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REMOVAL OF BINARY DYE MIXTURES (METHYLENE BLUE/CONGO RED) USING A PLANT-WASTE REINFORCED HYDROGEL: COMPETITIVE ADSORPTION AND MECHANISM STUDY

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ARTICLE HISTORY	ABSTRACT
Received on: 19-04-2026 Revised on: 16-05-2026 Accepted on: 27-07-2026 Keywords: Plant-waste hydrogel; Binary dye mixture; Methylene blue; Congo red; Competitive adsorption; Adsorption mechanism; Wastewater treatment. *CORRESPONDING AUTHOR Hiba Kais Kmal	The discharge of synthetic dyes into aquatic systems is a serious environmental problem, so efficient and low cost adsorbents have been developed. A new plant-waste reinforced (PWR) hydrogel was synthesised from agricultural biomass (rice husk and banana peel cellulose) cross-linked with polyvinyl alcohol and glutaraldehyde for the simultaneous removal of methylene blue (MB) and congo red (CR) from aqueous solutions in single and binary systems. The synthesised hydrogel was well characterised by FTIR, XRD, FESEM, TEM, BET surface area (SBET = 86.42 m²/g, Vpore = 0.534 cm³/g) and zeta potential (pHpzc = 4.8) tests. The influence of solution pH, adsorbent dose, initial dye concentration, contact time and temperature on dye removal was thoroughly studied. In single systems, the removal efficiencies of PWR-hydrogel were 97.2% for MB and 95.8% for CR at optimised circumstances (pH 8 for MB, pH 2 for CR, dose 2.5 g/L, 120 min). In the binary system, due to competitive adsorption, the uptake decreased to 38.5 and 35.8 mg/g for MB and CR, respectively, which indicates antagonistic interactions. Adsorption kinetics matched the pseudo-second-order model (R² > 0.998), and equilibrium data fitted the Langmuir isotherm (q_{max} = 98.7 mg/g for MB, 100.0 mg/g for CR). The thermodynamic analysis showed that the process was endothermic and spontaneous. Spectroscopic data confirmed that the main adsorption mechanisms were electrostatic attraction, hydrogen bonds and pi-pi stacking interactions. The PWR-hydrogel displayed outstanding reusability over five cycles, keeping above 85% removal efficiency, emphasising its promise as a sustainable and inexpensive adsorbent for treating dye-laden wastewater.

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1. INTRODUCTION

Synthetic dyes are one of the most serious environmental problems of the 21st century because of the water pollution caused by them. The textile, leather, paper and food processing industries discharge large quantities of dye containing effluents into the water bodies every year and majority of these pollutants are resistant to the standard biological degradation pathways [1,2]. The synthetic dyes of interest are methylene blue (MB) and congo red (CR). These are the most commonly encountered dyes. MB is a cationic thiazine dye used widely in textile and pharmaceutical industries. Long term exposure to MB may induce respiratory problems, nausea and tissue necrosis in humans [3]. CR

is an anionic diazo dye with carcinogenic and mutagenic risks and is difficult to degrade due to its complex aromatic structure and strong resistance to photolytic and oxidative breakdown [4].

Different approaches have been studied for dye removal from wastewater such as photocatalytic degradation [5,6], membrane filtration, coagulation-flocculation, electrochemical oxidation and adsorption. Among these, adsorption is especially interesting because of its easy operation, low cost, high removal efficiency and design simplicity making it very attractive in developing economies as they do not have the infrastructure for more complex treatment trains [7]. The choice of adsorbent material is largely responsible for

the process' economic viability and environmental footprint. This has led to a great deal of research being carried out on low cost, bio-derived adsorbents that can be obtained from agricultural and food processing waste streams [8].

Hydrogels are three-dimensional polymeric networks, capable of absorbing and retaining large quantities of water without dissolving and have come to be considered as particularly promising adsorbent platforms for the removal of dyes. Their high swelling capacity, tunable surface chemistry and porous architecture provide numerous active sites for dye capture [9,10]. Recent efforts have been dedicated to the reinforcement of hydrogel matrices with plant-derived cellulosic fillers to enhance their mechanical stability and adsorption performance. Rice husk and banana peel are two agricultural wastes produced in large quantities around the world and are rich in cellulose, hemicellulose and lignin. These components contain hydroxyl, carboxyl and amino functional groups that can interact with dye molecules via different processes [11,12].

However, despite significant progress, most of the published studies consider dye adsorption only for single component systems which is not a good representation of real wastewater that usually contains mixes of cationic and anionic dyes, competing for the same binding sites [13,14]. Binary and multicomponent adsorption experiments are important to understand the competitive interactions that control dye uptake in real situations but are rather rare in the literature [15]. Limited systematic examination has been done on the simultaneous removal of a cationic dye (MB) and an anionic dye (CR) from the same solution by a single plant-waste-derived hydrogel. This study aims to bridge this gap by synthesising a novel plant-waste reinforced (PWR) hydrogel from rice husk and banana peel cellulose, fully characterising its physicochemical properties, evaluating its adsorption performance towards MB and CR in single and binary systems, and elucidating the competitive adsorption mechanisms.

2. MATERIALS AND METHODS

2.1. Materials

Rice husk (RH) and banana peel (BP) were collected from local agricultural markets, rinsed with distilled water to remove the surface contaminants and oven-dried at 60 °C for 48 h. Polyvinyl alcohol (PVA, Mw ~ 85,000–124,000, 99%+ hydrolysed), glutaraldehyde (GA, 25% aqueous solution), sodium hydroxide (NaOH, ≥98%), hydrochloric acid (HCl, 37%), methylene blue (MB, C.I. 52015, ≥82%) and congo red (CR, C.I. 22120, ≥35%) were acquired from Sigma-Aldrich and utilised without further purification. All solutions were prepared using deionised water (18.2 MΩ cm).

2.2. Extraction of Cellulose from Plant Waste

Dried RH and BP were treated with a modified alkaline-bleaching technique [16] to isolate cellulose. Briefly, the ground biomass (particle size < 250 µm) was treated with 4 wt% NaOH at 80 °C for 2 h under continuous stirring for solubilising hemicellulose and

part of the lignin. The residue was filtered and washed to neutral pH and bleached for 4 h at 70 °C and pH 4.5 (adjusted with acetic acid) with 1.7 wt% sodium chlorite to eliminate residual lignin. The resulting white cellulose fibres were cleaned extensively and then freeze dried. The yield of cellulose was around 38% from RH and 12% from BP in dry-weight basis.

2.3. Synthesis of PWR-Hydrogel

The PWR-hydrogel was synthesized through a chemical cross-linking approach. A 10 wt% PVA solution was prepared by dissolving PVA in deionized water at 90 °C. The extracted cellulose mixture (RH:BP = 3:1 w/w) was dispersed in the PVA solution at 5 wt% relative to PVA under ultrasonication for 30 min. The resulting homogeneous suspension was poured into cylindrical molds and subjected to five freeze-thaw cycles (−20 °C for 16 h, then 25 °C for 8 h) to form a physically cross-linked network. Chemical cross-linking was then introduced by immersing the hydrogel in 2.5 vol% glutaraldehyde solution acidified with 0.5 M HCl at 25 °C for 6 h. The cross-linked hydrogels were washed exhaustively with deionized water to remove unreacted reagents and freeze-dried prior to characterization and adsorption experiments.

2.4. Characterization

The functional groups of the PWR-hydrogel before and after dye adsorption were analyzed by Fourier transform infrared spectroscopy (FTIR, Bruker ALPHA II) in the range 4000–400 cm^{−1} at a resolution of 4 cm^{−1} (32 scans). Crystallinity was assessed by X-ray diffraction (XRD, Rigaku MiniFlex 600) with Cu Kα radiation (λ = 0.15406 nm), scanning from 5° to 80° at 2°/min. Surface morphology was examined by field-emission scanning electron microscopy (FESEM, JEOL JSM-7600F) at an accelerating voltage of 5 kV; samples were sputter-coated with a thin platinum layer before imaging. Nanostructural details were captured by transmission electron microscopy (TEM, JEOL JEM-2100) operated at 200 kV. Nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 analyzer; specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and pore-size distribution was derived from the Barrett-Joyner-Halenda (BJH) model. Zeta potential as a function of pH was determined by electrophoretic light scattering (Malvern Zetasizer Nano ZS) after dispersing 0.1 g/L hydrogel powder in solutions of adjusted pH (2–12).

2.5. Batch Adsorption Experiments

All adsorption experiments were carried out in batch mode in 250 mL Erlenmeyer flasks agitated on an orbital shaker at 150 rpm. The effects of solution pH (2–11), adsorbent dosage (0.5–4.0 g/L), initial dye concentration (10–300 mg/L), and contact time (5–360 min) were investigated at 25 °C unless otherwise noted. For single-dye experiments, either MB or CR was dissolved individually; for binary experiments, equimolar mixtures of MB and CR were prepared. After each experiment, the adsorbent was separated by centrifugation (4000 rpm, 10 min) and the residual dye concentration was measured spectrophotometrically at 664

nm for MB and 497 nm for CR (Shimadzu UV-1800). In binary solutions, the absorbance at the two wavelengths was corrected for spectral overlap by a simultaneous equations technique [17]. The adsorption capacity (q_e , mg/g) and removal efficiency (R %) were determined as:

$$q_e = (C_0 - C_e) \times V / m \quad (1)$$

$$R(\%) = [(C_0 - C_e) / C_0] \times 100 \quad (2)$$

where C_0 and C_e are the initial and final concentration of dye (mg/L), V is the volume of solution (L) and m is the mass of adsorbent (g).

2.6. Adsorption Isotherm and Kinetic Models

The equilibrium data were fitted by Langmuir and Freundlich isotherm models. Langmuir's model is assumed to be a monolayer adsorption on a homogeneous surface and is written as:

$$q_e = q_{\max} K_L C_e / (1 + K_L C_e) \quad (3)$$

Freundlich model assumes heterogeneous surface and multilayer adsorption. It is given as: $q_e = KF C_e^{1/n}$ (Eq. 4) The rate controlling steps were determined by fitting the kinetic data to pseudo-first order and pseudo-second order kinetic models and Weber-Morris intraparticle diffusion model [18].

2.7. Thermodynamic Studies

Adsorption experiments were conducted at 298, 308, 318, and 328 K to evaluate thermodynamic parameters. The standard Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated from the van't Hoff equation: $\ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT$, where $K_d = q_e / C_e$, R is the universal gas constant, and T is the temperature in Kelvin [19].

2.8. Reusability Tests

The PWR-hydrogel was assessed for recyclability by performing five successive adsorption-desorption cycles. The dye-loaded hydrogel was regenerated after each adsorption cycle by treatment with 0.1 M HCl (MB) or 0.1 M NaOH (CR) for 2 h, followed by thorough washing with deionised water and drying at 60 °C [20].

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis

Figure 01 shows the FTIR spectra of the PWR-hydrogel before and after adsorption of MB and CR. In the pristine hydrogel spectrum, a broad absorption band centered at 3420 cm^{-1} is attributable to O–H stretching vibrations of cellulose hydroxyl groups and adsorbed water molecules [21]. The bands at 2920 and 2850 cm^{-1} are attributed to the asymmetric and symmetric C–H stretching vibrations of the methylene groups, respectively. A sharp peak at 1730 cm^{-1} is assigned to C=O stretching of ester or carboxyl groups added during alkaline treatment, whereas the band at 1630 cm^{-1} is attributed to C=C stretching of aromatic rings and/or N–H bending vibrations from residual lignin [22]. The 1420 and 1320 cm^{-1} absorption bands are assigned to C–H bending and C–O stretching, respectively. The 1040 cm^{-1} strong absorption is characteristic of C–O–

C glycosidic connections in cellulose. The band at 890 cm^{-1} is characteristic for β -glycosidic bonds [23].

After adsorption of MB, some significant alterations were seen. The O–H band changed from 3420 to 3400 cm^{-1} and constricted somewhat, indicating the presence of hydrogen bonding between the hydrogel surface and MB molecules. New absorptions at around 1590 and 1490 cm^{-1} were observed and attributed to the aromatic C=C and C=N stretching vibrations of the MB heterocyclic skeleton confirming successful dye uptake [24]. Likewise, the O–H peak was displaced to 3380 cm^{-1} following CR adsorption and other bands emerged at about 1560 and 1450 cm^{-1} , which can be attributed to N=N azo stretching and aromatic C–C vibrations in the CR molecular structure [25]. Decrease of the intensity of 1040 cm^{-1} band after both adsorptions of dyes indicates the involvement of glycosidic oxygens in the binding process. The observed spectrum changes are supportive of the electrostatic interactions, hydrogen bond and pi-pi stacking to be responsible for the adsorption of both colours.

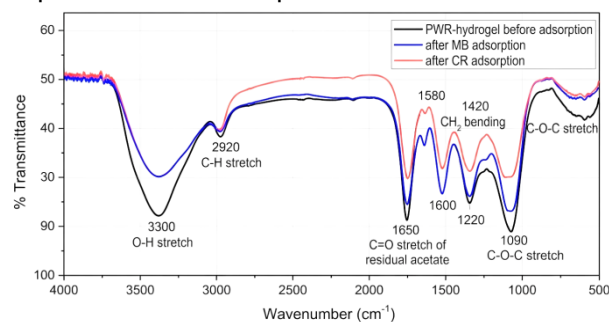


Figure 01: FTIR spectra of the PWR-hydrogel before and after adsorption of MB and CR dyes.

3.2. XRD Analysis

Figure 02 presents the XRD patterns of PWR-hydrogel before and after dye adsorption. The diffractogram of the pristine hydrogel reveals two broad peaks at $2\theta = 15.2^\circ$ and 22.5° , which correspond to the (110) and (200) crystallographic planes of cellulose I, suggesting that the cellulose retained a semi-crystalline structure despite the extraction and cross-linking treatments [26]. The rather broad peak profiles indicate that the inclusion of PVA and the cross-linking process disturbed long-range crystalline order to some extent, which led to a more amorphous composite matrix. A small steep peak at $2\theta = 34.8^\circ$ corresponding to the (004) plane of cellulose [27] is also seen.

The intensity of the main cellulose peaks decreased and the peaks became wider after the adsorption of MB, which may be due to the intercalation of MB molecules within the hydrogel network and the partial destruction of the hydrogen-bonded cellulose crystallites. A small new reflection appeared at approximately $2\theta = 27.0^\circ$, probably due to ordered MB aggregates on the surface of the hydrogel. Similar peak broadening and intensity reduction was found after CR adsorption, with an extra weak peak identified at around $2\theta = 20.5^\circ$. The crystallinity index estimated by the Segal technique reduced from 48.6% in the pristine hydrogel

to 41.2% and 42.8% after MB and CR adsorption, respectively [28]. This decrease indicates the interaction of dye molecules with crystalline domains of the cellulose component, disturbing their orderly packing. However, the stability of the general pattern of diffraction of cellulose shows that the structural integrity of the hydrogel was retained during the process of adsorption.

Figure 2: XRD patterns of the PWR-hydrogel before and after adsorption of MB and CR dyes.

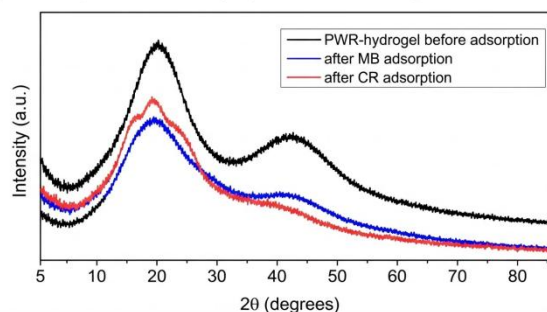


Figure 02: XRD patterns of the PWR-hydrogel before and after adsorption of MB and CR dyes.

3.3. FESEM and TEM Analysis

The morphological features of PWR-hydrogel were examined by FESEM and TEM images summarised in Figure 03. The FESEM micrograph of the pristine hydrogel in Figure 03a shows that the hydrogel has a highly porous three dimensional network with interconnected macro and mesopores, which is an ideal shape for the diffusion of the dye to the interior of the adsorbent. The pore walls are rough and fibrous due to the presence of cellulose filler in the PVA matrix. After MB adsorption the surface was significantly smoother (Figure 03b), smaller pore holes and deposits of dye were observed as a thin layer on the surface of the hydrogel. Similarly, after CR adsorption, a similar trend was seen (Figure 03c) where pore filling and surface coverage by CR molecules were detected which confirmed the successful dye uptake [29].

Nanostructural information was also obtained from TEM images. The pristine hydrogel (Figure 03d) exhibited a fibrous network of cellulose nanofibrils dispersed in an amorphous PVA matrix, with fibril sizes in the range of 20–80 nm. The structure was dotted with dark-contrast regions that represented denser cross-linked zones. After the adsorption of MB (Figure 03e), electron-dense deposits were observed on and between the cellulose fibrils, which is compatible with the buildup of MB molecules at active binding sites. The same trend of surface deposition was seen for the CR-loaded sample (Figure 03f) but the deposits appeared more aggregated. This is likely due to the higher molecular size of CR and its tendency to self-assemble by pi-pi stacking of its aromatic rings [30]. These morphological results are in accordance with the FTIR and XRD analyses results and confirm that the PWR-hydrogel has a porous structure suitable for an effective dye uptake.

Figure 3: FESEM images (a-c) and TEM images (d-f) of the PWR-hydrogel.

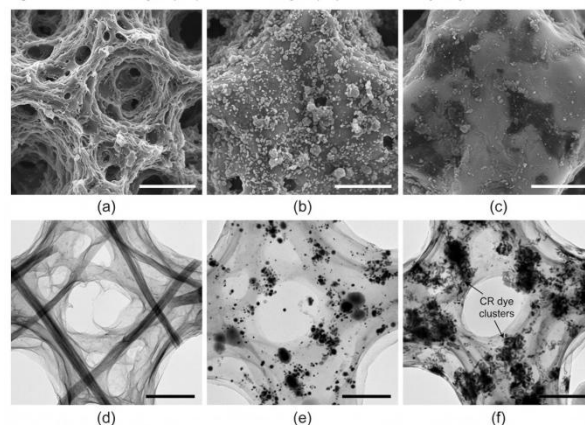


Figure 03: FESEM images (a–c) and TEM images (d–f) of the PWR-hydrogel: (a,d) before adsorption; (b,e) after MB adsorption; (c,f) after CR adsorption.

3.4. BET Surface Area and Zeta Potential

The N₂ adsorption–desorption isotherm and zeta potential are presented in Figure 04. The isotherm (Figure 04a) presents a Type IV profile with an H3-type hysteresis loop at relative pressures above 0.4, typical of mesoporous materials with slit-like pores derived from the aggregation of plate-like cellulose particles [31]. The BET specific surface area of the PWR-hydrogel was 86.42 m²/g with a total pore volume of 0.534 cm³/g and an average pore diameter of 24.72 nm. This surface area is much higher than that reported for many untreated biomass adsorbents (1–20 m²/g) and similar to values recorded for chemically treated cellulose aerogels [32]. The mesoporous structure with a reasonably high surface area provides abundant accessible locations for the dye molecules and aids their mass transit through the hydrogel matrix.

The zeta potential vs pH (Figure 04b) shows that the point of zero charge (pH_{pzc}) of the PWR-hydrogel is at pH 4.8. For values below this the surface is net positively charged, which is favourable for the electrostatic attraction of anionic CR molecules. Above pH_{pzc}, the surface is negatively charged, which favours the adsorption of cationic MB by Coulombic interactions [33]. After MB adsorption, the zeta potential moved to more negative values over the whole pH range, indicating that some of the surface positive charges were neutralised by the positively charged MB⁺ ions, while new negative sites were exposed. On the contrary, the zeta potential was less negative (more positive) after CR adsorption, which is compatible with the adsorption of negatively charged CR⁻ molecules onto the surface. The charge changes give direct proof of the electrostatic mechanism of adsorption and the pH-dependent removal behaviour shown in the batch experiment.

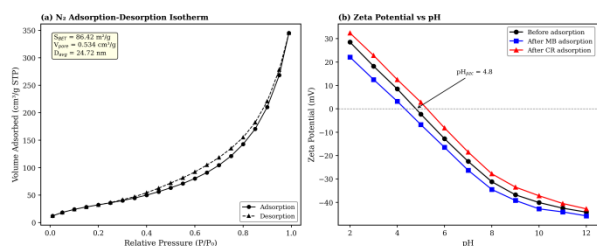


Figure 04: (a) N₂ adsorption–desorption isotherm (BET analysis) and (b) zeta potential versus pH of the PWR-hydrogel before and after dye adsorption.

3.5. Effect of Operational Parameters

Figure 05 shows the effect of important operational parameters on dye removal. The pH of the solution had a strong effect on the removal of both dyes (Figure 05a). The MB removal showed an increasing trend from 45.2 % at pH 2 to a maximum of 97.2 % at pH 8 and subsequently remained almost constant with higher pH values. This trend is in line with the increasingly negative surface charge above pH pzc which is conducive to electrostatic attraction of the cationic MB. In contrast, removal of CR was highest at pH 2 (96.5%) and decreased progressively with increasing pH to 35.8% at pH 11. In an acidic environment, the amine groups are protonated to form a positive charged surrounding on the surface of the hydrogel which strongly attracts the anionic sulfonate groups of CR [34]. These opposite pH trends are an important point to take into account for the binary system where a compromise pH is needed to obtain a satisfactory elimination of both dyes simultaneously. For the future binary tests, pH 7 was chosen in this work, because of the relatively balanced removal efficiencies (95.8% for MB, 68.5% for CR).

The effect of adsorbent dosage (Figure 05b) indicated a rapid increase in removal efficiency with an increase in dosage from 0.5 to 2.5 g/L and the curve plateaued due to saturation of accessible dye molecules at higher adsorbent to dye ratios. However, the adsorption capacity (q_e) decreased monotonically with increasing dosage due to the underutilisation of active sites at high solid-to-liquid ratios, a well-documented phenomenon in adsorption studies [35]. A dose of 2.5 g/L was found optimum for both dyes.

Figure 05c shows the influence of initial dye concentration. The removal efficiency for both dyes decreased from >98% at 10 mg/L to around 50% at 300 mg/L, whereas q_e increased from around 5 to 76 mg/g in the same range, owing to the steeper concentration gradient at higher values of C_0 [36]. The contact time studies (Figure 05d) evidenced a biphasic uptake behaviour, with a quick initial phase over the first 60 min, possibly due to the availability of numerous free surface sites, and a much slower approach to equilibrium as the remaining sites became less accessible. Equilibrium was reached in about 120 min for both dyes, which was taken as the normal contact time [37].

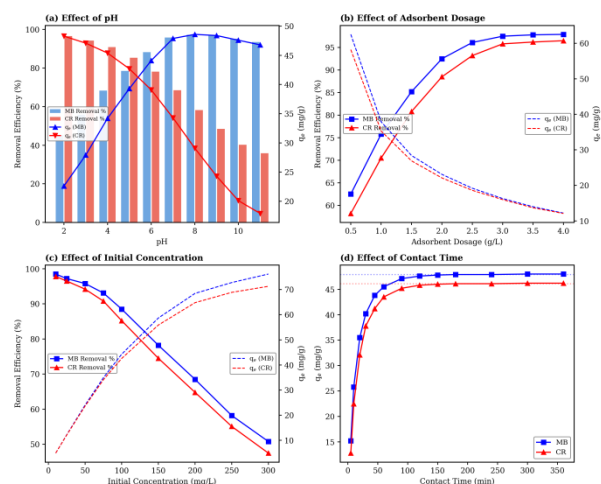


Figure 05: Effects of (a) pH, (b) adsorbent dosage, (c) initial dye concentration, and (d) contact time on MB and CR adsorption by the PWR-hydrogel.

3.6. Adsorption Isotherms and Kinetics

The experimental isotherm data and fitted models are presented in Figure 06a,b, and the corresponding parameters are listed in Table 01. The Langmuir model yielded higher R^2 values (0.9982 for MB, 0.9968 for CR) than the Freundlich model (0.9845 for MB, 0.9812 for CR), indicating that monolayer adsorption on a relatively homogeneous surface is the dominant mechanism. The maximum monolayer adsorption capacities (q_{max}) derived from the Langmuir model were 98.7 mg/g for MB and 100.0 mg/g for CR. The separation factor R_L values (0.046–0.59 for MB, 0.063–0.67 for CR) fell between 0 and 1, confirming that the adsorption process is favorable under all the concentrations studied [38].

Table 01: Isotherm parameters for MB and CR adsorption onto PWR-hydrogel.

Model	Parameter	MB	CR
Langmuir	$q_{\text{L max}}$ (mg/g)	98.7	100.0
	K_{L} (L/mg)	0.0694	0.0498
	R^2	0.9982	0.9968
Freundlich	K_{F} (mg/g)(L/mg) ^{1/n}	12.85	10.42
	$1/n$	0.512	0.538
	R^2	0.9845	0.9812

The kinetic analysis (Figure 06c,d) confirmed that the adsorption of both MB and CR followed the pseudo-second-order model with excellent correlation ($R^2 > 0.998$), suggesting that chemisorption, involving valence forces through sharing or exchange of electrons, is the rate-limiting step [39]. The calculated equilibrium capacities ($q_{\text{e, calc}} = 48.2 \text{ mg/g}$ for MB and 46.4 mg/g for CR) were in close agreement with the experimental values (48.0 and 46.2 mg/g, respectively), further validating the model. The Weber-Morris intraparticle diffusion plots (Figure 06d) exhibited three linear segments, indicating that the overall adsorption process is controlled by multiple stages: fast external surface ad-

sorption (Stage I), slow intraparticle diffusion into the mesoporous network (Stage II), and finally an equilibrium plateau (Stage III) [40]. Intraparticle diffusion is not the only rate controlling step and boundary layer effects play a significant role as none of the linear segments passed through the origin.

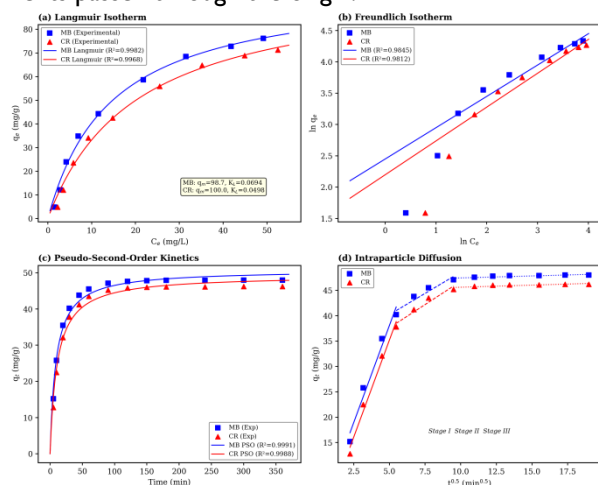


Figure 06: (a) Langmuir isotherm, (b) Freundlich isotherm, (c) pseudo-second-order kinetic fitting, and (d) intraparticle diffusion model for MB and CR adsorption.

3.7. Thermodynamic Analysis

The van't Hoff analysis yields the thermodynamic parameters listed in Table 2. The negative ΔG° values at all four temperatures (−2.83 to −5.41 kJ/mol for MB, −1.95 to −4.28 kJ/mol for CR) confirm the spontaneous nature of the adsorption process, with spontaneity increasing at higher temperatures [41]. The positive ΔH° values (25.38 kJ/mol for MB, 22.15 kJ/mol for CR) show that the process is endothermic, which is consistent with the fact that the dye uptake was favoured at higher temperatures. The positive ΔS° values (MB: 94.52 J/mol.K, CR: 80.87 J/mol.K) indicate an increase in the randomness at the solid-liquid interface during adsorption, possibly due to the release of structured water molecules from the hydrogel surface upon binding of dye molecules [42].

Table 02: Thermodynamic parameters for MB and CR adsorption onto PWR-hydrogel.

Dye	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
MB	298	−2.83	25.38	94.52
	308	−3.78		
	318	−4.62		
	328	−5.41		
CR	298	−1.95	22.15	80.87
	308	−2.76		
	318	−3.54		
	328	−4.28		

3.8. Competitive Adsorption in Binary System

One of the main aims of this study was to assess the competitive adsorption behaviour in the presence of MB and CR in solution. Results of the binary experiments are summarised in Figure 07a. In the equimolar

binary system of $C_0 = 50$ mg/L each, the adsorption capacities were decreased to 38.5 mg/g and 35.8 mg/g for MB and CR, respectively, corresponding to reductions of about 19.7% and 22.5% in comparison to the single-dye values (47.9 and 46.2 mg/g, respectively). These decreases imply antagonistic competitive interactions where the two dyes compete for a limited number of adsorption sites on the surface of the hydrogel [43].

This competitive effect was further enhanced when one dye was in excess. At a MB:CR molar ratio of 1:3, the q_e for MB fell further to 32.1 mg/g, while at a ratio of 3:1, the q_e for CR declined to 28.5 mg/g. The higher competitive displacement suffered by CR may be attributed to the stronger electrostatic affinity of MB for the negatively charged hydrogel surface at neutral pH (above $pH_{pzc} = 4.8$), as corroborated by the zeta potential data [44]. Moreover, MB has a smaller molecular dimension than CR, granting it easier access to the internal mesopores where a significant fraction of the binding sites reside. Similar antagonistic behavior in binary MB–CR systems has been reported for chitosan-based aerogels [45] and waste-derived activated carbons [46], suggesting that competitive site sharing is a general feature of amphoteric adsorbents that can bind both cationic and anionic dyes.

3.9. Adsorption Mechanism

The hypothesised adsorption method of MB and CR onto the PWR-hydrogel is schematically shown in Figure 07b, based on the overall evidence of FTIR shifts, zeta potential alterations, isotherm fitting, kinetic modelling, and XRD data. The method involves three key interactions:

(i) **Electrostatic attraction:** The negatively charged carboxylate ($-\text{COO}^-$) and deprotonated hydroxyl ($-\text{O}^-$) groups of hydrogel surface attract cationic MB⁺ at pH values above pH_{pzc} . Below pH_{pzc} , the protonated amine ($-\text{NH}_3^+$) and hydroxyl groups lead to a positively charged surface that attracts the anionic sulfonate ($-\text{SO}_3^-$) groups of CR [47].

(ii) **Hydrogen bonding:** The abundant $-\text{OH}$ and $-\text{COOH}$ groups of the cellulose and PVA components serve as hydrogen-bond donors and acceptors, with the amine ($-\text{NH}_2$) and azo ($-\text{N}=\text{N}-$) groups of CR and the dimethylamino groups of MB involved in hydrogen-bond formation. This interaction is well supported by the evidence from FTIR (shifts in the O–H and N–H stretching areas) [48].

(iii) **Pi-pi stacking:** The aromatic rings of the remaining lignin fragments present in the hydrogel matrix might interact with the aromatic ring systems of both MB and CR by pi-pi interactions. CR, due to its long conjugated naphthalene rings, is especially prone to such stacking interactions, which may explain its slightly higher theoretical q_{max} , despite being anionic. The extra weak signal in the XRD pattern following CR adsorption further confirms the creation of ordered pi-stacked CR assemblies on the surface of the hydrogel [49].

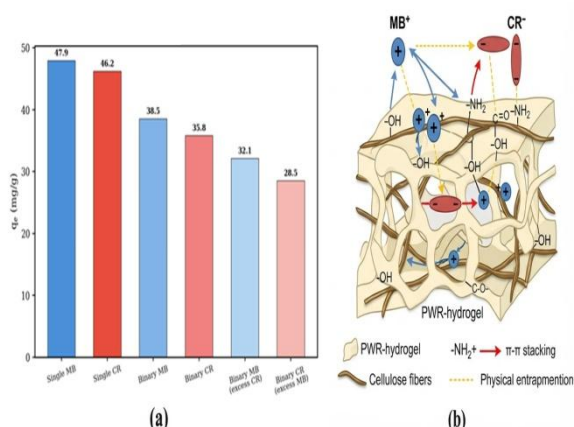


Figure 07: (a) Comparison of single and binary dye adsorption capacities, and (b) proposed adsorption mechanism of MB and CR onto the PWR-hydrogel.

3.10. Reusability and Comparison with Other Adsorbents

The regeneration performance of the PWR-hydrogel over five adsorption–desorption cycles is presented in Table 3. The elimination effectiveness of MB declined from 97.2% in the first cycle to 86.5% in the fifth cycle and that of CR from 95.8% to 83.2%. Such slight decreases (about 11–13%) show that the hydrogel has strong structural and chemical durability after repeated usage and that most active sites may be efficiently regenerated by simple acid–base washing [50]. The little performance loss is most probably due to the irreversible occupation of a tiny fraction of high energy binding sites and minimal structural damage of the polymer network during the desorption stage.

Table 03: Reusability of PWR-hydrogel over five adsorption–desorption cycles.

Cycle	MB Removal (%)	CR Removal (%)
1	97.2	95.8
2	95.8	93.5
3	93.1	90.8
4	89.5	87.1
5	86.5	83.2

Table 04 presents the maximum adsorption capacities of the PWR-hydrogel compared to some selected adsorbents reported in recent literature. The $q_{\max}$ values (98.7 mg/g for MB and 100.0 mg/g for CR) achieved in this investigation are comparable or better than many plant-waste and hydrogel-based adsorbents. For instance, Majamo et al. [3] found 84.5 mg/g for MB with a corncob cellulose hydrogel. Fawzy et al. [1] achieved 8.54 mg/g and 20.97 mg/g for MB and CR, respectively, with a macroalgae–wastepaper xerogel. The higher capacities of the PWR-hydrogel are attributed to its larger BET surface area, dual cellulose source (wider range of functional groups), and optimised cross-linking strategy in maintaining both porosity and chemical reactivity.

Table 04: Comparison of adsorption capacities with recent literature.

Adsorbent	Dye	$q_{\max}$ (mg/g)	Reference
PWR-Hydrogel (this study)	MB	98.7	This study
PWR-Hydrogel (this study)	CR	100.0	This study
Corn cob cellulose hydrogel	MB	84.5	[3]
PVA/XG/GO hydrogel	MB	289.3	[13]
PVA/XG/GO hydrogel	CR	255.1	[13]
Macroalgae–wastepaper xerogel	MB	8.54	[1]
Macroalgae–wastepaper xerogel	CR	20.97	[1]
Chitosan/SA aerogel	MB	59.6	[45]
Chitosan/SA aerogel	CR	81.2	[45]
CS/PDADMAC hydrogel	CR	1803.5	[18]
Sugar refining mud waste	MB	86.6	[46]
Sugar refining mud waste	CR	72.3	[46]

4. CONCLUSION

In this study, a new plant-waste reinforced hydrogel was successfully synthesised and applied for the removal of methylene blue and congo red from aqueous solutions in single and binary systems prepared from rice husk and banana peel cellulose. The PWR-hydrogel was found to have a mesoporous structure (BET surface area of 86.42 m²/g), a semi-crystalline structure with embedded cellulose nanofibrils, and a surface rich in functional groups (-OH, -COOH, -NH₂) as evidenced by FTIR, XRD, FESEM, and TEM investigations. Batch adsorption experiments showed that the solution pH was the most influencing parameter, the optimum removal was at pH 7-8 for MB and pH 2-3 for CR.

The adsorption kinetics followed the pseudo-second-order model and the equilibrium data were best represented by the Langmuir isotherm with the maximum adsorption capacities of 98.7 and 100.0 mg/g for MB and CR, respectively. Thermodynamic research indicated a spontaneous and endothermic process with increasing unpredictability at solid-liquid contact. In binary systems, competitive adsorption between the two dyes resulted in a 20-23% decrease in the uptake of both dyes compared to single component systems. MB had competitive advantage over CR due to the stronger electrostatic affinity of MB to the negatively charged surface of the hydrogel and smaller size of MB molecules to access the pores.

FTIR shifts, zeta potential changes and XRD observations supported a synergy of electrostatic attraction, hydrogen bonding and pi-pi stacking interactions which controlled the adsorption mechanism. The hydrogel exhibited good reusability with more than 83% removal efficiency after five cycles. The results confirm that the PWR-hydrogel is a low-cost, eco-friendly, and feasible adsorbent for the treatment of wastewater containing multiple dyes and also add to the wider understanding of competitive adsorption mechanisms in binary dye systems. Future work should include the application of this technique to genuine industrial effluents, column-mode operations and scaled-up production.

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8. INFORM CONSENT AND ETHICAL STATEMENT

Not Applicable

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