To overcome this constraint, we have limited the kinetic studies to 60 min The batch trials were carried out by taking 50 ml of altered concentration of dye solution (5, 10, 15, 20, 30, 60 mg L⁻¹) at room temperature (25°C), at pH 2.0 and with 30 mg of the adsorbent. The aliquots at regular time intervals are taken out, centrifuged and the concentration of dye in the supernatant solution was analyzed.

For isotherm analysis, a standard solution of DB-53 dye made of different concentrations from 5 to 60 mg L⁻¹ was used. Using either 1 N NaOH or 1 N HCl the pH of the stock solution was maintained at 2. The mixture of catalyst and dye solution was kept for magnetic stirring in the reactor for 30 min (equilibrium time). The supernatant liquid is taken after centrifugation to measure the magnitude of adsorption using the Shimadzu model 1800 UV visible spectrophotometer. The concentrations were made appropriate so that the absorbance of the dye authenticates the Beer- Lambert’s law. The percentage of dye adsorption is calculated using the below formula [16].

\[
% \text{Adsorption} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{1}
\]

Adsorption at equilibrium \(q_e\) (mg/g) is estimated using the below equation,

\[
q_e = (C_0 - C_e) \frac{V}{w} \tag{2}
\]

Where, \(C_0\) is initial and \(C_e\) is the equilibrium concentration of dye (mg/L) respectively: \(v\) is the volume of the solution (ml) and \(w\) is the amount of adsorbent (mg).

Adsorption \(q_t\) (mg/g) at time interval \(t\) is calculated using the equation,

\[
q_t = (C_0 - C_t) \frac{V}{W} \tag{3}
\]

Where, \(C_0\) is initial concentration(mg/L) and \(C_t\) is concentration (mg/L) at time t. \(V\) is the volume of the solution (ml) and \(w\) is the amount of adsorbent (mg).

### 2.5. Determination of point of zero charge

The acidic or basic nature of the surface explains the surface chemistry of any material. It’s known that positive surface charge indicates acidic and negative surface charge indicates basic nature. It’s been very important to know the surface charge of the materials in aqueous media especially in adsorption studies, as we can produce material with the high surface area but if its charge opposes the adsorption with like charges, then we have to alter the pH conditions to make adsorption favorable. The pH_{pzc} (pH point of zero charge) of the adsorbent material was estimated using a pH drift method. In a typical study, 50 ml of 0.01 M sodium chloride (NaCl) solution was taken in a glass beaker and then pH 2 was adjusted using 1 N HCl and 1 N NaOH. 30 mg of the adsorbent material was added to that solution and kept for stirring for 24 h at room temperature. After the time evolved final pH attained was noted. A similar procedure was followed for different pH (2, 4, 6, 8, 10 and 12) and the final pH values attained were noted. Figure S1 shows the graph of initial pH (x-axis) Vs final pH (y-axis) is plotted. The point of transition of adsorbent material from acidic to basic was noted (where the charge will be zero) as a zero-point charge of the material and was found to be 6.97.
2.6. Statistical error computation

In the present study various kinetic and equilibrium isotherm models, nonlinear regression analysis was computed with SOLVER tool, Microsoft Excel (Microsoft Office 2019, USA). SOLVER software designed on the Generalized Reduced Gradient (GRG) nonlinear system of repetition available in Microsoft Excel-2019. SOLVER-2019 was utilized for fitting the experimental data on selected models. Twelve statistical parameters such as sum of absolute error (SAE), Nonlinear Chi-square (χ²), Hybrid Fractional Error Function (HYBRID), sum of square error (SSE), average relative error (ARE), Absolute Percentage Error (APE), Marquardt’s percent standard deviation (MPSD), Root mean square error (RMSE), normalized standard deviation, Akaike information criterion (AIC), Akaike information corrected criterion (AICC) and R² as prime criterion were carried out to evaluate the best fit among various different models. Statistical data were calculated using the succeeding mathematical expressions (equations (4)–(15)). Where \( Q_{e,\text{cal},i} \) and \( Q_{e,\exp,i} \) represents the calculated and experimentally measured adsorbate on adsorbate phase, concentration on adsorbent at any instant \( i \) respectively. \( Q_{e,\exp,\text{avg}} \) is the average of experimentally measured observations. The number of observations referred by \( N \) and the number of parameters is referred by \( P \) is in the model [17–19].

Mathematical equation equation no.

\[
\text{SSE} = \sum_{i=1}^{N} (Q_{e,\exp} - Q_{e,\text{cal}})^2
\] (4)

\[
\text{HYBRID} = \frac{100}{n-p} \sum_{i=1}^{n} \left( \frac{(Q_{e,\exp} - Q_{e,\text{cal}})^2}{Q_{e,\exp}} \right)
\] (5)

\[
X^2 = \sum_{i=1}^{N} \frac{(Q_{e,\exp} - Q_{e,\text{cal}})^2}{Q_{e,\text{cal}}}
\] (6)

\[
\text{SAE} = \sum_{i=1}^{N} |Q_{e,\exp} - Q_{e,\text{cal}}|
\] (7)

\[
\text{ARE} = \frac{100}{n} \sum_{i=1}^{N} \left( \frac{Q_{e,\exp} - Q_{e,\text{cal}}}{Q_{e,\exp}} \right)
\] (8)

\[
\text{RMSE} = \left( \frac{1}{n-2} \sum_{i=1}^{n} (Q_{e,\exp} - Q_{e,\text{cal}})^2 \right)^{1/2}
\] (10)

\[
\text{MPSD} = 100 \sqrt{\frac{1}{N-P} \left( \frac{Q_{e,\exp} - Q_{e,\text{cal}}}{Q_{e,\exp}} \right)^2}
\] (11)

\[
\text{NSD} = 100 \sqrt{\frac{1}{N-1} \left( \frac{Q_{e,\exp} - Q_{e,\text{cal}}}{Q_{e,\exp}} \right)^2}
\] (12)

\[
\text{AIC} = 2P - n \left( \ln \left( \frac{\text{SSE}}{N-P} \right) \right)
\] (13)

\[
\text{AICC} = n \ln \left( \frac{\text{SSE}}{N} \right) + 2P + \frac{2P(P+1)}{N-P-1}
\] (14)

\[
R^2 = \frac{\sum(Q_{e,\text{cal}} - Q_{e,\exp})^2}{\sum(Q_{e,\text{cal}} - Q_{e,\exp})^2 + \sum(Q_{e,\text{cal}} - Q_{e,\exp})^2}
\] (15)

2.7. Regeneration and reusability studies

0.6 g of adsorbent is added to the 1000 ml of 10 mg l⁻¹ of dye solution to carry out regeneration and reusability studies. The 6 cycles of adsorption and desorption were carried out using different strength of NaOH between 0.02 to 0.2 M for a fixed equilibration contact time 30 min Later the mixture is centrifuged to separate the spent adsorbent and it is dried at 65 °C. The dried spent adsorbent is treated with optimized 0.25 M NaOH for 3 h to get maximum leaching of DB-53 dye efficiency in each cycle.
3. Results and discussion

3.1. Powder x-ray diffraction (XRD)

Figure 2(A) represents the PXRD patterns of the nanoparticles calcined at 900°C for 2 h. All the diffraction peaks in XRD can be attributed to the pure phase of the rhombohedral perovskite crystal structure and agrees well with the (JCPDS 85–848) with the space group R3m and lattice parameter $a = 3.789$ Å. The intense sharp peaks indicate the crystalline nature of the sample.

The particle size was calculated from the x-ray line broadening of the diffraction peak using the Scherrer’s formula:

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (16)

Where $D$ refers particle size in nm, $\lambda = 1.5418$ Å the Cu Kα x-ray wavelength, $\theta$ refers to the angle of x-ray diffraction and $\beta$ refers to the full width of the peak at half maximum intensity. The estimated mean crystallite size is found to be in the range of 30–46 nm. Further, employing Williamson-Hall plots strain present in the nanoparticles was calculated.

$$\beta \cos \theta = \frac{0.9 \lambda}{D} + 4\varepsilon \sin \theta$$  \hspace{1cm} (17)

Where ‘$\varepsilon$’; the strain related to the nanoparticles. The plot between ‘$4 \sin \theta$’ (x-axis) and ‘$\beta \cos \theta$’ (y-axis) gives a straight line as shown in figure 2(B). The strain ($\varepsilon$) and grain size ($D$) are given by the slope and y-intercept of this line respectively.

The small discrepancy in the values attributed to the fact that the in Scherrer’s formula strain component is assumed to be zero and reducing grain size is only considered to affect the observed broadening of the diffraction peak. The existence of nonstoichiometric oxygen and grain boundary defects results in variation in strain values [21]. Table 1 depicts the average crystallite size of the LA, LAS, and LASB nanoparticles as tabulated.

3.2. Scanning electron microscopy (SEM)

SEM observations reveal detailed information about the structure and morphology of the synthesized samples. Figure S2 is available online at stacks.iop.org/MRX/6/1250i5/mmedia shows SEM images and EDX patterns of (a), (b) LA, (c), (d) LAS and (e), (f) LASB nanoparticles. As a result of combustion, the excess heat released during the process creates the porous nature and agglomeration of the nanoparticles. This is clearly observed in the SEM images. The TEM pictures also show the non-uniformity of individual particles that are aggregated. Energy-dispersive x-ray spectrum (EDXS) shows the peaks allocated to Al$^{3+}$, La$^{3+}$, O$_2$, Sm$^{3+}$ and Bi$^{3+}$ ions.
3.3. Transmission electron microscopy (TEM)

Figures 3(a) and (b) represent the TEM image and SAED pattern of the LASB nanoparticles respectively. SAED pattern is identified to be originated from the lattice planes as identified in PXRD confirming the formation of crystalline nanoparticles. Also, as per the observed TEM images, the size of the LASB nanoparticles is in the range 30–46 nm and which agree well with the XRD results.

3.4. Fourier transforms infrared (FTIR) spectroscopy

Figure 4 shows the FTIR spectra of the (a) LA, (b) LAS, (c) LASB nanoparticles before dye adsorption and (d) DB-53 dye and (e) LASB nanoparticles after dye adsorption. A broad peak in the spectrum around 3400 cm\(^{-1}\) shows the existence of an adsorbed water molecule. The absorption of CO\(_2\) can be assigned to the peak at 2300 cm\(^{-1}\). The vibrational stretching modes of the carboxylate ions are shown by the sharp absorption bands at 1384 cm\(^{-1}\). However, it is evident that the peaks at 1595–1384 cm\(^{-1}\) (strong bands) are due to the stretch vibrations in NO\(_3\)\(^-\). The C–O–C crosslinking between the hydrocarbon chains resembles by the peak at 1045 cm\(^{-1}\). The perovskite structure compound comprised of characteristic M–O (possible La–O and Al–O stretching frequencies) vibrations which are observed specifically at 826 cm\(^{-1}\) and 657 cm\(^{-1}\) in the 820–400 cm\(^{-1}\) region of the IR spectrum. The presence of organic molecules in the calcined samples is indicated by a very low-intensity band at 1080 cm\(^{-1}\)\(^{[22, 23]}\). The enhanced peak at 834 cm\(^{-1}\) clearly confirms dye adsorption. The characteristic IR bands of asymmetric S=O stretching, C–O stretching of the phenolic and epoxy group at 1050 cm\(^{-1}\), 1115 cm\(^{-1}\)\(^{[24, 25]}\).

3.5. UV-Visible spectroscopy and bandgap analysis

Figure S3(A), (B) represents the absorption spectra and Tauq’s plots of LA, LAS, LASB nanoparticles. In order to estimate the optical energy bandgap from UV-Visible absorption spectroscopy, Wood and Tauc relation is used. It is mentioned below as the relation between photon energy and absorbance\(^{[24–26]}\):

\[
\alpha h\nu = A(h\nu - E_g)^n
\]

Where \(\alpha\) indicates the absorption coefficient, \(h\) is the Planck’s constant, \(\nu\) is the frequency of the incident photon, \(E_g\) refers optical energy bandgap, \(A\) refers proportionality constants and values of \(n\) depend on the nature of the electric transitions. The estimated value of the bandgap energy for LA, LAS, LASB by linear extrapolation of the curve to the x-axis was found to be in the range 4.7–5.5 eV and is tabulated in table 1. The bandgap is decreasing by doping the Sm\(^{3+}\) ion to the host lattice indicating the effect of SmO\(_8\) clusters on the
electronic assembly. By the incorporation of the trivalent transition metal ion (Bi$^{3+}$), there is a drastic change in the optical behavior of the host lattice and it induces ferromagnetism in non-magnetic perovskite materials having a wide bandgap. As a result, there occurs a reduction of the bandgap to 4.7 eV [27].

3.6. BET measurements
Specific surface area, pore volume and mean pore diameter of nanoparticles were measured using N$_2$ adsorption-desorption cycles. The linear adsorption-desorption isotherms with the inset of the BJH plot for LASB nanoparticles are shown in figure 5 and table 2. The isotherms of these nanoparticles depicted mesoporous materials of type—IV nature and also it is confirmed by observed pore diameters. The specific surface area is found to be 26.314 m$^2$ g$^{-1}$, the pore volume is found to be 0.086 cm$^3$ (at STP)/g and mean pore diameter is 12.993 nm for the LASB nanoparticles [1].

Figure 4. FTIR spectra of (a) LA, (b) LAS, (c) LASB nanoparticles before dye adsorption and (d) Pure DB-53 dye. (e) LASB nanoparticles after dye adsorption.

Figure 5. N$_2$ adsorption –desorption isotherms with inset of BJH plot for LASB nanoparticles.
3.7. Adsorption of DB-53 dye

Figure S4 shows the adsorption of DB-53 dye using a) LA b) LAS and c) LASB nanoparticles. It clearly indicates that compared to LA and LAS nanoparticles, LASB shows the maximum adsorption. Hence further processes are carried out using LASB nanoparticles alone.

3.7.1. Equilibrium studies

3.7.1.1. Impact of adsorbent dosage on dye removal

The effect of adsorbent dosage on the DB-53 dye removal is as shown in figure S5(a). In order to find the optimization of the dosage, the amount of adsorbent was varied from 10–50 mg in 50 ml of 5 mg/L dye solution. The efficiency of adsorption increased with an increase in the concentration of the catalyst. Since active sites available for the adsorption on the catalyst surface increases up to 30 mg /50 ml. Further increase in the concentration of the catalyst increases the turbidity of the solution which leads to lesser availability of free hydroxides and superoxide. Hence optimal dosage was found to be 30 mg /50 ml [28].

3.7.1.2. Impact of pH on adsorption

The adsorption of 5 mg/L DB-53 dye solution using 30 mg of dosage is investigated under different pH conditions (2, 4, 6, 8, and 10) as shown in figure S5(b) with the inset of % adsorption with pH. The figure S5 indicates that the adsorption process is intensely reliant on the pH of the dye solution. The efficiency of adsorption is more in acidic conditions compared to basic conditions. The dissociation of dye molecules is dependent on the surface properties of the nanoparticles which are controlled by pH. On increasing pH, the adsorption is decreased. At low pH, the interaction between the dye and the positively charged surface is active and thus higher adsorption can be observed. At basic conditions, the electrostatic interactions of SO₃⁻ group with the surface of the adsorbate will be more active leading to the higher intake of dye. The pH studies finally reveal that only 65% is adsorbed at natural pH and the highest adsorption of around 97.9% was observed at pH 2. The pHpzc value of the LASB nanoparticle is found to be 6.97 as shown in figure S1.

3.7.1.3. Dye concentration-dependent adsorption

The effect of dye concentration on the adsorption using LASB nanoparticles is illustrated in figure S6. The trial concentration of DB-53 dye was ranging from 5 to 60 mg L⁻¹, the catalytic load was maintained as 30 mg /50 ml at pH 2. As the concentration of dye increases from 5 to 60 mg L⁻¹, time increased as expected for the complete adsorption. At higher concentrations, active sites on the catalyst decreases since a greater number of dye molecules are adsorbed on the surface of the catalyst [29].

3.7.2. Adsorption isotherm models

Adsorption isotherms provide the information about the adsorption affinity towards the surface and retention period of the sorbent at a particular temperature. To know the mechanism, surface properties, maximum adsorption uptake designing of isotherm models and interaction of the adsorbent and adsorbate is very important. The present study focuses on the six two-parametric models (Langmuir, Freundlich, D-R, Temkin, Halsey, Harkin-Jura) and two three-parameter models (Redlich-Peterson and Sips) to analyze the experimental isotherm equilibrium data [16, 30–33]. The coefficient R² and statistical error data values give the applicability of these isotherm equations to describe the adsorption capacity of the adsorbent. Figure 6 indicates the nonlinear modelled isotherm profiles for the adsorption of DB-53 dye [2, 34–36]. A comparison of the adsorption parameters of different isotherm models for the adsorption of DB-53 dye onto LASB NPs is tabulated in table 3 and computed statistical data from the eight-equilibrium model presented in table S3.

All the nonlinear mathematical parameteric expressions and equational descriptions presented in table S1. All Nonlinear equilibrium models fitted ranking order best to worst presented in table S4.

Langmuir isotherm assumes that all the active sites are independent of each other and adsorption sites are equivalent [16, 37]. Once adsorbate occupies the vacant sites of a monolayer of the adsorbent, there will be no further lateral interaction hence plateau is observed in the curve. From table 3 lower R² values (<1) reflect that

| Parameters         | BET     | BJH     | Langmuir |
|--------------------|---------|---------|-----------|
| Surface area (m²/g) | 26.31   | 25.43   | 28.09     |
| Pore Volume (cc/g)  | 0.086   | 0.078   | —         |
| Average pore size (nm) | 12.99   | 14.27   | —         |
| R²                 | 0.999   | —       | 0.998     |

Table 2. BET surface area analysis of LASB nano particles.
adsorption is more favorable and a monolayer formation is taking place. For $C_o$ from 5 to 60 mg l$^{-1}$ is used in the present study. From table 3, monolayer maximum adsorption capacity is found to be 105.85 mg g$^{-1}$. Coefficient $R^2$ is 0.995 indicates strong linear relationships with predicted and experimental data but not confirmed with statistical error function values compared to a few other models.

Freundlich equilibrium isotherm model explains heterogeneous sites with uniform distribution energy and interaction which occurs between the adsorbed adsorbate and new adsorbate interactions forming the multilayer. As the concentration of adsorbate dye increases on adsorbent, graph does not reach saturation. Lower AIC, AICC, $R^2$ values and higher statistical error data shows Freundlich equilibrium model is not in good agreement. Furthermore, the value of $n$ is 2.0 which lies between 1–10 hence, favours physical adsorption process on the adsorbent.

The D-R equilibrium empirical model is used to predict the Gaussian energy distribution on heterogeneous sites of the adsorbent. D-R model is temperature dependent and mean free energy value at room temperature is 0.042 kJ mol$^{-1}$ which is less than 8 kJ mol$^{-1}$ suggested that adsorbate-adsorbent interaction is physical in nature. From the computed nonlinear statistical error data and order of most visited isotherm from table S4, it is observed that D-R equilibrium isotherm model is well fitted with the experimental data. Regression value $R^2$ is 0.9952 is higher compared with all other fitted equilibrium models. Hence, the D-R model can be concluded as suitable for experimental data representation at lab temperature.

The indirect interaction of adsorbate-adsorbent and the extent of coverage over the surface of adsorbate applied is determined by Temkin equilibrium model. This model is limited to a lower concentration of adsorbate. The model poorly fit with all other model data, it shows lower $R^2$ value and higher statistical error functions. The $B_T$ values 0.147 (kJ/mol) which indicates the physical nature of adsorption.

Harkin-Jura equilibrium model equation explains the multilayer adsorption on hetero-porous adsorbent. By observing coefficient $R^2$ from table 3, this model is also experimentally poor fitted with most of the other model and has higher statistical error function. Hence, it is concluded that Harkin-Jura is the worst fitted model.

Redlich-Peterson Hybrid three parametric model is derived from the combined mathematical modified equation of both Freundlich and Langmuir equilibrium isotherm equation. From table 3, $\beta$ value 0.5 indicates that the adsorption neither fits Langmuir nor Freundlich isotherm. One more three parametric Sips equilibrium model is the combined form of Freundlich and Langmuir express the heterogeneous adsorption mechanism. Sips model fitted well next to the D-R model when observed the statistical computed table S4.
The Halsey model explains adsorption occurs at large layer distance from the surface of the adsorbent. Halsey isotherm is poor fitted as observed in table 3. $R^2$ value 0.94 indicates that the present adsorbent fails to adsorb multilayer at relatively large distance. Comparison of computed statistical error data and most fitted isotherm model best to worst for 2-parametric and 3-parametric models were carried out. D-R model has the highest $R^2 > 0.995$ value with lowest statistical error values SSE, HYBRID, $\chi^2$, ARE, MPSD, NSD and higher Value of AIC, AICC, $R^2$. Three parametric Sips equilibrium model with $R^2 > 0.9955$ and $n_s = 0.860$ indicate adsorbent allows monolayer adsorption at high concentration.

### Table 3. Different parameters of selected nonlinear isotherm models for adsorptive removal of DB-53 dye using LASB nanoparticles.

| Isotherm                  | Parameters | Nonlinear model |
|---------------------------|------------|-----------------|
| Freundlich                | $K_F \text{mg. G}^{-1} (L\text{.mg}^{-1})^{1/n}$ | 23.46 |
|                           | $N$        | 2.0             |
|                           | $R^2$      | 0.988           |
| Langmuir                  | $K_L(L\text{.mg}^{-1})$ | 0.256 |
|                           | $Q_m(\text{mg.g}^{-1})$ | 105.85 |
|                           | $R_L$      | 0.992           |
|                           | $R^2$      | 0.995           |
| Dubinin-Radushkevitch (D-R) | $E(kJ.\text{mol}^{-1})$ | 0.042 |
|                           | $Q_{D-R}(\text{mg.g}^{-1})$ | 24.2 |
|                           | $B_{D-R}$ | $2.83 \times 10^{-3}$ |
|                           | $R^2$      | 0.99949         |
| Tempkin                   | $B_T(L.\text{mol}^{-1})$ | 147.23 |
|                           | $A_T(L.\text{g}^{-1})$ | 5.23 |
|                           | $R^2$      | 0.924           |
| Harkin-Jura isotherm      | $A_HJ$     | 930             |
|                           | $B_{HJ}$  | 2.63            |
|                           | $R^2$      | 0.884           |
| Redlich-Peterson isotherms | $A_{rp}(L.\text{mg}^{-1})$ | $76.0 \times 10^4$ |
|                           | $K_{rp}(L.\text{g}^{-1})$ | $1.78 \times 10^7$ |
|                           | $B$       | 0.5             |
|                           | $R^2$      | 0.987           |
| Halsey isotherm           | $N_h$      | -1.4            |
|                           | $K_H$      | 0.022           |
|                           | $R^2$      | 0.949           |
| Sips                      | $K_S$      | 27.4            |
|                           | $B_s$      | 0.860           |
|                           | $A_s$      | 0.224           |
|                           | $R^2$      | 0.996           |

The Halsey model explains adsorption occurs at large layer distance from the surface of the adsorbent. Halsey isotherm is poor fitted as observed in table 3. $R^2$ value 0.94 indicates that the present adsorbent fails to adsorb multilayer at relatively large distance. Comparison of computed statistical error data and most fitted isotherm model best to worst for 2-parametric and 3-parametric models were carried out. D-R model has the highest $R^2 > 0.995$ value with lowest statistical error values SSE, HYBRID, $\chi^2$, ARE, MPSD, NSD and higher Value of AIC, AICC, $R^2$. Three parametric Sips equilibrium model with $R^2 > 0.9955$ and $n_s = 0.860$ indicate adsorbent allows monolayer adsorption at high concentration.

#### 3.7.3. Kinetic studies

To ascertain the efficiency of LASB adsorbent and better indulgence of the adsorption dynamics with the prospect for future industrial applications, the reaction kinetics were assessed. In order to investigate the controlling mechanism of dye sorption such as chemical reaction, diffusion control, mass transfer onto LASB nanoparticles, pseudo first order [33], pseudo second order [34] and Elovich [35] models were adopted. These kinetic models along with Bangham kinetic diffusion model are represented in Figure 7. Kinetic parameters of DB-53 dye adsorption onto the LASB nanoparticles at room temperature and at pH 2 are charted in table 4. All the parameters of equations and their descriptions are represented in table S2. Computed statistical error data are given in table S5 and ranking fitting order from best to worst is shown in table S6.

From the nonlinear kinetic and statistical error parameter we observe that pseudo first-order model (PFO) best fitted by an increase in concentration between 5–60 mg L$^{-1}$ and $R^2 > 1$ from table S5. At higher concentrations pseudo second-order (PSO) shows higher statistical error computed values. This indicated that adsorption of LASB well explained using the PFO mechanism. At lower concentration of adsorbate, $q_e$ was found to be 7.48 mg g$^{-1}$ to 89.29 mg g$^{-1}$.

The layered structure and indirect optical transition of LASB play a vital role in its outstanding adsorption activity. During the indirect transition, an excited electron has to reach the valence band by traveling certain k-space distance. Hence the recombination probability is reduced for the electron-hole pair. The layered structure of LASB polarizes the atoms and orbitals by providing large enough space. As a result, electron-hole separation efficiency increases through the appeared dipole, and thus enhances the adsorption activity.
From the values of initial adsorption rate $H$ (mg/g min) from table 4, we can observe the gradual increase initially and then it decreases along with the increasing dye concentration indicating the physisorption. All these results indicate that the adsorption kinetics of DB-53 dye onto LASB nanoparticles are better fitted using PFO model.

The Elovich kinetic model describes the PSO nonlinear kinetic model for the heterogeneous materials. The $\alpha$ is the initial adsorption rate and value of $\beta$ is related to the extent of surface coverage and activation energy for chemisorption. From table S5, the observed values of coefficient $R^2$ and increased statistical error values it can be concluded that the Elovich model fails to give satisfactory results hence, adsorbent not favours chemical adsorption $[17, 19]$.

3.7.4. Mechanism of adsorption

PFO, PSO and Elovich models are not enough to identify the pore diffusion mechanism. So, the intraparticle diffusion model (Weber-Morris) and Bangham kinetic model were used to explain the rate-controlling step.
According to Weber-Morris studies, in most of the cases adsorption is proportional to t^{0.5} instead of its contact time. If the rate-limiting step followed only intraparticle diffusion it can be confirmed with Bangham kinetic model as presented in figure 8\cite{14, 35}. In the present study, the plot does not pass through the origin, it shows multilinear curves which confirms that intraparticle diffusion is not the only rate-limiting step\cite{35}. Hence, the rate-limiting step is the multistep involving intraparticle diffusion.

**Table 4.** Different parameters of selected nonlinear kinetic model for adsorptive removal of DB-53 dye using LASB nanoparticles.

| Model Type | Model Type | Parameters | 5 mg/L | 10 mg L^{-1} | 20 mg L^{-1} | 30 mg L^{-1} | 60 mg L^{-1} |
|------------|------------|------------|--------|--------------|--------------|--------------|--------------|
| pseudo first order nonlinear model | Q_e (exp) | 7.489 | 15.051 | 31.23 | 35.97 | 89.295 |
| | K_1 (min^{-1}) | 0.3734 | 0.474 | 0.274 | 0.159 | 0.0468 |
| | R^2 | 0.987 | 0.999 | 0.999 | 0.997 | 0.992 |
| pseudo second order nonlinear model | Q_e (mg G^{-1}) | 7.90 | 15.45 | 33.34 | 40.10 | 125.13 |
| | K_2 (g mg^{-1}.min^{-1}) | 0.101 | 0.108 | 0.0162 | 0.0056 | 0.0003 |
| | H (mg G^{-1}.min^{-1}) | 6.33 | 25.87 | 18.03 | 9.14 | 4.70 |
| | R^2 | 0.996 | 0.999 | 0.996 | 0.993 | 0.992 |
| Elovich kinetic nonlinear model | B (mg^{-1}) | 1.6 | 1.72 | 0.31 | 0.15 | 0.025 |
| | A (g. Mg^{-1}.min^{-1}) | 3756 | 7.12*10^{-1} | 2054 | 40.28 | 5.54 |
| | R^2 | 0.999 | 0.998 | 0.986 | 0.977 | 0.991 |

**Table 5.** Different parameters of Intraparticle particle diffusion and Bangham kinetic adsorption model for adsorptive removal of DB-53 dye using LASB nanoparticles.

| Model type | Parameters | Initial Concentration of DB-53 dye solution |
|------------|------------|------------------------------------------|
| Intraparticle diffusion model | K_d (mg g^{-1} min^{-0.5}) | 5 mg/L | 10 mg L^{-1} | 20 mg L^{-1} | 30 mg L^{-1} | 60 mg L^{-1} |
| | P-I | 0.331 | 0.570 | 3.348 | 6.174 | 13.127 |
| | P-II | 0.203 | 0.073 | 0.315 | 0.38 | 6.086 |
| | C_d (mg g^{-1}) | P-I | 5.804 | 12.633 | 16.963 | 7.302 | 7.33 |
| | | P-II | 6.483 | 14.703 | 29.408 | 38.053 | 37.003 |
| | | R^2 | 0.994 | 0.898 | 0.937 | 0.989 | 0.991 |
| | | | P-I | 0.999 | 0.999 | 0.984 | 0.887 | 0.985 |
| Bangham kinetic diffusion model (nonlinear) | A (g/ mg.min^{-1}) | | 5.64 | 13.22 | 21.83 | 17.14 | 6.09 |
| | K_b (g/mg) | | 5.64 | 13.22 | 21.83 | 17.14 | 6.09 |
| | R^2 | | 0.999 | 0.998 | 0.984 | 0.969 | 0.986 |

[34]. All the details of the model equations and the parameters are presented in tables 5 and S5 respectively.
Table 6. Comparative studies related to adsorption of DB-53 using various adsorptive materials.

| Adsorbent                          | Adsorbent state and size | Concentration range (mg/L) | Dosage (gL$^{-1}$) | Temperature (°C) | PH | Eq. Time (h) | Langmuir Capacity (mg g$^{-1}$) | References |
|------------------------------------|--------------------------|-----------------------------|---------------------|------------------|----|--------------|---------------------------------|------------|
| Multi-walled CNT                  | Powder                   | 80–1000                     | 0.3                 | 25               | 2.0 | 24           | 334.8                           | [37]       |
| Activated carbon                  | Powder                   | 80–1000                     | 0.3                 | 25               | 2.0 | 24           | 88.36                           | [37]       |
| Zn$_2$Al layered double hydroxide | Powder                   | —                           | 2.5                 | 25               | 7.0 | 7            | 49.51                           | [38]       |
| Aqai stalks as bio sorbent        | Powder                   | 0–70                        | 2.5                 | 25               | 2.0 | 16           | 45.1                            | [39]       |
| Mg-Al-CO$_3$                       | Powder                   | 50                          | 0.5                 | 25               | 6.0 | 20           | 107.5                           | [17]       |
| Euphorbia antiquorum L AC         | Powder                   | 25–100                      | 0.5                 | 25               | 8.22| 2            | 58.40                           | [18]       |
| PLA nano particles                | Powder                   | 5–30                        | 0.6                 | 28 ± 2           | 7.0 | 0.5          | 40.82                           | [19]       |
| Rare earth doped laalo$_3$        | Powder                   | 5–60                        | 0.6                 | 25 ± 2           | 2   | 0.5          | 100                             | Present study |
control of the adsorption process occurred in multiple steps [31]. Table 5 shows that the rate constant increases with increased dye concentration. Higher adsorbate concentration creates a concentration gradient hence causes the quicker and faster adsorption rate. The coefficient $R^2$ for the Webber–Morris model was $>0.9$ at all concentrations of deviated curves from the origin suggested that some degree of boundary layer effect. Also, the Bangham model is well fitted nonlinearly with value of coefficient $R^2 > 0.96$ at all concentration as presented in table S6 [28]. Therefore, one may predict that both intraparticle, as well as film diffusion, administers the rate-limiting mechanism. Comparison of adsorption of DB-53 capacity on to rare-earth doped Lanthanum aluminate and other parameters obtained from the present work against already reported materials has been tabulated in table 6. Hence, we can say that these materials have a better potential towards adsorption of DB-53 dye at ambient conditions (room temperature and pressure).

3.7.5. Regeneration and reusability studies
The figure 9 depicts the regeneration and reusability studies and the regenerated adsorption efficiency found to be in the percentage order of 89, 77.5, 69.2, 60.8, 53.3 and 41.8 as presented in graph. Among the six adsorption-desorption cycles, the first 5 cycles work effectively. Hence the present study recommended LASB as a prominent adsorbent for removal of azo dye [28, 35].

4. Conclusions
We successfully synthesized LA, LAS, LASB nano aluminates via a non-toxic and eco-friendly approach using sugar and studied the structural properties and adsorption of DB-53 dye. Hence nano aluminate prepared by sugar (natural fuel) is an alternative method to produce large nano aluminate compounds with low cost. Using x-ray diffraction analysis crystallite size was calculated by Scherrer’s formula. The TEM image also shows that we obtain a nanopowder with a particle size of about 60 nm. The incorporation of Bi$^{3+}$ ions reduces the bandgap to 4.7 eV. Also, LASB nanocomposites show the significant potential in adsorption of DB-53 dye. The kinetic study revealed that the equilibrium time of contact was about 30 min for different dye concentrations at room temperature. We achieved maximum DB-53 dye adsorption using LASB nanoparticles with acidic pH 2 in 30 min The pseudo first-order kinetic model and D-R equilibrium model were good fitted and confirmed with nonlinear statistical error computation studies. The coefficient $R^2 > 0.99$ of PFO, the mean energy value of D-R model (0.042 kJ mol$^{-1}$) and value of initial adsorption rate H in PSO indicates that the physisorption is dominant in the present study. These physisorbed molecules are further confirmed with infrared spectroscopy.

The maximum Langmuir adsorption capacity is found to be 105.85 mg g$^{-1}$. Adsorption mechanism predicted using Bangham kinetic and intraparticle diffusion models. Multi-linearity of the intraparticle diffusion curves shows adsorption follow different steps at higher concentrations. Overall, from the structural studies, adsorption isotherms and kinetic modelling, the synthesized LASB nanoparticles are expected to be possible potential nano adsorbent materials for the future analytical applications.
Acknowledgments

The author S. Pratibha would like to convey sincere thanks to BMSITM, Bangalore for the providing research facilities and Dr N. Dhananjaya acknowledges DST -SERB, Govt. Of India, for financial support to carry out this research under Seed Money to Young Scientist for Research (Ref: SERB/F/6219/2014–15, Grant: DST/SERB No: SR/FTP/PS-188/2013).

ORCID iDs

N Dhananjaya  https://orcid.org/0000-0002-7973-1353
C R Manjunatha  https://orcid.org/0000-0001-5203-4462

References

[1] Gugulothu S, Sing S A and Madras G 2017 Superior adsorption capacity of strontium titanate and titania composites for anionic dyes removal J. Environ. Chem. Eng. 5 4663–75
[2] Jegathesan V, Pramanik B K, Chen J, Navarathna D, Chang C Y and Shu L 2016 Treatment of textile wastewater with membrane bioreactor: a critical review Bioreours. Technol. 264 302–12
[3] Manenti D R, Módenes A N, Soares P A, Espinoza-Quiñones F R, Boaventura R A, Bergammasco R and Vilar J 2014 Assessment of a multistage system based on electrocoagulation, solar photo-Fenton and biological oxidation processes for real textile wastewater treatment Chem. Eng. J. 252 120–30
[4] Santos A G, Leite J O, Souza M J, Gimenez I F and Pedrosa A G 2018 Effect of the metal type in perovskites prepared by modified protein method in dye adsorption from aqueous medium Ceram. Int. 44 5743–50
[5] Venkatesh S, Venkatesh K and Quaff A R 2017 Dye decomposition by combined ozonation and anaerobic treatment: Cost effective technology J. Appl. Res. Technol. 15 340–5
[6] GilPavas E, Dobrosz-Gómez I and Gómez-García M A 2017 Coagulation–flocculation sequential with Fenton or Photo-Fenton processes as an alternative for the industrial textile activated carbon j. Taiwan Inst. Chem. Eng. 53 112–21
[7] Saraf R, Shivakumara C, Rehera S, Nagabhushana H and Dhananjaya N 2015 Photoluminescence, photocatalysis and Judd–Ofelt analysis of Eu3+ activated layered BiOCl phosphors RSC Adv. 5 4109–20
[8] Li Y et al 2013 Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes Chem. Eng. Res. Des. 91 361–8
[9] Fan J, Shi Z, Lian M, Li H and Yin J 2013 Mechanically strong graphene oxide/sodium alginate/polyacrylamide nanocomposite hydrogel with improved dye adsorption capacity J. Mater. Chem. A 1 7433–43
[10] Dylani C, Zaghdoudi R, Djazi F, Boucheikima B, Balamam A, Madarresi A and Rogalski M 2015 Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon j. Taiwan Inst. Chem. Eng. 53 112–21
[11] Haque E, Jun W and Jhung S H 2011 Adsorptive removal of methyl orange and methyl blue from aqueous solution with a metal-organic framework material, iron terephthalate (MOF-235) J. Hazard. Mater. 185 507–11
[12] Duman O, Tung S, Bozoğlan B K and Polat T G 2016 Removal of triphenylmethyl and reactive azo dyes from aqueous solution by magnetic carbon nanotube-κ-carrageenan-Fe3O4 nanocomposite J. Alloys Compd. 687 370–83
[13] Kim S H and Choi P P 2017 Enhanced Congo red dye removal from aqueous solutions using iron nanoparticles: adsorption, kinetics, and equilibrium studies Dalton Trans. 46 4677–85
[14] Palas B, Ersöz G and Atalay S 2018 Catalytic wet air oxidation of reactive black 5 in the presence of LaNiO3 perovskite catalyst as a green process for azo dye removal Chemosphere 209 623–30
[15] Bradha M, Vijayaraghavan T, Suriraj S P, Selvakumar R and Ashok A M 2015 Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon j. Taiwan Inst. Chem. Eng. 53 112–21
[16] Liang S, Guo X, Feng N and Tian Q 2010 Isotherms, kinetics and thermodynamic studies of adsorption of Cu2+ from aqueous solutions by Mg+2–K+ type orange peel adsorbents J. Hazard. Mater. 174 756–62
[17] Boursa M, Beshaa H and de Méroval L C 2014 Removal of evans blue and yellow thiazole dyes from aqueous solution by Mg–Al–CO3 Layered Double Hydroxides as anion-exchanger Mediterranea Journal of Chemistry. 3 894–906
[18] Sivakumar P and Palamisamy P N 2011 Non-conventional low-cost adsorbent from Euphorbia antiquorum L for the removal of Direct Blue 53 from its aqueous solution Indian Journal of Chemical Technology 18 188–96 http://mctdhhlab.com
[19] Manjunatha C R, Nagabhushana B M, Raghu M S, Pratibha S, Dhananjaya N and Narayana A 2019 Perovskite lanthanum aluminate nanoparticles applications in antimicrobial activity, adsorptive removal of Direct Blue 53 dye and fluoride Mater. Sci. Eng. –C
[20] Raveeshya H R, Sivakumara C R, Nagaswarupa H P and Dhananjaya N 2019 Costus Pictus leaf extract mediated biosynthesis of Fe and Mg doped CuO nanoparticles: structural, electrochemical and antibacterial analysis Mater. Res. Express 6 115005
[21] Anupama M K, Rudaewsamy B and Dhananjaya N 2017 Investigation on impendence response and dielectric relaxation of Ni–Zn ferrites prepared by self-combustion technque J. Alloys Compd. 706 554–61
[22] Williet-Gijs T, Delong E and Zollner S 2014 Vibrational properties of bulk LaAlO3 from Fourirer–transform infrared ellipsometry Thin Solid Films 571 620–4
[23] Singh V, Rai V K, Singh N, Pathak M S, Rathiaah M, Venkatramu V, Patel R V, Singh P K and Dhoble S J 2017 Visible upconversion in Er3+/Yb3+ co-doped LaAlO3 phosphors Spectrochim. Acta A 171 229–35
[24] Pratibha S, Dhananjaya N and Lokesh R 2020 Investigations of enhanced luminescence properties of Sm3+ doped LaAlO3 nanophosphors for field emission displays Mater. Res. Express 6 125007
[25] Pratibha S, Dhananjaya N, Manohara S R and Yadav I R 2019 Effect of Sm3+, Bi3+ ion doping on the photoluminescence and dielectric properties of phosphosynthesized LaAlO3 nanoparticles J. Mater. Sci., Mater. Electron. 30 674–59
[26] Lokesh R, Pratibha S, Dhananjaya N, Manohara S R and Kumar K S 2019 Reformed solution combustion approach for probing of structural and dielectric properties of Sm3+ doped GdAlO3 nanoparticles. Materials Research Express 6 105066
[27] Wu G, Deng H, Wang W, Zhang K, Cao H, Yang P and Chu J 2014 Effect of Co doping on the structure, optical and magnetic properties of LaAlO$_3$ thin films J. Mater. Sci., Mater. Electron. 25 3137–40
[28] Manjunatha C R, Nagabhushana B M, Narayana A, Pratibha S and Raghu M S 2019 Effective and fast adsorptive removal of fluoride on CaAl$_2$O$_4$: Ba nanoparticles: isotherm, kinetics and reusability studies Mater. Res. Express 6 115089
[29] Yadav L S, Thippeswamy R, Shekarappa P, Kempegowda R G and Ganganagappa N 2019 Photocatalytic activities, kinetics and adsorption isotherm studies of CeO$_2$ nanoparticles synthesized via low temperature combustion method Current Nanomaterials. 4 223–34
[30] Kumar K V and Porkodi K 2007 Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using Paspalum notatum J. Hazard. Mater. 146 214–26
[31] Wu F C, Liu B L, Wu K T and Tseng R L 2010 A new linear form analysis of Redlich–Peterson isotherm equation for the adsorptions of dyes Chem. Eng. J. 162 21–7
[32] Elmosri T M 2011 Equilibrium isotherms and kinetic studies of removal of methylene blue dye by adsorption onto miswak leaves as a natural adsorbent Journal of Environmental Protection. 2 817
[33] Porkodi K and Kumar K V 2007 Equilibrium, kinetics and mechanism modeling and simulation of basic and acid dyes sorption onto jute fiber carbon: Eosin yellow, malachite green and crystal violet single component systems J. Hazard. Mater. 143 311–27
[34] Inyinbor A A, Adekola F A and Olatunji G A 2016 Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto Raphia hookerie fruit epicarp Water Resources and Industry. 15 14–27
[35] Manjunatha C R, Nagabhushana B M, Adarsha J R, Pratibha S and Dhananiya N 2019 One pot solution combustion synthesis of nano Dicalcium magnesium aluminate and effective utilization of hazardous fluoride removal: kinetics, equilibrium and reusability studies Mater. Res. Express 6 115025
[36] Chen H, Motuzas J, Martens W and da Costa J C 2018 Degradation of azo dye Orange II under dark ambient conditions by calcium strontium copper perovskite Appl. Catalysis B 221 691–700
[37] Prola L D, Machado F M, Bergmann C P, de Souza F E, Gally C R, Lima E C, Adebayo M A, Dias S L and Calvete T 2013 Adsorption of Direct Blue 53 dye from aqueous solutions by multi-walled carbon nanotubes and activated carbon J. Environ. Manage. 130 166–75
[38] Marangoni R, Bouhent M, Taviot-Guého C, Wypych F and Leroux F 2009 Zn-Al layered double hydroxides intercalated and adsorbed with anionic blue dyes: a physico-chemical characterization J. Colloid Interface Sci. 333 120–7
[39] Prola L D, Acayanka E, Lima E C, Bestetti C, Santos W O, Pavan F A, Dias S L and Tarley C R 2013 Application of aqai stalks as biosorbent for the removal of Evans Blue and Vilmafix Red RR-2B dyes from aqueous solutions Desalin. Water Treat. 51 4582–92