



Adsorptive removal of acid blue dye 113 using three agricultural waste biomasses: The possibility of valorization by activation and carbonization – A comparative analysis

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ABSTRACT

The presence of various organic and inorganic contaminants in wastewater leads to serious health effects on humans and ecosystems. Industrial effluents have been considered as noticeable sources of contaminating water streams. These effluents directly liberate the pollutants such as dye molecules and heavy metal ions into the environment. In the present study, three biowaste materials (groundnut shell powder, coconut coir powder and activated corn leaf carbon) were utilized and compared for the removal of acid blue dye 113 from aqueous solutions. The characterization study of newly prepared sorbent material (H₃PO₄-activated corn leaf carbon) and the other utilized sorbents was carried out by Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectrophotometer (FTIR), along with Energy Dispersive X-Ray (EDX) Analysis. The influence of experimental conditions such as pH, initial dye concentration, temperature, contact time, and sorbent dosage on the removal efficiency of the dye were appraised. The adsorption isotherm and kinetic result of acid blue dye 113 adsorption onto the sorbents best obeyed from Sips and pseudo-second-order kinetic model. Overall, the outcomes confirmed that the newly synthesized sorbent material (carbonized H₃PO₄-activated corn leaf) has superior adsorption capacity, rapid adsorption, and higher suitability for the removal of toxic dyes from the contaminated waters.

1. Introduction

Our blue planet has covered with abundance of water resources. Nevertheless, only 0.3% of the existing water on the earth is utilizable by humans and animals. The remaining 99.7% consists of the shares of oceans, icecaps, etc. which are not drinkable. Over the decades, the quality of water is declining, owing to contamination which mainly comes about from anthropogenic activities like population growth, industrialization, unplanned urbanizations and unskilled utilizations of water (Kumar et al., 2019; Saravanan et al., 2020; Dutta et al., 2021).

Among the aforementioned activities, industries consume a large amount of water, especially in the wet processing of fabrics in textile industries. In India, the textile industry is one of the major industry sectors and it is contributing to employment and revenue generation (Tianzhi et al., 2021; Nidheesh et al., 2022). At the same time, textile wastewater causes a deep impact on the environment, due to the high concentration of dyes, salts, and organic and inorganic compounds (Keskin et al., 2021; Keerthi and Vani, 2022). In recent years, the treatment of wastewater has been a foremost research area engaging in the field of science and technology.

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Various methods which have been recruited for the removal of heavy metals and dyes include physicochemical methods like precipitation, membrane filtration, incineration, adsorption, ion exchange, coagulation and flocculation, electrochemical treatments, oxidations/reductions, etc. (Ahmad et al., 2022; Kumar et al., 2022). Even though the conventional methods have few remarkable demerits, including chemicals consumption, initial operation cost, less degradation of dye molecules, system regeneration, and elimination of adsorbate and membrane fouling, adsorption has many advantages which make it a useful technology for water and wastewater treatments purposes (Kumar et al., 2018; Hemavathy et al., 2021). In wastewater treatment, energy and environmental sustainability are major concerns of environmental engineers. In recent years, researchers have developed the exploitation of various agriculture waste sources for effluent treatment (Bhatnagar et al., 2015; Saravanan et al., 2016; Mo et al., 2018). India generates about 350 million tons of agricultural waste every year. This agriculture waste can be utilized for power production, composting, mushroom cultivation, enzyme production, and biofuel production. Also, they can be used to produce adsorbents for retrieving contaminants, like dye molecules and heavy metal ions, from water and wastewater streams (Ren et al., 2022).

Dyes discharged to environment are of the imperative contaminants threatening both the environment and the human life (Shayesteh et al., 2016; Ahsani-Namin et al., 2022). Numerous dyes have been used in textile industries; among them, Azo dyes consumption is 10000 tonnes per year. As a result, these industries produce effluents which contain high amounts of azo dyes. These azo dyes-containing effluents can lead to harmful effects on living organisms, changing water colour, inhabitation of photosynthesis in water plants, and reducing dissolved oxygen (Dihom et al., 2022; Koulini et al., 2022). Also, these dyes are threatening human beings and cause serious impacts on their health, leading to allergies, skin irritation, cancer, and mutagenesis. On the other hand, azo dyes contain aromatic amine structures, and degradative circumstances can lead to the formation of aromatic amine compounds from such dyes, which may lead to carcinogenicity, neurotoxicity, genotoxicity, and frequent headaches in adults (Dong et al., 2019; Kashefi et al., 2019; Zhang et al., 2019). Because of the ecotoxicological nature and harmful effects of the azo dyes, the azo-dyes-containing industrial effluents must undergo a treatment stage before discharging into the environments, for removing the dye content (Ertugay and Acar, 2017; Mahmoud et al., 2017). As mentioned above, comparatively, the adsorption process is recognized as a valuable alternative in wastewater treatments due to its simplicity of design, convenience, and ease of operation (El-Sewify et al., 2022; Hu et al., 2022). Hence, in the last years, agricultural wastes such as maize husk, groundnut shell and coconut coir, etc. have been utilized for dye removal and effluent treatment. However, it falls upon the researchers to valorize the agricultural wastes for waters and wastewater treatments.

Beside exploitation of the agro-waste biomasses for the removal of acid blue dye 113 from the aqueous solutions, one of the principal goals of this research is to appraise if H_3PO_4 -activation and carbonization of a leaf-based waste could lead to production of an added-valued adsorbent. For these purposes, three sorbent materials, i.e., groundnut shell and coconut coir, and carbonized H_3PO_4 -activated corn leaf, were appraised for their potential in removing acid blue dye 113 from the aqueous media. The surface morphology and the presence of functional moieties on these sorbent materials were characterized by SEM, EDX, and FTIR analyses. Batch experimental studies were accomplished to determine the optimum values of several parameters like pH, contact time, dosage, and temperature for the sorption system. The adsorption experimental data were applied to various kinetic models and isotherms to scrutinize the adsorption properties and grasp information about the mechanism of adsorption in the studied adsorption systems.

2. Materials and methods

2.1. Preparation of adsorbents

Corn leaves, groundnut shells and coconut coir were collected from the local market and washed thoroughly to remove dirt and unwanted particles adhered to them. In order to activate the corn leaves, it was impregnated in a boiling solution of 30% H_3PO_4 for 2 h and soaked in the same solution for 24 h. In the end, the excess solution was decanted, and the biomass was air-dried and carbonized in a muffle furnace at 400 °C for 20 min and at 800 °C for 10 min. Coconut coir and groundnut shell were dried and crushed in a mixer grinder until they become fine powders. The powders were sieved so that the particles of similar size (300 µm) were selected for the sorption experiments.

2.2. Preparation of adsorbate

In this present adsorption study, acid blue 113 (Molecular formula: $\text{C}_{32}\text{H}_{21}\text{N}_5\text{Na}_2\text{O}_6\text{S}_2$; molecular weight: 681.64 g/mol) was used as an adsorbate which was procured from E.Merck, India. A stock solution of acid blue dye 113 (1000 mg/L) was prepared by dissolving the prerequisite amount of acid blue dye in 1 L of deionised water. From the stock solution, different concentrations of acid blue dye solution were prepared by dilution of the requisite amount of stock solution with deionised water. The pHs of dye solutions were adjusted to the appropriate value by exploiting the 0.1 M HCl or 0.1 M NaOH.

2.3. Characterization study

2.3.1. Energy dispersive X-ray (EDX) and Scanning Electron Microscopy (SEM) analyses

Scanning Electron Microscopy analysis is carried out to comprehend the surface morphology of the adsorbent by striking electron beams onto the sample and analyzing the signals received by the detector. These signals indicate the surface structure of the samples under study include activated corn leaf carbon, groundnut shell & coconut coir powders. The samples were gold-coated and scrutinization at different magnifications at 20 kV was carried out using Zeiss Field Emission Scanning Electron Microscope equipped with an Oxford Instruments, UK, making energy dispersive X-ray analysis (EDX) system. EDX analysis is exploited to identify the chemical composition and the type of elements in the samples. The intensity of secondary electrons generated is correlated with the atomic number of the element which gives different components present in the sample. Hence, quantitative elemental information of the sample can be known. The elemental composition of activated corn leaf carbon, groundnut shell & coconut coir was identified.

2.3.2. Fourier transform infrared (FTIR) analysis

FT-IR analyses were carried out to confirm the presence of functional moieties in the adsorbents as these could play a role in the adsorption processes. The samples (activated corn leaf carbon, groundnut shell & coconut coir) were incorporated with KBr pellets and the FTIR spectra were measured employing FTIR (IR Affinity-1s) Shimadzu, Japan within the range of 400–4000 cm^{-1} before and after adsorption.

2.3.3. BET surface analysis

Surface area and overall pore volume of three utilized samples were quantified in exact via the controlled N_2 system operated at temperature range of 77 K, through a standard physisorption device (Belsorp mini II Model, BEL company, JAPAN) supporting BET analysis (Khalesi et al., 2022).

2.3.4. GC/MS

The Gas Chromatography/Mass Spectrometry (GC/MS) instrument separates chemical mixtures (the GC component) and identifies the components at a molecular level (the MS component) and the probable

metabolites. The GC works on the principle that a mixture will separate into individual substances when heated. The heated gases are carried through a column with an inert gas (such as helium). Low concentrations of dye at low levels after treatment were analysed using GCMS.

2.3.5. UV-visible spectrophotometer

The instrument uses light in the UV and visible range (190 nm–1100 nm) of the electromagnetic spectrum. When a beam of radiation passes through the solution some of the light will be absorbed and the remaining will be transmitted. Absorbance of the sample is the negative logarithm of transmittance. Absorbance is used to find the concentration of dye before and after treatment. The maximum wavelength for Acid blue 113 is 566 nm, by which the extent of adsorption can be determined.

2.4. Batch adsorption study

The adsorption of acid blue 113 using low-cost adsorbents (Corn leaves, groundnut shell, and coconut coir) was studied using the batch technique. Dissolving 0.1 g of dye in 100 mL of water, a stock solution of 1000 mg/L of dye was prepared. The stock solution was diluted to prepare working solutions with various concentrations (mg/L). Standard values for all these solutions were taken and their absorption was determined at 566 nm in the UV-Visible spectrophotometer. To test the potential of adsorbents for adsorptive removal of the acid blue dye, a suitable amount of each groundnut shell powder, activated corn leaf carbon, and coconut coir powder were added to the dye solution and left undisturbed for a pre-determinate time, while agitated at 100 rpm. A portion of all the solutions was filtered immediately and UV (or GC/MS) readings were recorded at 566 nm to calculate the adsorption percentage. For equilibrium and thermodynamic studies, the solutions were kept in a shaker incubator and this process was repeated until a constant UV (or GC/MS) reading was obtained. From the standard values and absorbance values, the percentage removal of acid blue dye 113 was calculated using the below formula:

$$\text{Removal percentage (\%)} = \frac{C_o - C_f}{C_o} \times 100 \quad (1)$$

C_o - Initial concentrations of the dye and C_f - Final concentrations of the dye.

2.5. Effect of pH & temperature

The initial pH of the dye solution was measured to be 6.5. The pH was lowered to acidic values by adding several drops of 1.0 N HCl and brought to higher basic values by adding a suitable amount of 1.0 N NaOH. The effect of the different pHs on decolourization was studied. Similarly, the effects of temperature on decolourization were scrutinized by varying the temperature from 15 °C to 45 °C, apart from the studies at room temperature (28 °C). A predefined value of each sorbent was added to the dye solutions with varied conditions. It was agitated for 10 h. Some amount of solution was filtered to calculate removing percentage.

2.6. Adsorption isotherm study

The results of the effects of initial concentration were scrutinized to determine the capacity of various adsorption isotherm models (Açiksel and Göze, 2017; Kumar et al., 2021). The adsorption isotherms study is used to evaluate the relationship betwixt the acid blue dye 113 in the liquid solution and the biosorbent material at an equilibrium condition. The experimental studies were carried out by varying the dye concentration from 100 to 500 mg/L. In each experiment, a fixed amount of biosorbent material was loaded into each flask which contains 100 mL of dye solution. After the equilibrium time, the biosorbent materials were filtered out using Whatman filter paper. The residual dye concentration

was analysed recruiting a UV-Visible spectrophotometer or GC/MS instrument. The amount of acid blue dye 113 adsorbed onto the surface of the biosorbent at equilibrium condition was calculated using the following formula:

$$q_e = \frac{(C_o - C_f)V}{m} \quad (2)$$

where q_e represents adsorption capacity at equilibrium (mg/g), V represents the volume of acid blue dye 113 solution (g) and m represents the mass of adsorbent (g). In this adsorption study, Langmuir and Freundlich isotherm models were utilized to fit with the results obtained from studying the effects of initial dye concentrations. The following isotherms were exploited.

Langmuir isotherm model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Freundlich isotherm model:

$$q_e = K_F C_e^{1/n} \quad (4)$$

Sips isotherm model:

$$q_e = \frac{q_{max} (K_S \cdot C_e)^{1/n}}{1 + (K_S \cdot C_e)^{1/n}} \quad (5)$$

Goodness-of-fit was evaluated by comparing R^2 values and various statistical indices which can be obtained by the following relations:

$$R^2 = 1 - \frac{\sum (q_{e,exp} - q_{e,cal})^2}{\sum (q_{e,exp} - q_{e,mean})^2} \quad (6)$$

$$\chi^2 = \sum_{i=1}^N \left(\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \right) \quad (7)$$

$$\Delta q(\%) = \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(\frac{q_{exp} - q_{cal}}{q_{exp}} \right)^2} \quad (8)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (q_{exp} - q_{cal})^2} \quad (9)$$

where $q_{e,exp}$, $q_{e,mean}$ and $q_{e,cal}$ are the experimental adsorption capacity (mg/g), the average value of the experimental adsorption capacity (mg/g) for three experiments for which the standard errors were lower than 4.3%, and the adsorption capacity calculated by the model (mg/g), respectively.

2.7. Adsorption kinetic studies

The adsorption kinetic study was exploited to determine the adsorption rate and the mechanism of present adsorption systems. The experimental study was carried out by varying the contact times from 5 to 60 min. In each experiment, a fixed amount of biosorbent material was loaded into each flask which contains a 100-mL portion of dye solution. After the equilibrium time, the biosorbent material was filtered out using Whatman filter paper. The residual dye concentration was analysed using a UV-Visible spectrophotometer or GC/MS instrument. The amount of acid blue dye 113 adsorbed onto the surface of the biosorbent at different contact times was computed recruiting the following formula:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (10)$$

where C_t represents the concentration of acid blue dye 113 in the

solution at time t .

The following models were exploited for kinetic studies.

Pseudo-first order kinetic model:

$$q_t = q_e \cdot [1 - \exp(-k_1 t)] \quad (11)$$

where k_1 represents the rate constant of pseudo-first order kinetic (min^{-1}) and t represents time (min).

Pseudo-second order kinetic model:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (12)$$

where k_2 represents the rate constant of pseudo-first order kinetic ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$).

3. Results and discussion

Agricultural wastes can be utilized for generating power, composting, mushroom cultivation, vermicomposting, etc. In this study, the waste materials were used for removing the acid blue dye 113 from aqueous solutions. In fact, the focus of the study was on the adsorption of acid blue dye 113 and the primary treatment of textile effluents, using organic wastes (activated corn leaf carbon, coconut coir and groundnut shell), separately. The substrates were prepared and their characteristics were brought under investigation. The effect of pH and temperature on the sorption and removal of the dye and the removal mechanism of the dye have also been studied.

3.1. Characteristics of substrates

3.1.1. Physical features

The properties of all three substrates, namely, moisture content, pH, pore volume and porosity were evaluated. Although all the studied sorbent almost has similar pore volumes, activated corn leaf carbon had the maximum BET surface area. Higher surface area may be very effective in possessing higher level of adsorption ability (Table 1).

3.1.2. SEM and EDX analyses

Scanning electron microscopy (SEM) was recruited to determine the surface topology, morphology of the substrates and their porous nature which is the key in adsorption studies. Additionally, SEM is unique for the characterization of sorbents as it can display sample features which are even less than 1 nm in size. Therefore, even micropores can be exposed by SEM micrographs. The SEM image of the utilized biosorbents (Fig. 1a, b and 1c) shows that the surface is faintly rough and uneven with minute pores that may assist in the adsorption process. The elements present in the substrates were determined using EDX and the results are provided in Fig. 2. Earlier reports suggested that activation at 800 °C leads to the formation of a more porous surface due to the release of more volatile compounds in activated carbon from waste tea. The EDX analysis revealed the presence of three elements in activated corn leaf carbon, namely carbon, oxygen and phosphorous with their weight percentages being 17.74, 57.66 and 24.61% and their atomic percentages being 25.13, 61.34 and 13.52%, respectively. The SEM micrograph also shows that the surface of groundnut shell powder appeared to be uneven compared to the other two substrates. The elements identified in

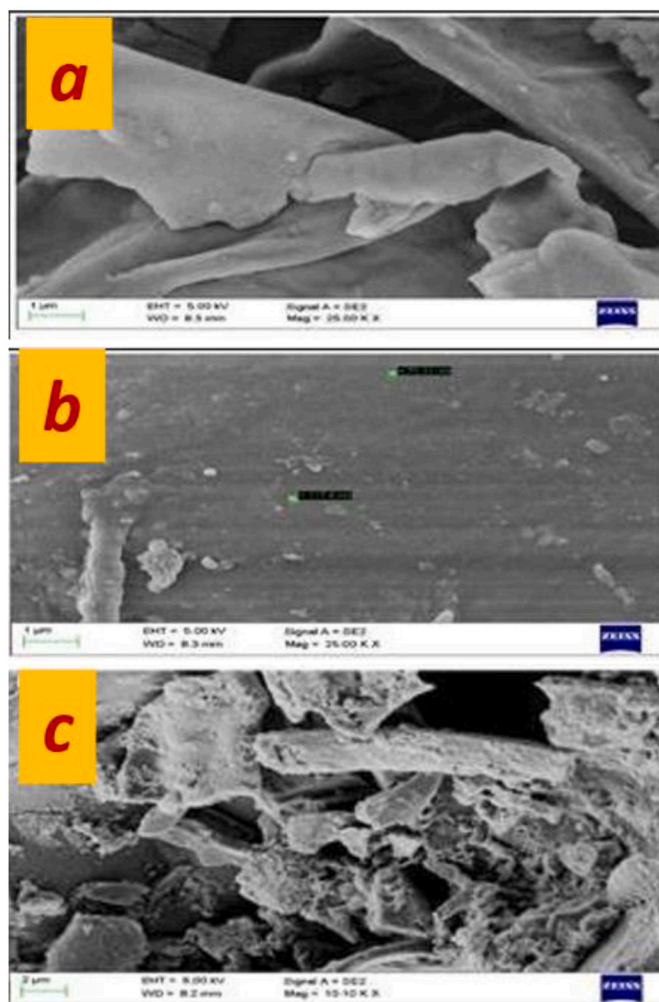


Fig. 1. SEM analysis of the exploited sorbent materials: (a) groundnut shell powder, (b) coconut coir powder and (c) activated corn leaf carbon.

groundnut shell powder, using EDX, were carbon, oxygen, and sodium with their weight percentages being 47.64, 50.65 and 1.71% and their atomic percentages being 55.04, 43.93 and 1.035%, respectively. The presence of C and O is due to the organic nature of the biomass (Ikla-dious et al., 2017). The surface of coconut coir is a little more even and smooth and the number of pores was found to be very less in the case of coconut coir powder. Carbon, Oxygen and Silicon were found to be present elements in coconut coir powder. The mass and percentages were 50.52, 48.18, and 1.29%, and the atomic percentages were 57.90, 41.46 and 0.63%.

3.1.3. FTIR analyses of the adsorbents before and after adsorption

FTIR is a technique that uses infrared radiation to produce spectra which enables the identification and even quantification of the compounds and functional groups. Each peak corresponds to a particular functional group. By using this technique, the functional groups that may be active in the substrate and play a role in the adsorption and removal process can be identified.

3.1.3.1. Groundnut shell. The FTIR spectra (Fig. 3a) of the groundnut shell included 8 peaks with smaller peaks at 3315.63 cm^{-1} and 2949.16 cm^{-1} which correspond to the stretching vibrations of O–H and C–H groups. Peaks at 1679 cm^{-1} and 1413 cm^{-1} are ascribed to C=O stretching vibration and O–H bending vibration, respectively. A long narrow peak at 1116 cm^{-1} correlates to O–C stretching and another peak

Table 1
Physical features of the sorbents.

Substrate	Moisture content (g)	pH	Pore volume (cm^3/g)	Surface coverage (m^2/g)
Activated corn leaf carbon	0.46	6.5	1.08	484.14
Coconut coir	0.45	7.0	0.92	62.14
Groundnut shell	0.50	7.0	1.07	93.45

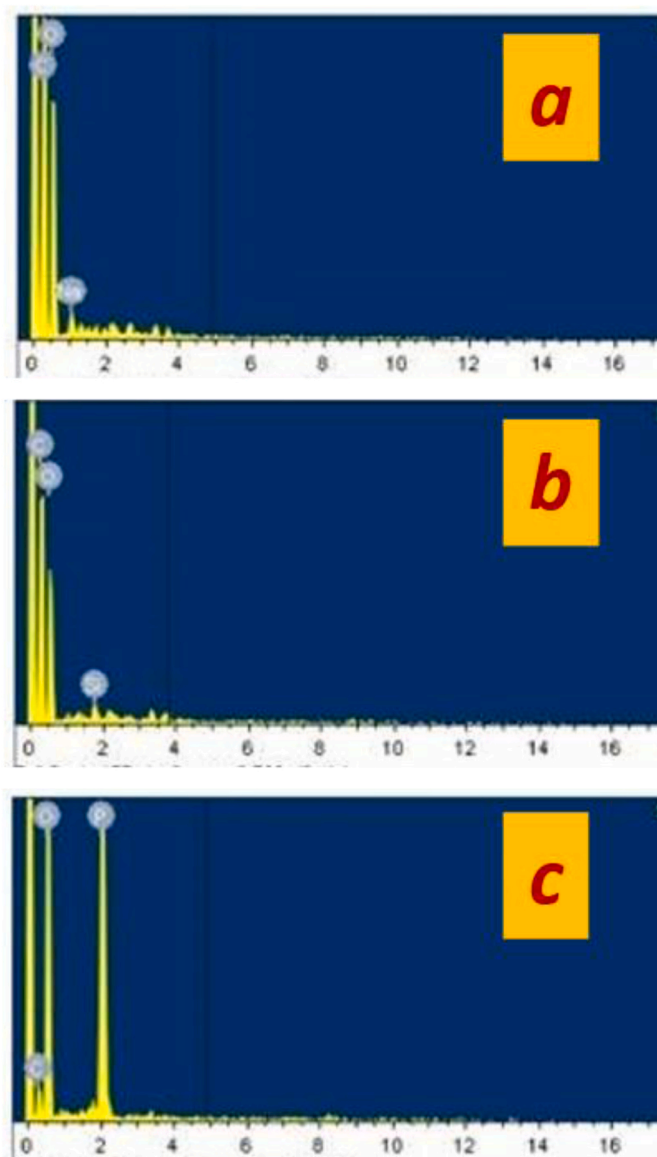


Fig. 2. EDS analysis of adsorbent materials: (a) groundnut shell powder, (b) coconut coir powder and (c) activated corn leaf carbon.

at 615 cm^{-1} corresponds to C–H bending. FTIR analysis of the adsorbent was carried out before and after the adsorption process. It is evident from the FTIR spectra that the peaks before adsorption which were at 3315 and 2949 cm^{-1} disappeared in the spectrum obtained after dye adsorption (Fig. 3b) indicating that the functional groups in these regions would have been involved in the adsorption process. Peaks at 1670 cm^{-1} and 1413 cm^{-1} were not recorded after treatment while a new peak was formed at 1533 cm^{-1} which relates to the N–H bending vibration of the dye. The peak at 1100 cm^{-1} showed an increase in the area after adsorption while the peaks in the fingerprint region were not found after the adsorption process. These results indicate that the disappearance and appearance of certain functional groups are related to the suitable adsorption of the dye onto the sorbent.

3.1.3.2. Activated corn leaves carbon. FTIR spectra of groundnut powder before the adsorption process showed 5 prominent peaks. The peaks at 3317 cm^{-1} correspond to O–H stretching vibrations while a smaller peak at 2374 cm^{-1} is related to P–H vibration. Peaks at 1676 , 1400 and 1114 cm^{-1} are associated with C=O stretching vibrations, O–H bending vibrations and O–C stretching vibrations, respectively (Fig. 3c). Smaller

peaks in the fingerprint region at 752 , 653 and 603 cm^{-1} are of O–H and C–H bending vibrations. After the adsorption process, the FTIR spectra of activated corn leaf carbon clearly showed variations in the peaks. The peaks at 3313 cm^{-1} which were small inflicted a variation after treatment so that a broad peak was obtained at 3403 cm^{-1} ascribable to N–H and O–H groups. The narrow peaks at 1676 , 1400 and 1143 cm^{-1} were modified and new peaks at 1730 and 1052 cm^{-1} were obtained with smaller peaks corresponding to C=O and O–C, respectively (Fig. 3d). Small narrow peaks in the fingerprint region disappeared with the formation of only one peak at 667 cm^{-1} . These changes indicate the roles of their functional groups in the adsorption process.

3.1.3.3. Coconut coir powder. The FTIR spectra of coconut coir powder showed characteristic peaks at 3321 and 3197 cm^{-1} which corresponded to O–H stretching vibration while a small peak was observed at 2935 cm^{-1} which denoted C–H stretching vibration (Fig. 3e). Peaks at 1658 , 1402 and 1118 cm^{-1} correlated to C=C, O–H and C–N stretching and bending vibrations respectively. The peak at 611 cm^{-1} represented C–H bending vibrations. After the adsorption process, the FTIR spectra showed differences that could be attributed to the functional groups that could be involved in the adsorption process. There is a broadening of the peak at 3266 cm^{-1} corresponding to the O–H group and a formation of a new peak at 2353 cm^{-1} compared to that of the control. A significant change was noticed in the peaks in the region from 1700 to 1000 cm^{-1} where there is a clear disappearance of the peak at 1402 cm^{-1} and reduction in the size of the peak at 1118 cm^{-1} and a formation of a peak to 1038 cm^{-1} (Fig. 3f). These peaks correspond to O–H, C–N and O–C respectively (Aravind et al., 2021). These changes in the spectra suggest their possible role in the adsorption process.

3.2. Decolourization tests of acid blue dye 113

Different concentrations of the dye solutions were prepared and readings were recorded using a UV–Visible spectrophotometer, at 566 nm , or GC/MS instrument. The standard values and the values obtained after the adsorption process occurred in the samples were used to calculate the adsorption and removal percentage values under various circumstances.

3.2.1. Activated corn leaf carbon

5 g of activated corn leaf carbon sample was added to various concentrations of the dye (100 mg/L – 2500 mg/L) solution. The adsorption capacities of the sample at various time intervals were tested by taking readings in the UV–Visible spectrophotometer, at 566 nm . It was observed that the sample reacted very fast when the concentration was lesser than 100 mg/L , as the adsorption was completed in several hours. For 200 mg/L , the completion of the adsorption process took almost 3 h. Since complete adsorption (almost 100%) did not occur for 250 mg/L , the concentration of the substrate was increased to 10 g . For 500 mg/L , the adsorption dosage was increased to 20 g to achieve complete adsorption, i.e. nearly 100%. As the concentration of the dye increases, the adsorbent material takes more time to react with adsorbate molecules. By increasing the amount of the sorbent, higher concentrations of the dye can be treated. Since the corn leaf has been activated and carbonized, it does have useful functional groups and thus can remove the dye rapidly.

3.2.2. Groundnut shell powder

5 g of sorbent substance was added to different concentrations of the dye solution, ranging from 100 mg/L to 5000 mg/L . The adsorption and removal capacity of the agricultural waste was determined by taking readings in the UV–Visible spectrophotometer at 566 nm (or in GC/MS instrument). Since 5 g of the substrate was not sufficient to treat the dye solutions with concentrations larger than 750 mg/L , the dosage of the sorbent was increased to 10 g , and readings were taken. Similarly, the

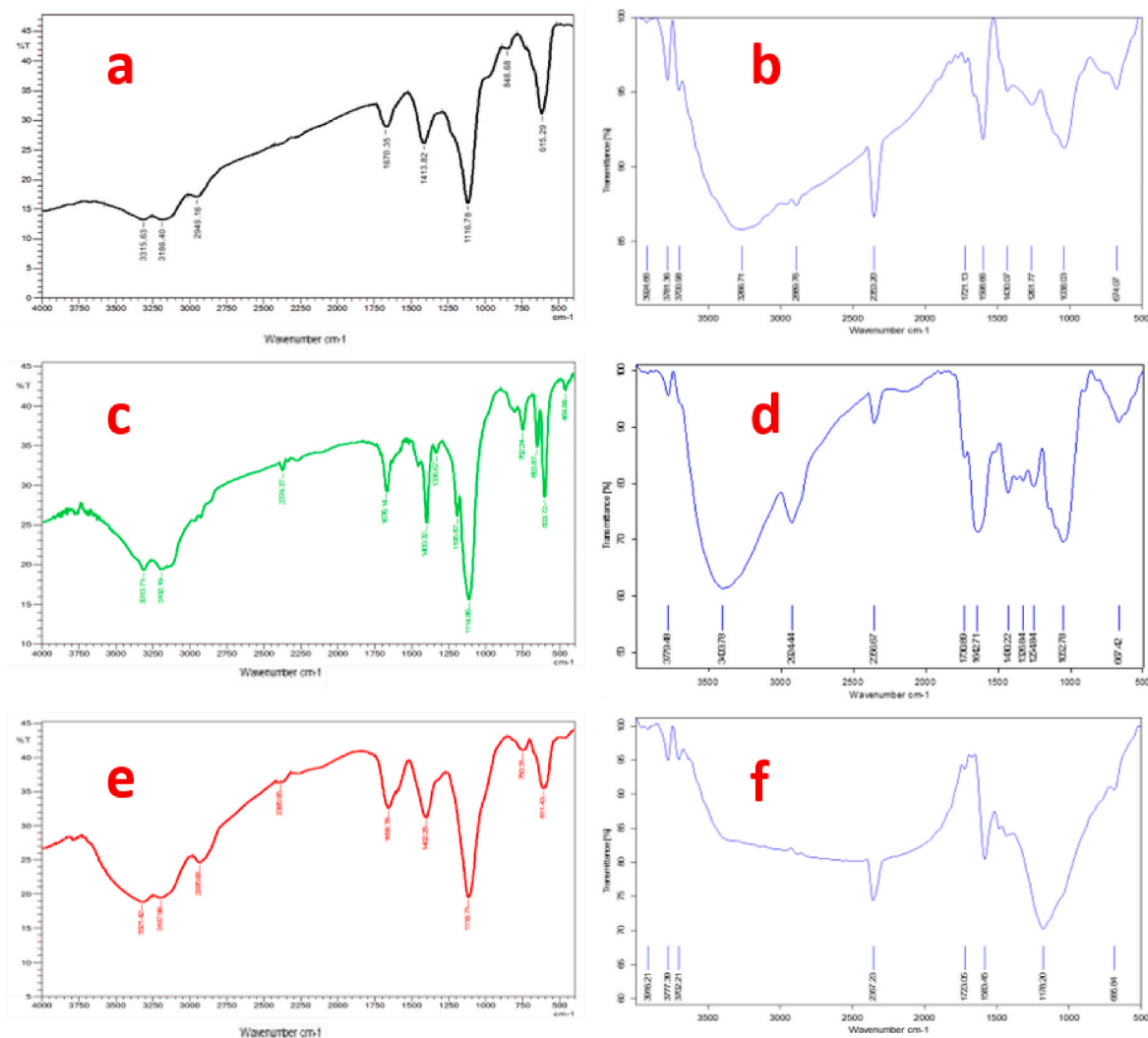


Fig. 3. FTIR analyses of groundnut shell– before (a) and after (b) dye adsorption, FTIR analyses of activated corn leaf carbon – before (c) and after (d) dye adsorption, and FTIR analyses of coconut coir – before (e) and after (f) dye adsorption.

sorbent dosage was increased gradually until the sorbent amount was sufficient to treat the dye solution with a concentration of 5000 mg/L. Higher concentrations of dyes can be treated by further increasing the concentration of the substrate. This sorbent was also able to remove the interested dye since it has some valuable functional moieties in its structure which are capable of forming adsorptive interactions with the dye molecules.

3.2.3. Coconut coir powder

10 g of substance was added to various concentrations of dye solutions from 100 mg/L to 5000 mg/L. The adsorption capacity of coconut coir powder was estimated by taking readings in the UV–Visible spectrophotometer at 566 nm (or in GC/MS instrument). 10 g was able to completely remove the dye existing in the solution when the concentration of dye was lower than 750 mg/L. At higher concentrations of dye, the sorbent dosage was increased by 5 g each time, since the sorbent was not able to completely remove the dye (Sathish et al., 2021; 2022). Like groundnut shell powder, coconut coir powder also has some suitable functional groups which can degrade and adsorb the dye on its surface.

3.3. Effect of pH and temperature on dye

The effects of pH and temperature on dye adsorption were studied

using each of the studied three sorbents with a dye concentration of 100 mg/L. The original pH of the dye solution was found to be 6.5. The pH of the solution was altered to lower amounts by adding several drops of 1 N HCl and to higher amounts by adding some amount of 1 N NaOH. After an incubation/shaking period of 1 day, UV readings were taken at 566 nm and it was observed that the original pH of the dye, that is 6.5, is the most favourable for the maximum activity of the sorbent materials. Similarly, three different temperatures (15, 25, 35 and 45 °C) were tested to find out the effect of temperature on the adsorption process (Lagergren, 1898). Of the three different temperatures maintained, room temperature (25 °C) favoured the complete decolourization of the dye, even though a higher temperature (35 and 45 °C) gave slightly better results for decolourization of the solutions, indicating the positive influence of higher temperatures on the process.

3.4. Adsorption isotherm study

The dye-binding interaction with the three different adsorbents was evaluated by isothermal equations such as Freundlich, Langmuir, and Sips isotherm models. The present studies were postulated with varying dye concentrations from 100 mg/L – 500 mg/L at pH 6.5, and the studies were conducted at three differing temperatures 15, 25, 35, and 45 °C.

The graphs (Fig. 4a-c) were given for the visual evaluation of the

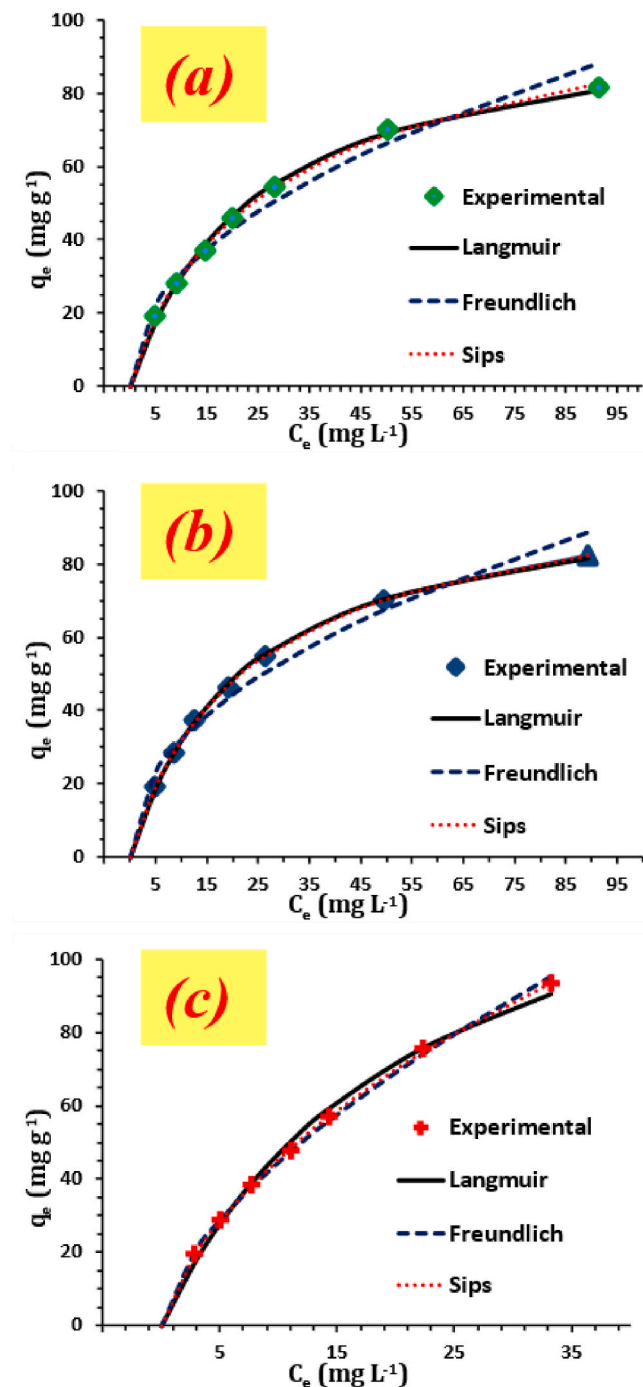


Fig. 4. Adsorption isothermal fit for the removal of dye onto groundnut shell (a), coconut coir (b), and activated corn leaf carbon (c). (Dye solution volume: 100 mL, pH 6.5, dye concentration 100–500 mg/L, contact time 90 min, sorbent dose 5.0 g/L, temperature 25 °C (298 K)).

goodness-of-fit of different models with experimental data. Also, the obtained parameters and statistical indices were reported in Table 2 for a detailed comparison.

Langmuir model was evaluated to find out if there is homogenous adsorption between the three different adsorbents and dye molecules (Açikel and Göze, 2017; Ho and McKay, 1999). According to this study, and the lower fitness of the Langmuir model with the results, the dye molecule is not adsorbed on the surface of the sorbent homogeneously (Dhaif-Allah et al., 2020). On the other hand, the three-parameter model (Sips model) showed a high goodness-of-fit for adsorption processes

Table 2

Parameters obtained for different isotherms. (Dye solution volume: 100 mL, pH 6.5, dye concentration 100–500 mg/L, contact time 90 min, sorbent dose 5.0 g/L, temperature 25 °C (298 K)).

Models	Parameters	Adsorbent		
		Activated corn leaf carbon	groundnut shell powder	Coconut coir powder
Freundlich	K_F ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$)	10.47	10.38	11.10
	N	1.59	2.11	2.16
	R^2	0.9992	0.9904	0.9891
	Δq (%)	7.63	8.60	10.74
	RMSE	1.09	3.51	3.75
	χ^2	0.15	1.58	2.02
Langmuir	q_{max} (mg g^{-1})	150.29	101.86	101.44
	b (L mg^{-1})	0.05	0.04	0.05
	R^2	0.9975	0.9980	0.9988
	Δq (%)	5.24	6.22	3.58
	RMSE	1.88	1.14	0.96
	χ^2	0.56	0.29	0.15
Sips	q_{max} (mg g^{-1})	336.09	118.74	107.59
	n_s	1.33	1.17	1.07
	K_s (L g^{-1})	0.01	0.03	0.04
	R^2	0.9999	0.9995	0.9999
	Δq (%)	0.93	1.13	0.74
	RMSE	0.43	0.28	0.28
	χ^2	0.02	0.04	0.01

between all three adsorbents and the dye molecules (Kumar et al., 2022).

Freundlich model shows heterogeneous adsorptions and reveals multilayer sorption processes, which happen between the dye and the adsorbent surface (Vishnu and Dhandapani, 2021). Based upon the correlation coefficients, R^2 values, the interaction between the three adsorbents and the dye molecule follows the Freundlich adsorption pattern. The R^2 value for Freundlich was not greater than those of Langmuir and Sips models for all three adsorbents' interaction with the dye molecules (Prakash et al., 2021). In fact, with higher R^2 amounts and lesser values of the sum of squared errors and root mean square errors for the Sips model, one can claim that the system is obeying the Sips pattern (Ho and McKay, 1999). This means that in the overall process, mono-layer sorption happens first and dye molecules get distributed on the surface and, then, some multilayer adsorptions also happen on the sorbents (Arshadi et al., 2014).

3.5. Adsorption kinetics study

Adsorption kinetics is performed to understand the ability of a sorbent to adsorb the dye concerning time (Azizian et al., 2018). Adsorption kinetics is performed for substances that only adsorb and do not react with the dye (i.e., for substances that do not degrade the dye) (Sathish et al., 2019). The substance can either follow pseudo-first-order kinetics or pseudo-second-order kinetics, etc. The kinetic studies were done by varying the concentrations of the dye from 100 mg/L to 400 mg/L. The experiments were carried out at optimal conditions which were found above. The temperature was at 25 °C with the concentration of the adsorbent at 0.5 g/L, pH was at 6.5, and contact time varied from 5 to 60 min.

Fig. 5 shows a visual evaluation of the goodness-of-fit of the kinetic data with the studied models. In this study, the agro-waste adsorbents were found to follow pseudo-second-order kinetics, since the R^2 values for these models were approximately equal to 1 for all dye concentrations from 100 mg/L to 400 mg/L. The results of the evaluation of various kinetic models of pseudo-first-order and pseudo-second-order, and the vital parameters like correlation coefficients (R^2) were postulated using MATLAB programming and are reported in Table 3. The results show that, in addition to the higher values of R^2 for the pseudo-second-order, the values of statistical indices are lower for this model

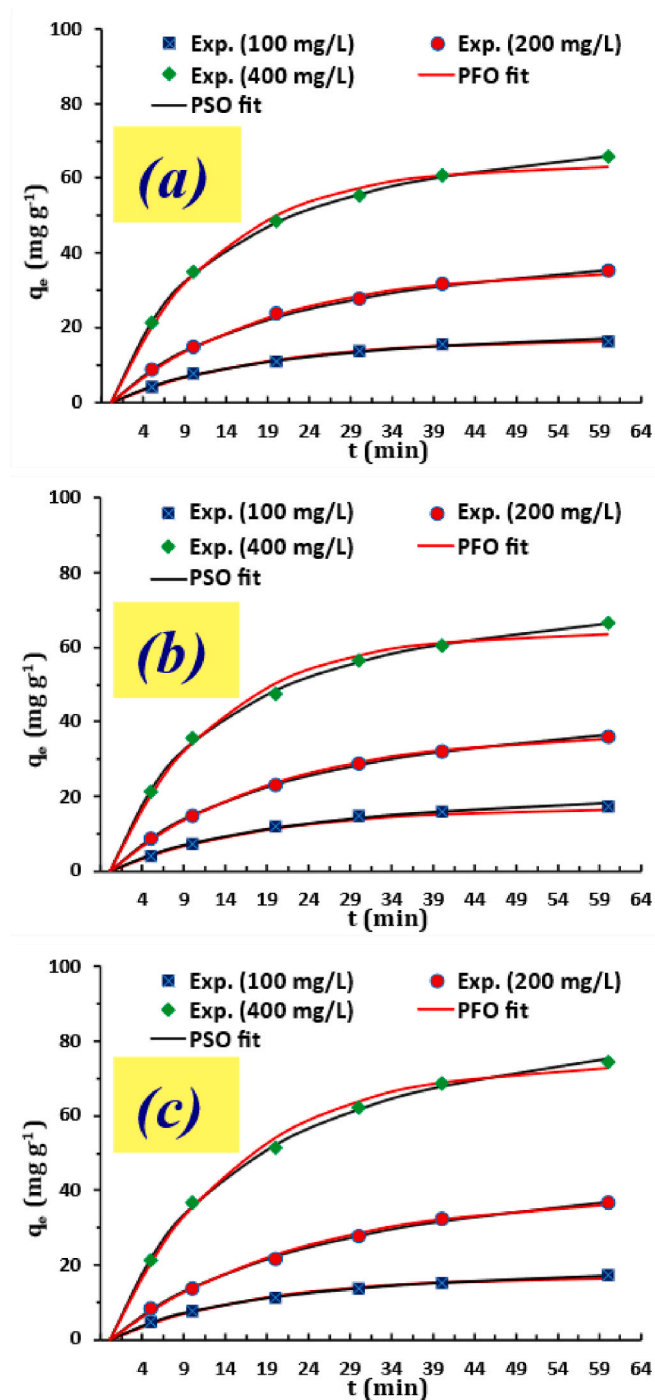


Fig. 5. Adsorption kinetic fitting for the dye removal by groundnut shell (a), coconut coir (b), and activated corn leaf carbon (c). (Dye solution volume: 100 mL, pH 6.5, dye concentration of 100, 200, and 400 mg/L, contact time 5–60 min, sorbent dose 5.0 g/L, temperature 25 °C).

which ascertains the obedience of the kinetic data from the pseudo-second-order kinetics. Such outcomes reveal that the interaction between the adsorption sites with the dye is the rate-controlling step in the adsorption processes (Mohammadzadeh et al., 2023).

3.6. Adsorption thermodynamic study

Assessing the change in the thermodynamic parameters during the adsorption processes is essential for the practical application of the adsorption systems.

Table 3

Kinetic results for the adsorption of the interested dye on the groundnut shell powder, coconut coir powder and activated corn leaf carbon. (Dye solution volume: 100 mL, pH 6.5, dye concentration of 100, 200, and 400 mg/L, contact time 5–60 min, sorbent dose 5.0 g/L, temperature 25 °C).

Adsorbents	Models	Parameters	Concentrations (mg/L)		
			100	200	400
Activated corn leaf carbon	Pseudo-first order	k_1 (min ⁻¹)	5.88E-02	4.40E-02	6.54E-02
		$q_{e,cal}$ (mg g ⁻¹)	17.11	39.00	74.08
		R^2	0.9908	0.9977	0.9988
		Δq (%)	4.72	5.39	3.45
		RMSE	0.41	0.75	1.55
		χ^2	0.10	0.20	0.27
	Pseudo-first order	k_2 (g mg ⁻¹ min ⁻¹)	2.26E-03	6.30E-04	6.09E-04
		$q_{e,cal}$ (mg g ⁻¹)	22.72	54.86	96.72
		R^2	0.9996	0.9990	0.9997
		Δq (%)	1.28	3.22	2.11
		RMSE	0.09	0.50	0.77
groundnut shell powder	Pseudo-first order	k_1 (min ⁻¹)	5.55E-02	5.08E-02	7.70E-02
		$q_{e,cal}$ (mg g ⁻¹)	17.04	37.17	64.25
		R^2	0.9765	0.9981	0.9975
		Δq (%)	5.25	3.70	4.43
		RMSE	0.73	0.45	1.97
		χ^2	0.22	0.26	0.45
	Pseudo-first order	k_2 (g mg ⁻¹ min ⁻¹)	1.65E-03	8.19E-04	9.04E-04
		$q_{e,cal}$ (mg g ⁻¹)	25.44	50.98	81.45
		R^2	0.9990	0.9997	0.9996
		Δq (%)	2.04	0.92	2.27
		RMSE	0.20	0.24	0.34
Coconut coir powder	Pseudo-first order	k_1 (min ⁻¹)	5.55E-02	5.30E-02	7.73E-02
		$q_{e,cal}$ (mg g ⁻¹)	17.04	36.01	63.72
		R^2	0.9957	0.9982	0.9984
		Δq (%)	4.64	3.88	5.53
		RMSE	0.49	0.43	1.56
		χ^2	0.14	0.18	0.28
	Pseudo-first order	k_2 (g mg ⁻¹ min ⁻¹)	2.01E-03	8.95E-04	9.19E-04
		$q_{e,cal}$ (mg g ⁻¹)	23.09	49.09	80.65
		R^2	0.9992	0.9994	0.9999
		Δq (%)	1.78	2.06	1.24
		RMSE	0.23	0.17	0.16

The following equation can be applied as a basis for deriving proper thermodynamic equilibrium constants for the studied adsorbents (Peiravi-Rivash et al., 2023):

$$Adsorbate_{(aq)} + Adsorbent = Adsorbate.Adsorbent \quad (13)$$

The thermodynamic parameters, ΔG° , ΔH° and ΔS° , of acid blue dye adsorption on agro-waste sorbents were used to grasp information on the mechanism involved in the sorption processes. These parameters were calculated by the following relations:

$$\Delta G^\circ = -RT \ln K_{eq} \quad (12)$$

$$\ln K_{eq} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

$$K_{eq} = \frac{(K_s \times \text{molecular weight of acid blue dye}) [\text{Acid blue dye}]^\circ}{\gamma} \quad (14)$$

K_{eq} is the thermodynamic equilibrium constant, R is the universal gas constant (8.314 J/(mol·K)), T is the absolute temperature (K), K_s is Sips isotherm model constant (L/g), γ is the coefficient of activity (dimensionless), and $[Acid\ blue\ dye]^\circ$ is the standard concentration of the acid blue dye (1 mol/L). The computed parameters from Eq. (12) and the plot of Eq. (13) (Fig. 6) were reported in Table 4. The negative ΔG° values revealed that the adsorption processes of acid blue dye on the studied adsorbents were all spontaneous. Lower values of negative ΔG° at higher temperatures indicated that the adsorption was more advantageous and feasible at higher temperatures. The higher ΔG° values obtained for the adsorption of acid blue dye on the activated corn leaf carbon reveals that this adsorbent is more advantageous than the two other studied one for this purpose. The positive values of ΔS° (38.52–41.07 J/mol K) indicated high affinity of the adsorbents for acid blue dye and a slight increase in disorder and randomness at the solid/liquid interface during the adsorption processes, while the positive values of ΔH° (4.83–7.30 kJ/mol) implied that the removal of acid blue dye on all the studied adsorbents was endothermic (Mohammadzadeh et al., 2023). Also, the higher value of ΔH° for activated corn leaf carbon again shows that this adsorbent has stronger adsorptive interactions with acid blue dye than the two others. Usually, the absolute magnitudes of ΔH° ranging from 2.0 to 20 kJ/mol indicate physisorption processes (Tran et al., 2016; Khamirchi et al., 2018). Low ΔH° magnitudes (4.83–7.30 kJ/mol) implies that physical sorption is the major mechanism existing in the system. In fact, such results reveal that the sorption is proceeded via electrostatic interactions and hydrogen bonding (Prabu et al., 2022). However, the value of ΔH° for activated corn leaf carbon is higher than those of groundnut shell and coconut coir (Table 4). The more positive value of ΔH° for activated corn leaf carbon indicate that, except electrostatic interactions and hydrogen bonding, there is another adsorption force which can be attributed to the π - π interactions between the dye molecule and the stacked graphitic planes present in the structure of activated carbons (Alahabadi et al., 2017; Alahabadi et al., 2020).

3.7. Comparison with other adsorbents

The adsorption capacity of groundnut shell, coconut coir, and

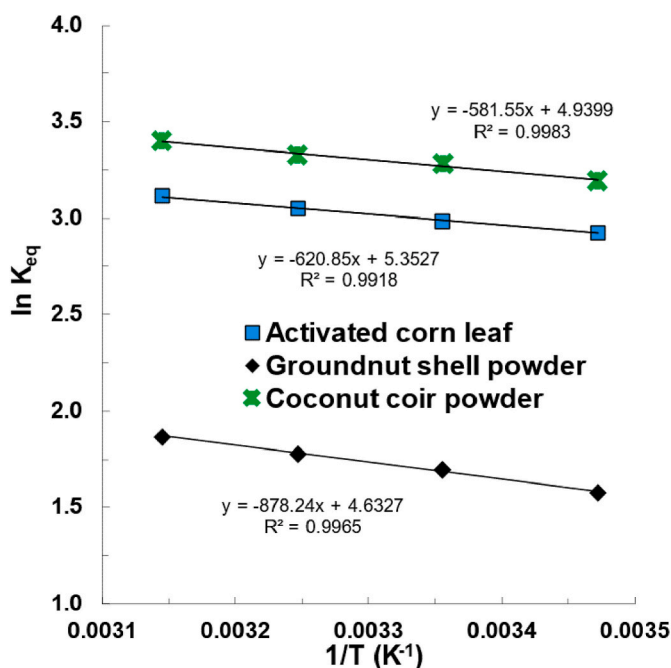


Fig. 6. The plot of $\ln K_{eq}$ against $1/T$. (Dye solution volume: 100 mL, pH 6.5, dye concentration 100–500 mg/L, contact time 90 min, sorbent dose 5.0 g/L, temperatures of 288, 298, 308, and 318 K).

Table 4

Parameters of the adsorption thermodynamic. (Dye solution volume: 100 mL, pH 6.5, dye concentration 100–500 mg/L, contact time 90 min, sorbent dose 5.0 g/L, temperatures of 288, 298, 308, and 318 K).

Adsorbent	Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
Activated corn leaf carbon	288	−26.78	7.30	38.52
	298	−28.41		
	308	−30.47		
	318	−32.32		
Groundnut shell powder	288	−7.00	4.83	41.07
	298	−7.39		
	308	−7.81		
	318	−8.23		
Coconut coir powder	288	−3.78	5.16	44.50
	298	−4.20		
	308	−4.56		
	318	−4.94		

activated corn leaf carbon was compared with several adsorbent used for removal of Acid blue dye 113. The adsorption capacities of these adsorbents have been tabulated in Table 5. As can be seen, in comparison to the other reported adsorbents, Activated corn leaf carbon has a higher potential in the treatment of waters and wastewater containing Acid blue dye 113. Such results shows that activation and carbonization of waste biomass (corn leaf) has an imperative effect on its valorization for removal of Acid blue dye 113.

4. Conclusion

In the present research, the agro-waste material (groundnut shell powder, coconut coir powder and activated corn leaf carbon) was effectively recruited as an adsorbent for the removal of acid blue 113 dye from the aqueous solutions. The surface morphology and the presence of functional groups on the adsorbent material were evaluated using SEM, EDX and FTIR analyses. The factors influential parameters like solution pH, contact time, biosorbent dosage and temperature were optimized by conducting batch experimental studies. The optimal sorption occurred at 6.5 for all the studied adsorbents, and the share of adsorption after 60 min was marginal. The adsorption isotherm and kinetic study were appraised, indicating that the Sips isotherm and Pseudo-second order kinetic model gave the best fit with experimental data. The maximum adsorption capacity for groundnut shell powder, coconut coir powder and activated corn leaf carbon 118.74, 107.59, and 336.09 mg/g. One can conclude that, among the studied sorbents, activated corn adsorbent material has superior adsorption capacity for the effective removal of acid blue 113 dye from the contaminated

Table 5

Comparing the sorption capacities of the studied sorbents towards Acid blue dye 113 with other adsorbents.

Sorbent	Adsorption capacity of acid blue dye 113 (mg.g ^{−1})	Ref.
<i>Cucumis sativus</i> peel	59.81	(Lee et al., 2016)
<i>Abelmoschus esculentus</i> seed	169.9	(Lee et al., 2015)
Lemna minor adsorbent	395.7	(Prakash et al., 2021)
Chitin	102	(Açikel and Göze, 2017)
Chitosan	143	(Açikel and Göze, 2017)
<i>Prunus Dulcis</i> leaves	97.09	(Jain and Gogate, 2017)
Groundnut shell powder	118.74	Present study
Coconut coir powder	107.59	Present study
Activated corn leaf carbon	336.09	Present study

solutions. The higher adsorption capacity of activated corn leaf carbon in the adsorption of acid blue 113 dye can be assigned to H_3PO_4 -activation and carbonization which were inflicted on this agro-waste material.

Credit author statement

Swetha Sunkar: Investigation, Writing-original draft, Writing-Reviewing and Editing; **Prakash.P:** Data curation, Writing-original draft **Balaji. D:** Conceptualization; **Omirsarik Baigenzhenov:** Data modelling, Writing-Reviewing and Editing **J. Aravind Kumar:** Supervision, Writing-Reviewing and Editing, Correspondence; **Valli Nachiyaar:** Funding acquisition; **Sara Zolfaghari:** Data modelling, Writing-Reviewing and Editing **Sara:** Data curation;; **Tejaswini:** Data curation; **Ahmad Hosseini-Bandegharai:** Writing-Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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