CHAPTER-4

Corn husk derived mesoporous carbon (CHMACs) for Orange G and Rhodamine B dyehouse effluents removal from wastewater: Characterization and Removal Study

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4.1. Topography Analysis (SEM):

An analysis of the morphology and elements present in CHMAC 2 Imp 7 days adsorbent was conducted at 20 kV using a standard SEM with an energy dispersive spectroscopy (EDS) instrument. The surface topography and chemical changes of the samples were assessed using EDS (EDS:51N1000 – EDS System), elemental mapping of CHMAC 2 Imp 7 days, and normal SEM (CARL ZEISS MICROSCOPY LTD. of Oxford Instruments Nanoanalysis) before and after the adsorption of Orange G and RhB dye, respectively. The surface topography of the adsorbent was uniformly porous before adsorption; **Figure 4-2 (e) and (f)** at 300 µm and 100 µm resolutions, respectively, depict a cube-type or solid porous structure. The EDS spectrum of supplemental **Figure 4-1 (a)-(b)** displays the elements on the surface of the CHMAC 2 Imp 7 days adsorbent, together with an atomic percentage value. **Figure 4-1 (c)-(d)** from the elemental mapping analysis reveals a significant density of oxygen and carbon before adsorption. The CHMAC 2 Imp 7 days is significantly better at removing the OG and RhB dye from wastewater because of the properties of the extremely unorganized particles.

4.2. XRD, FTIR, RAMAN and BET Analysis:

The produced adsorbents were characterized using an HR-X-ray diffractometer (Rigaku Miniflex Cu Kα radiation of 30 mA and 40 kV). As seen in **Figure 4-2 (a)**, all of the CHMAC samples displayed two distinctive peaks at approximately 24° and 44°, indicating the disordered (semicrystalline) and graphitic peaks in the adsorbent (JCPDS card No.75-1621). Nevertheless, the CHMAC 2 Imp 7 days showed superior crystallinity with a strong peak at 24° among all six adsorbents. This could be because H_3PO_4 was loaded more heavily onto the corn husk biomass for several days (7 days) [214].

Fourier-transform infrared spectroscopy (FT-IR) spectra in the mid-infrared band of 4000-400 cm^{-1} were generated using a spectrophotometer (Model: Nicolet iS5 Company: THERMO Electron Scientific Instruments LLC) with a resolution of 4 cm^{-1}. Following analysis, the Fourier Transform Infra-Red Spectrum of CHMAC 2 Imp 7 days is displayed in **Figure 4-2 (b)**. Strong stretching of the -OH functional group is responsible for the peaks at 3420 cm^{-1}, symmetric and asymmetric stretching from C-H (alkane) is responsible for the peak at 1705 cm^{-1}, C-C/C-O-C in the aromatic moiety is responsible for the peak at 1587 cm^{-1}, bending vibrations from C-H and C=O are observed in the range of 1250 1400 cm^{-1}. The peak at 1105 cm^{-1} arises due to alkyl or phenyl ether or ester linkage bending vibrations, C-O bond, and an out-of-plane C-H and δ-OH at around 700-800 and 545 cm^{-1} were characterized in CHMAC 2 Imp 7 days adsorbent surface [108,111,173].

The inelastic scattering principle causes molecules to vibrate in the presence of visible light in this spectroscopic approach, which is simply the reverse of FTIR analysis. the Raman spectroscopy was used to characterize at a 532 nm wavelength for CHMAC. Three distinct peak types known as the D, G, and 2D bands are seen in the analysis of carbon-type compounds [113]. Raman spectroscopy is the traditional, rapid, and non-destructive characterization technique for understanding the variety of carbon's structural forms. To check the graphitic “G” (sp^2 carbon form) and defects “D” (sp^3 carbon form) abundance in the adsorbent, the ID/IG ratio value was calculated using Origin Software 2018 by the peak area of the D and G bands and found to be 1.33. The I_D/I_G of 1.33 indicates the increase in sp^2 carbon because of chemical activation [114]. Three distinct bands, designated G (graphitic), D (disordered), and 2D band at approximately 1580, 1360 (first-ordered Raman spectrum), and 2700 cm^{-1} (second-ordered Raman spectrum), are presented in the Raman spectrum for CHMAC 2 Imp 7 days, which ranges from 3500 to 100 cm^{-1}, as shown in **Figure 4-2 (c)** [112 178]. The CHMAC 2 Imp 7 days adsorbent was subjected to specific surface area and porosity measurements using BET/BJH instruments at 77 K in N_2 for 18 hours of degassing. A total of 500 mg of adsorbent was used for analysis; the Type I (b) isotherms' rapid increase in

adsorption at low relative pressures (P/P0) and slowdown at intermediate pressure, as shown in **Figure 4-2 (d)** [215] demonstrate the presence of micropores and mesopores in the adsorbent (CHMAC 2 Imp 7 days). The IUPAC takes into account macropores with r > 50 nm, transition pores with r < 50 nm, and micropores with r < 2 nm. The primary adsorption sites are micropores, while mesopores facilitate intraparticle diffusion and reduce the adsorption time [216]. The mesoporosity on the adsorbent surface by adsorption of N_2 is confirmed by the CHMAC 2 Imp 7 days' high specific surface area of around 1668.18 m^2/g, BJH average porosity, and pore diameter of about 5.4 nm. The high specific surface area and good micro-mesoporosity on the adsorbent surface, along with well-active sites, are the only factors contributing to the great amount of adsorption of both dyes by this adsorbent.

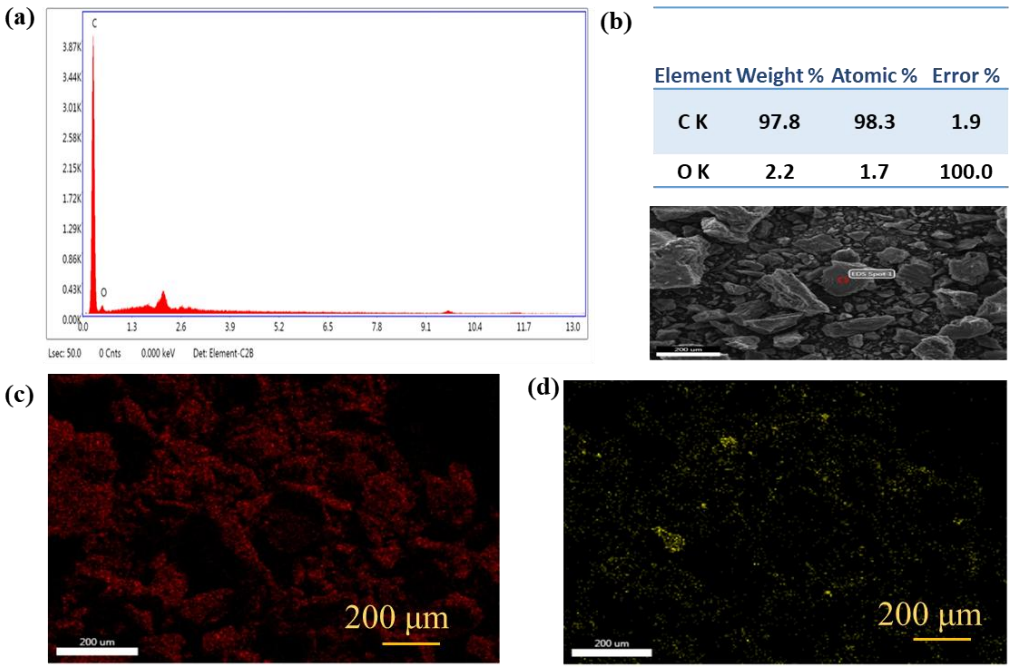


Figure 4-1 (a) EDAX of CHMAC 2 Imp 7 days. **(b)** Element percentage with error for the particular image**.**

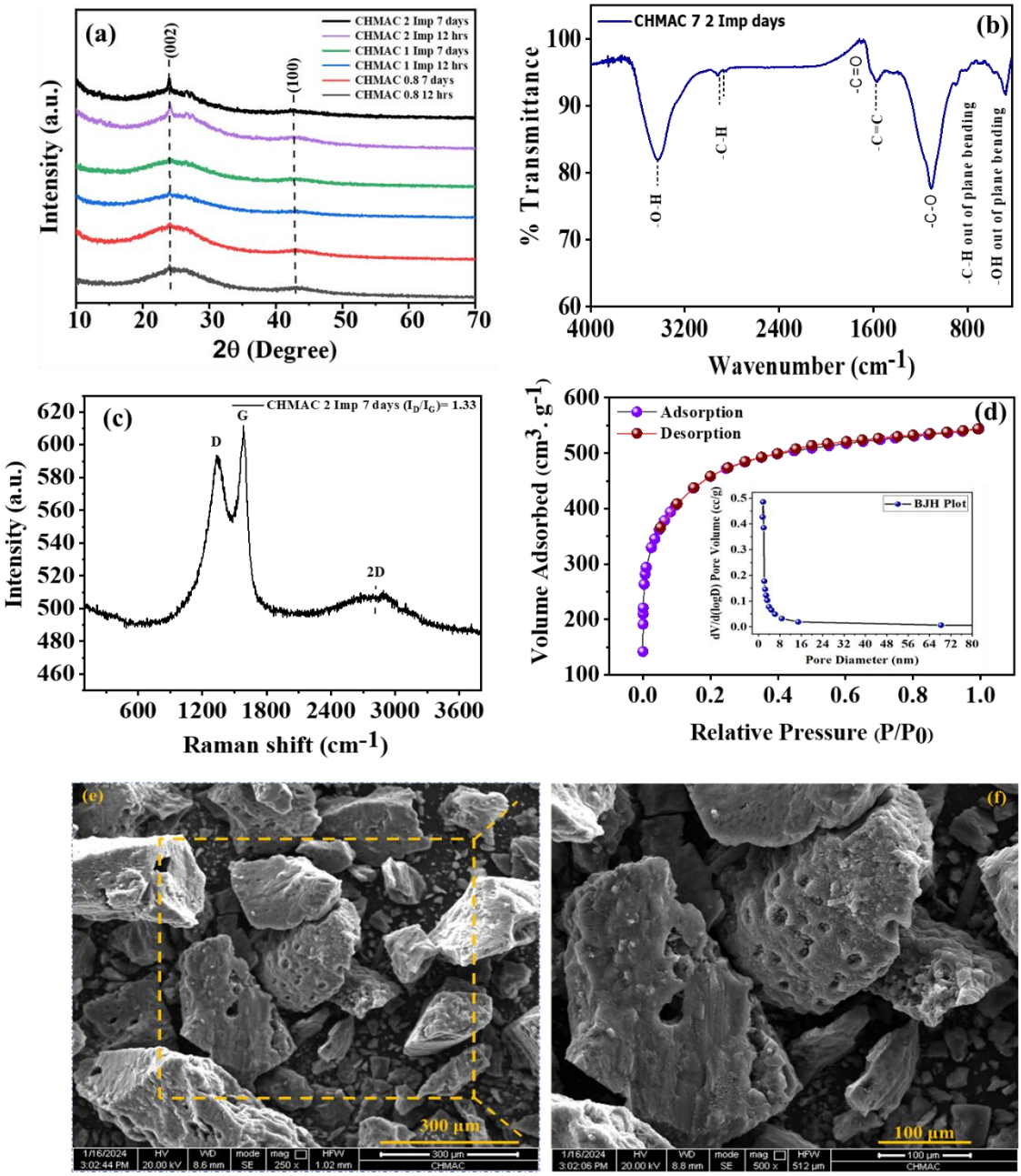


Figure 4-2 (a) XRD all adsorbents, **(b)** FTIR, **(c)** Raman, **(d)** BET/BJH plot, **(e)** and **(f)**

Normal SEM images of synthesized CHMAC 2 Imp 7 days adsorbent.

4.3. X-ray Photoelectron Spectroscopy Analysis:

The presence of atoms and functional groups on the surface of a solid sample can be identified with the help of this surface-sensitive method. To extract electrons from atoms on the surface of the analyte, X-rays with sufficient energy are directed towards the sample by a photon source in the XPS model K-alpha of Thermo Fisher Scientific [140]. These electrons are captured by a hemispherical analyzer, which then measures their kinetic energy and electron amount (intensity). The electron's binding energy is linked to the intensity of the kinetic energy, which provides information on the chemical composition of the surface and is related to the amount of a specific atom or functional group present on the material being studied. The most popular technique for assessing the surface chemistry, bonding structure, and composition of surfaces and interfaces is X-ray photoelectron spectroscopy (XPS). Here, **Figure 4-3 (b) (c)** displays the analysis of the effective CHMAC 2 Imp seven days before adsorption. In contrast, in O 1s, a band around 532.5 eV and 531.8 eV are for O-C and O=C, respectively, and a peak around 530.5 eV is defined with the charge effect in the polymer surface [110]. In the case of C 1s, C-C was around 284.02 eV, C-O-C bond was at 285.18 eV, C=O was at 287.5 eV, and a π-π* satellite peak was above 290 eV [217]. The survey peak of CHMAC 2 Imp 7 days adsorbent is displayed in **Figure 4-3 (a).**

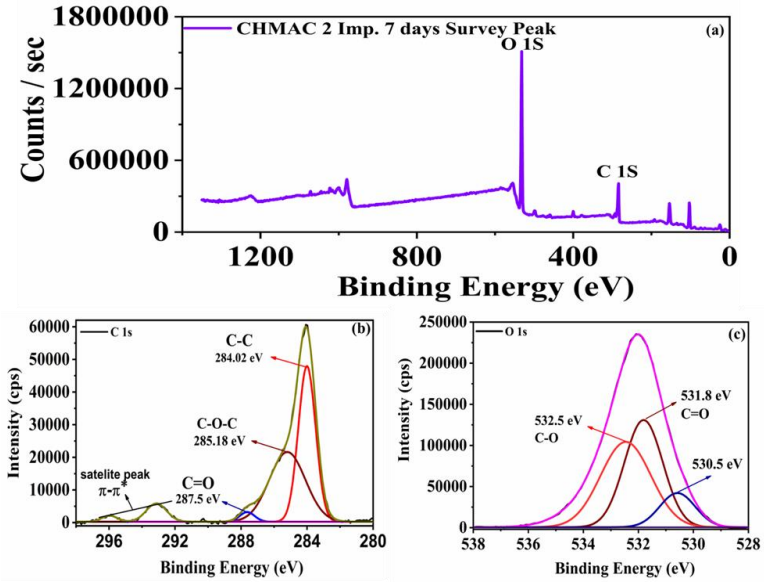


Figure 4-3 XPS survey **(a),** C 1s **(b),** and O 1s **(c)** of synthesized CHMAC 2 Imp 7 days adsorbent.

4.4. Adsorption Performance Comparability Study

In order to choose the best adsorbent, the ability of 50 mg of each CHMAC sample for adsorbing 100 ppm of OG and RhB was compared by recording comparative UV-Vis spectra. In Figure 4-4 (a), a removal comparison of 100 ppm RhB and OG dye with a 50 mg dose of adsorbents in a 60 mL dye solution was performed for 1 hour. All the spectra exhibited a λmax at 550 nm corresponding to RhB. As seen from the figure, only the CHMAC 2 samples demonstrated a significant decrease in the absorbance, indicating the adsorption of the dye on the CHMAC 2 samples. Of all the six samples, CHMAC 2 Imp 7 days showed maximum reduction in absorbance, manifesting its highest efficiency for the adsorption of RhB. Similar measurements were done for OG. The comparative UV-Vis spectra are shown in Figure 4-4 (b). Other concentrations of OG, as well as of RhB dye, were opted for removal investigation comparison using adsorbents with a dose of 50 mg, shown in Figures 4-4 (i) with CHMAC 2 Imp 7 days and CHMAC 2 Imp 12 hrs. All the spectra showcased maximum absorbance at 488 nm, corresponding to OG. Both CHMAC-1 and CHMAC-2 were found to be effective adsorbents for removing OG, showcasing a significant decrease in the absorbance. Nevertheless, CHMAC 2 Imp 7 days was found to be most effective for the adsorption of OG, which is inferred from the maximum decrease in the absorbance of OG after adding CHMAC 2 Imp 7 days. Therefore, CHMAC 2 Imp 7 days was considered for further investigations.

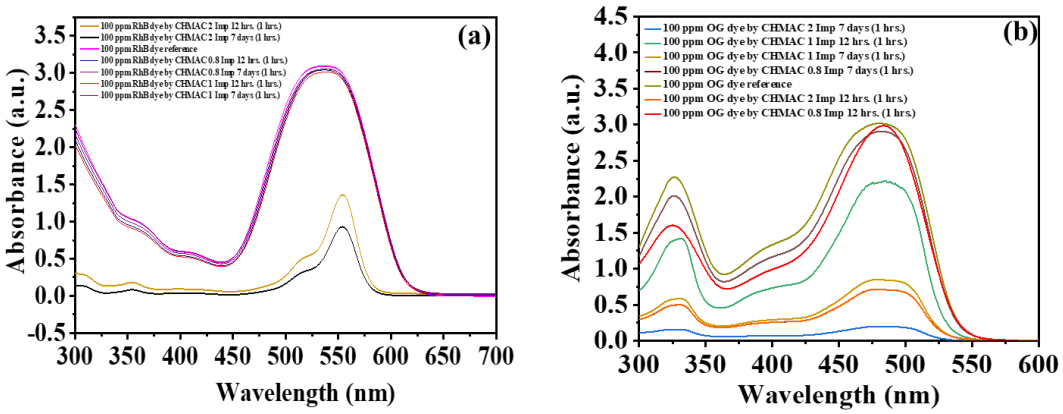


Figure 4-4 100 ppm RhB **(a)** and OG **(b)** removal comparison using all adsorbents within 1 h.

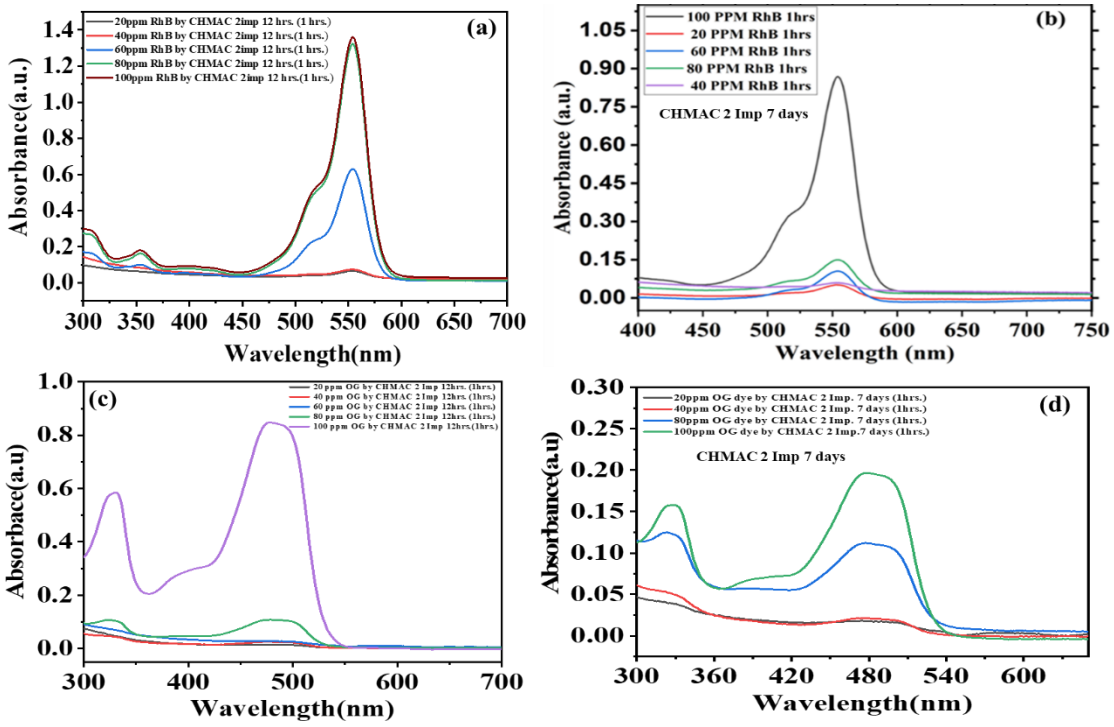
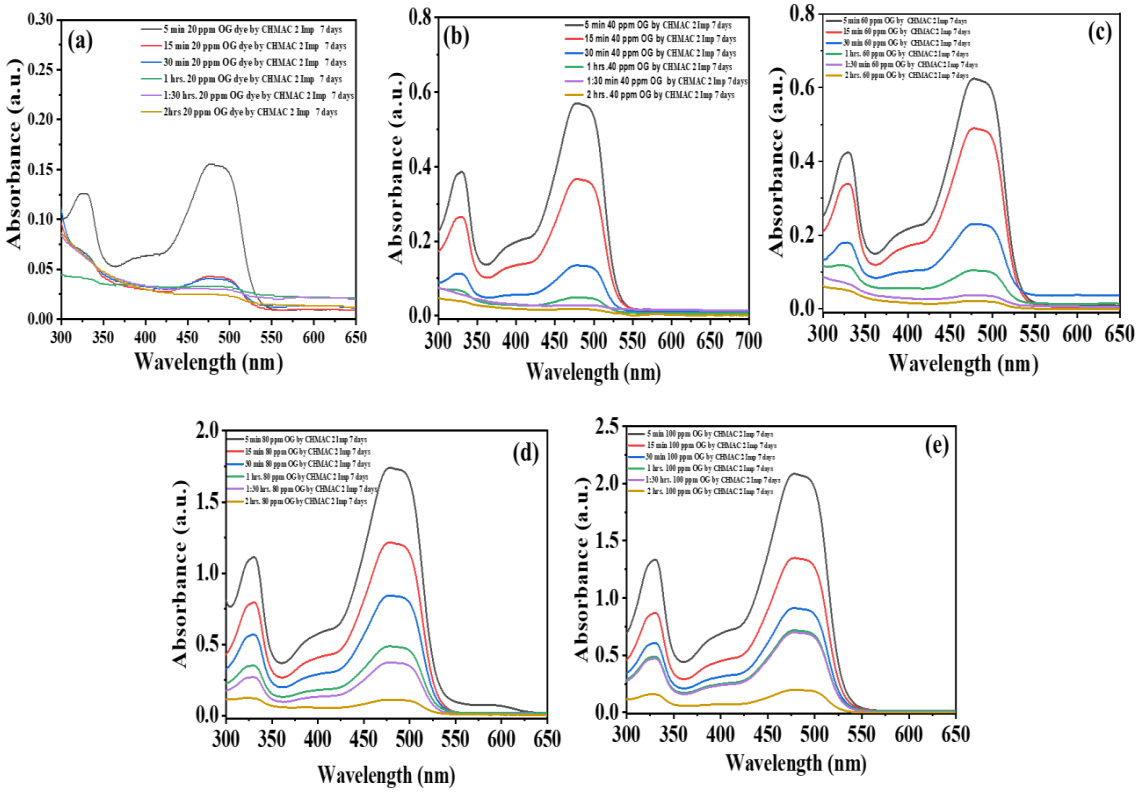


Figure 4-4 (i) CHMAC 2 Imp 12 hrs. and CHMAC 2 Imp 7 days UV-Vis plot to compare removal of OG and RhB dye within 1 hour of adsorption

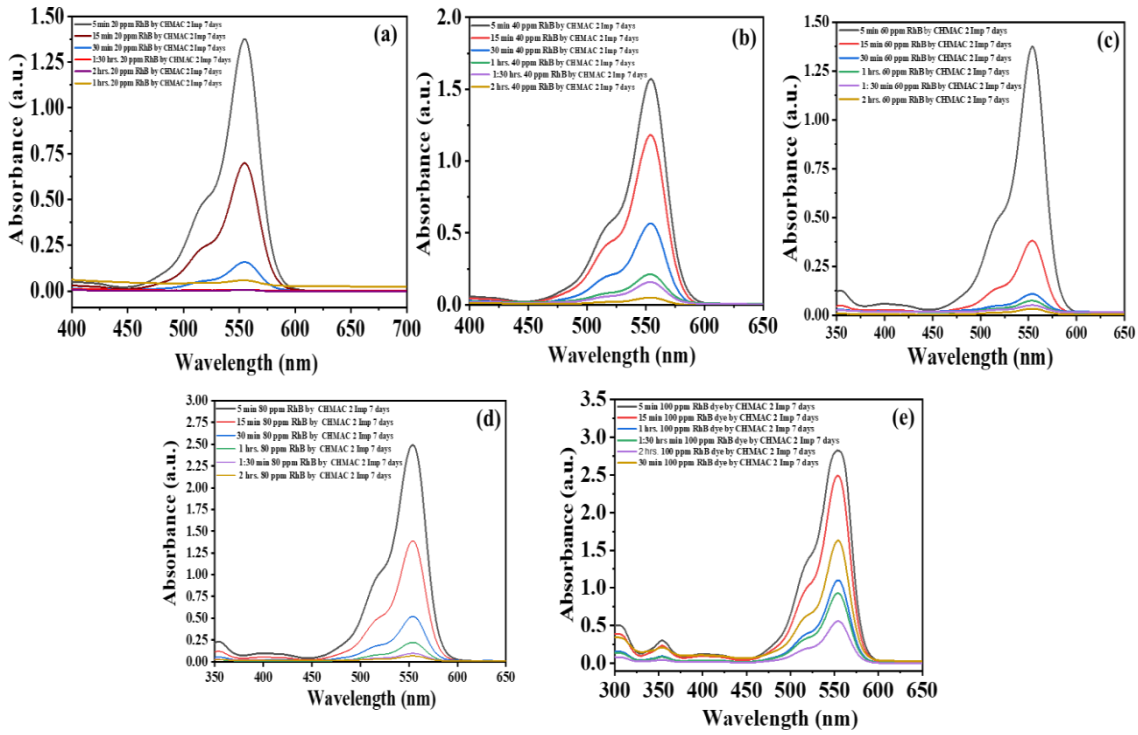
4.5. Optimization of Adsorption Parameters:

For both OG and RhB dye, the 250-ppm stock solution was diluted to 20, 40, 60, 80, and 100 ppm. The diluted adsorbates of both dyes at varying concentrations were stored in a 60 mL bottle containing 50 mg of CHMAC 2 Imp adsorbent for 7 days at 200 rpm for 5, 15, 30, 60, 90, and 120 minutes at 30 °C. Before usage, the adsorbate was kept at pH 7. After varying adsorption durations, the sample was filtered through a 125 mm Cytiva Whatman filter paper, and the filtrate was used for UV-vis analysis. To find the residual concentration at various time intervals, a UV-vis spectrophotometer (UV-1800) was used to plot a calibration curve (for both dyes), which is displayed in Figures 4-5 (e) and (f). Equation (1) examined and computed the removal %, while Equation (2) computed the capacity. For RhB and OG dye, respectively,

Figure 4-5 (a) and (c) display the removal percentage graph, while Figure 4-5 (b) and (d) provide the removal capacity graph. In the case of both dye concentrations (20-100 mg/L), the removal was thoroughly examined for two hours, and the equilibrium time was maintained within 60 minutes, as the graph indicates. At a dye concentration of 100 mg/L, the removal capacity is greater. The calculated loading capacity value within 120 minutes for 100 mg/L dye concentrations was 118 mg/g and 119 mg/g, respectively. The percentage removal of OG and RhB dyes is higher (greater than 95%) in the case of all concentrations using 0.83 g/L dose. The UV-Vis absorbance spectrum of both dyes using CHMAC 2 Imp 7 days adsorbent is provided in Figure 4-5 (i) and (ii), for all the concentrations



(i) 20-100 ppm OG dye all the time UV-Vis absorbance spectrum using CHMAC 2 Imp 7 days

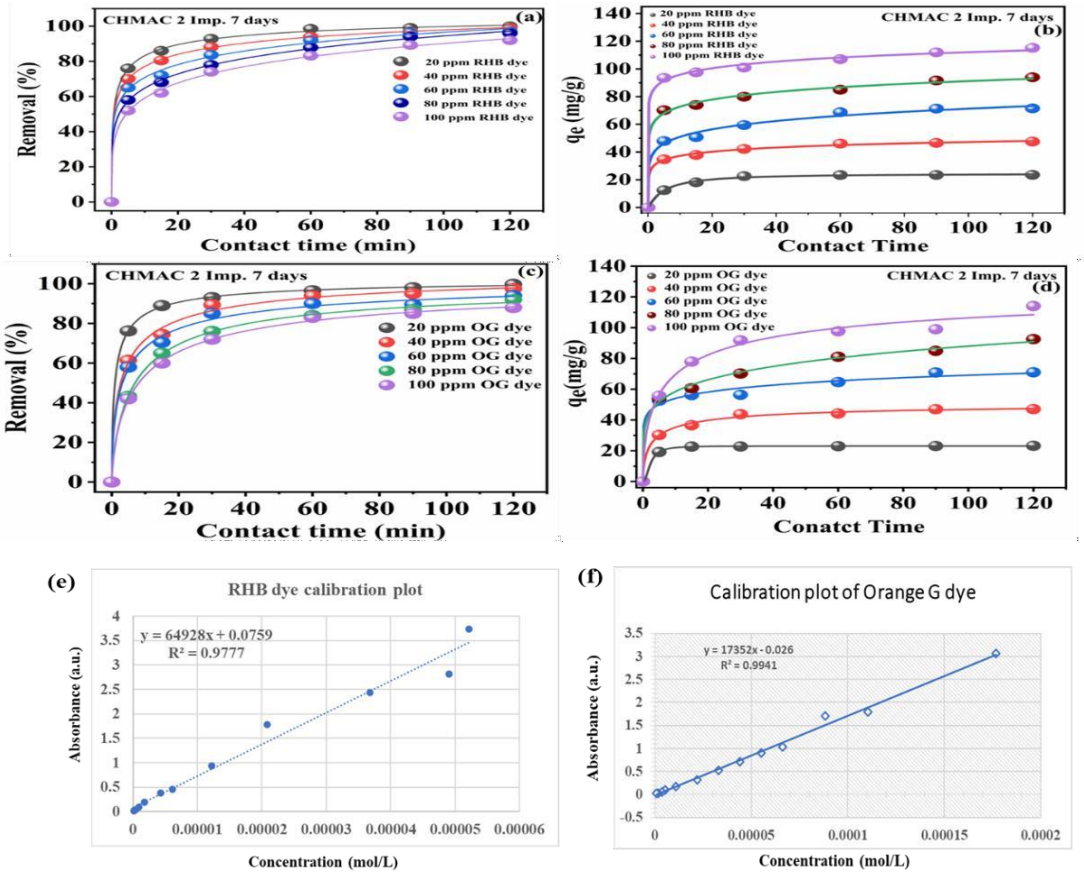


(ii) 20-100 ppm RhB dye of all the time UV-Vis absorbance spectrum using CHMAC 2 Imp 7 days

Figure 4-5 20-100 ppm OG (i) and RhB (ii) dye UV-Vis absorbance plot at times 5, 15, 30, 60, 90, and 120 minutes.

4.6. pH_{ZPC}, pH and adsorbent dose analysis:

The pH_{ZPC}, or pH of zero point of charge, is the pH value at which the surface of a solid is considered neutral. It is essential for ionic species to sorb onto solid surfaces from watery environments. Note that **Figure 4-6 (c)** displays the pHzpc plot. In this process, 0.1 g of CHMAC 2 Imp 7 days was added to 0.1 M of KCl solution in a 60 mL container with 50 mg of adsorbent dosage, and the suspension was stirred for 24 hours at 30 °C while being maintained at various pH levels (3, 4, 5, 7, 9, 10, and 11). The pH of the solutions was tested after a day. When $pH_{fnal} = pH_{initial}$, the adsorbent's pHzpc is determined [218]. This figure makes it evident that the surface of the CHMAC 2 Imp 7 days is neutral at roughly 6.9 pHzpc; the adsorbent's surface is negative above this pH value and positive below it, respectively. indicates that the adsorbent's acidic range will work well if the adsorbate has negative sites on its surface, and vice versa. with a 1M solution of NaOH/KOH and HCl from the Merck



Figures 4-5 (a)-(d) Contact time vs removal percentage and adsorption capacity plot for both dyes (for 20, 40, 60, 80, 100 mg/L dye concentration) using CHMAC 2 Imp 7 days adsorbent. (e) calibration plot of RhB dye, (f) calibration plot of OG dye.

The adsorbent's pH was examined with dye pH fluctuations ranging from pH 3, 5, 7, 9, 10, and 12. For two hours, the 60 mL dye (OG and RhB) stocks at a concentration of 60 mg/L were examined for pH analysis at 30 °C. The experiment used a dosage of 50 mg of adsorbent and was conducted in an incubation shaker at 200 rpm. As the pH rose to 7, the clearance of both dyes increased; however, from 9 to 12, it reduced, as seen in **Figure 4-6 (a).** The greatest dye removal occurred at neutral pH, where it showed good adsorbent properties to adsorb a broad range of cationic and anionic dyes. pHZPC analysis was then performed. The removal of both dyes at pH 7 was greater than 98%. RhB (>98%) had a larger removal percentage than OG dye (<20%) at the initial pH (acidic) range, mostly because of the adsorbate's surface structure at this pH. Using an adsorbate concentration of 60 mg/L at pH 7, the adsorbent's dose study was examined for both dyes. **Figure 4-6 (b)** illustrates that the elimination of

adsorbate increased as the dose was raised from 10, 20, 30, 40, and 50 mg. In every analytical parameter of dye adsorption, the maximum amount of adsorbate was removed at the optimal dose of 50 mg. The analysis was carried out at 30 °C in an incubation shaker. The figure, which was analysed after two hours of adsorption, displays the elimination% and adsorption capacity at various dosage concentrations of CHMAC 2 Imp 7 days. Additionally, **Figure 4-6 (b)** shows that RhB dye elimination accelerated relative to OG dye as the dose was raised from 10 to 50 mg.

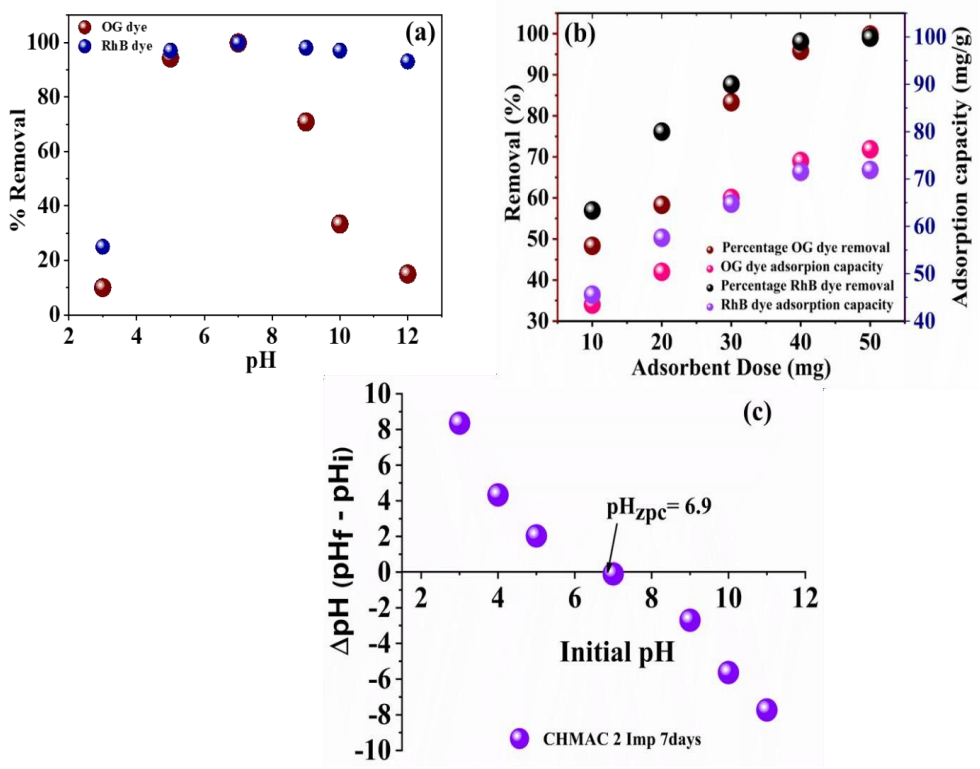


Figure 4-6 Various parameters were studied for adsorbent CHMAC 2 Imp 7 days **(a)** pH effect of dyes on adsorbent at 30 °C for 2 hrs. for 60 ppm concentration. **(b)** adsorbent dose study for 60 ppm dye concentration at 30 °C for 2 hours. **(c)** pHzpc study for adsorbent using NaCl salt solution at 30 °C for 24 hrs.

4.7. Adsorption Isotherm Study

Adsorbent and adsorbate-based interaction by distribution is shown by the adsorption isotherms. The adsorption equilibrium period for both dyes was 60 minutes, whereas the optimal removal times ranged from 5 minutes to 2 hours. The Temkin isotherm, Dubinin-

Radushkevich, Freundlich, and Langmuir (both linear and non-linear) isotherms were used to analyse the dyes' adsorption on the surface of CHMAC 2 Imp 7 days. The Langmuir isotherm can be used for a variety of adsorbents, even though it was first created for gas-solid interactions. Under equilibrium conditions, adsorption-desorption rates on the surface are equal, and there is no buildup because this empirical model is founded on kinetic principles [219]. A separation factor smaller than one indicates the favourable adsorption of OG dye, and the Langmuir adsorption isotherm displays both linear and non-linear best fits with R^2 values of 0.994 and 0.998 with mono-layer adsorption capacity values of 96.27 and 97 mg/g. With R^2 values of 0.99 and 0.99, respectively, the linear and non-linear Langmuir isotherms for RhB dye fit the data the best. RhB dye has a favourable adsorption on the CHMAC 2 Imp 7 days adsorbent, as indicated by the separation factor R_L being smaller than 1. **Table 4-7-1** contains all of the data. In the case of RhB dye, the maximum monolayer adsorption capacity was 106.5 mg/g in a non-linear manner and 107 mg/g in a linear manner. This model can be utilized for heterogeneous surface adsorption with a multilayer phenomenon. It assumes that there are irregularities in the affinities and the distribution of adsorption heat toward the heterogeneous surface [220]. For Langmuir and Freundlich, the linear plot is between $1/C_e$ vs $1/q_e$, as depicted in **Figure 4-7-1 (b, d, f, and h) and (a, c, e, and g).** The non-linear plot is between C_e and q_e. OG dye adsorption at 303 K is shown to have a favourable adsorption on the surface of CHMAC 2 Imp 7 days, as evidenced by the isotherm fitting with R^2 0.986 and 0.988 in non-linear and linear Freundlich adsorption isotherms, with 1/n value smaller than 1. All other data are shown in **Table 4-7-1.** In the case of RhB dye adsorption, the R^2 is 0.975 and 0.978 with n values of 0.42 and 0.47 for non-linear and linear Freundlich isotherms.

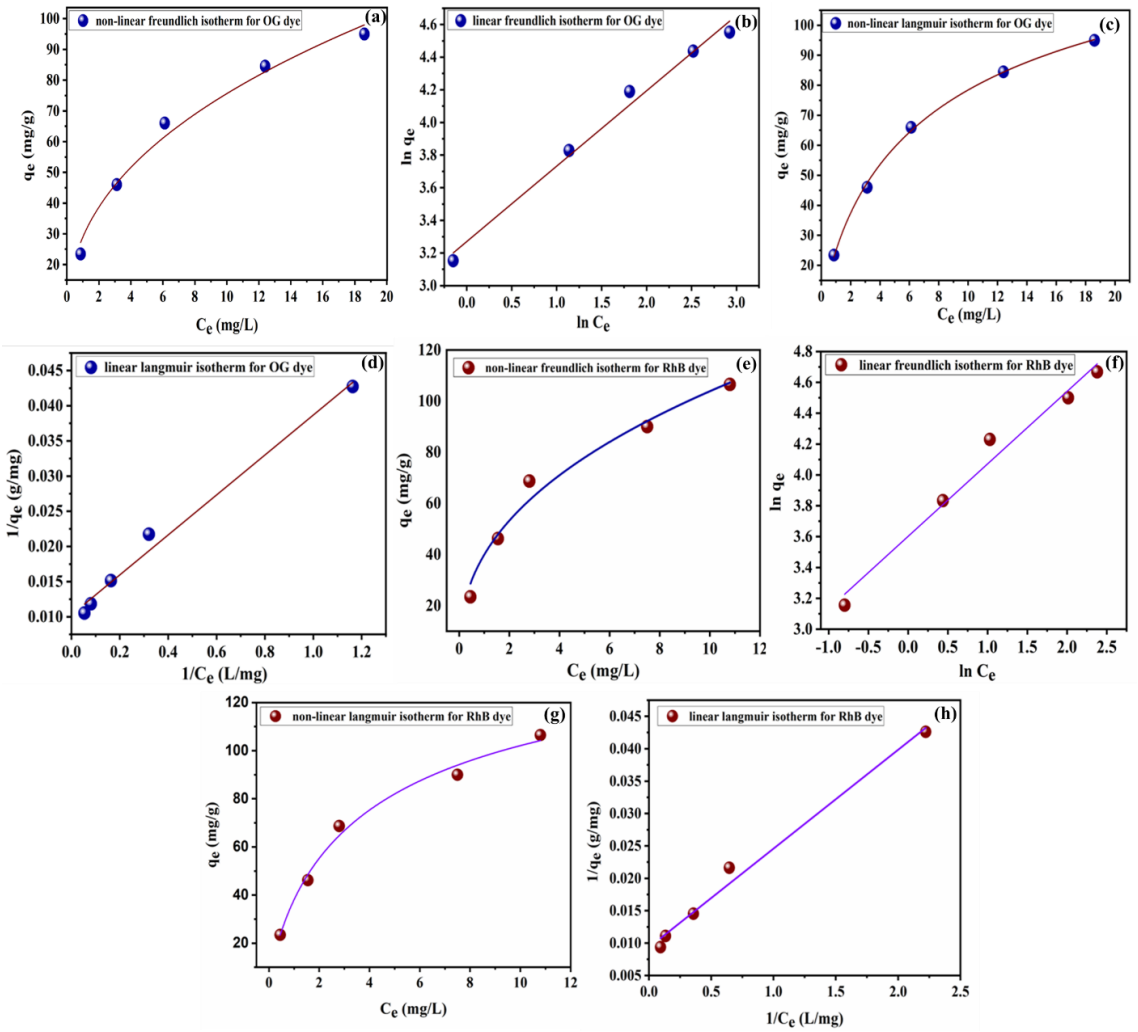


Figure 4-7-1 Linear (b, d, f, and h) and Non-linear (a, c, e, and g) Langmuir and Freundlich isotherms plot.

The linear Temkin plots for the OG and RhB dyes are shown in **Figure 4-7-2 (a) and (c)**. Based on the b_T and A_T values listed in **Table 4-7-2**, the neighbouring R^2 for OG and RhB dye is 0.988 and 0.983, respectively. But the D-R isotherm provides information on biomass porosity and adsorption energy in a general model that does not need a consistent surface or adsorption potential. Additionally, considering the adsorption energy value indicates whether the method of adsorption is physical or chemical. **Table 4-7-2** revealed that the fitting R^2 for OG and RhB dye was not close to 0.9 in D-R models, indicating that it is not very uniform. However, the mean free energy of adsorption, E, which was calculated to be greater than 16 kJ/mol, demonstrated the chemical nature of adsorption between the adsorbent and the

adsorbate. In the cases of OG and RhB dye, the sorption capacities were 22.44 and 82.26 mg/g, respectively. D-R model plot is shown in **Figure 4-7-2 (b)-(d).**

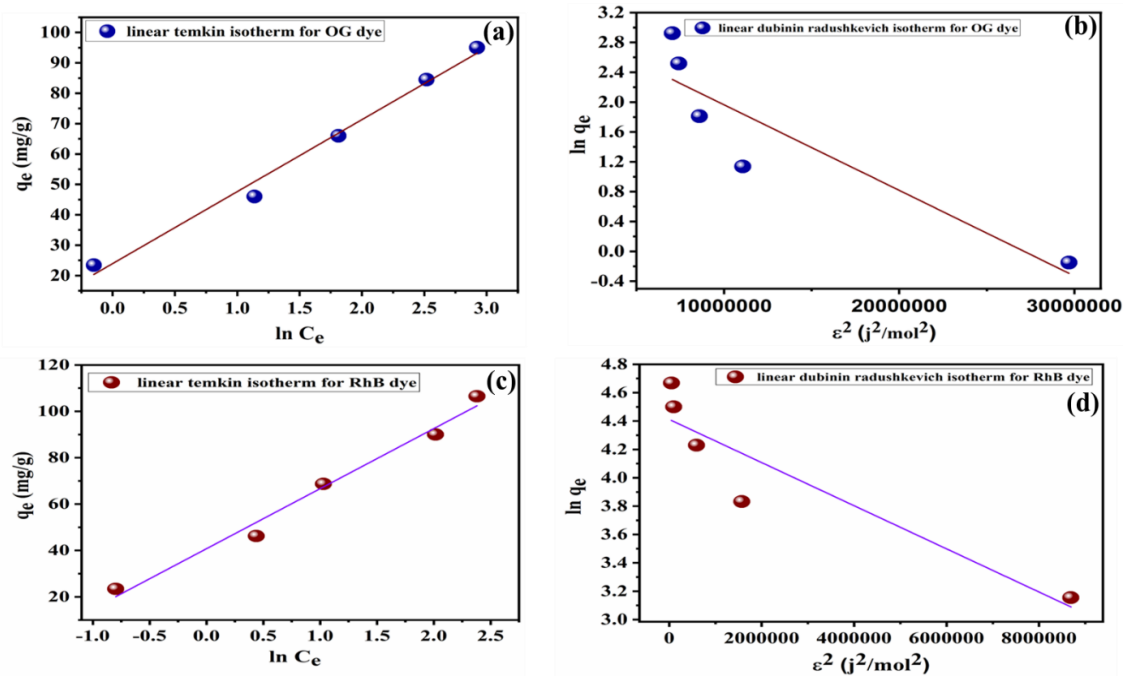


Figure 4-7-2 (a)-(d) Linear Temkin and Dubinin-Radushkevich isotherm plot for both dyes using CHMAC 2 Imp. 7 days.

4.8. Kinetics Analysis

Figure 4-8-1 (a) and (b) depict the plot for pseudo-first-order (PFO), whereas **Figure 4-8-1 (c) and (d)** depict the plot for pseudo-second-order (PSO) for both dyes at a concentration of 80 mg/L. The rate constants for PFO and PSO kinetics are denoted by k_1 and k_2, respectively, expressed in min^{-1} and g/mg/min. For both dyes in **Figure 4-8-1 (c) and (d)**, pseudo-second-order kinetics was the best fit, and the outcomes are provided in **Table 4-8-1**. From the outcomes, the dye was chemically adsorbed on the surface of the adsorbent CHMAC 2 Imp. 7 days. The Elovich equation is often used to study the kinetics of gas chemisorption on a solid surface. All kinetics were done using the equations of the kinetics in **Chapter 2**. **Figure 4-8-1 (e) and (f)** are drawn and shown for the Elovich model. **Figures 4-8-1 (g) and (h)** show the plot of q_t vs. $t_{1/2}$ for the two adsorbates, respectively. The diffusion constant k_{diff}, intercept C, and R-squared values following plotting are listed in **Table 4-8-2**. The overall R^2 value

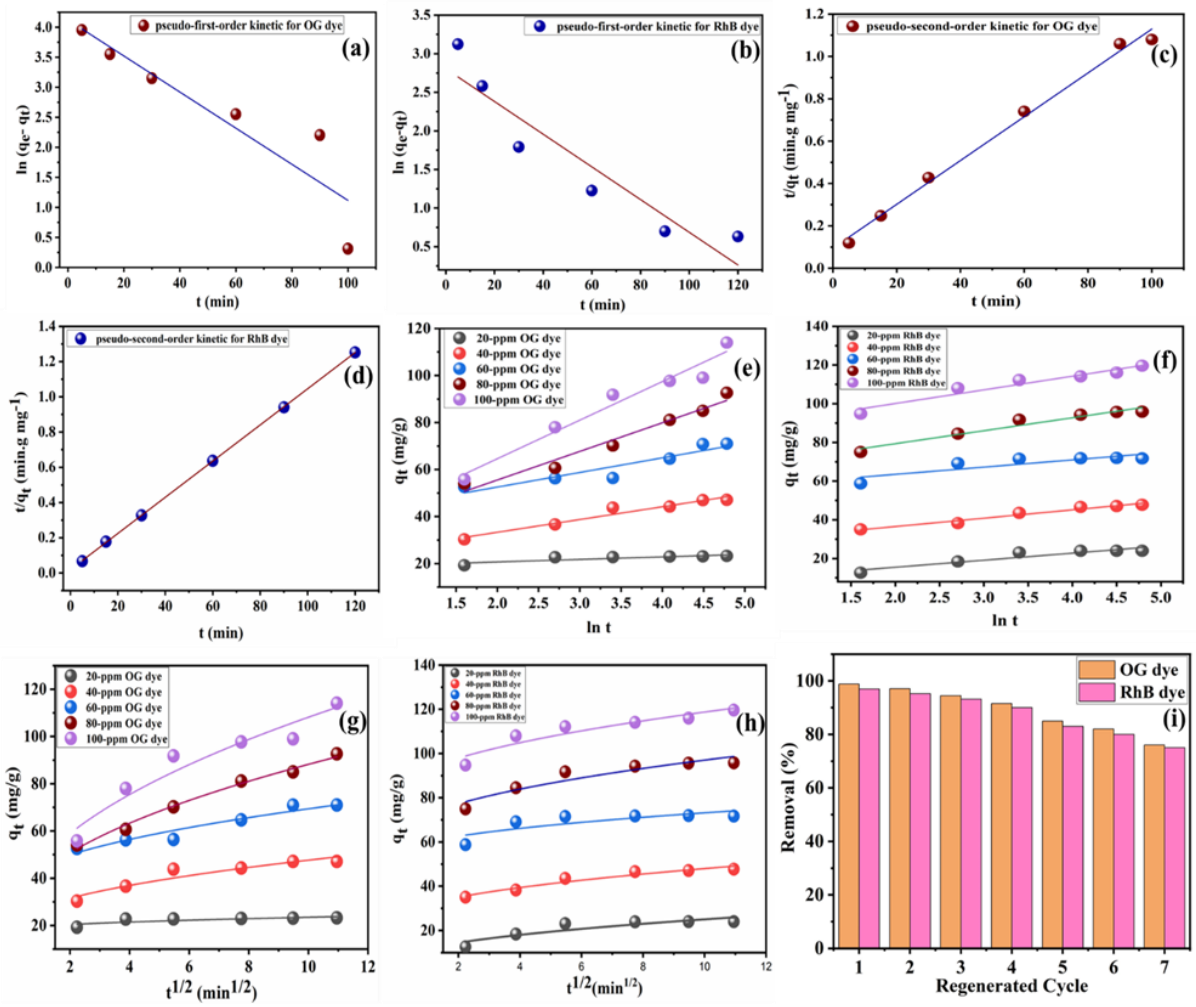
following modelling was 0.98, and the figure indicates that it is not elevated from the origin. Adsorption onto the active site, internal diffusion (also called intraparticle diffusion), and external diffusion (also called film diffusion), which entails the movement of adsorbate in the solution or film surrounding the adsorbent, are the three mass transfer processes that are part of the adsorption kinetics [155,221–223].

Parameters Notations	OG non-linear Freundlich	OG linear Freundlich	RhB non-linear Freundlich	RhB linear Freundlich	OG non-linear Langmuir	OG linear Langmuir	RhB non-linear Langmuir	RhB linear Langmuir
K_F	28.95 ($mg^{1-1/n}$ $L^{1/n}/g$)	26.50 ($mg^{1-1/n}$ $L^{1/n}/g$)	39.90 ($mg^{1-1/n}$ $L^{1/n}/g$)	37.50 ($mg^{1-1/n}$ $L^{1/n}/g$)				
1/n	0.41	0.46	0.42	0.47				
R^2	0.986	0.988	0.975	0.978	**0.998**	**0.994**	**0.999**	**0.999**
T (K)	303	303	303	303	303	303	303	303
K_L					0.023 L/mg	0.028 L/mg	0.76 L/mg	0.62 L/mg
q_m					95.5 mg/g	95.27 mg/g	106 mg/g	105.89 mg/g
R_L					0.42 (for 60 ppm)	0.37 (for 60 ppm)	0.05 (for 60 ppm)	0.025 (for 60 ppm)

Table 4-7-1 Freundlich and Langmuir Isotherms, all Constant parameter values after analysis

Parameters Notation	For OG dye Linear Temkin	For RhB dye, the Linear Temkin	For OG dye Linear D-R model	For RhB dye, the Linear D-R model
R^2	**0.988**	**0.983**	**0.82**	**0.85**
B	23.69	25.89		
b_T	106.33 J/mol	97.3 J/mol		
A_T	2.74 L/g	4.80 L/g		
K_{ad}			0.114×10^{-8}	0.152×10^{-8}
E			20.96 KJ/mol	18.14 KJ/mol
q_m			22.44 mg/g	82.26 mg/g

Table 4-7-2 All parameter values for linear Temkin and D-R adsorption isotherm models.



Figures 4-8-1 Pseudo-first-order kinetics for **(a) and (b),** Pseudo-second-order kinetics for **(c) and (d),** Elovich kinetics **(e) and (f),** Intra-particle diffusion plot **(g) and (h),** and regeneration plot for both dyes **(i),** for CHMAC 2 Imp 7 days adsorbent for OG and RhB dye.

Parameters notations	For OG dye PFO model	For the RhB dye PFO model	For OG dye PSO model	For the RhB dye PSO model
R^2	0.845	0.883	0.993	0.999
k_1	0.030 min^{-1}	0.021 min^{-1}		
q_e	63.49 mg/g	16.53 mg/g	93.50	97.37
k_2			0.0012	0.0055

Table 4-8-1 Data after PFO and PSO analysis for the dyes.

4.9. Regeneration Analysis

CHMAC 2 Imp was used to evaluate the reusability of both dyes upon desorption. 30 mL of the (1:1) ratio for RhB dye, C_2H_5OH: H_2O, was employed as an adsorbent for seven days, while 30 mL of an aqueous (1M) HCl solution was utilized for OG dye. 50 mg was the starting weight for adsorption at a dye concentration of 60 mL and 60 ppm. Post adsorption, drying was done for the adsorbent for six hours at 50 °C in an air oven. Any residual amounts in both dye cases were then examined in the filtrate using a UV-vis spectrophotometer. A 30 mL volume of ethanol-water mixture was then used to desorb the adsorbent for RhB dye adsorbed adsorbent and aqueous HCl for OG dye adsorbed adsorbent, respectively. Both adsorbent-containing solutions were maintained in an incubator shaker at 200 rpm for 15 minutes at 303 K. After that, the solution was removed and subjected to a 5-minute sonication using a sonicator. After six cycles of the cyclic process, the adsorbent
was finally separated using Whatman filter paper with adsorbate, and the sample residue was dried and left behind. This graph, which is displayed in **Figure 4-8-1 (i),** plots the percentage removal and the regenerated cycle to demonstrate the removal percentage rate using the desorbed adsorbent. This reusability investigation demonstrated the adsorbent's stability in eliminating dye contamination from wastewater on multiple occasions, indicating its potential for commercialization. By lowering the reusability feature, the seventh cycle removal percentage was gradually lowered from 80 %. By the eighth cycle, the removal had dropped to 70 % as the adsorbent gradually reached its maximum capacity, allowing the dyes to adsorb numerous times. Future scope scientists are working on it to be utilized in various civil and other domains of work because it is unclear what spent adsorbent will be after several adsorption cycles.

Parameters notations	For OG dye Elovich model	For RhB dye Elovich model	For the OG dye, the Intra-Particle diffusion model	For RhB dye Intra-Particle diffusion model
R^2 (20-100 ppm)	0.65, 0.95, 0.87, 0.964, 0.958	0.88, 0.96, 0.75, 0.94, 0.93	0.62, 0.90, 0.92, 0.98, 0.93	0.80, 0.94, 0.65, 0.88, 0.88
β (20 ppm)	0.930 g/mg	0.275 g/mg		
β (40 ppm)	0.184 g/mg	0.232 g/mg		
β (60 ppm)	0.161 g/mg	0.268 g/mg		
β (80 ppm)	0.082 g/mg	0.149 g/mg		
β (100 ppm)	0.060 g/mg	0.141 g/mg		
α (20 ppm)	33,264,456 mg/g/min	34.63 mg/g/min		
α (40 ppm)	336.9 mg/g/min	2779 mg/g/min		
α (60 ppm)	3904 mg/g/min	121,15 546 mg/g/min		
α (80 ppm)	157.27 mg/g/min	123, 007 mg/g/min		
α (100 ppm)	111 mg/g/min	12,89802 mg/g/min		
k_{diff} (20 ppm)			1.75	6.04
k_{diff} (40 ppm)			9.21	7.38
k_{diff} (60 ppm)			11.15	6.042
k_{diff} (80 ppm)			21.44	11.27
k_{diff} (100 ppm)			28.16	11.92
C (20 ppm)			17.90	5.93
C (40 ppm)			18.50	24.02
C (60 ppm)			34.11	54.08
C (80 ppm)			20.40	61.37
C (100 ppm)			19.07	81.08

Table 4-8-2 Elovich (linear) and Intra-particle diffusion models (kinetics) parameters data for dyes (20-100 ppm).

4.10. Thermodynamic Study (Temperature Impact Investigation)

Thermodynamic dye removal was examined at three distinct temperatures (303, 313, and 323 K). The Van't Hoff equation was utilized to get the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) by graphing $\ln K_c$ vs 1/T. K_c, which is the ratio of adsorbed solute concentration over free solute concentration at equilibrium, is a measure of adsorption strength. **Figure 4-10-1 (b)** displays the thermodynamic plot for both OG and RhB dye. R^2 values for OG and RhB dyes were found to be 0.99 and 0.97, respectively. Using an incubation shaker, various 60 ppm concentrations were fixed for two hours of stirring, with

the highest removal of adsorbates occurring at the temperatures indicated above at pH 7. According to the computation, Gibbs' free energy was negative (spontaneous) at all temperatures. Despite being negative, ΔH and ΔS for OG dye demonstrates the exothermic character of adsorption and reduced randomness on the adsorbent surface, respectively. RhB dye exhibits endothermic adsorption with slightly increased unpredictability on the surface of the CHMAC 2 Imp 7 days adsorbent, as evidenced by the fact that ΔH and ΔS are both positive (near zero) [224,225]. **Table 4-10-1** contains all of the computed information about the thermodynamics analysis for both dyes. To compare other adsorbent-based OG and RhB dye removal capabilities in mg/g with our investigated adsorbent, a few research gaps are listed in **Table 4-10-2**.

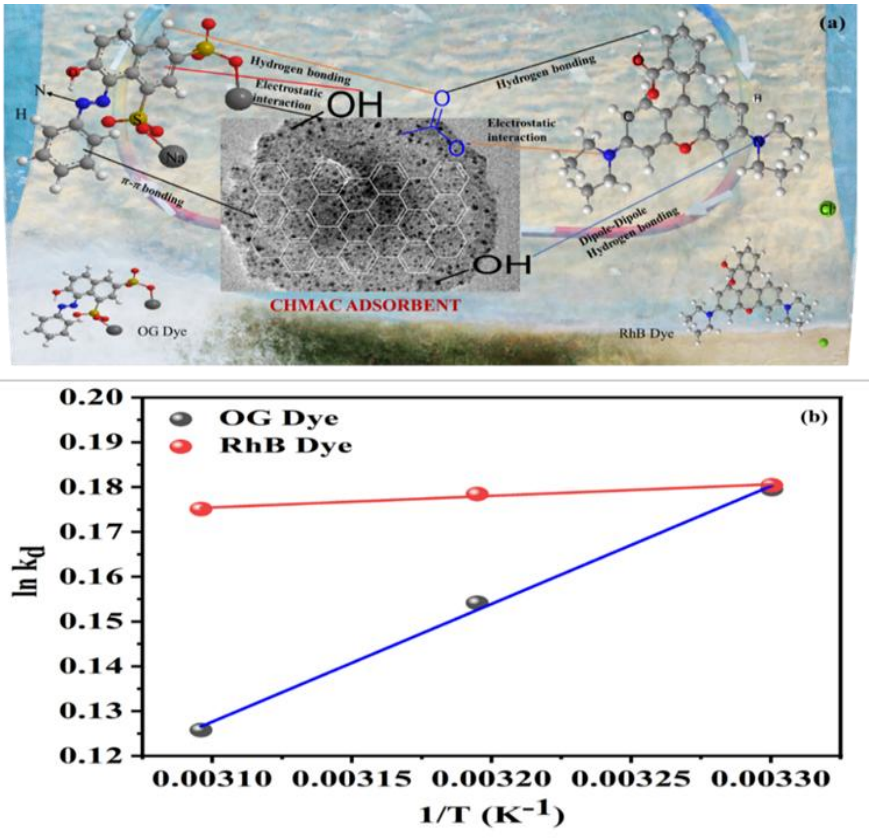


Figure 4-10-1 (a) Probable Mechanism for OG and RhB dye removal by using CHMAC 2 Imp 7 days adsorbent. **(b)** Thermodynamic Van't Hoff plot for OG and RhB dye at different temperatures.

S.NO.	Temperature (K^{-1})	ΔG (Joule)		ΔH (kJ/mol)		ΔS (J/mol. K)		R^2	
		OG dye	RhB dye	OG dye	RhB dye	OG dye	RhB dye	OG dye	RhB dye
1	303	-455	-22.4	-2.18	0.215	-5.711	0.792	0.99	0.97
2	313	-398.4	-32.89						
3	323	-341.3	-40.81						

Table 4-10-1 Thermodynamic data (enthalpy, entropy and Gibbs free energy) obtained experimentally by the Van't Hoff plot.

4.11. Proposed Mechanism of OG and RhB Dye Removal

Several characterizations, including Raman, FTIR, and XPS measurements after adsorption, were needed to evaluate the mechanism because of the OG and RhB dye. **Figure 4-11-1. (a), (b)** after dye adsorption, show the FTIR and Raman spectra. Before and post adsorption of RhB and OG dye, the FTIR of the adsorbent CHMAC 2 Imp 7 days was assessed. Seven days after OG dye was adsorbed to the surface of CHMAC 2 Imp, the bending vibration's initial peak position, which was at about 1105 cm^{-1}, changed to a higher wavenumber value with two spikes, indicating that polar and non-polar moieties in the adsorbent and adsorbate interacted to adsorb OG dye. The interaction of S=O in RhB dye with the adsorbent confirms the interaction of the adsorbent with the dye. In the case of RhB adsorption on the surface of CHMAC, the FTIR shows variation by obtaining a new asymmetric C=C around 2250 cm^{-1} with shifting to the C-O bond (1105 cm^{-1}) bending vibration, resulting in a higher value after adsorption. For FTIR investigation, a 60-ppm dye concentration was applied to the surface of CHMAC 2 Imp for two hours of adsorption over seven days [234]. The OG and RhB dyes are adsorbed in Raman analysis following dye adsorption, resulting in a shift in the I_D/I_G ratio of the defects that increases and decreases, respectively, as a result of adsorption on the adsorbent surface. Defects on the adsorbent's surface decreased after adsorption in the case of RhB dye adsorption when the I_D/I_G ratio value was relatively low in comparison to the

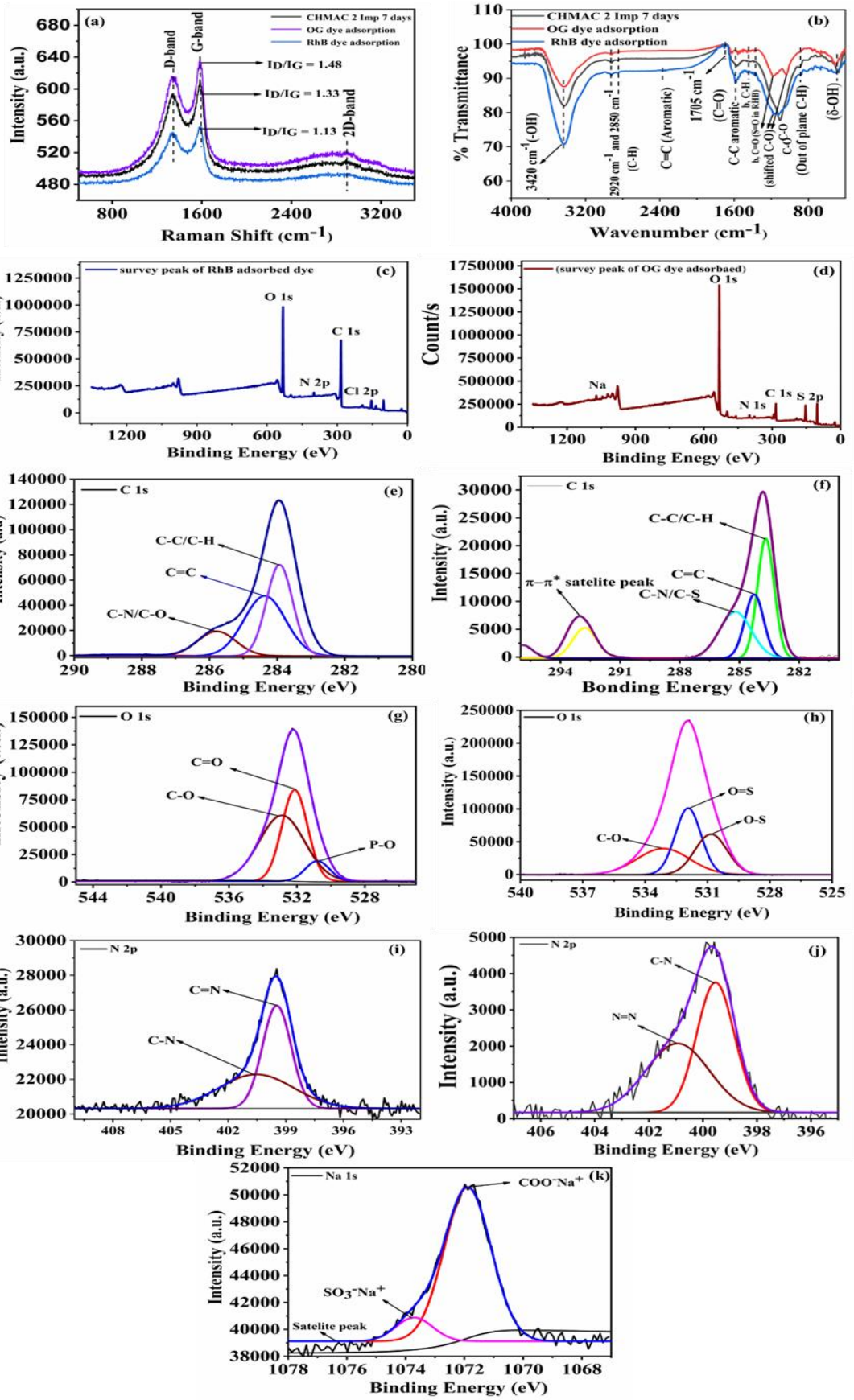
original adsorbent; however, this is not the case for OG dye adsorption [179].The CHMAC 2 Imp 7 days adsorbent was analysed using XPS to look for interaction and variations in binding energy from the basic value following the adsorption of RhB and OG dyes. The binding energy at different times for C 1s, O 1s, and N 2p of RhB dye adsorption on CHMAC 2 Imp 7 days is shown in **Figure 4-11-1 (e), (g), and (i).** The mechanism of OG and RhB dye is shown in **Figure 4-10-1 (a)** by a schematic presentation by varying the interaction of the adsorbent with adsorbates Orange G and Rhodamine B. Since CHMAC 2 Imp 7 days has adsorbed both the dyes to a greater extent, but the OG dye adsorption capacity is greater than RhB dye, this may be due to some cationic surface functionality on carbon, and hence in future, from this material, anionic dye loading capacity may be higher as compared to cationic dye. Water adsorption on the surface results in the bond C-C/C-H at about 283.9 eV, whereas C=C 284.3 eV, C-N/C-O at about 285.85 eV, and C=N at 399.5 eV and 400.5 eV show the C-N in the case of N 2p. For O 1s, the band at 532.08 eV, 530.8 eV, and 532.98 eV for C=O, P-O, and C-O, respectively, is displayed in the figure for RhB dye adsorption on the adsorbent surface [235–237]. The orange G dye adsorption on CHMAC 2 Imp 7 days adsorbent is now discussed. **Figure 4-11-1 (f), (h), (j), and (k)** illustrate this process for C 1s, O 1s, N 2p, and Na 1s, respectively. In C 1s, 283.8 eV, 284.3 eV, 285.5 eV, and a peak above 290 eV defined the C-C/C-H (due to adsorbed water on the surface), C=C, C-N/C-S, and π-π* satellite peaks [238]. In the case of O 1s and N 2p bands around 531.9 eV, 530.8 eV, 533.08 eV, 399.5 eV, and 400.9 eV are defined for O=S, O-S, O-C, N-C, and N=N, respectively. Orange G, which contains Na, also showed a band on XPS by a peak at about 1071.93 eV and 1073.83 eV, respectively, because of the COO-Na and SO_3-Na bonds [239]. **Figure 4-11-1 (c) and (d)** exhibit the survey peaks of RhB and OG dye adsorbed CHMAC 2 Imp 7 days, respectively. Overall, it was determined from the XPS data analysis that both dyes had successfully adsorbed onto the adsorbent surface. Both dyes' adsorption was impacted by pH and pHzpc [240]. Following the adsorption of both dyes, FTIR demonstrated that the adsorbent's functionality somewhat alters its wavenumber value, as well as the width and intensity of the peak displayed in the earlier graph [59]. Every study demonstrates that the interfaces between

the adsorbent and adsorbate surfaces have hydrogen bonds in addition to ionic and covalent interactions. The neutral pH range outperformed the basic and acidic pH ranges in terms of dye adsorption (covalent linkage between adsorbent and adsorbate). According to FTIR, the adsorbent's surface -OH group attaches itself to the hydrogen molecule of the adsorbate with aromatic and other functions. The sodium ion in OG dye and the nitrogen ion in RhB dye are electrostatically contacted by the carboxylic or ketonic functionality of the adsorbent, respectively. Dipole-dipole hydrogen bonds and the π-π contact between the adsorbent and the adsorbate are two more possible interactions. Additionally, both dye examples showed improved pseudo-second-order kinetics and the Langmuir adsorption isotherm, suggesting homogenous chemisorption [149].

Adsorbents Materials (in Orange G dye)	Adsorbents Materials (in Rhodamine B dye)	Orange G removal capacity (mg/g)	Rhodamine B removal capacity (mg/g)	References
Polyaniline/AS (almond shell) and WS (walnut shell)	Sulphur tethered adsorbent of Tapioca peel (S@TP) biochar	9.0 and 17.79	33.10	[226] [227]
Active formaldehyde-modified ragi husk	Activated Carbon prepared from stalk corn	14.66	5.6	[228] [229]
Alumina Nanoparticle	Coconut shell-activated carbon loaded with cobalt ferrite ($CoFe_2O_4$)	93.3	94.08	[230] [231]
Activated carbon from empty fruit bunches	Magnetic K_2CO_3-activated carbon From a bamboo shoot	18.76	53.94	[232] [233]
Rice husk modified Char	Cassava Slag biochar	38.8	105.3	[227,233]
CHMAC 2 Imp 7 days	CHMAC 2 Imp 7 days	97	107	This Work

Table 4-10-2 Research gap on adsorbents in the literature for the synthesized adsorbent for OG and RhB removal.

Overall, the mechanism of dye adsorption has been elucidated based on these results. Since the adsorption of both dyes on the surface of the adsorbent is different in the case of thermodynamic study may be due to the interaction and availability of functionality and physico-chemical properties of adsorbent and adsorbate, which makes them endo and exothermic. SEM examination was carried out to know the adsorption changes on the surface of the sample of CHMAC 2 Imp 7 days for both OG and RhB dyes. The results are given in **Figure 4-11-1 (l) (i)-(ii)** for RhB dye and **Figure 4-11-1 (l) (iii)-(iv)** for OG dye. The existence of dye-molecule-related components on the surface of adsorbents is further confirmed by the EDS spectra obtained following the adsorption of RhB and OG dye. **Figure 4-11-1 (l) (v)-(vi)** displays it for RhB dye and OG dye, respectively. From the point of view of the regeneration study of both dye using HCl and water-ethanol mixture for OG and RhB dye it can generate an acidic waste solution, and an alcoholic waste solution with this organic dye. The performance is decreased after a few cycles of regeneration due to surface activity loss, pore filling, and may be due to pore disruptions on the adsorbent surface, as well as due to functionality. So, these contaminants can be drawn out and read sorbed by the adsorbents for safe environmental atmospheres


(a)
CHMAC 2 Imp 7 days
OG dye adsorption
RhB dye adsorption
D-band
G-band
2D-band
ID/IG = 1.48
ID/IG = 1.33
ID/IG = 1.13
Intensity (a.u.)
Raman Shift (cm-1)
(b)
CHMAC 2 Imp 7 days
OG dye adsorption
RhB dye adsorption
% Transmittance
3420 cm-1 (-OH)
2920 cm-1 and 2850 cm-1 (C-H)
C=C (Aromatic)
1705 cm-1 (C=O)
C-C aromatic
(shifted C-O)
(Out of plane C-H)
(δ-OH)
Wavenumber (cm-1)
(c)
survey peak of RhB adsorbed dye
O 1s
C 1s
N 2p
Cl 2p
Intensity (a.u.)
Binding Energy (eV)
(d)
(survey peak of OG dye adsorbaed)
O 1s
Na
N 1s
C 1s
S 2p
Count/s
Binding Enegy (eV)
(e)
C 1s
C-C/C-H
C=C
C-N/C-O
Intensity (a.u)
Binding Energy (eV)
(f)
C 1s
C-C/C-H
π–π* satelite peak
C=C
C-N/C-S
Intensity (a.u.)
Bonding Energy (eV)
(g)
O 1s
C=O
C-O
P-O
Intensity (a.u.)
Binding Energy (eV)
(h)
O 1s
O=S
O-S
C-O
Intensity (a.u.)
Binding Enegry (eV)
(i)
N 2p
C=N
C-N
Intensity (a.u.)
Binding Energy (eV)
(j)
N 2p
C-N
N=N
Intensity (a.u.)
Binding Energy (eV)
(k)
Na 1s
COO-Na+
SO3-Na+
Satelite peak
Intensity (a.u.)
Binding Energy (eV)

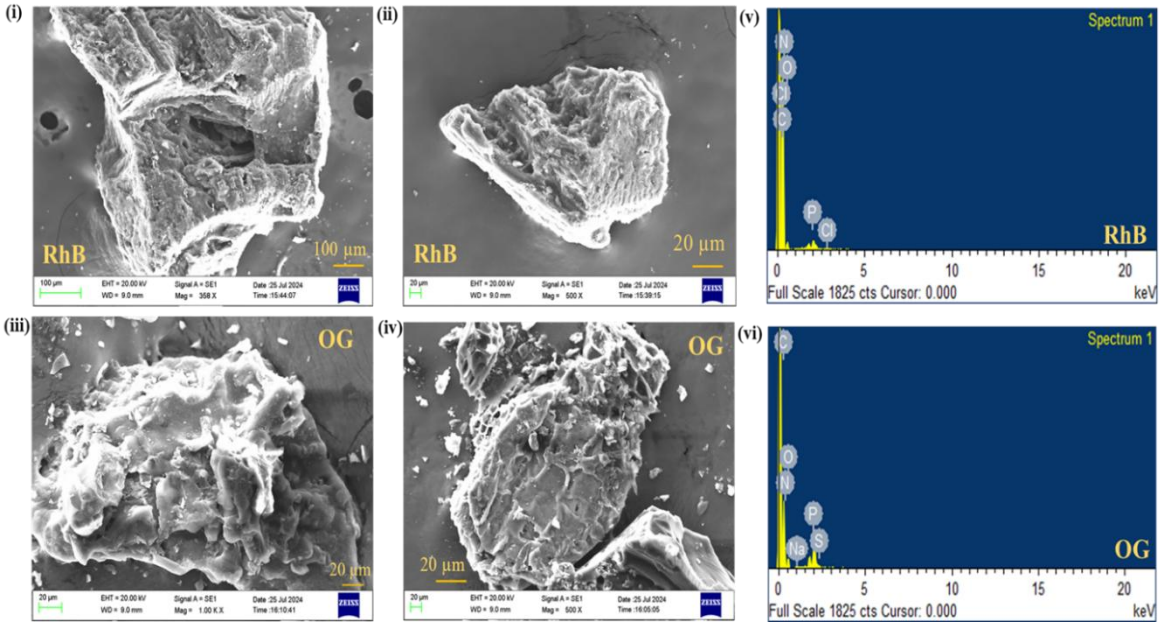


Figure 4-11-1 Raman **(a),** FTIR **(b),** Survey peaks **(c) and (d),** with **(e), (g), (i) and (d), (f), (h), and (k)** XPS analysis of CHMAC 2 Imp 7 days adsorbent after adsorption of RhB and OG dye respectively **(l)** SEM of RhB **(i)-(ii)** and OG **(iii)-(iv)**, EDS RhB **(v)** and EDS OG **(vi)** dye after adsorption by CHMAC 2 Imp 7 days.