Adsorptive decontamination of paper mill effluent by nano fly ash: response surface methodology, adsorption isotherm and reusability studies
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ABSTRACT
In the present study, adsorption of colour and other pollutants from agro-based paper mill effluent onto fabricated coal fly ash nanoparticles (CFA-N) have been investigated. Response surface methodology was applied to evaluate the operational conditions for maximum ouster of colour from effluent by nano structured CFA-N. Maximum reduction in colour (92.45%) and other pollutants were obtained at optimum conditions: 60 min interaction time, 60 g/L adsorbent dosage and 80 rpm agitation rate. The regression coefficient values (adjusted $R^2 = 0.7169$; predicted $R^2 = 0.7539$) established harmony between predicted and the experimental data. The adsorption equilibrium results matched perfectly with both Langmuir and Freundlich isotherms with maximum adsorption capacity of 250 platinum–cobalt/g. Additionally, the efficacy of CFA-N was also assessed in a continuous column mode. Furthermore, the feasibility of treated effluent for irrigation purpose was checked by growing the plant *Solanum lycopersicum*. Overall, the findings demonstrated the outstanding role of inexpensive and abundantly available CFA-N in treatment of paper mill effluent to the required compliance levels.

Key words | adsorption isotherm, BBD design model, colour removal, column adsorption study, nano fly ash, pulp and paper mill effluent

HIGHLIGHTS

- Nano fly ash was successfully utilized for removal of colour and other pollutants from agro-based paper mill effluent.
- RSM using BBD was used to optimize the operational conditions.
- Quadratic models have been established for the response variables.
- Fixed-bed column adsorption studies illustrated the feasibility of nano fly ash for pilot-scale applications.
- The reusability of treated effluent for irrigation was examined.
INTRODUCTION

The need of water for fulfilment of basic requirements has increased with the rise in industrialization and population. According to the Central Pollution Control Board, India, the pulp and paper industry is considered as one of the largest patrons of water and is positioned sixth in adulteration of the environment after cement, leather, steel, textile and oil industries (Ashrafi et al. 2015). Pulp and paper industries require large amounts of water during manufacturing, and consequently release equivalent amounts of coloured wastewater generated during various processes of paper making. Colour in pulp and paper effluent is because of the presence of synthetic dyes, tannins, wood extracts, and lignin and its derivatives (Lacorte et al. 2003). Apart from being coloured, these effluents are also identified by high pH, odour, chemical oxygen demand, biological oxygen demand, total suspended solids, and chlorinated organic compounds like adsorbable organic halides (AOX), furans and dioxins (Singh & Chandra 2019, Zainith et al. 2019a). Therefore, there is an urge to develop methods that are effective, profitable and eco-friendly for the treatment of such effluents.

Recently, the idea of utilizing wastes as adsorbents in the decontamination of wastewater has led to the use of coal fly ash, which is considered a major source of pollution (Mush-taq et al. 2019). Coal fly ash, represented as industrial waste and rich in alumina, silica, ferrous, lime, mullite, hematite and gypsum, is produced as a derivative from the combustion of coal in thermal power plants (Paul et al. 2007). Presently, India has about 155 thermal power stations that generate approximately 170 million tons of fly ash annually (Singh & Pillai 2019). Dumping of fly ash can result in the degradation of acres of land, eventually causing a negative effect on the environment. A significant step in achieving a sustainable environment would be to utilize fly ash as a low-cost adsorbent for wastewater treatment that would also contribute to the minimization of waste and the problem of its dumping. To enhance the efficiency of fly ash as an adsorbent, it can be modified from micro-sized fly ash to nano-sized fly ash. The characteristics of fly ash nanoparticles, like high surface area, water holding capacity, presence of multiple metal oxides, bulk density, particle size distribution, porosity and hydrophilicity, will make it a prospective contender to remediate the pulp and paper wastewater (Bello et al. 2015).

Since the conventional optimization process for maximum removal of pollutants by adsorbents is time consuming and needs a lot of experimental runs, the use of statistical techniques like response surface methodology (RSM) can help in minimizing these issues. RSM is an effective, statistical and mathematical tool employed to optimize and model the process at different independent parameters (Box & Wilson 1951; Kumar et al. 2019; Munawar et al. 2019; Khan et al. 2020).

After the suitable treatment, the toxicity assessment of decontaminated water before discharging it into the environment or reuse is of vital in view of eco-friendly remediation. For this purpose, researchers have reused the treated effluent for irrigating Solanum lycopersicum (Al-Lahham et al. 2007; Disciglio et al. 2015) and various other vegetable crops, like Capsicum frutescens, Lagenaria siceraria, Cucumis sativus and Allium cepa (Ramana et al. 2019).
Saravanamoorthy and Kumari found in their study that there are both favourable and unfavourable effects of wastewater on crops even after decontamination (Saravanamoorthy & Kumari 2007). Therefore, it is necessary to analyze the impact of effluents (untreated/treated) on crops before recommendation for irrigation.

Previous works have been limited to the batch adsorption of colour and other pollutants from pulp and paper effluent onto fly ash (Fu & Salahin 2018; Malik et al. 2018). The application of nano-sized fly ash in reduction of colour, along with other pollutants from wastewater, has not been investigated to our knowledge. Thus, to fill this reported research gap, the main objective of the present work was to explore the efficiency of nano-sized fly ash in colour removal from paper mill effluent in both batch and continuous column experiments. The second objective was to optimize the colour removal process and establish a model with independent variables, namely, interaction time, agitation rate and adsorbent dosage using RSM, and to perform isotherm and kinetic studies for colour removal. The third objective was to check the appropriacy of the treated effluent for irrigation by growing S. lycopersicum. Thus, the removal of colour and other pollutants from paper mill effluent by nano fly ash will deliver an efficient and low-cost technology for the overall improvement of effluent and will allow people to have access to water with negligible contaminants that can be successfully reused for irrigation and other purposes.

MATERIALS AND METHODS

Fabrication of nano fly ash and characterization

Coal fly ash (CFA) was acquired from the coal-based thermal power plant of National Thermal Power Corporation Limited, Dadri, Gautam Budh Nagar, Uttar Pradesh and was used without any pre-treatment. Two grades of coal fly ash, based on size, were used for this work – electrostatic precipitator fly ash (CFA-E) and nano fly ash (CFA-N). CFA-N was prepared at the National Metallurgical Laboratory, Jamshedpur, by processing the CFA-E through attrition. A continuous-type attrition mill (Labstar, Netzch, Germany) was used for fine (wet) grinding and mechanical activation of fly ash. To calculate the size of the particle, a Mastersizer 3000 (Malvern Panalytical, UK) was used which utilizes the laser diffraction technique to measure particle size distributions from 10 nm up to 5.5 mm using a single optical measurement path.

The physico-chemical characteristics of CFA-E and CFA-N were analyzed as per the standard procedure prescribed by APHA (2005). Chromium (Cr) and cadmium (Cd) were determined using a Microwave Plasma Atomic Emission Spectrophotometer (ICP OES 5800, Agilent). Other heavy metals including arsenic (As) and selenium (Se) were determined using an Atomic Absorption Spectrophotometer. All the chemicals used in the present study for the preparation of solution were of analytical grade and bought from Hi-Media, India.

Collection and characterization of paper mill effluent

The effluent utilized in this study was collected from a medium sized agri-based paper mill located in Uttarakhand from the discharge point of secondary treatment in clean plastic bottles and stored at 4 °C before use, to avoid any change in biological or physico-chemical properties. The effluent was then analyzed for various physical and chemical properties using the standard method reported in APHA (2005). Colour and pH was observed using a spectrophotometer (Shimadzu UV-1650, Japan) and pH meter (Cole Parmer, Canada), respectively. All the experiments were conducted in sets of triplicates.

Response surface methodology

In this investigation, the 3-level Box–Behken design (BBD) model of RSM with categorical factors was employed to establish the individual and synergistic effects of process parameters for colour removal from paper effluent using CFA-N. The interactions time (A), adsorbent dosage (B) and agitation rate (C) were chosen as independent parameters and the percentage of colour removal (%) from effluent was selected as the response. Table 1 depicts the range of levels and independent factors employed in the present study. During the preliminary trial experiments of individual independent factors on colour removal efficiency of CFA-N, a minimum and maximum level was obtained.

| Independent factors | -1 | 0 | +1 |
|---------------------|----|---|----|
| Interaction time (A)| 10 | 60| 110|
| Adsorbent dosage (B)| 20 | 60| 100|
| Agitation rate (C)  | 20 | 80| 100|
A BBD model gave a total of 17 experiments or runs using Design-Expert Software (version 12.0).

In the process of optimization, the response (percentage colour removal) can be related to the process parameters by quadratic or linear model, represented as:

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ij} x_i^2 + \sum_{i<j}^{k} \beta_{ij} x_i x_j + \epsilon \]  
(1)

where \( Y \) is the response; \( x_i \) and \( x_j \) are coded variables; \( \beta_i \), \( \beta_{ij} \) and \( \beta_{ij} \) are interaction coefficients of linear, quadratic and second order terms, respectively; \( \beta_0 \) is the constant coefficient and \( \epsilon \) is the error. The significance of quadratic regression model was ascertained by analysis of variance (ANOVA). The statistical significance of the model terms was established using the \( p \)-value and F-value. A \( p \)-value less than 0.05 and insignificant lack-of-fit F-value are required for the entire model to be significant. The synergistic impact of various process parameters on the colour removal was depicted by 3D response surface plot.

### Batch studies

The colour removal from effluent by fly ash (CFA-E, CFA-N) was performed in 2-L conical flasks. A known amount of adsorbent was added to 1 L of effluent and agitated at fixed speed and time, obtained through BBD design model. The pH of the effluent was unaltered for all the experiments to reduce the expense and effort of the pH adjustments. A definite number of samples were taken from each flask and centrifuged at 5,000 rpm (15 min). The supernatant obtained was analyzed for residual colour and agitated at 465 nm by UV-visible spectrophotometer using Platinum–Cobalt (Pt–Co) colour units. The percentage of colour removal in Pt–Co units was determined using the following equation:

\[ \text{Colour removal (\%)} = \frac{A_o - A}{A_o} \times 100 \]  
(2)

where \( A_o \) (Pt–Co/L) is the initial concentration of colour and \( A \) (Pt–Co/L) is the concentration of colour in the effluent at time \( t \) (min). The amount of colour adsorbed was calculated using the following relationship:

\[ q_e = \frac{(A_o - A)V}{W} \]  
(3)

where \( q_e \) (Pt–Co/g) is the amount of colour adsorbed per unit weight of adsorbent, \( V \) (L) is the volume of the solution and \( W \) (g) is the weight of the adsorbent.

### Adsorption isotherm studies

The adsorption isotherms are mathematical models that illustrate the dispersion of adsorbate molecules between liquid and solid (adsorbent) surface, based on the assumptions that are chiefly associated with the homogeneity/heterogeneity of the adsorbent, type of coverage and plausibility of interaction between adsorbate molecules (Bartczak et al. 2018). Adsorption data obtained through batch studies are generally expressed by various adsorption isotherm models, i.e. Langmuir, Freundlich, Elovich, Temkin and Redlich–Peterson. These isotherm models relate the amount of adsorbate adsorbed per unit gram of adsorbent to the adsorbate concentration in the bulk fluid phase at equilibrium. The data obtained through adsorption experiments in the present study were fitted with two widely used models, i.e. Langmuir and Freundlich isotherm models.

#### Langmuir isotherm

Langmuir adsorption isotherm is used to determine the maximum amount of colour bound to the CFA-N when all the binding sites have the same affinities for the colour molecules and are independent of each other (Langmuir 1916). The linear form of Langmuir isotherm model is depicted by the following equation:

\[ \frac{1}{q_e} = \frac{1}{bq_m} (\frac{1}{A_{eq}}) + \frac{1}{q_m} \]  
(4)

where \( q_e \) (Pt–Co/g) and \( A_{eq} \) (Pt–Co/L) is the amount of colour adsorbed and concentration of colour at equilibrium, respectively; \( q_m \) (Pt–Co/g) is the maximum amount of colour adsorbed onto CFA-N particles; and \( b \) (L/Pt–Co) is the constant associated with the degradation energy. The values of \( q_m \) and \( b \) can be obtained from the slope and intercept of the linear plot of \( 1/q_e \) versus \( 1/A_{eq} \).

#### Freundlich isotherm

The Freundlich isotherm model assumes that the multilayer adsorption takes place on the heterogeneous surface of adsorbent with non-uniform distribution of active sites and
The linear form is represented by the following equation:

\[
\log (q_{eq}) = \log K_T + \left(\frac{1}{n}\right) \log A_{eq}
\]

(5)

where \(K_T\) (Pt-Co/g) is the adsorption constant related to the quantity of colour adsorbed onto CFA-N for unit equilibrium constants; and \(n\) is the dimensionless factor representing the favourability of the adsorption process. The values of \(K_T\) and \(n\) were calculated from the slope and intercept of the graph between \(\ln q_e\) and \(\ln A_{eq}\).

**Continuous column adsorption studies**

A brief study on the fixed-bed column experiments were conducted to explore the dynamic behaviour of the adsorbent. A 30-g sample of CFA-N was packed into the glass column, which had an inner diameter of 2.5 cm and length of 25 cm (Figure 1). The CFA-N was packed between the layers of medium sand with an average particle size of 0.5 mm to 0.32 mm to increase the porosity, subsequently leading to the easy flow of influent in the column. At the bottom, glass frit was placed to provide mechanical support to the packing material and also to prevent the loss of adsorbent. All the experiments were performed at 30 ± 5 °C. Then 500-mL of untreated effluent of known concentration was pumped into the column at the flow rate of 1 mL/min using a peristaltic pump. During trial runs at different flow rates of 1, 5, 10 mL/min, it was observed that the flow rate of 1 mL/min had a longer breakthrough time, thus this flow rate was chosen for the final column experiments. The treated effluent sample was collected at regular time intervals and analyzed for residual colour concentration. The column was considered exhausted when the equilibrium concentration of the effluent contained 95% of the influent concentration.

**Thomas model**

The Thomas model was used to understand the dynamic behaviour of the column in the adsorption of colour by CFA-N. The Thomas model is based on the principle that the entire process will follow Langmuir adsorption isotherm without any axial dispersion and the model will fit the second-order reversible reaction kinetics. The linear form of the given model is expressed as:

\[
\ln \left[\frac{C_0}{C_t} - 1\right] = \frac{k_{TH} q_e W}{Q} - k_{TH} C_0 t
\]

(6)

where \(C_0\) is the influent concentration (mg/L); \(C_t\) is the effluent concentration (mg/L) at time \(t\); \(k_{TH}\) is the Thomas rate constant (mL/min·mg); \(q_e\) is the maximum colour adsorption capacity of the adsorbent (mg/g) at equilibrium; \(W\) is the mass of the adsorbent (mg/g); \(Q\) is the flow rate (mL/min) and \(t\) is the flow time (min).
Reusability study of treated effluents

Utilizing the treated effluent for agricultural purpose is the most common and simple way of reusing it efficiently, and these days even governments of many countries are supporting this initiative. Reusing the treated wastewater not only solves the problem of water scarcity but it also provides a more insightful way to utilize wastewater sustainably (Mehrotra et al. 2019). For the present analysis, the cherry tomato (S. lycopersicum) plant, one of the major vegetables grown worldwide, was chosen because it has a short lifespan and can easily be cultivated outdoors in pots. The seeds of S. lycopersicum were purchased from a local agro-seed shop and sterilized with sodium hypochlorite (5%), and then washed properly in tap water and dried for 20 min. The healthy seeds were sown in three pots and watered regularly; one of the pots with tap water (control), one with untreated effluent and the other with treated effluents. The plant growth parameters were observed after 8 weeks of incubation under controlled conditions. Plant height (shoot length), leaf number and flower number (including the emerging buds) were evaluated manually after the incubation period. Average weight of the tomato fruit and the vegetative (shoot) dry weight were ascertained using a calibrated weighing balance (Mettler Toledo, USA).

RESULTS AND DISCUSSION

Characteristics of CFA-N

The physical and chemical analysis of both the adsorbents (CFA-E and CFA-N) revealed the presence of oxides of Si, Al and Fe (SiO₂, Al₂O₃ and Fe₂O₃) as major elements, and other oxides like CaO, MgO, SO₃, Na₂O and unburnt carbon as minor constituents, in addition to other trace elements like Cr and Cd (Table 2). The existence of more than 88% of major oxides in the procured fly ash and lack of agglomeration in water played a major role in the removal of colour and other pollutants from the effluents. A similar observation was reported by Visa et al. (2011). According to the American Society for Testing and Materials standards, the procured fly ash belongs to class F because the total of total silica (SiO₂), aluminium (Al₂O₃) and iron (Fe₂O₃) is more than 70% (Lee & Deventer 2002). The process of fabrication of nano-sized fly ash from micro-sized through a simple wet mechanical attrition method involved no change in physico-chemical properties of fly ash, but the size was reduced to nanoscale. Particle size distribution as illustrated in Table 3 shows that CFA-N is the finest compared to CFA-E and the size of 90% particles are of 10 μm.

RSM analysis

As the statistical analysis offers a clear conception of the reaction process and minimizes the experimental errors, in the present study the RSM–BBD approach was applied to optimize the colour removal process from the paper mill effluent using adsorbent CFA-N. In order to statistically optimize the operational factors (interaction time, A; adsorbent dose, B; agitation rate, C) and determine the influence of these factors on colour removal by CFA-N, 17 experimental runs were carried out and results are shown in Table 4.

On the basis of the statistical evaluation carried out by Design-Expert Software with the experimental data (Table 4), the final equation (Equation (7)) generated from the percentage colour removal by CFA-N based on BBD

| Table 2 | Physical and chemical characteristics of fly ash |
|---------|-----------------------------------------------|
| Properties | CFA-E | CFA-N |
| pH | 8.1 | 8.1 |
| Ash (%) | 87.2 | 88.6 |
| Moisture (%) | 7.3 | 6.4 |
| Volatile organic carbon (%) | 6.5 | 6.4 |
| Specific gravity | 2.10 | 2.2 |
| Total silica (SiO₂) (%) | 57.10 | 57.1 |
| Calcium oxide (CaO) (%) | 1.91 | 1.91 |
| Iron oxide (Fe₂O₃) (%) | 5.63 | 5.63 |
| Magnesium oxide (MgO) (%) | 2.34 | 2.34 |
| Aluminium oxide (Al₂O₃) (%) | 26.47 | 26.47 |
| Sulphur trioxide (SO₃) (%) | 0.70 | 0.70 |
| Unburnt carbon (%) | 1.93 | 1.93 |
| Chromium as Cr (ppm) | 20.60 | 18.35 |
| Cadmium as Cd (ppm) | 0.34 | 0.31 |
| Mercury as Hg (ppm) | ND | ND |

ND, Not detected.

| Table 3 | Particle size distribution in fly ash |
|---------|-------------------------------------|
| Adsorbents | Weight % |
| 1 μm | 10 μm | 25 μm | 45 μm | 75 μm | 100 μm |
| CFA-E | 0.15 | 5.20 | 18.0 | 50.0 | 85.0 | 97.0 |
| CFA-N | 20.0 | 90.0 | 99.0 | 100 | 100 | 100 |
was found to be well fitted to the quadratic model:

\[
\text{Colour removal (\%) = + 92.45 + 0.1600A + 0.3700B + 0.6875C + 1.69AB - 0.6050AC + 0.0150BC - 3.63A^2 - 1.18B^2 - 2.86C^2} (7)
\]

The model Equation (7) describes how the colour removal (\%) by CFA-N was influenced by three factors (A, B and C) in the quadratic or interactive model. As given in Equation (7), coefficients with a positive sign represent synergistic effects, i.e., they enhance the colour removal, whereas those with negative coefficients affect inversely to the response. Thus, the positive values of interaction time, adsorbent dosage and agitation rate in Equation (7) states that all these parameters play a significant role in reduction of colour from the paper mill ef fluent. Moreover, it is essential to carry out ANOVA and R² analysis in order to determine the appropriacy of the quadratic model to sufficiently explain the colour removal process (Zhang et al. 2016). The detailed results of ANOVA for colour removal by CFA-N are presented in Table 5. Generally, the significant factors are based on the F-values and p-values with 95% confidence level. The large F-value and small p-value represents the significance of the model coefficients.

The model F-value 5.50 for the maximum colour removal implies that the quadratic model is significant and there is only a 1.75% chance that this large F-value could occur due to noise. The significance of the model parameters is also validated by p-values because p-value less than 0.05 reflects that model terms are significant. Herein, the p-values of interaction (AB) and quadratic (A² and C²) terms are less than 0.05, indicating that these model terms are significant.

The lack-of-fit (F = 1.94) from ANOVA states that it is not significant, which is considered good and desirable for the model to fit. There is a 26.46% chance that a lack-of-fit F-value this large could occur due to noise. The high value of R² (0.8761) indicates that the data are well fitted to the quadratic model. Moreover, the value of predicted R² (0.7539) is in good agreement with the value obtained for adjusted R² (0.7169) because the difference between them is less than 0.2 (Hiew et al. 2019). Thus, it can be proclaimed that this design model can sufficiently explain the relationship between factors (A, B and C) and response (percentage colour removal).

Adequate precision measures the signal-to-noise ratio and compares the range of predicted values at the design points to average prediction error. A ratio greater than 4

| Run | Interaction time (A) (min) | Adsorbent dosage (B) (g) | Agitation rate (C) (rpm) | Experimental response (% decolourization) | Predicted response, RSM (% decolourization) |
|-----|--------------------------|--------------------------|--------------------------|-------------------------------------------|-------------------------------------------|
| 1   | 60                       | 60                       | 80                       | 91.13                                     | 92.45                                     |
| 2   | 60                       | 20                       | 120                      | 88.87                                     | 88.72                                     |
| 3   | 10                       | 60                       | 120                      | 86.89                                     | 87.10                                     |
| 4   | 60                       | 20                       | 40                       | 85.99                                     | 87.38                                     |
| 5   | 60                       | 60                       | 80                       | 91.00                                     | 92.45                                     |
| 6   | 110                      | 60                       | 120                      | 84.88                                     | 86.21                                     |
| 7   | 10                       | 20                       | 80                       | 88.87                                     | 88.81                                     |
| 8   | 60                       | 60                       | 80                       | 92.91                                     | 92.45                                     |
| 9   | 110                      | 20                       | 80                       | 86.92                                     | 85.74                                     |
| 10  | 60                       | 60                       | 80                       | 93.23                                     | 92.45                                     |
| 11  | 60                       | 100                      | 40                       | 87.94                                     | 88.09                                     |
| 12  | 10                       | 60                       | 40                       | 85.84                                     | 84.51                                     |
| 13  | 60                       | 100                      | 120                      | 90.88                                     | 89.49                                     |
| 14  | 10                       | 100                      | 80                       | 84.98                                     | 86.16                                     |
| 15  | 60                       | 60                       | 80                       | 94.00                                     | 92.45                                     |
| 16  | 110                      | 60                       | 40                       | 86.25                                     | 86.04                                     |
| 17  | 110                      | 100                      | 80                       | 89.81                                     | 89.87                                     |
signifies adequate model discrimination (Noordin et al. 2004; Mourabet et al. 2017). Herein, the ratio of 6.574 indicates an adequate signal, confirming that the model can be used to navigate the design space and is unaffected by the system noise. The coefficient of variance (CV%) measures the reproducibility of the design model. A CV% less than 10% confirms high reproducibility of the experimental data. The results in Table 5 demonstrate a low value of CV%, indicating the reproducibility of the data. The graphical plots were also utilized to evaluate the significance of the developed design model. Figure 2(a) shows the graph of normal (%) probability versus externally studentized residuals. It was observed that maximum data points were distributed around a straight line, with less deviation from normality. This supports the fact that the model is suitable for the colour removal from the effluent. Figure 2(b) presents the plot between the actual (experimental) and predicted values obtained from the regression equation for colour removal using CFA-N. The graph established that the significance of the model as the actual and the predicted data were in close proximity and followed a straight line.

### Response surface plot

The 3D surface curves were plotted to determine the interactive effects of the independent process parameters on the

### Table 5 | ANOVA results for colour removal using the BBD model

| Source | Sum of squares | df | Mean square | F-value | p-value | Remarks |
|--------|----------------|----|-------------|---------|---------|---------|
| Model  | 122.82         | 9  | 13.65       | 5.50    | 0.0175  | Significant |
| A (time) | 0.2048         | 1  | 0.2048      | 0.0826  | 0.7822  |          |
| B (dose) | 1.10           | 1  | 1.10        | 0.4415  | 0.5277  |          |
| C (agitation) | 3.78        | 1  | 3.78        | 1.52    | 0.2568  |          |
| AB     | 11.49          | 1  | 11.49       | 4.63    | 0.0484  |          |
| AC     | 1.46           | 1  | 1.46        | 0.5902  | 0.4674  |          |
| BC     | 0.0009         | 1  | 0.0009      | 0.0004  | 0.9853  |          |
| A²     | 55.54          | 1  | 55.54       | 22.39   | 0.0021  |          |
| B²     | 5.83           | 1  | 5.83        | 2.35    | 0.1690  |          |
| C²     | 34.37          | 1  | 34.37       | 13.86   | 0.0074  |          |
| Residual | 17.36         | 7  | 2.48        |        |         |          |
| Lack-of-fit | 10.30       | 3  | 3.43        | 1.94    | 0.2646  | Not significant |
| Pure error | 7.07        | 4  | 1.77        |        |         | Pure error |
| Correlation total | 140.19     | 16 |             |         |         |          |

Df, degree of freedom; $R^2 = 0.8761$; adjusted $R^2 = 0.7169$; predicted $R^2 = 0.7539$; adequate precision $= 6.57$; CV% $= 1.57$. 

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![Graphs](Figure 2) | Plot between (a) normal % probability and studentized residuals for the colour removal by CFA-N. (b) Predicted and actual output for the colour removal by CFA-N.
percentage of colour reduction and also to estimate the optimum value of each parameter for obtaining maximum color removal (%). Figure 3(a) shows the 3D plot for the effect of interaction time (10–110 min) and adsorbent dosage (20–100 g/L) on the colour removal from the effluent by CFA-N at a fixed agitation rate. It was observed that the percentage of colour removal increased with increasing time and dosages up to 60 min and 60 g/L, respectively. With a further increase in adsorbent dosages and time, it started decreasing after achieving equilibrium. This may be because the availability of the active sites, such as Al₂O₃ and SiO₂, on CFA-N increases with an increase in the adsorbent dosage until equilibrium is achieved. The continuous agitation beyond 60 mins caused the desorption of colour from adsorbent surface, thus leading to a decrease in percentage of colour removal (El Alouani et al. 2017). The higher removal of colour in the initial stages can be attributed to the availability of a greater number of active vacant sites on the adsorbent, which is gradually occupied by adsorption of pollutants from the wastewater as the time progressed (Li et al. 2018). The equilibrium time was found to be 60 min, as no appreciable change in the removal of colour was observed beyond 60 min. The highest colour removal percentage (approximately 92%) was obtained at adsorbent dosage and interaction time of 60 g/L and 60 min, respectively. Parameters, interaction time (10–110 min) and agitation rate (10–100 rpm) had a significant effect on colour removal at a fixed adsorbent dose i.e. 60 g/L (Figure 3(b)). It was observed that the colour removal efficiency of the CFA-N increased by increasing the agitation rate from 10 to 80 rpm. This could be due to the increase in the external mass transfer coefficient leading to faster removal of colour by CFA-N (Singh & Prasad 2000). However, at an agitation rate above 80 rpm, there was slight decrease in the colour removal. The highest efficiency (approximately 90%) was obtained when the agitation rate and interaction time were at 80 rpm and 60 min, respectively (Figure 3(b)). The impact of adsorbent dosage (10–90 g/L) and agitation rate (10–100 rpm) at a constant time (60 min) on the percentage of colour removal by CFA-N is shown in Figure 3(c). It was noticed that at lower fly ash concentrations and agitation rates, the percentage of colour removal was much less. However, with the increase in the dosage and agitation, up to 60 g/L and 80 rpm, respectively, there was a significant increment in decolourization. The maximum colour removal of approximately 91% was obtained at adsorbent dosage and agitation rate of 60 g and 80 rpm, respectively.

The optimum conditions for the three process variables (interaction time, adsorbent dosage and agitation rate) for maximum removal of colour by CFA-N was evaluated by numerical optimization based on the desirability function. The desired goal according to the software optimization for every process variable was chosen ‘within the range’ and the response (percentage of colour removal) was set at maximum to attain highest performance. As per the above optimization process, the most favourable conditions for maximum colour removal efficiency were observed at interaction time of 60 min, oscillations of 80 rpm and adsorbent dosage of 60 g/L. The colour removal efficiency of CFA-N under these optimized conditions was 92.45%, while the experimental value was 91.13%.

**Batch studies**

A 500-mL sample of paper mill effluent was treated with both CFA-E and CFA-N under the optimum conditions obtained through the RSM design model, i.e. adsorbent dose (60 g/L), interaction time (60 min) and agitation rate (80 rpm). The physical and chemical properties of the effluent before and after treatment with adsorbents are illustrated in Table 6. The reduction in the colour intensity was determined to be ~92% and ~85% by CFA-N and CFA-E, respectively. The treated effluent under the optimized conditions was observed to be clear, with almost complete removal of colour by CFA-N. Apart from colour, other pollutants in the effluent also showed a significant decrease in concentration, while the value of dissolved oxygen (DO)
increased after treatment by both CFA-E and CFA-N. However, the best results were achieved by CFA-N, which might be due to its large surface area and higher reactivity compared to CFA-E. The findings of the batch studies also suggest that in the statistical model RSM not only successfully reduced the cost but also the time required to perform large number of experiments to optimize the conditions for successful treatment of waste water. Thus, the BBD model can be regarded as an efficient strategy to improve overall quality of water by removing pollutants, especially when large numbers of chemicals are required.

**Comparison of various adsorbents or processes utilized for the treatment of paper mill effluent**

A wide selection of adsorbents and techniques have been used to treat pulp and paper mill wastewater. The removal efficiency of CFA-N for chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS), AOX and colour in the present study with respect to other adsorbents as reported in the literature are shown in Table 7. The percentage reduction of colour and other pollutant parameters from the effluent achieved in the present investigation were higher than those achieved in other reported biological and chemical methods (Table 7). However, electrocoagulation and advanced oxidation processes combined with biological methods also showed comparable results. But the requirement of energy and chemical reagents to operate the system makes the technique costly, thus limiting its pilot-scale application for small industries. The commercially available activated carbon was found to be a highly efficient adsorbent because it removed 100% colour from paper and pulp industrial effluents, but the high cost

### Table 6 | Physicochemical parameters of the agri-based paper mill effluent before and after treatment with CFA-E and CFA-N

| Parameters               | Permissible limit<sup>b</sup> | Effluent before treatment | Effluent after treatment with CFA-E | Effluent after treatment with CFA-N |
|--------------------------|--------------------------------|---------------------------|------------------------------------|-----------------------------------|
| pH                       | 6.5–7.5                        | 8.2                       | 7.2                                | 7.3                               |
| Electrical conductivity  | 0.6                            | 2.56                      | 0.5                                | 0.56                              |
| Total suspended solids   | 200                            | 197                       | 99                                 | 94                                |
| TDS                      | 500                            | 1,236                     | 394                                | 350                               |
| COD                      | 250                            | 596                       | 171                                | 165                               |
| BOD                      | 30                             | 86                        | 29                                 | 23                                |
| DO                       | 4–6                            | 3                         | 5                                  | 6                                 |
| Chloride                 | 1,000                          | 845                       | 715                                | 635                               |
| AOX                      | –                              | 4.72                      | 2.1                                | 1.34                              |
| Sulphate                 | 200                            | 122                       | 158                                | 152                               |
| Phosphate                | 10                             | 4.33                      | 1.1                                | 0.33                              |
| Colour                   | –                              | 878                       | 136.5                              | 78                                |

<sup>a</sup>Except pH, electrical conductivity (mS/cm) and colour (Pt-Co/g), all parameters are expressed in mg/L.

<sup>b</sup>Permissible limits are according to the World Health Organization guideline value.

### Table 7 | Different adsorbents/processes employed for the treatment of pulp and paper mill effluent

| Adsorbent/processes                                         | COD (%) | BOD (%) | TDS (%) | AOX (%) | Colour (%) | References                      |
|------------------------------------------------------------|---------|---------|---------|---------|------------|---------------------------------|
| *Rhodococcus* sp NCIM 2891                                 | 53.23   | 81.25   | 81      | –       | –          | Nadaf & Ghosh (2014)            |
| Lignolytic bacterial strain RJH-1                           | 69      | 39      | 47      | 67      | 86         | Hooda et al. (2015)             |
| *Bacillus aryabhatti*                                       | 85      | –       | –       | –       | 86         | Zaminth et al. (2019b)          |
| Fly ash                                                    | –       | –       | –       | –       | 86         | Malik et al. (2018)             |
| Electrocoagulation                                         | 85      | 100     | –       | 100     |            | Azadi et al. (2016)             |
| Combination of advanced oxidation process and biological method | 55    | 100     | 100     | 91.13   |            | Brink et al. (2018)             |
| Activated carbon                                           | 71.97   | 86.05   | 68.52   | 71.6    | 91.13      | Malik et al. (2018)             |
| CFA-N                                                      |         |         |         |         |            | Present study                   |
limits its industrial applications. Fly ash, on the other hand, is a waste, abundantly present in nature, safe and has a good adsorptive property. Nevertheless, to increase the adsorption efficiency of fly ash, several mechanical and chemical modification must be done (Mushtaq et al. 2019). In the current study, the adsorption capacity of pristine fly ash was increased by reducing its size to nano level, which involved a little processing without the use of any harmful and costly chemicals. Undoubtedly, results from the present batch study and statistical modelling inferred that the nano fly ash (CFA-N), a low-cost material, has immense capability as an adsorbent and it can create wonders in the remediation process (Ahmaruzzaman 2010; Chikri et al. 2020).

Adsorption isotherm studies

The calculated parameters and statistical values of Langmuir and Freundlich isotherm models are depicted in Table 8. Both Langmuir and Freundlich isotherms showed good fit with high correlation coefficient ($R^2$) values of 0.9884 and 0.989, respectively (Figure 4(a) and 4(b)). The excellent fit of the Langmuir model demonstrated the homogenous distribution of binding sites on the CFA-N surface with monolayer arrangement of adsorbed molecules (Langmuir 1916). Maximum adsorption capacity ($q_m$) of CFA-N was found to be 250 Pt-Co/g.

The good fit of Freundlich isotherm model indicated a non-uniform distribution of binding energy for each active binding site (Freundlich 1906). In the present study, class F fly ash with high content of SiO$_2$, Al$_2$O$_3$ and other oxides was used to prepare the CFA-N sorbent. These silica and alumina oxides are highly active and act as adsorption sites (Visa et al. 2018). It is also evident from the Freundlich isotherm that the surface of the CFA-N consists of small heterogeneous adsorption patches which are similar to each other in relation to adsorption. Therefore, it can be inferred that the colour removal by the CFA-N is a multi-step process that involves more than one mechanism including electrostatic interactions, hydrogen bonding, surface complexation, ion exchange or chemisorption between pollutants and active sites present on the surface of adsorbent as shown in the inset of Figure 1 (Sinha et al. 2016; Zhang et al. 2019). The value of $K_f$ in the Freundlich isotherm indicates the adsorption capability of the adsorbent. The higher value favours the high adsorption of colour and other pollutants on the surface of CFA-N. The parameter $1/n$ establishes the impact of concentration on the adsorption capacity and depicts the adsorption intensity. Therefore, the value of $1/n$ less than unity (0.5) in the present study revealed the favourable adsorption of pollutants onto the heterogeneous surface of CFA-N. A similar isotherm was observed by Adeyi et al. (2019), who found a good fitting of the experimental data with both Langmuir and Freundlich isotherm models ($R^2 = 0.8712$ and 0.9993, respectively) during the adsorptive removal of methylene blue using Thiourea-Modified Poly (Acrylonitrile-co-Acrylic Acid) as an adsorbent indicating the multilayer adsorption system. Boonpoke (2015) also reported that both Langmuir and Freundlich isotherm models described the adsorption characteristics of COD and colour from pulp and paper mill wastewater using water hyacinth-based activated carbon.

| Table 8 | Langmuir and Freundlich isotherm constants for the adsorption of colour onto the CFA-N |
|-----------|-------------------------------|----------------------|--------------|----------|--------|
| Langmuir adsorption isotherm | Freundlich adsorption isotherm |
| $q_m$ | b | $R^2$ | $K_f$ | n | $R^2$ |
| 250 Pt-Co/g | 0.00050 | 0.9884 | 1.07 | 1.69 | 0.989 |

Figure 4 | Adsorption of colour from pulp and paper wastewater using CFA-N at optimized conditions: (a) Langmuir isotherm model, (b) Freundlich isotherm model.
Evaluation of column studies

Adsorption in fixed-bed columns has numerous benefits due to its easy modus operandi and high efficacy compared to batch analysis. Moreover, the column studies give accurate scale-up information for industrial applications and are widely used for wastewater treatment (Biswas & Mishra 2015). Figure 5(a) shows the breakthrough curve for the colour adsorption from pulp effluent by CFA-N. It was observed that the breakthrough occurred quite rapidly. At 20 min, the outlet-inlet concentration of the effluent (C_{out}/C_{inlet}) was 0.1. At 40 min, the C_{out}/C_{inlet} concentration increased to 0.46. The column was considered saturated at 60 min when the outlet-inlet concentration reached the value of 0.95.

Thomas model

The values of $k_{TH}$ and $q_e$ were estimated by the slope and intercept of the linear graphical representation between ln($C_0/C_t - 1$) and time (t), utilizing the data obtained from the column experiments (Figure 5(b)). The $k_{TH}$ and $q_e$ values of 0.000037 mL/min.mg and 950 mg/g were obtained. This may be due to the higher driving force of the high effluent concentration. The low value of $k_{TH}$, high value of $q_e$ and correlation regression coefficient ($R^2$) value of 0.8917 revealed that the Thomas model fitted well with the experimental breakthrough data. The Thomas model predicts the monolayer adsorption of the adsorbate on the adsorbent, which is also established in our prior batch adsorption isotherm studies where the experimental data fits efficiently with the Langmuir isotherm. The present findings are in agreement with the research work reported by Sugashini & Sheriffa (2013), which revealed the low $k_{TH}$ and high $q_e$ values of 0.00367 mL/min.mg and 2,535.07 mg/g, respectively, in column adsorption studies for the removal of Cr(VI) by ethylamine-modified chitosan carbonized rice composite beads. Another study carried out by Alardhi et al. (2020) also reported lower ($k_{TH}$) values and greater $q_e$ values in the Thomas model of continuous column adsorption analysis of methyl green dye using mesoporous materials MCM-41.

Reusability of the treated effluent

In the present study, a preliminary examination of the effluent’s toxicity was assessed using the phytotoxicity test to determine its possible application in the irrigation of tomato plants. The results obtained after 8 weeks of incubation are shown in Table 9, which reveal that the shoot length, leaf number and flower number drastically reduced in the plant exposed to untreated effluent. However, all the plant growth parameters substantially increased, causing enhanced yield and significant improvement in the average weight of the tomato fruit in the plant grown in treated effluent. As shown in Table 9, all the plant growth parameters of the tomato plant grown in treated effluent were found comparable with the control plant. These findings are in agreement with the study reported by Tsadilas & Vakalis (2003), which concluded the possibility of reuse of wastewater after treatment for the irrigation of corn and cotton (Tsadilas & Vakalis 2003). The encouraging results obtained in terms of enhanced yield and growth of the tomato plant exposed to treated effluent indicate significant quantitative reduction of the toxic pollutants from the mill effluent after treatment with CFA-N. A detailed study including cytotoxicity and genotoxicity examination is required for complete authenticity of the reuse of effluent treated by CFA-N for irrigation purposes.

CONCLUSION

The current study demonstrates the effect of nano-sized fly ash on the removal of colour and other pollutants present

| Parameters | Plant exposed to tap water (control) | Plant exposed to untreated effluent | Plant exposed to treated effluent |
|------------|-------------------------------------|-----------------------------------|----------------------------------|
| Plant height (cm) | 58 ± 0.21 | 15 ± 0.34 | 42 ± 0.25 |
| Leaf number | 19 ± 0.14 | 06 ± 0.22 | 17 ± 0.15 |
| Flower number | 6 ± 0.16 | 0 | 4 ± 0.18 |
| Average weight of tomato fruit (g) | 48 ± 0.18 | 14 ± 0.33 | 39 ± 0.24 |
| Vegetative dry weight (g) | 142 ± 0.23 | 51 ± 0.45 | 128 ± 0.31 |

Values are Mean ± standard deviation.
in pulp and paper effluent. Based on RSM, a maximum of 92.45% of colour removal was achieved at optimum conditions: 60 g CFA-N dosage, 60 min interaction time and 80 rpm agitation rate. At optimum parameters, the inorganic pollutants such as total suspended solids, TDS, sulphates, chlorides, phosphates were successfully removed, leading to the improved quality of effluent by increasing the DO and reducing the BOD and COD in a batch method. In a continuous column analysis, the breakthrough time was observed at 20 min and the adsorption data fitted well with the Thomas model. Additionally, the treated water showed potential for agriculture use by supporting better growth of *S. lycopersicum* compared to the untreated effluent. The encouraging results of the current study demonstrate that nano fly ash is a lucrative adsorbent for successful decontamination of paper and pulp mill effluent. We hope that our research will serve as a base for further studies on the removal of complex pollutants using nano fly ash from industrial effluents involving different statistical models together with some more developed and innovative techniques.

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**CONFLICT OF INTEREST**

The authors declare that there is no conflict of interest.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

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