Solution combustion synthesis of calcium aluminate nanocomposite using coffee husk extract as green fuel and its application in adsorptive amputation of anionic dyes

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Abstract

Solution combustion synthesis of calcium aluminate (CaAl₂O₄) nanocomposite using coffee husk extract and its adsorption capacity for removal of Congo red (CR) and Indigo carmine (IC) are reported. Physicochemical properties of adsorbent were studied by PXRD, SEM, TEM and point of zero charge. Batch adsorption studies were conducted to study the effect of adsorbent dosage, pH, contact time, initial dye concentration and temperature on adsorption efficiency of coffee husk derived calcium aluminate nanocomposite (CHCA). Among the isotherms used, Langmuir model explained best the equilibrium data and the maximum monolayer adsorption capacity was found to be 377 and 135 mg/g for CR and IC, respectively. Mass transfer analysis indicated adsorptive removal of dyes was controlled by both external and internal diffusion. Pseudo-first-order model fitted best with experimental kinetic data and adsorption efficiency increased with an increase in the initial bulk concentration of CR and IC. Thermodynamic analysis indicated that adsorption of CR and IC on CHCA is feasible, spontaneous and exothermic in nature. The magnitude of enthalpy and heat of adsorption suggested that the adsorption is physical in nature. The present study explores the potential of coffee husk extract, an agro-based bio-waste, as a novel and eco-friendly fuel in the synthesis of CHCA and the synthesised nanocomposite as a potential adsorbent for the removal of synthetic dyes.

Introduction

Colour is a major water containment notable even at small amounts. Significant use of synthetic dyes by industries such as textile, leather, paper, printing, cosmetic, food etc., has led to increased dye effluent associated water pollution. Textile industry alone contributes to >50% dye effluent discharge [1, 2]. Presently, more than 100,000 commercial dyes are known with an annual production rate of over 7 × 10⁷ tones [3]. Apart from changing the properties of water, dye effluent also inhibits penetration of light into the water, making it unsuitable for aquatic life. Due to the toxic, carcinogenic, mutagenic and allergic nature of dyes, the direct discharge of untreated dye effluent can cause hazardous effects on living systems [4–8].

Various physicochemical and biological methods such as chemical coagulation, ozonation, chemical and electrochemical oxidation, adsorption, photocatalysis, aerobic and anaerobic digestion etc., are widely used for decolourisation of dye-containing wastewater [9–12]. Despite several techniques available, adsorption is considered most promising due to its extensive applicability, ease of operation and cost-effectiveness. Adsorption technique is not only efficient for the removal of soluble and insoluble organic pollutants, it is also an environmentally benign process owing to the non-generation of hazardous by-products [13–15]. Activated
carbon, because of its textural properties, larger surface area, pore volume and pore structure, is the widely used conventional adsorbent material for the removal of pollutants from aqueous systems [16]. However, high cost and difficulty in regeneration are still concerns with the use of activated carbon. This has motivated researchers to develop economical and efficient alternative adsorbents for the removal of dyes [17–19].

In the recent decade, nanomaterials, due to their unique characteristics such as small size, greater surface area, and presence of a large number of active sites, have emerged as excellent adsorbents over conventional adsorbents [20]. Although various metal and metal oxide nanoparticle are explored as adsorbents for water purification, there is limited literature available on the usage of calcium aluminate (CaAl2O4) as adsorbent. Majorly, calcium aluminate derived compounds are used in the cement industry as hydraulic binders [21, 22] and in the bio-medical field as bioceramics [23]. Present work, therefore, emphasises on exploring the potential of calcium aluminate nanocomposite for adsorptive removal of organic dyes.

There are numerous strategies available for the synthesis of nanomaterials such as sol-gel, chemical co-precipitation, chemical vapour deposition, mechanical alloying, solvothermal synthesis, microwave heating and reverse micelle synthesis. The major drawback of these methods includes longer reaction time, high temperature and need for specialised equipment [24]. Solution combustion synthesis - a simple, fast, cost-effective wet chemical method yielding products of high purity, overcomes the major drawbacks of most of the other techniques [25]. The properties of solution combustion-derived nanoparticles such as particle shape and size, structure, crystallinity and specific surface area are dependent on adiabatic combustion temperature and released gaseous quantity which in turn is dependent on the nature of fuel and fuel to oxidant ratio [26]. Fuel selection is based on several features such as low decomposition temperature, chelating capability, high solubility, availability and cost [27]. It is evident from the literature that carbohydrates and amines are widely used as fuels in the solution combustion synthesis [28, 29]. Presence of biomolecules such as carbohydrates (58%–85%), proteins (8%–11%), polyphenols, tannins etc play an important role as fuel and amine-containing molecules possess good chelating ability and aid in better combustion [30, 31]. Despite several reports on the use of various organic compounds as fuels, use of agro-waste extract as a cost-effective and eco-friendly fuel is limited. Hence, the main objective of this research is to utilise an extract of the coffee husk, agro-waste as fuel for the synthesis of calcium aluminate nanocomposite (CHCA).

Two anionic dyes, viz. Congo red (CR) and Indigo Carmine (IC) are considered as model dyes to study the adsorptive removal efficiency of CHCA. Azo dyes are the largest class of synthetic dyes with 60%–70% of total dye consumption [32]. CR, a benzidine-based anionic diazo dye, has a complex chemical structure and high solubility in aqueous solutions. Sewage from the printing, textile, plastic and paper industries release a substantial amount of CR in the effluent. CR causes serious eye, skin, alimentary tract, genital, and respiratory irritation and is also human carcinogen [33]. IC is another water-soluble disulphonate vat dye having wide application in many industries like paper, textile, cosmetic, medicine, and food [34, 35]. IC is highly toxic, causes skin, respiratory and gastrointestinal irritation and leads to permanent injury of cornea and conjunctiva. IC dye is also carcinogenic in nature and can be reproductive, developmental, neuro and acute toxic [36, 37]. Therefore, it is very crucial to eliminate these toxic dyes from the effluents prior to discharge into the environment.

In the present study, solution combustion derived calcium aluminate nanocomposite are employed in adsorptive removal of two anionic dyes viz. CR and IC. The influence of batch adsorption operating parameters such as adsorbent dose, solution pH, initial adsorbate concentration, temperature and time are studied. The experimental adsorption data is systematically analysed using adsorption isotherms, kinetic and thermodynamic models to understand the mode and mechanism of adsorption.

Materials and methods

Materials

Aluminium nitrate nonahydrate (Al(NO3)3·9H2O, 99% purity), Calcium nitrate tetrahydrate (Ca(NO3)2·4H2O, 99% purity), Congo red (C32H22N6Na2O6S2, λmax~497 nm) and Indigo Carmine (C16H8N2Na2O8S2, λmax~610 nm) were purchased from SD Fine-Chem Limited, India. All chemicals are of analytical grade and used without further purification. Double distilled water was used throughout the experiments. The molecular structure of CR and IC is given in figure S1 is available online at stacks.iop.org/MRX/7/035503/mmedia.

Preparation of coffee husk extract

Coffee husk sample used in this study was collected from coffee curing industry located in Hassan (13.0753 °N, 76.1784°E), Karnataka, India. Coffee husk was manually cleaned to remove impurity and dried at 40 °C for 24 h. Dried coffee husk was ground to powder in a domestic grinder. Approximately 15 gm of coffee husk powder was...
refluxed with 250 mL of water for 1 h and the extract was filtered to remove solids. The obtained extract was utilized for the synthesis of calcium aluminate (CaAl₂O₄) nanocomposite.

**Synthesis of calcium aluminate nanocomposite absorbent**

In a typical synthesis, 2.36 g of Calcium nitrate tetrahydrate and 7.50 g of Aluminium nitrate nonahydrate were dissolved in coffee husk extract solution (10 ml of coffee husk extract diluted with 10 ml of double-distilled water). The mixture was stirred for 1 h to obtain a homogenous mixture and kept in muffle furnace preheated to 500 °C. Milky white product obtained from combustion process was ground to a uniform size. The experiments were conducted at different volumes viz. 20, 30, 40, 50 and 60 mL of coffee husk extract for optimization of fuel. Obtained Calcium aluminate was heated at different temperature viz. 700, 800, 900 and 1 000 °C to optimise calcination temperature. The obtained calcium aluminate nanocomposite was named as CHCA.

**Characterization of CACH nanoparticles**

The crystalline phase of CHCA nanoparticles was analyzed by powder x-ray diffraction (PXRD) using (Rigaku’s, Smartlabs, Japan) rotating anode Cu Kα (1.5406 Å). The accelerating voltage and current were 30 kV and 40 mA respectively. The PXRD patterns were collected in the 2θ range from 10° to 70° with a step size of 0.02°. Scanning electron micrographs (SEM) were recorded to investigate the surface morphology using JEOL (JSM-840A) instrument. Particle size was determined using HRTEM (Jeol/JEM 2100).

**Determination of point of zero charge**

Solid addition method described elsewhere was employed for the estimation of point of zero charge (PZC) of the CHCA adsorbent [38, 39]. A Series of 50 mL solution of 0.01 N NaCl solution was taken in 250 ml conical flask and solution pH was adjusted between 2 and 12 using 0.01 N NaOH and 0.01 N HCl. Then, 0.01 g of CHCA absorbent was added to these solutions and pH was recorded after 48 h of equilibration under 150 rpm agitation at 303.15 K. The point of zero charge was estimated from the plot of the change in pH (final pH—initial pH) versus initial pH.

**Adsorption studies**

Batch experiments, to study the adsorption behaviour of CR and IC on CHCA, were carried out using 50 mL of dye solution at 150 rpm and 303.15 K in a thermostatic shaker. Working solutions of CR and IC were prepared by diluting a stock solution of 1 g l⁻¹. The effect of adsorbent dosage was studied using a known concentration of CR or IC solution contacted with CHCA varied between 0.1 to 3 g/l at neutral pH. Effect of pH on CR adsorption was assessed in the pH range of 2–10 at 303.15 K. Isotherm studies were conducted by varying initial concentration of dye between 50–800 mg l⁻¹ and temperature between 303.15–323.15 K. Kinetic studies were conducted with the initial concentration of dye ranging from 50–500 mg l⁻¹ at 303.15 K for different time intervals (0–120 min). Post adsorption, the dye solutions were centrifuged at 15000 rpm for 5 min to remove CHCA and the absorbance of the supernatant was measured at λmax 497 nm and 610 nm for CR and IC respectively using UV−visible spectrophotometer (UV-1800, Shimadzu, Japan). The dye removal efficiency, equilibrium capacity of adsorption (qe) and adsorption capacity at time t (qt) were calculated using equations

\[
\text{Dye removal efficiency(%) } = \frac{100(C_i - C_e)}{C_i} \text{ or } \frac{100(C_i - C_t)}{C_i} \quad (1)
\]

\[
q_e = \frac{(C_0 - C_e)V}{m}, \quad \text{mg/g} \quad (2)
\]

\[
q_t = \frac{(C_0 - C_t)V}{m}, \quad \text{mg/g} \quad (3)
\]

where C₀ is the initial dye concentration (mg/L), Cₑ and Cₜ are dye concentration after equilibrium and kinetic time respectively, V is the volume of dye solution (L) and m is the mass of adsorbent (g).

**Statistical analysis**

Adsorption experiments in this study were carried out in duplicates and average values were used for further analysis. The experimental adsorption data was fitted to selected isotherm and kinetic models. Non-linear regression analysis was performed in Microsoft Excel® 2019 using the SOLVER tool based on the Generalized Reduced Gradient (GRG) method of iteration. The goodness of the fit was evaluated using three statistical parameters viz, coefficient of determination (R²), residual sum square (RSS), average relative error (ARE). Statistical parameters were calculated from the following mathematical expressions (equations (4) to (6))

\[
R^2 = \frac{\sum(q_{exp, i} - q_{exp, avg})^2}{\sum}
\quad (4)
\]

\[
\text{average relative error (ARE)} = \frac{100}{n} \sum \left| \frac{q_{exp, i} - q_{pre, i}}{q_{exp, avg}} \right|
\quad (5)
\]

\[
\text{coefficient of determination (R²)} = 1 - \frac{\text{RSS}}{\text{TSS}}
\quad (6)
\]
where $q_{\text{e,exp},i}$ is experimentally measured and $q_{\text{e,pre},i}$ is model predicted adsorbate solid phase concentration on adsorbent at any observation $i$. $q_{\text{e,exp,avg}}$ is the average of experimentally measured observations. $N$ and $p$ are number of observations and number of model parameters respectively [10, 29].

**Regeneration studies**

After batch adsorption, dye adsorbed CHCA nanocomposite was regenerated by calcinating at 450 °C for 30 min in a muffle furnace. The obtained CHCA nanoparticles were used for dye removal to study the capacity of the regenerated nanocomposite. The experiment was repeated for 5 cycles [40, 41].

**Results and discussion**

**Characterization of adsorbent**

CHCA prepared using 40 ml of coffee extract was calcinated at different temperatures (700, 800, 900 and 1000 °C) and the corresponding PXRD patterns are shown in figure 1. From the diffraction patterns obtained, it is observed that the as-formed product is completely amorphous without any crystalline peaks (figure 1(a)). A similar observation is also seen in the samples that are calcinated at 700 and 800 °C (figures 1(b) and (c)). Further, the XRD pattern of the sample (figure 1(d)) calcinated to 900 °C show crystalline and well-defined diffraction peaks. However, in order to obtain a highly crystalline product, the sample was further calcinated to 1000 °C. For samples calcined at 1000 °C, highly crystalline well-defined diffraction peaks (figure 1(e)) that can be readily indexed to the monoclinic phase of CaAl$_2$O$_4$ were obtained. The diffraction peaks obtained are found

![Figure 1. PXRD of CHCA.](image)
to have a high intensity that indicates to highly crystalline nature of CaAl$_2$O$_4$. All the diffraction peaks match with the standard JCPDS: 70–0134 without any impurity phases and is in good agreement with the literature [42].

The SEM images of the adsorbent (CHCA) before (prepared using 40 ml of coffee fuel extract and calcinated at 1000 °C) and after adsorption of CR and IC are shown in figure 2 and S2 respectively. From the SEM micrographs, it is clear that there is a difference in the surface morphology of the adsorbent before and after dye adsorption. Figures 2 and S2a surface morphology of CHCA before dye adsorption shows highly agglomerated particles with more number of voids. Each particle interconnected to one another forming agglomerated clusters is clearly visible in the micrograph. The reusability of adsorbent is one of the important parameters for practical application in terms of economic and cost-effectiveness. As shown in fig S the CR and IC removal

![Figure 2. SEM micrographs of CHCA before adsorption.](image)
efficiency remained at a relatively higher level for up to three cycles but decreased slightly thereafter. This reduction might be related to the loss of active sites during adsorption−desorption processes and due to repeated calcination. Nevertheless, these findings showed that CHCA nanoparticles could be regenerated and recycled successfully after being used for CR and IC removal. However, CHCA after adsorption of CR (figure S2b) and IC (figure S2c) dyes shows changes in the surface morphology. The rough surface before adsorption has changed to a relatively smoother surface (not significant) and the number of voids/pores are reduced significantly. The reason for the variation in the morphology may be due to the accumulation of dye particles on the surface. Further, during batch adsorption experiments stirring causes collision of adsorbent molecules and may cause variation in the surface morphology.

Figure 3 shows the transmission electron microscopic images of CaAl2O4 prepared using coffee husk extract as fuel. In order to determine the precise size of the particles, TEM is carried out and is presented in figure 3(a). The particles seen in TEM images are found to have different sizes and are agglomerated. The average size of the particles is found to be ~40–60 nm. The agglomerated nature of the particles observed in TEM images are consistent with the SEM results and similar nature of the particles are also reported in the literature for combustion synthesised particles. Figure 3(b) shows the SAED pattern, and the nature of the diffracted pattern is found to be ring pattern with bright spots. This indicates to nanocrystalline nature of the prepared samples [42]. The HRTEM images show well-defined lattice fringes with d spacing ∼0.22 nm corresponding to (230) plane of monoclinic CaAl2O4.

Effect of adsorbent dosage
Adsortent dosage is the major factor that significantly influences the economic viability and efficiency of an adsorption process [43]. The effect of CHCA adsorbent dosage on removal of dyes was studied in the concentration range of 0.1–1 g l−1 for CR and 0.3–3 g/l for IC with an initial concentration of 100 mg l−1 and 50 mg l−1 of CR and IC, respectively. Figures 4(a) and (b) depict the influence of CHCA dosage on dye adsorption efficiency and adsorption capacity at neutral pH. Percentage dye removal increases with increase in the adsorbent dosage for both the dyes, owing to an increase in the number of sorption sites [10]. The dye adsorption capacity at lower adsorbent dose is high due to better access to the available active sites. However, at high adsorbent dosage, available active sites become relatively higher with respect to dye molecules and hence saturation is reached. [44]. Maximum adsorption efficiency (>90%) was achieved at 1 g l−1 and 2 g l−1 of CHCA for CR and IC, respectively. Further adsorption experiments were carried out at these adsorbent dosages.

Effect of pH
The pH of the dye solution is an important factor which effects the absorbent surface charge and degree of ionization of dye molecules. Charge on the adsorbent surface and degree of ionisation of dye molecules have a significant influence on the adsorption capacity of dyes [29]. The influence of pH on adsorption of CR on to CHCA was studied in the pH range 6–11 using 0.3 g l−1 of CHCA with an initial dye concentration of 100 mg l−1 at 303.15 K for 2 h. Lower pH (<6) conditions were not considered because of the shift in λmax of the dye. In the case of IC, studies were conducted in the pH range 2–10 using 1 g l−1 of CHCA with an initial dye concentration of 50 mg l−1 at 303.15 K for 2 h. From figures 5(a) and (b), it is observed that maximum dye removal efficiency and adsorption capacity for both dyes occurs around 7–8 pH. PZC of the adsorbent was found to be 8.3 (figure 4(c)). At pH lower than PZC, CHAC will have a positive charge and at pH higher than PZC, CHAC acquires a negative charge. Hence, lower pH favours dye adsorption due to the electrostatic attraction between
anionic dye and adsorbent surface, while electrostatic repulsion results in a decrease in dye removal efficiency at higher pH [45, 46].

**Adsorption isotherms**

Adsorption equilibrium and its mathematical expression are significant in the framework of adsorption theory. Adsorption equilibrium data helps to assess the process of adsorption and to design the adsorber for effective removal of pollutants. It is also essential to characterize the adsorbability of the pollutants in a considered adsorbate/adsorbent system in order to choose a suitable adsorbent [47, 48]. In general, adsorption isotherm is an invaluable curve representing the relationship between the extent of adsorption (amount of adsorbate adsorbed by the unit weight of adsorbent) and the equilibrium concentration of adsorbate at a constant temperature. At various equilibrium concentrations, adsorption isotherms give information about the distribution of adsorbate between solid and liquid phases [49–51]. The experimental adsorption equilibrium data of CR and IC onto CHCA was correlated using two well-known isotherm models namely Langmuir and Freundlich.

The Langmuir adsorption isotherm was originally developed for gas-solid adsorption on to activated carbon, which has been conventionally used to quantify the adsorption capacity of various adsorbents. This model assumes monolayer adsorption and all the adsorption sites have the same adsorption energy with no lateral interaction or steric hindrance between the adsorbed molecules [52]. The nonlinear form of Langmuir isotherms is expressed as:

\[
q_e = \frac{q_mK_LC_e}{1 + K_LC_e}
\]

where \(q_m\) (mg/g) is the maximum saturated monolayer adsorption capacity of adsorbent, \(C_e\) (mg/L) is adsorbate equilibrium concentration, \(q_e\) (mg/g) is the equilibrium adsorption capacity and \(K_L\) is Langmuir constant.
The important feature of the Langmuir isotherm can be expressed as dimensionless separation factor $R_L$:

$$R_L = \frac{1}{1 + K_L C_0}$$

where $C_0$ (mg/L) is the initial adsorbate concentration.

$R_L$ represents the type of adsorption: unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$).

Freundlich adsorption isotherm is another widely used and earliest empirical model developed to describe the characteristics of adsorbents with heterogeneous surfaces [53]. The nonlinear Freundlich isotherm is expressed as:

![Figure 5. Effect of pH on adsorption capacity of CHCA nanocomposite (a) Congo Red (b) Indigo Carmine (c) PZC of the adsorbent.](image-url)
where $K_F$ (mg/g) is Freundlich constant. $1/n$ (dimensionless) is the intensity parameter representing the magnitude of surface heterogeneity and indicate the favorability of adsorption process: irreversible ($1/n = 0$), favourable ($0 < 1/n < 1$) and unfavourable ($1/n > 1$). The adsorbent surface becomes more heterogeneous as $1/n$ value gets closer to 0. Freundlich isotherm is unable to describe the saturation behaviour of adsorbent because it can neither describe linear range at lower concentrations nor the saturation effect at high adsorbate concentrations [10, 50, 54, 55].

The values of model and statistical parameters obtained through nonlinear regression of isotherm models at various temperatures for adsorption of CR and IC on CHCA is summarized in table 1. Clearly for both the dyes, Langmuir isotherm fitted better with experimental data than Freundlich isotherm, with a strong correlation between experimental and predicted data as indicated by high $R^2$ value. The lower values of RSS and ARE further confirm that the Langmuir model reproduces the adsorption data more precisely compared to Freundlich isotherm. It is evident from the results that monolayer adsorption of CR and IC occurs on CHCA. Figures 6(a) and (b) represents the Langmuir plot at various temperatures. As shown, equilibrium adsorption capacity increased with an increase in dye concentration and decreased with increase in temperature. This shows the exothermic nature of adsorption process with lower temperature favouring the adsorption of CR and IC on CHCA. The theoretical maximum adsorption capacity was calculated to be 338 and 135 mg/g for CR and IC respectively at 303.15 K. With an increase in temperature from 303.15 K to 323.15 K, the adsorption capacity decreased by 33% and 11% for CR and IC, respectively. Langmuir constant $K_L$ also decreased indicating that affinity between adsorbent and adsorbate decreased with increase in temperature. The RL values in the range $0 < RL < 1$ (figures S3a and b) and the Freundlich intensity parameter in the range $1 < 1/n < 10$ (table 1) indicates that the adsorption of both CR and IC on CHCA is favourable at the concentration and temperature range studied [56]. The adsorption capacities obtained in this study was compared with various adsorbents reported in the literature for the removal of CR and IC and is summarized in tables S1 and S2 respectively. Calcium aluminate nanocomposite synthesized using coffee husk extract as a green fuel is found to have better adsorption capacity compared to other nano-adsorbents reported in the literature. It is also economically attractive and very promising compared to other adsorbents due to the low-cost synthesis.

### Adsorption kinetics and mechanism of adsorption

Adsorption kinetics is essential to describe the rate of adsorbate (solute) uptake and helps to determine the time required for reaching equilibrium. Kinetic analysis is also important to evaluate the mass transfer limitation during the adsorption process and provides the most valuable information for the design of adsorption systems [57, 58]. In liquid phase systems and porous materials, the course of adsorption of solutes from bulk to pores generally includes the following four consecutive steps:

1. Transfer of solute from the bulk of the solution to the liquid phase/film localized around the adsorbent.

### Table 1. Estimated model and statistical parameters of selected isotherm models for adsorption of CR and IC on CHCA.

| Dye           | Isotherm | Temperature, K | Model constants | Statistical parameters |
|---------------|----------|----------------|-----------------|------------------------|
|               |          |                | $Q_L$ | $K_L$ | $R^2$ | RSS | ARE |
| Congo Red     | Langmuir | 303.15         | 337.4415 | 0.0666 | 0.9635 | 860.0892 | 7.0785 |
|               |          | 313.15         | 265.1243 | 0.0230 | 0.9632 | 400.1351 | 5.1186 |
|               |          | 323.15         | 228.8830 | 0.0202 | 0.9694 | 355.7948 | 5.3206 |
|               | Freundlich | 303.15      | 4.1669 | 88.2920 | 0.9551 | 2817.7948 | 10.7282 |
|               |          | 313.15         | 2.7123 | 34.3343 | 0.9218 | 1334.8635 | 10.4010 |
|               |          | 323.15         | 3.3833 | 36.3937 | 0.9112 | 1432.2185 | 10.1764 |
| Indigo Carmine| Langmuir | 303.15         | 134.6782 | 0.0603 | 0.9586 | 256.5471 | 11.2880 |
|               |          | 313.15         | 125.8056 | 0.0352 | 0.9806 | 90.4010 | 6.4487 |
|               |          | 323.15         | 118.0249 | 0.0249 | 0.9787 | 78.8696 | 6.5350 |
|               | Freundlich | 303.15      | 2.6438 | 21.8624 | 0.8430 | 903.4645 | 21.9633 |
|               |          | 313.15         | 2.3065 | 13.7456 | 0.9170 | 365.0313 | 14.5294 |
|               |          | 323.15         | 2.1985 | 10.3220 | 0.9150 | 297.2277 | 14.6030 |

\[ q_e = K_F C_r^{1/n} \] (9)
2. Transport of solute across the hydrodynamic boundary layer to the external surface of the adsorbent. This is termed as film or external diffusion.

3. Diffusion of solute species from the surface into the pores of the adsorbent via intraparticle/internal or pore diffusion.

4. Energetic interaction of solute molecules to adsorption sites by physical forces or surface reaction.

The overall adsorption rate is usually controlled by the slowest among the above-mentioned steps. The initial step is negligible or can be overcome by increasing the agitation speed in batch adsorption process and the last step is considered to be spontaneous. Generally, the adsorption of pollutants on to porous materials is governed by either film or intraparticle diffusion [59, 60].

In this study, to better understand the adsorption kinetics, two categories of kinetics models were employed i.e., diffusion-controlled, and reaction controlled. The mathematical details and description of the selected models are presented below [61]:

Figure 6. Langmuir isotherm plot for adsorption of (a) Congo Red and (b) Indigo Carmine onto CHCA.
Diffusion-based models

Intraparticle diffusion (IPD) model

The IPD model also called as Weber and Morris model explains the adsorption kinetics limited by intraparticle diffusion, especially in porous adsorbent materials.

\[ q_t = k_{id} \sqrt{t} + C \]  

(10)

where \( k_{id} \) (mg g\(^{-1}\) min\(^{-0.5}\)) is intraparticle diffusion rate constant and \( C \) (mg/g) is the parameter which represents the interfacial film resistance or a boundary layer effect. Intraparticle diffusion is the sole rate-limiting step if the plot of \( q_t \) versus \( t^{0.5} \) straight line passes through the origin. However, two or more steps influence the adsorption if the plot exhibits multilinearity.

Bangham model

To further evaluate the pore diffusion-controlled mechanism of the adsorption process, Bangham model was used and the equation is as follows:

\[
\log \left\{ \log \left[ \frac{C_0}{C_0 - Mq_f} \right] \right\} = \log \left[ \frac{k_{0m}}{2.303V} \right] + \alpha \log t
\]

(11)

where \( C_0 \) represents the initial dye concentration (mg/L), \( m \) and \( V \) are the weight of adsorbent (g/L) and volume of dye solution (mL), respectively. \( k_0 \) and \( \alpha \) (<1) represent the Bangham constants.

Liquid film diffusion (LFD) model

Liquid film diffusion model can be applied to understand if the adsorbent surface is surrounded by a liquid film that controls the process of adsorption. Mathematically LFD model can be expressed as follows:

\[
\ln (1 - F) = k_{fl} t
\]

(12)

where \( F = \frac{q_t}{q_e} \) is fractional attainment of equilibrium and \( k_{fl} \) (min\(^{-1}\)) is film diffusion rate constant.

Reaction based models

Pseudo First Order (PFO) Model

In 1898, Lagergren proposed pseudo-first-order (PFO) equation and it has the following nonlinear form:

\[
q_t = q_e(1 - \exp^{-k_1t})
\]

(13)

where \( q_t \) and \( q_e \) (mg/g) are the amount of dye adsorbed at time \( t \) (min) and at equilibrium per unit weight of the adsorbent. \( k_1 \) (min\(^{-1}\)) is the pseudo-first-order rate constant which is a function of process conditions.

Pseudo Second Order (PSO) Model

Ho and McKay in 1998 proposed PSO model and the mathematical expression in nonlinear form is as follows:

\[
q_t = \frac{k_2q_e^2t}{1 + k_2q_et}
\]

(14)

where \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is pseudo-second-order kinetics.

It is evident from figures 7(a) and (b), the IPD plot of \( q_t \) versus \( t \) does not pass through the origin for both CR and IC. It is suggested that multiple rate-controlling steps such as film and intraparticle diffusion are involved in the adsorption of anionic dyes on CHCA. The piecewise linear regression was employed and the values of \( k_{id} \) and \( C \) for the linear portions calculated from slope and intercept at various concentrations are presented in table 2. The three main regions represented in figure 7 are: (1) the first linear region signifying the external film diffusion and instantaneous surface adsorption of dye molecules on CHCA, (2) The second region corresponding to interparticle or pore diffusion, where dye molecules diffuse into the pores of CHCA with gradual adsorption of dyes and (3) the third region indicating the equilibrium adsorption of dyes [62]. The \( R^2 \) values of the linear fit were in the range of 0.75–0.99 and \( k_{id} \) values calculated from the slope of the piecewise linear plots increased with increase in concentration for both CR and IC. This indicates that the increase in concentration gradient significantly influences the diffusion process thereby increasing the adsorption efficiency by overcoming the resistances along with the movement of dye molecules from the bulk to adsorption sites. It can also be seen from table 2 that the order of rates of adsorption kinetic is the first stage \((k_{i1}) > \) second stage \((k_{i2}) > \) third stage \((k_{i3})\). The values of \( C \) calculated from the intercepts of the linear plot is proportional to the thickness of the boundary layer in each step and larger the value more is the boundary layer effect. With an increase in time and concentration, the value of \( C \) also increased for both the dyes. From all these results it is clear that both
Figure 7. Intraparticle diffusion plot (a) Congo Red (b) Indigo Carmine.

Table 2. Weber-Morris Intraparticle diffusion model parameters for adsorption of Congo red and Indigo Carmine onto CHCA.

| Co, mg/L | k_d | C    | R²   | Co, mg/L | k_d | C    | R²   |
|--------|------|------|------|----------|------|------|------|
| 100    | Step-1 | 16.7989 | 1.0753 | 0.9715 | 50 | Step-1 | 3.4608 | 4.1601 | 0.9618 |
|        | Step-2 | 2.7840 | 68.6193 | 0.9135 | | Step-2 | 0.3274 | 18.3603 | 0.9280 |
|        | Step-3 | 1.6887 | 76.3913 | 0.7303 | | Step-3 | 0.0613 | 20.6383 | 0.7946 |
| 300    | Step-1 | 26.6934 | 3.8929 | 0.9830 | 150 | Step-1 | 8.2203 | 0.2289 | 0.9695 |
|        | Step-2 | 9.6228 | 108.4644 | 0.9569 | | Step-2 | 3.1069 | 27.7735 | 0.9590 |
|        | Step-3 | 6.2673 | 144.6011 | 0.9616 | | Step-3 | 0.6598 | 46.9708 | 0.9696 |
| 500    | Step-1 | 36.2967 | 6.7601 | 0.9798 | 250 | Step-1 | 9.4922 | 2.8338 | 0.9952 |
|        | Step-2 | 15.5728 | 125.5164 | 0.9748 | | Step-2 | 6.2357 | 24.9563 | 0.9702 |
|        | Step-3 | 5.1707 | 228.9133 | 0.9979 | | Step-3 | 1.1925 | 64.6829 | 0.9998 |
intraparticle and film diffusion are rate-controlling steps. To further substantiate this, adsorption kinetic data were fitted to Bangham and liquid film diffusion mass transfer models (LFD). Figures S4 and S5 show the plots for Bangham and LFD model respectively for CR and IC. The model and regression parameter values for Bangham and LFD model is presented in tables 3 and 4 respectively. For the Bangham model, the logarithmic plot for all the concentrations shows some linearity, however, the line does not pass through the origin (Intercept≠0) indicating the involvement of film diffusion along with intraparticle diffusion. The LFD model results are in good agreement with the Bangham model and the linear plot did not pass through origin suggesting the possible involvement of film diffusion during the adsorption process [63, 64].

In order to describe the kinetics involved in the process of adsorption of CR and IC on CHAC, PFO and PSO models were fitted with experimental data. The values of model parameters and statistical parameters are presented in table 5. From the results, it is observed that in the concentration range studied, the PSO model fitted well with high R² value and lower values of RSS and ARE for both the dyes. Compared to the PSO model, PFO model was best suited to describe the adsorption dynamics with the predicted values of maximum adsorption capacities closer to the experimental adsorption capacity. Hence, while the PFO model is best suited to explain the physical nature of the adsorption process, the PSO model describes the chemical nature of the interaction between adsorbate and adsorption sites [65]. kₜ values for CR and IC adsorption onto CHCA were found to decrease with increasing concentration which can be attributed to an increase in the time required to reach equilibrium with an increase in initial bulk concentration. [61]. Diffusion of dyes increases with the increase in mass transfer gradient and increase the adsorption capacity [66]. The plots of the nonlinear form of the PFO model are shown in figures 8(a) and (b) for adsorption of CR and IC respectively. As can be seen, CR and IC adsorption capacity increases with an increase in time and reaches saturation at ∼80 min and ∼60 min for CR and IC respectively. Faster adsorption kinetics observed during initial stages can be attributed to a large number of active sites available for adsorption which becomes less available and slow down the adsorption kinetics near equilibrium.

**Thermodynamics studies**

Adsorption is a temperature-dependent process and in the design of adsorption system assessment of thermodynamic parameters such as equilibrium constant (Kₑ), Gibbs free energy (ΔG⁰), enthalpy (ΔH⁰), entropy (ΔS⁰) and isosteric heat of adsorption (ΔHₛ) delineates the feasibility and mechanism (physical or chemical) of adsorption process [67, 68]. The thermodynamic parameters were determined using the following equations:

\[ G^0 = -RT \ln K_C \]  \hspace{1cm} (15)

Kₑ is calculated from the distribution coefficient (Kᵢₜ). The intersection on the vertical axis of the extrapolated line in the plot of ln(qₑ/Cₑ) versus Cₑ provides the value of Kᵢₜ [69].

Equations for evaluating ΔG⁰, ΔH⁰ and ΔS⁰ are given as follows:

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]  \hspace{1cm} (16)

By substituting equation XX into equation XX, the well-known van’t Hoff equation is obtained as given below:

| Table 3. Bangham model parameters for adsorption of Congo red and Indigo Carmine onto CHCA. |
|-------------------------------------------------------------|
| Cₒₐ mg/L | kₒ | α | R² | Cₒₐ mg/L | kₒ | α | R² |
|-----------|----|---|---|-----------|----|---|---|
| 100       | 0.0447 | 0.5424 | 0.7663 | 50        | 0.1152 | 0.3254 | 0.8614 |
| 300       | 0.0294 | 0.5452 | 0.9533 | 150       | 0.0703 | 0.4816 | 0.9501 |
| 500       | 0.0241 | 0.5687 | 0.9596 | 250       | 0.0590 | 0.5053 | 0.9697 |

| Table 4. Liquid film diffusion model parameters for adsorption of Congo red and Indigo Carmine onto CHCA. |
|-------------------------------------------------------------|
| Cₒₐ mg/L | kₕ₁ | I | R² | Cₒₐ mg/L | kₕ₁ | I | R² |
|-----------|----|---|---|-----------|----|---|---|
| 100       | 0.0341 | 1.127 | 0.878 | 50        | 0.0462 | 1.0985 | 0.9477 |
| 300       | 0.0285 | 0.282 | 0.98  | 150       | 0.0456 | 0.2515 | 0.9955 |
| 500       | 0.0261 | 0.236 | 0.963 | 250       | 0.0418 | 0.2515 | 0.9978 |
Table 5. Values of Model Constants and statistical parameters for reaction kinetic models of CR and IC dye adsorption onto CHAC.

| Model | \( C_0 \), mg/L | \( k_1 \) | \( q_e \) | \( R^2 \) | RSS | ARE | \( C_0 \), mg/L | \( k_1 \) | \( q_e \) | \( R^2 \) | RSS | ARE |
|-------|-----------------|----------|----------|----------|----|-----|-----------------|----------|----------|----------|----|-----|
| PFO   | 100             | 0.1070   | 92.0926  | 0.9582   | 440.9049 | 7.4328 | 50              | 0.1393   | 20.9358  | 0.9974   | 1.1351 | 1.4967 |
|       | 300             | 0.0492   | 202.8157 | 0.9884   | 481.5845 | 4.5909 | 150             | 0.0603   | 53.3708  | 0.9967   | 11.1125 | 1.8957 |
|       | 500             | 0.0372   | 289.0473 | 0.9924   | 820.2879 | 4.3733 | 250             | 0.0488   | 76.7274  | 0.9958   | 32.3233 | 3.2324 |
| PSO   | 100             | 1.430 \times 10^{-03} | 103.0407 | 0.9423   | 602.5356 | 8.6616 | 100             | 0.4712   | 3.2683   | 0.9874   | 5.4730 | 3.4087 |
|       | 300             | 2.247 \times 10^{-04} | 243.9957 | 0.9948   | 285.6365 | 2.8946 | 150             | 0.2673   | 4.0801   | 0.9941   | 19.8831 | 3.5600 |
|       | 500             | 1.079 \times 10^{-04} | 356.7294 | 0.9899   | 1111.5701 | 4.7354 | 250             | 0.2332   | 4.6250   | 0.9930   | 46.9438 | 3.7434 |
Where $R$ is the universal gas constant ($8.3144 \times 10^{-3}$ kJ mol$^{-1}$ K$^{-1}$) and $T$ is the absolute temperature in Kelvin.

The values of thermodynamic parameters obtained from equation (15) and van’t Hoff plot (figure S6) for adsorption of CR and IC on CHCA are listed in table 6. The negative values of $\Delta G^0$ at all temperatures for both the dyes confirms the feasibility and spontaneous nature of the adsorption process. Increase in value of $\Delta G^0$ with an increase in temperature demonstrated that lower temperatures are favourable for adsorption of the selected anionic dyes on CHCA [68]. In general, $\Delta G^0$ in the range of $-20$ to $0$ kJ mol$^{-1}$ indicates physisorption and values between $-80$ and $-400$ kJ mol$^{-1}$ corresponds to chemisorption [70]. The negative value of $\Delta H^0$ confirms the exothermic behaviour of adsorption reaction suggesting that higher temperature is unfavourable for the adsorption process. $\Delta H^0$ value $< -42$ kJ mol$^{-1}$ further confirms that adsorption in physical in nature.
The negative values of $\Delta S^0$ denote decreased randomness at the solid-liquid interface during the adsorption of CR on CHCA [68]. Multilayer adsorption on CHCA possibly reduces the randomness [72, 73]. The isosteric heat of adsorption is another relevant thermodynamic parameter that efficiently describes the heat effects during the adsorption process and is a basic requirement for optimization of the adsorption process. Information about isosteric heat of adsorption is crucial in the design of adsorption equipment and in identifying the energetic characteristics (homogenous or heterogeneous surfaces) of the adsorbent [74–76]. $\Delta H_X$ at a constant surface loading ($q_e, \text{mg/g}$) is calculated using the Clausius–Clapeyron equation:

$$\ln C_e = -\frac{\Delta H_X}{R} \frac{1}{T} + C$$

where $C$ is the integration constant. $\Delta H_X$ values were obtained from the slope of isosteres (figure S7 a and b) corresponding to different equilibrium adsorption uptake of CR and IC by CHCA and are presented in table 7. The linear fit of $\ln C_e$ versus $1/T$ obtained using the LINEST function available in Microsoft Excel® 2019 showed good correlation with high $R^2$ values. For both the dyes, it is evident that $\Delta H_X$ varied with surface loading indicating that CHCA has an energetically heterogeneous surface. The dependency of $\Delta H_X$ on surface loading can be due to adsorbate-adsorbate interaction followed by adsorbate-adsorbent interaction. Higher values of $\Delta H_X$ at lower $q_e$ is due to adsorbate-adsorbate interaction. As $q_e$ increases, adsorbate-adsorbent interaction will occur resulting in lower values of $\Delta H_X$. The negative and lower values of $\Delta H_X$ further confirm the exothermic and physical nature of the adsorption process. [74, 76].

### Regeneration studies

The reusability of adsorbent is one of the important parameters for practical application in terms of economic and cost effectiveness[5, 77]. As shown in figure S8, the CR and IC removal efficiency remained at a relatively higher level for up to three cycles but decreased slightly thereafter. This reduction might be related to the loss of active sites during adsorption-desorption processes and due to repeated calcination. Nevertheless, these findings showed that CHCA nanoparticles could be regenerated and recycled successfully after being used for CR and IC removal.

### Conclusion

This study demonstrated the usage of agro-based waste, namely coffee husk, in the synthesis of calcium aluminate nanocomposite and their application in adsorptive removal of anionic dyes. Langmuir isotherm model and pseudo-first-order reaction-based kinetic model fitted best with experimental data. Mass transfer analysis indicated that both intraparticle diffusion and film diffusion were rate-controlling steps in the adsorption process. The separation factor calculated for the concentration and temperature range studied indicated favourable adsorption. CR and IC adsorption on CHCA was mainly of physisorption type with low values of adsorption energy. The estimated values of the thermodynamic parameters indicate the spontaneous and exothermic nature of the adsorption processes.

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### Conflict of interest

The authors declare that they have no conflict of interest.

| Table 7. Isosteric heat of adsorption calculated from Clausius–Clapeyron equation. |
|--------------------------------|-----------------|-----------------|-----------------|
| $q_e, \text{mg/g}$ | $\Delta H_X, \text{kJ/mol}$ | $R^2$ | $q_e, \text{mg/g}$ | $\Delta H_X, \text{kJ/mol}$ | $R^2$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 100            | -59.5730        | 0.9372          | 30              | -43.7339        | 0.9837          |
| 130            | -68.3204        | 0.9572          | 45              | -44.3192        | 0.9881          |
| 160            | -75.9230        | 0.9738          | 60              | -45.5448        | 0.9958          |
| 190            | -93.1693        | 0.9968          | 75              | -48.5682        | 0.9912          |
| 220            | -114.3870       | 0.9965          | 90              | -49.5096        | 0.9932          |
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