

Reactive dyes adsorption by chestnut shells coated with nanoparticles of zinc oxide: Characterization, isotherm and kinetic studies

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ABSTRACT

This investigation employed a new adsorbent composed of chestnut shell powder and covered with ZnO nanoparticles. Coated chestnut shell (CCS) was examined to assess the adsorption of Reactive Blue-19 Dye and Red Reactive-2 from a water-based mixture. Considerable increases in the capability of adsorption of the chestnut shell were recognized following the coating of the powder particles with ZnO nanoparticles. The adsorbent was analyzed using surface area analysis, FTIR, SEM, and XRD to verify its structural and morphological properties. Batch adsorption Research was done to ascertain the optimum Situations, including the solution pH, adsorbent dosage, contact period, speed of shaking, and initial dye concentration, all conducted at room temperature, which is 25 °C. Both the Freundlich and Langmuir isotherm models were used to describe the equilibrium information on adsorption. As a result revealed that the process of adsorption followed Langmuir's isotherm model, using correlation values (R^2) of 0.9886 for Reactive Red-2 and 0.9955 for Reactive Blue-19, demonstrating monolayer adsorption onto a uniform surface. The greatest CCS adsorption capacity was observed for Reactive Blue-19 (172.413 mg/g), followed by Reactive Red-2 (114.942 mg/g). Kinetic information was correlated using both pseudo-first-order and pseudo-second-order models. The findings demonstrated that the model of pseudo-second order gave greater results compared to the pseudo-first order model, considering correlation coefficients (R^2) of 0.9951 for Reactive Red-2 and 0.9975for Reactive Blue-19, demonstrating that the process of chemisorption step that limits the rate of adsorption mechanism. Thus, these results show that CCS is among the best and most efficient adsorbents for getting rid of wastewater tainted with reactive dye residues.

Keywords: adsorption, coating, dyes, wastewater, sustainable process.

INTRODUCTION

The industry of textiles is among the greatest contributions to industrial wastewater, driven by population growth, urbanization, and intensive chemical use, particularly dyes (Periyasamy, 2025). Reactive dyes, though widely used for their bright colors and strong covalent bonding to cellulosic fibers, are problematic because 10–15% remain unfixed during dyeing and are discharged into effluents (Dutta et al., 2024). Their aromatic amine structure provides strong chemical stability and biodegradation resistance, while breakdown

products can be carcinogenic and mutagenic (Kamati et al., 2024). Discharge of dye-laden wastewater elevates BOD/COD, reduces dissolved oxygen and photosynthesis, and disrupts aquatic biodiversity (Islam et al., 2025), with human exposure linked to bioaccumulation, endocrine disruption, and carcinogenesis (Kolya and Kang, 2024). Treating such wastewater before discharge is therefore essential (Valli Nachiyar et al., 2023). The absorption of sunlight by colorants, crucial for the photosynthesis of aquatic plants, hinders their penetration into the water, which presents a serious risk to the ecosystem. This phenomenon

demands attention due to the visibility of dyes, even at low concentrations. Consequently, wastewater treatment containing dyes must adhere to legal standards and consider aesthetic criteria (Tripathi et al., 2023). Elevated amounts of such colors in water may restrain re-oxygenation and sunlight penetration, harming aquatic organisms' biological activity and disrupting the process of photosynthesis in vegetation or seaweed (Alguacil et al., 2024). Traditional approaches to therapy, AOPs, membrane filtration, coagulation-flocculation, electrocoagulation, and photocatalysis face limitations such as high cost and incomplete removal at scale (Senthil Rathi et al., 2024), but biological methods are mainly useless against non-biodegradable reactive dyes (Lellis et al., 2019). In adsorption, thus developed as a straightforward, low-cost, and effective alternative, offering sludge-free operation and easy regeneration (Athira and Sumi, 2024; Dutta et al., 2021). While activated carbon is still the benchmark, the high cost of adsorbent and difficult regeneration have driven interest in low-cost agricultural waste materials such as walnut, chestnut, and hazelnut shells, and various peels and husks as renewable alternatives (Aftab et al., 2024; Aragaw and Bogale, 2021). Nanoparticle-based adsorbents (e.g., ZnO, TiO₂, Fe₂O₃, Ag, CuO) offer a large surface area in relation to ratios of volume, and improved active sites (Chaisorn et al., 2023; Doondani et al., 2024), and coating traditional adsorbents with nanoparticles improves stability, adsorption efficiency, and surface area (Van et al., 2021). However, standalone nanoparticles face challenges including high synthesis cost, difficult separation, agglomeration, and instability (Rashtbari et al., 2020; Rorissa et al., 2025). Nanoparticle-coated low-cost adsorbents thus represent a practical compromise, combining the benefits of nanomaterials with the affordability of biosorbents (Sayed et al., 2024). This study evaluated ZnO-coated chestnut shell (CCS) as an adsorbent in reactive eliminating dyes from aqueous solutions. The manufactured CCS was examined under Fourier transform infrared (FTIR), Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM), and X-ray diffractometer (XRD). Using manipulation, the adsorption capabilities were studied by examining pH and dosage of adsorbent effects, time of contact, shaking speed, and initial dye concentration, alongside both an isotherm and kinetic modeling to clarify the adsorption methodology as well as optimize treatment conditions.

MATERIALS AND METHODS

Adsorbent preparation

Chestnut shells (CS) were gathered locally and manually cleaned, and entirely cleaned using water that has been distilled to remove any impurities. After that, these shells were they kept dry at 105 °C. Within an oven for a full day, the dried shells were ground, and sieved until the particles were small 87 µm (Kuyucu et al., 2025), prior to surface coating with ZnO nanoparticles. The leftover generated CS was analyzed in tiny quantities, and its surface was coated with ZnO nanoparticles. The ZnO nanoparticles were provided by Xi'an Biotec Co., Ltd. Lyphar. In China, covering the CS using ZnO nanoparticles, an ultrasonic apparatus. An appropriate dispersion (acetone) was used with the ZnO nanoparticles (Hong et al., 2006) for 30 minutes in an ultrasonic device. Preliminary experiments were conducted using several CS: ZnO weight ratios (e.g., 7:1, 5:1, 9:1) to determine the optimal formulation for composite preparation. Among the ratios tested, the 5:1 (w/w) CS: ZnO ratio yielded the most homogeneous and stable composite, and was therefore selected for subsequent experiments. Accordingly, chestnut shell biomass was combined with ZnO nanoparticles at this optimized 5:1 ratio (CS: ZnO, g/g) and agitated vigorously until a homogeneous mixture was produced. Then, after the liquid was decanted, the precipitate of coated chestnut shell with ZnO nanoparticles was filtered, and then dried completely in an oven at 60 °C. At last, the drying CCS was kept in stoppered bottles for the necessary experiments (Figure 1).

Preparation of dye solutions

A stock Reactive Red-2(RR-2) solution with a concentration was created by dissolution 1 g of 1000 mg/L of RR-2 (Reactive Red-2) dye in a liter of distilled water. Similarly, a stock Reactive Blue-19(RB-19) solution containing to make 1000 mg/L, 1.0 g of Reactive Blue-19 dye in a liter of distilled water. Various concentrations in the working dilutions of the solutions were according to (Mubarak et al., 2017). Standard curves were developed within the absorption and the concentration for each dye. The chemical structures of dyes are shown in (Figures 2a and 2b).

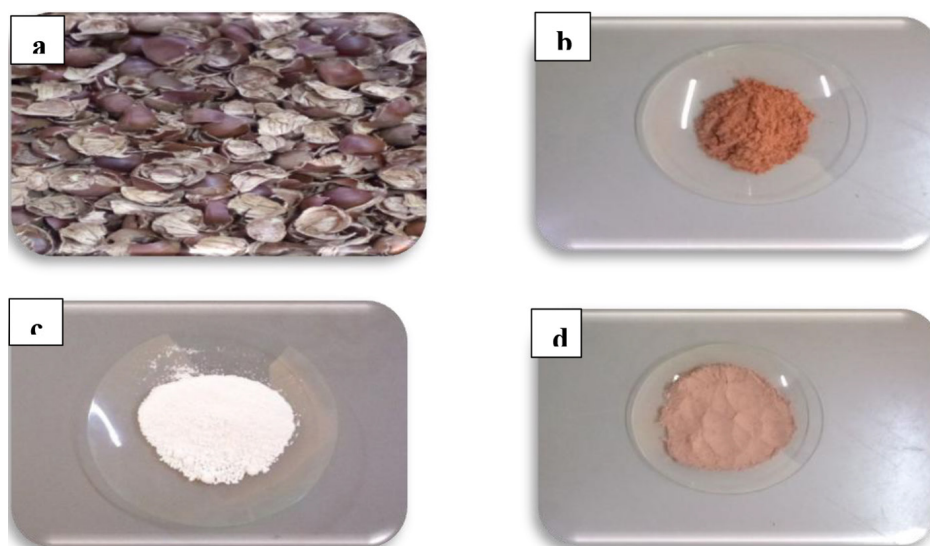


Figure 1. Chestnut shell with ZnO nanoparticles preparation (a) chestnut shell, (b) chestnut shells after ground and sieved, (c) ZnO nanoparticles, and (d) chestnut shell coated with nano zinc oxide

EXPERIMENTAL WORK

Experiments on adsorption in batches was carried out to determine the ideal operating circumstances namely pH, adsorbent dose, time of contact, shaking speed, and initial dye concentration, in order to eliminate dyes Red Reactive -2 and Reactive Blue-19 from water-based solution by utilizing zinc oxide-coated chestnut shell as the adsorbent. For each experiment, conical flasks within 250 milliliters capacity included 100 milliliters of the dye solution recognized concentration. The pH value of each solution was quantified with a pH meter (German, WTW-3110) and modified to the necessary amount by incorporating 0.1 M either HCl or NaOH as required. A known mass of CCS was then introduced into each flask, and the flasks were placed on a mechanical shaker (Heidolph Unimax 2010, Germany) and agitated continuously for a predetermined contact time at a controlled the temperature of 25 ± 2 °C. After

every experiment, samples were withdrawn and passed via filter paper (Whatman, 12.5 cm) to remove suspended particles that are adsorbent. The remaining dye concentration of the filtrate was assessed with a UV-Visible spectrophotometer (UV-Vis) (NANOCOLOR VIS, Macherey-Nagel, Germany) at $\lambda_{\max}$ 535nm (RR-2) and $\lambda_{\max}$ 572nm (RB-19). All analyses were performed at the Chemistry Department Sciences, Science College, University of Baghdad. The consequences of the operating parameters on dye removal studies were conducted by systematically varying one parameter while holding the others constant, over the following ranges: pH (2–12), CCS dose of (0.02–0.4 g/100 mL), time of contact (5–180 min), agitation speed (50–250 rpm) and the starting concentration of dye (10–250 mg/L). The effectiveness of removal (R%) and the capacity for equilibrium adsorption (q_e , mg/g) of CCS for the Reactive Red-2 and Reactive Blue-19 were computed utilizing Equations 1 and 2, respectively (Nguyen and Pho, 2014).

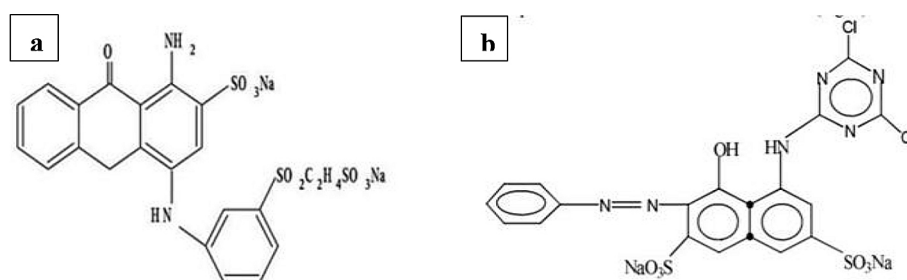


figure 2. (a) chemical structure of rr-2 dye, and (b) chemical structure of RB-19 dye

$$R\% = \frac{(C_o - C_e)}{C_e} \times 100\% \quad (1)$$

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

where: C_o stands for the initial concentration of dye prior to adsorption, C_e for the amount of dye at equilibrium following adsorption, m for the quantity of adsorbent utilized (g), and V for the dye solution volume (L).

Characterization techniques

The samples were examined both before and after adsorption employing a variety of methods to comprehend surface and structural changes. FTIR was utilized to find functional groupings; SEM was used to examine morphological and surface features; BET was used to assess surface area and porosity; and XRD was used to analyze crystalline structures. These methods produced a comprehensive analysis of the results of adsorption on the material's characteristics.

RESULTS AND DISCUSSION

Adsorbent characteristics

FTIR spectroscopy

The FTIR spectrum of chestnut shell (Figure 3a) revealed characteristic peaks reflecting its lignocellulosic composition. The broad absorption region at 3410–3547 cm^{-1} is equivalent to the O–H stretching vibrations of cellulose molecules' hydroxyl groups that are hydrogen bound, however the peak at 2916 cm^{-1} is attributed to C–H stretching vibrations of methylene groups. The peak at 1732 cm^{-1} is assigned to C=O stretching of ester and carboxyl groups of hemicellulose, and the bands at 1637–1616 cm^{-1} correspond to hydrogen-bonded O–H bending as well as aromatic C=C stretches of lignin. The band at 1519 cm^{-1} is characteristic of aromatic C=C vibrations of lignin, although the region at 1232–1159 cm^{-1} reflects C–O–C glycosidic linkage. The polysaccharide's extension backbone, and the strong absorption at 1035–1056 cm^{-1} represents C–O stretching of the cellulosic structure (Tolkou et al., 2024; Yadav et al., 2024). Coated chestnut shell before adsorption upon incorporation of ZnO nanoparticles onto the chestnut shell

surface, notable spectral changes were observed. The intensity of the –OH stretching band (3541–3234 cm^{-1}) decreased compared to CS, indicating partial occupation of surface hydroxyl sites through Zn–O–C bond formation. A slight shift of the C=O band and modification in the 1056–1033 cm^{-1} region confirm chemical anchoring of ZnO onto the biomass. New absorption bands at 503.42 and 441.70 cm^{-1} are indicative of Zn–O stretching vibrations, indicating that ZnO nanoparticles were effectively incorporated onto the adsorbent surface. These findings align with earlier research findings reporting that ZnO impregnation onto biomass partially occupies –OH and –COOH sites while introducing Zn–O stretching contributions below 600 cm^{-1} (Belhaj et al., 2025). CCS after Reactive Red-2 adsorption following adsorption of Reactive Red-2 dye, significant spectral changes were recorded relative to CCS. The –OH stretching band shifted from 3408 to 3473 cm^{-1} with reduced intensity, indicating participation of hydroxyl groups in establishing hydrogen bonds with the sulfonate ($-\text{SO}_3^-$) groupings of the anionic dye. A new intensified band at 1556 cm^{-1} appeared, attributed to asymmetric –COO[−] stretching arising from dye surface complexation. The Zn–O stretching bands shifted from 503.42, 476.42 cm^{-1} and 441.70, 428.20 cm^{-1} (red shift), confirming Lewis acid–base coordination between Zn^{2+} surface sites and the electron-rich azo ($-\text{N}=\text{N}-$) and sulfonate groups of RR-2. Modifications in the C–O–C region (1247–1035 cm^{-1}) further reflect engagement of polysaccharide oxygen-containing groups in dye binding. The sulfonate group of reactive dye compounds has been identified as the most reactive zone for interaction with the carboxyl and hydroxyl groups in the biomass surface (Koc-Bilican et al., 2025), as shown in Figure 3b. The FTIR spectrum of CCS after Reactive Blue-19 adsorption exhibited distinct spectral changes. The –OH band showed pronounced broadening and intensity reduction with new shoulders at 3541 and 3466 cm^{-1} , consistent with extensive hydrogen bonding between surface –OH groups and the anthraquinone ring system and sulfonate groups of Reactive Blue-19. The C=O band at 1734 cm^{-1} persisted with altered intensity, confirming carboxyl group involvement. New peaks at 1315 and 1255 cm^{-1} emerged, attributed from C–N stretching also aromatic Vibrations of C–O from in the adsorbed dye. In the Zn–O bands shifted from 503.42, 484.13 cm^{-1} and 441.70, 453.27 cm^{-1} , FTIR

analysis demonstrated that π - π stacking interactions of aromatic dye structures contacting the adsorbent surface, hydrogen bonds that connect sulfonate as well as functional groupings with oxygen, and electrostatic attraction all contribute to the high adsorption efficiency (Gürses et al., 2023), as seen in Figure 3c.

SEM

The unmodified chestnut shell exhibits a compact, stratified surface with overlapping irregular platelets and lamellar microstructures. This native lignocellulosic framework (lignin, cellulose, and hemicellulose) produces inherent micro-roughness, shallow micro-cracks, and stepped fracture planes, offering a moderately textured surface with limited adsorption site density (Enache et al., 2023), as shown in the Figure 4a. After ZnO nanoparticle functionalization, the CCS shows a pronounced morphological change: elongated fibrous structures densely decorated with uniformly anchored ZnO nanocrystallite clusters along fiber surfaces and junctions.

This homogeneous distribution reflects high interfacial bonding within the ZnO phase and the organic structure (Rashtbari et al., 2022), producing a hierarchically roughened surface that significantly increases surface area and reactive site density, as illustrated in Figure 4b. Following Reactive Red-2 (RR-2) adsorption, the CCS surface shows the most pronounced change, with a densely packed, globular aggregate exhibiting a rough, cauliflower-like texture that occupies most of the field of view indicating extensive dye accumulation and near-complete saturation of surface active sites, consistent with a chemisorption-dominated mechanism. As illustrated in Figure 4c. After Reactive Blue-19 (RB-19) adsorption, as illustrated in Figure 4d. dye nanoparticle deposits are distributed as smaller, discrete particulates along multiple interlaced fiber edges and at inter-fiber junctions, without forming large globular clusters, confirming a more dispersed pattern of electrostatic and coordinative interactions between ZnO active sites and the dye's anionic groups (Rashtbari et al., 2020).

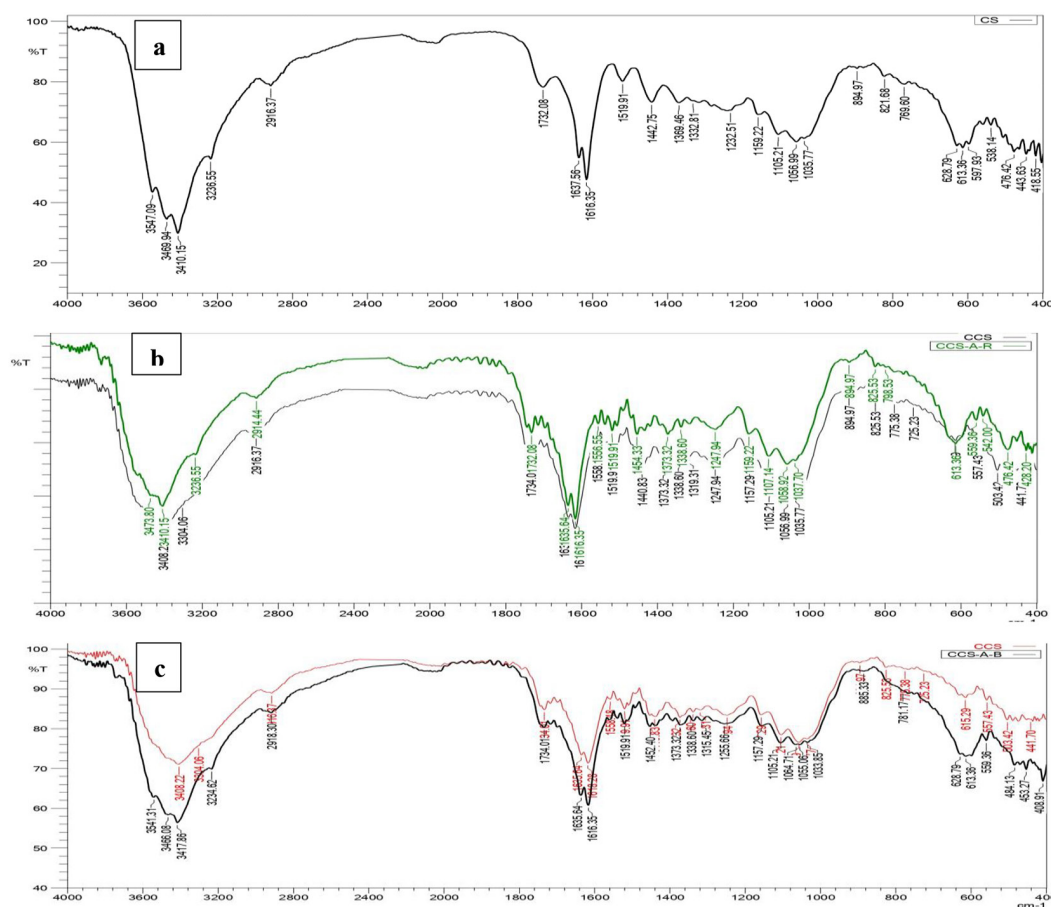


Figure 3. FTIR spectrum of (a) CS, (b) CCS before and after RR-2 adsorption, (c) CCS before and after RB-19 adsorption

Brunauer-Emmett-Teller

Chestnut shells were methodically described using Brunauer–Emmett–Teller (BET) evaluation to assess the results of surface modification in the structural characteristics of the material. The chestnut shells demonstrated a specific surface area of $3.0269 \text{ m}^2/\text{g}$, a total pore volume of $0.011969 \text{ cm}^3/\text{g}$, and a typical pore diameter of 15.817 nm , representative of a naturally compact lignocellulosic matrix with limited porosity. Following the coating process with ZnO nanoparticles, a remarkable enhancement in all morphological parameters was observed, as the particular surface area increased considerably to $6.7682 \text{ m}^2/\text{g}$, a pore volume expanded to $0.021224 \text{ cm}^3/\text{g}$, considering the average diameter of the porous was recorded at 12.544 nm .

X-ray diffraction (XRD)

The synthetic ZnO nanoparticles' XRD pattern confirmed 100% phase purity, with sharp diffraction peaks at 2θ positions in line with the (100), (002), (101), (102), (110), and (103) planes, characteristic of the hexagon-shaped wurtzite structure (space group $P6_3mc$, JCPDS card No. 36-1451) (Flores et al., 2025). Refined lattice parameters were determined as $a = b = 3.308 \text{ \AA}$ and

$c = 5.196 \text{ \AA}$ (Munna et al., 2025). The mean size of crystallites, computed via the Debye–Scherrer equation ($D = 0.89\lambda/\beta\cos\theta$), was 20.9 nm , consistent with values reported for chemically synthesized ZnO nanoparticles (Khorsand Zak and Hashim, 2025). As shown in Figure 5a, chestnut shell (CS), the XRD pattern showed a wide amorphous hump centered at $2\theta \approx 20\text{--}22^\circ$. As shown in Figure 5b, the typical XRD pattern of lignocellulosic biomass due to the disordered arrangement comprising lignin, hemicellulose, and cellulose (Halder and Purkait, 2020). Quantitative phase analysis identified three constituents: lignocellulosic matrix (78.3%), silica SiO_2 (11.3%), and periclase MgO (10.4%), both naturally present in plant-derived biomass (Lamponi et al., 2026). The elevated Rwp of 32.0% reflects the inherent structural disorder of amorphous biological materials. In coated chestnut shell, the XRD analysis of the CCS composite showed sharp ZnO diffraction peaks (Figure 5c) superimposed over the broad biomass background, confirming successful nanoparticle deposition while retaining crystalline integrity. Rietveld refinement confirmed the hexagonal wurtzite ZnO phase ($P6_3mc$), with phase composition of ZnO (77.5%), cristobalite SiO_2 (21.1%), and trace MgO (1.4%), with a satisfactory Rwp of 23.4% (Lopes de Almeida et al.,

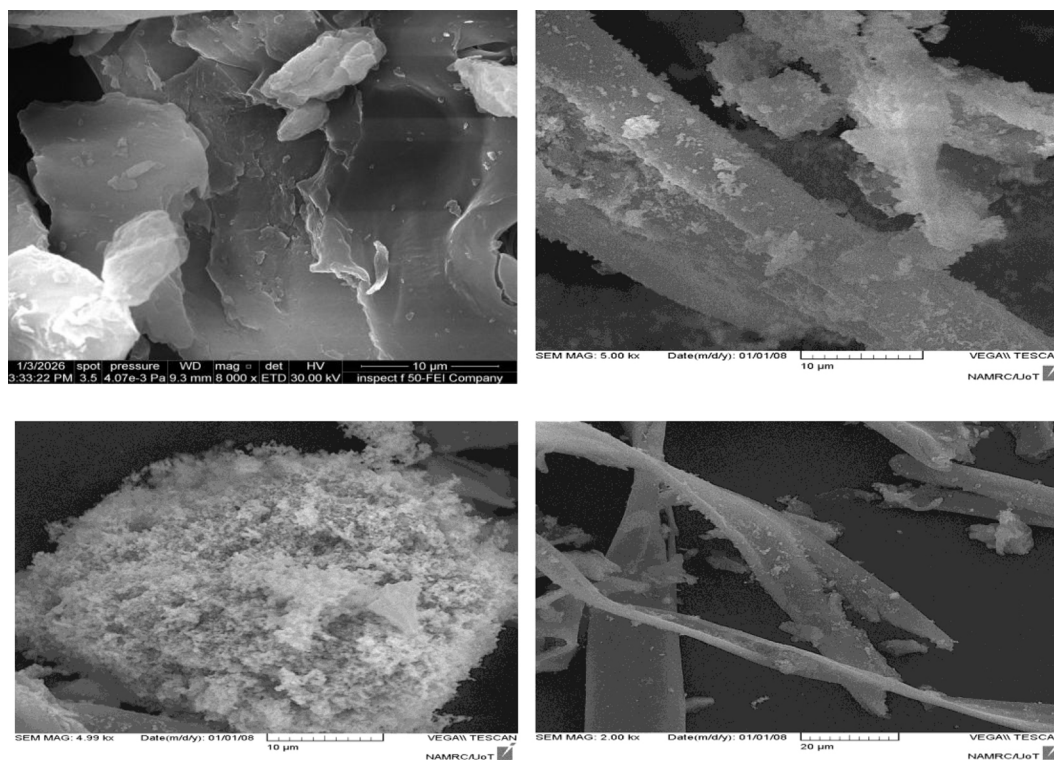


Figure 4. SEM images for CS (a), CCS (b), CCS after RR-2 adsorption (c), and CCS after RB-19 adsorption (d)

2021). These results collectively confirm uniform and effective coating of chestnut shell particles with highly crystalline ZnO nanoparticles.

Batch adsorption investigations for dye removal

The tested pH levels

Solution pH was identified as a decisive parameter governing the removal efficiency of Red-2 Reactive (RR-2) and Blue-19 Reactive (RB-19) dyes by the ZnO nanoparticle-coated chestnut shell (CCS) composite. (Figure 6) illustrates how pH affects dye removal over the range pH 2–12 (dosage of adsorbent 0.1 g/100 ml, contact time 120 min, initial dye concentration 50 mg/l, 200 rpm, $25^{\circ}\text{C} \pm 5$). Removal efficiency increased markedly under acidic conditions, reaching a maximum at pH 2 (78.4% for Reactive Red-2 and 77.34% for Reactive Blue-19), and then declined progressively as the pH shifted toward alkaline values. The surface can explain this pattern charge behavior of the ZnO-coated adsorbent: under acidic conditions, Hydroxyl groups on the outside become protonated, generating a net

positive surface charge that establishes a strong electrical attraction to the negatively charged sulfonate with charge ($-\text{SO}_3^-$) groups of the reactive dye anions, improving adsorption as a result. As the pH increases, this positive surface charge diminishes and is progressively replaced by a negative surface charge. This induces both the adsorbent and the electrostatic repulsion of anionic dye molecules, producing a marked reduction in removal efficiency (Yang et al., 2022).

Dosage of adsorbent

The outcome of CCS composite dose in the process of removing dyes Reactive Red-2 and Reactive Blue-19 was investigated over the range of 0.02–0.4 g/100 ml, while other parameters were held constant (pH 2, 120 minutes of contact, initial dye concentration 50 mg/l, 200 rpm, and $25^{\circ}\text{C} \pm 5$). (Figure 7) shows that removal efficiency increased progressively with dosage, reaching a maximum of 81.61% for Reactive Red-2 at an optimum 0.1 g/100 ml dosage, and 86.303% for Reactive Blue-19 at a slightly lower The The best dosage is 0.08 g /100 ml, owing to the greater quantity of active adsorption sites made available by the increased

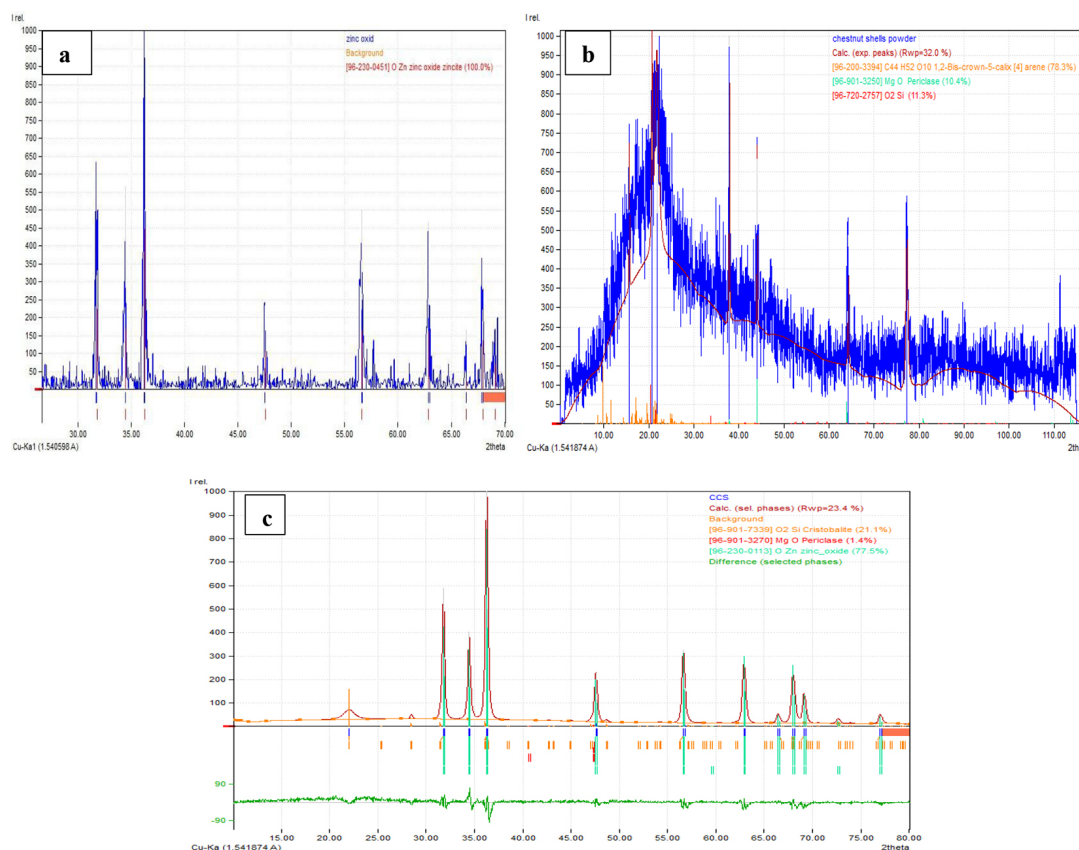


Figure 5. XRD images of the ZnO (a), CS (b), and CCS(c)

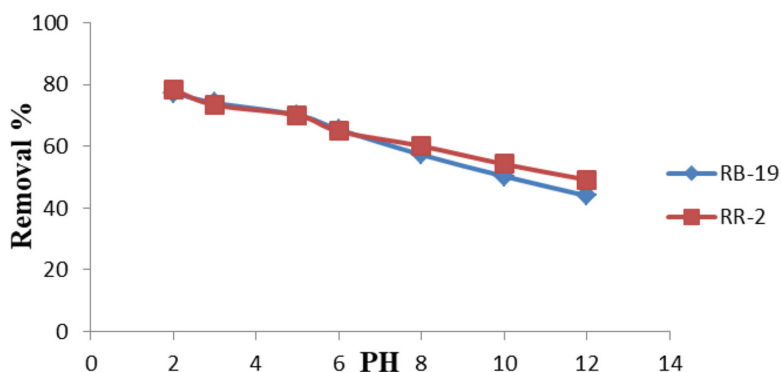


Figure 6. Effect of pH on the adsorption of RR-2 and RB-19 using coated chestnut shell

surface area from the composite (Van et al., 2021). Beyond these optimum dosages, no significant further improvement in removal was observed for either dye, a plateau due to the creation of a balance between dissolved and adsorbed dye ions, in addition to particle agglomeration at increased doses. Consequently, the effective surface area decreases per unit mass constraints as well as further uptake (Rápó and Tonk, 2021).

Contact time

The impact of adsorption on contact time of the dyes Reactive Red-2 and Reactive Blue-19 onto the ZnO nanoparticle-coated chestnut shell (CCS) composite was investigated over a range of 5–180 min, while other parameters were held constant (pH 2, adsorbent dosage 0.1 g/100 ml RR-2 and adsorbent dosage 0.08 g/100 ml RB-19, initial dye 50 mg/l of dye, 200 rpm of agitation, and temperature $25\text{ }^{\circ}\text{C} \pm 5$). As demonstrated in (Figure 8), the efficiency of removal of both dyes increased progressively with a rise in contact time, which is ascribed to the large number of vacant active sites initially available on the composite surface, allowing quick absorption of dye during

the initial phases of the adsorption procedure (Al-Arjan, 2022). For Reactive Red-2, equilibrium was attained at a contact time of 120 min, corresponding to a maximum elimination effectiveness of 87.49%, while for Reactive Blue-19, equilibrium was likewise attained at 90 min, with a maximum removal efficiency of 93.12%. Beyond this point, the adsorption rate for both dyes slowed markedly and eventually plateaued, as the active binding sites of the CCS composite became progressively saturated with dye molecules, leaving fewer accessible sites for further uptake (Li et al., 2019). Its behavior conforms to the usual biphasic adsorption pattern reported for ZnO-based composites derived from agricultural waste, in which an early stage of fast uptake governed by surface adsorption is after which there is a slower phase managed by intraparticle diffusion once the readily accessible sites are occupied (Abdelrazek et al., 2025).

Speed of agitation

The impact of agitation rate at the adsorption of Red-2 Reactive as well as Reactive Blue -19 dyes onto the ZnO nanoparticle-coated chestnut shell (CCS) composite was investigated at 50,

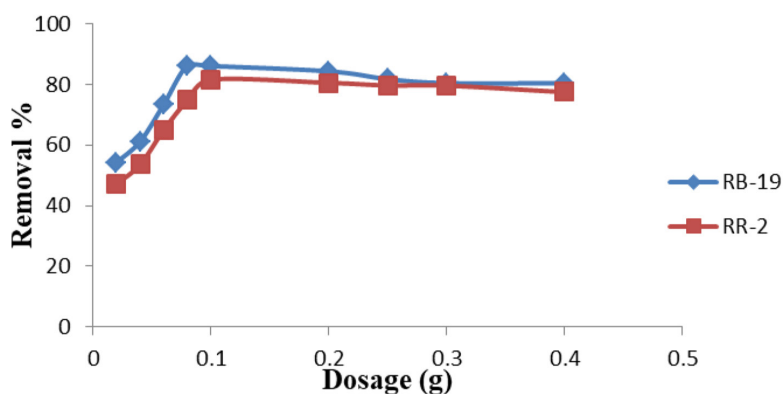


Figure 7. Effect of dose on the adsorption process adsorbent RR-2 and RB-19 using coated chestnut shell

100, 150, 200, and 250 rpm, while other conditions were held constant (pH 2, contact time 120 min and 90 min of RR-2 and RB-19, adsorbent dosage 0.1 g/100 ml and 0.08g/100ml of RR-2 and RB-19, 50 mg/l of dye at the beginning, temperature $25\text{ }^{\circ}\text{C} \pm 5$). According to (Figure 9), the result revealed that each dye exhibited its own distinct optimal agitation speed. For Reactive Red-2 dye, removal efficiency increased progressively with agitation speed up to an optimum of 200 rpm, at which a maximum removal efficiency of 88.22% was achieved, beyond which no further improvement was observed. For Reactive Green dye, removal efficiency similarly increased with agitation speed, reaching its own optimum at 150 rpm with a maximum removal efficiency of 94.39%, after which additional increases in agitation speed yielded no significant enhancement. This conduct might be clarified by the fact that greater agitation speeds reduce the thickness of the liquid level of boundaries encircling the CCS molecules and enhance the dispersion rate of dye molecules in the bulk mixture in the direction of the layer, thereby increasing their accessibility to the active adsorption sites on the composite surface and consequently improving adsorption effectiveness (Andrade-Guel et al., 2022). This trend is consistent with the outcomes seen for other ZnO- nanoparticle-based adsorbents, where an increase in agitation speed similarly minimized external mass-transfer resistance and improved dye uptake up to an optimum point specific to each dye system (Eleryan et al., 2023; Palai et al., 2021). Beyond the optimum speed of each dye, the boundary layer resistance is already minimized, so further agitation offers negligible additional mass-transfer benefit and may instead risk desorption or particle attrition.

Initial dye concentration

The influence of starting dye concentration on the Reactive Red-2 and Reactive Blue-19 dyes' adsorption onto the CCS composite was investigated across a range of 10 to 250 mg/l, with all other conditions fixed at pH 2, 0.1 g/100 ml dose of adsorbent and 0.08g/100ml of RR-2 and RB-19, contact time 120 min and 90 min of RR-2 and RB-19, agitation speed 200 rpm and 150rpm of RR-2 and RB-19, and temperature $25\text{ }^{\circ}\text{C} \pm 5$. As shown in (Figure 10), at low initial concentrations (10 mg/l), elimination effectiveness reached its maximum values of 93.18% and 96.92% for the dyes Reactive Red-2 and Reactive Blue-19, respectively. Because from the abundance of active adsorption sites in the CCS surface in relation to the quantity of dye molecules present in solution, which allowed nearly complete uptake. However, as the initial concentration progressively rose to 250 mg/l, removal efficiency declined markedly to 44.95% and 51.50% for dyes Reactive Red-2 and Reactive Blue-19, respectively. The inverse connection between the initial dye concentration and removal efficiency is inverse is ascribed to the finite number of adsorption sites that are active on the CCS composite surface; at higher dye loadings, these sites become increasingly preoccupied and ultimately arrive at saturation, rendering the adsorbent incapable of accommodating the rising quantity of dye molecules entering the system. Furthermore, intensified rivalry among dye molecules for the few available active sites at elevated concentrations further diminishes overall adsorption efficiency (Alhares et al., 2023). This trend is compatible with the findings reported for ZnO-based adsorbents and related composite materials, where removal effectiveness consistently declined as the initial dye concentration exceeded

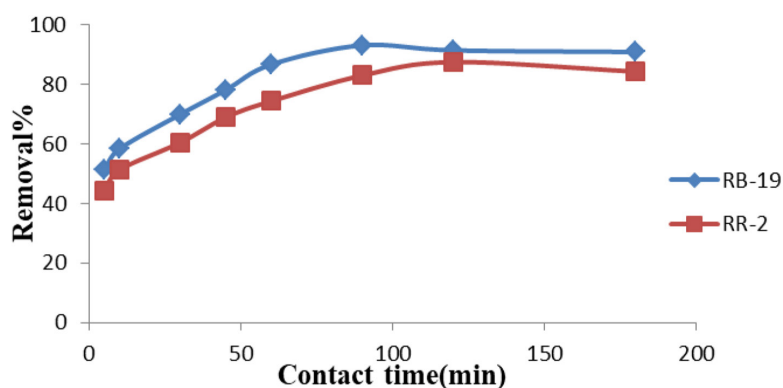


Figure 8. Effect of contact time on the percentage removal of RR-2 and RB-19 using coated chestnut shell

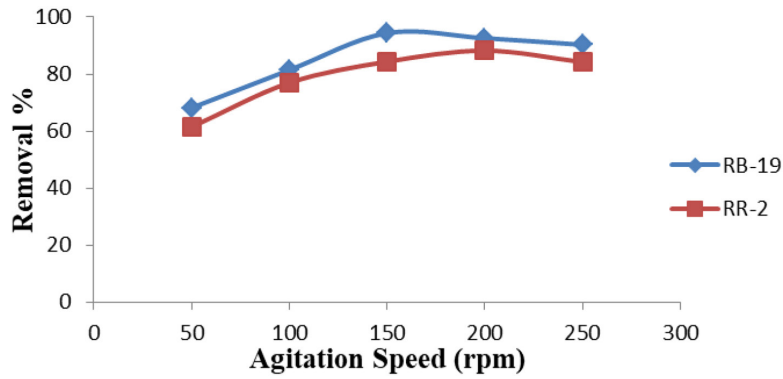


Figure 9. Effect of agitation speed on the adsorption process RR-2 and RB-19 using coated chestnut shell

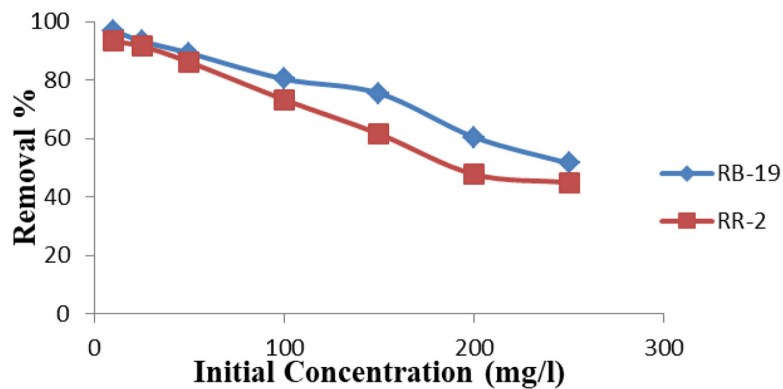


Figure 10. Effect of initial concentration on the adsorption process of RR-2 and RB-19 using coated chestnut shell

the ability for adsorption capacity of the adsorbent surface (Doondani et al., 2024).

Isotherm models for adsorption

The equilibrium method was examined employing Freundlich and Langmuir models. The Langmuir model is used to investigate homogeneous surface adsorption. The procedure is founded on the assumption that a saturated monolayer of dye solute on the external surface of the adsorbent, adsorption energy is constant, and adsorption occurs at homogeneous sites. Langmuir's model is explained by Equation 3 (Al-Ma'abreh et al., 2022).

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

The level of equilibrium for the dye in solution is represented by C_e (mg/L), the amount of dye adsorbed per unit mass of adsorbent at equilibrium is represented by q_e (mg/g), the maximum adsorption capacity of the adsorbent surface (monolayer capacity) is represented by q_m (mg/g), and the Langmuir constant, which represents the

energy of adsorption, is represented by K_L (L/mg) in Equation 4 (Abdelrazek et al., 2025).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

The C_e/q_e versus. The linear plot's slope and intercept were used to calculate K_L and q_m 's values. Adsorption on heterogeneous, multilayer surfaces is described by the Freundlich model (5), which has the following expression (Reda et al., 2025):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where: C_e (mg/L) is the equilibrium dye concentration in solution, K_f is the Freundlich constant linked to adsorption capacity, n is the Freundlich constant linked to adsorption intensity, and q_e (mg/g) is the quantity of dye adsorbed in relation to the mass of adsorbent at equilibrium, indicating the process's favorability.

The intercept and slope of the linear plot of $\log q_e$ vs $\log C_e$ yielded the values of K_f and n ,

respectively. Figures 11 and 12 show how the criteria on the Langmuir and Freundlich modeling were determined using the experimental data to fit for the isotherm models. Table 1 displays every parameter along with the correlation coefficients (R^2). The correlation coefficient values for the Langmuir are 0.9886 and 0.9955 for RR-2 and RB-19, respectively, and for Freundlich models they are 0.9561 and 0.9767 for RR-2 and RB-19, respectively; According to correlation coefficient values, the Langmuir model thus depicts better adsorption than the Freundlich model.

Models of kinetic analysis

Kinetic models of first and second order were utilized to assess the process of adsorption kinetics from the reactive dye onto the coated chestnut shell. When a model's correlation coefficient (R^2) is strong and close to unity, it is deemed to adequately reflect the process. Equation 6 provides the PFO (Gürses et al., 2023):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

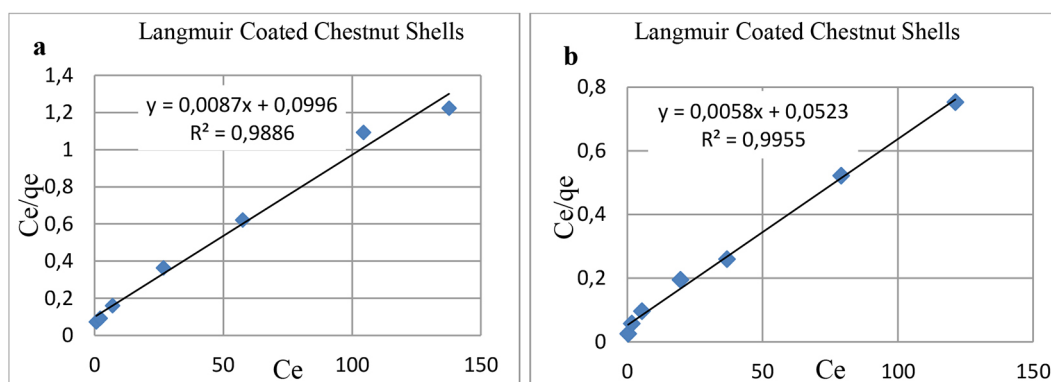


Figure 11. Langmuir model for RR2 adsorption onto coated chestnut shell (a), and RB-19(b)

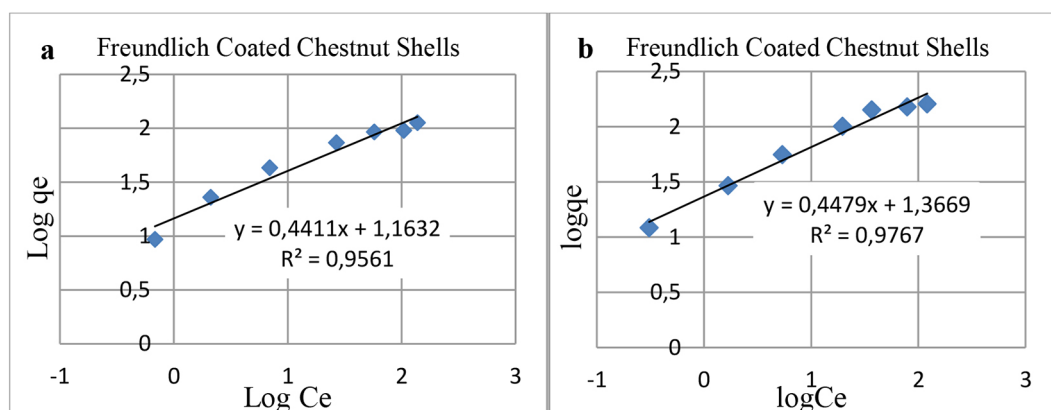


Figure 12. Freundlich model for RR2 adsorption onto coated chestnut shell (a), and RB-19(b)

Table 1. Parameters of the isotherm for RR-2 and RB-19 Reactive Dyes onto coated chestnut shell

Isotherm	Parameters	Red-2 Reactive (RR-2)	Reactive Blue (RB-19)
		CCS	CCS
Langmuir	q_m (mg/g)	114.942	172.413
	K_L	0.0875	0.1125
	R^2	0.9886	0.9955
Freundlich	$K_f((\text{mg/g})/(\text{mg/L})^{1/n})$	14.564	23.286
	n	2.2662	2.2333
	R^2	0.9561	0.9767

where: the amount of dye adsorbed in balance is denoted by q_e (mg/g), the quantity of adsorbed over time t by qt (mg/g), and the pseudo-rate constant of first order is denoted by k_1 (1/min).

As seen in Figure 13, both the intercept and slope of the linear graph of $\ln(q_e - qt)$ against t yielded the corresponding values of K_1 and q_e . Equation 7 shows the pseudo-second-order model: (Ahlawat et al., 2023).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where: the pseudo-second-order rate stability is denoted by K_2 (g/mg·min).

The slope and intercept show the linear plot of t/qt vs t , as displayed in Figure 14, which were used to calculate the values of K_2 and q_e . Table 2 summarizes the computed parameters and experimental findings. The pseudo-second-order

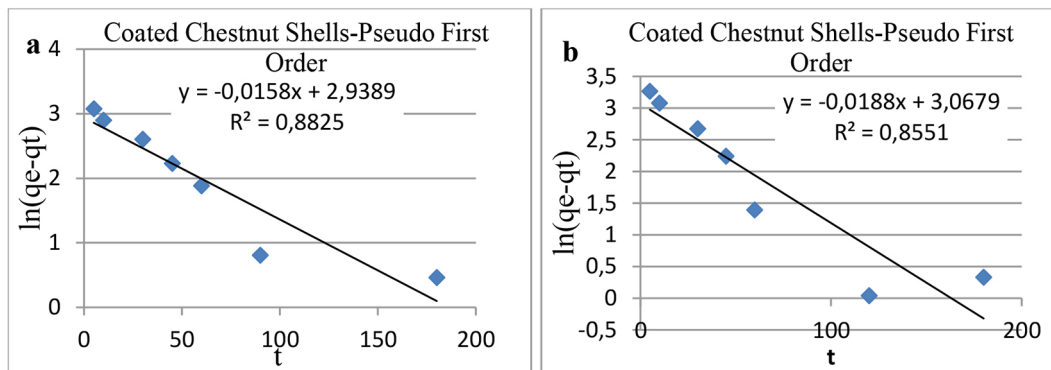


Figure 13. Sorption kinetic model Pseudo-first order RR-2 onto coated chestnut shell kinetic model (a) and Pseudo-first order RB-19 onto coated chestnut shell kinetic model (b)

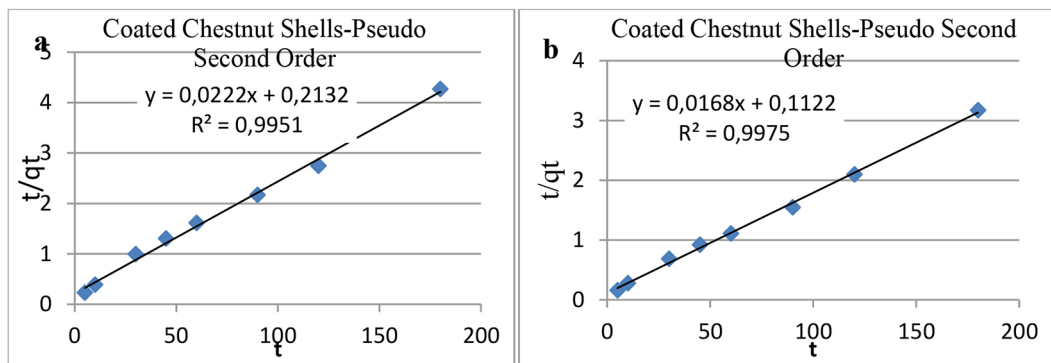


Figure 14. Sorption kinetic model (a) A pseudo-second order RR-2 onto coated chestnut shell kinetic model, and (b) A pseudo-second order RB-19 onto coated chestnut shell kinetic model

Table 2. Parameters of kinetic for RR-2 and RB-19 Reactive dyes onto coated chestnut shell

Kinetics model	Parameters	Reactive Red (RR-2)	Reactive Blue (RB-19)
		CCS	CCS
First-order pseudo	$q_{e(\text{exp.})}$ (mg/g)	43.745	58.2
	$q_{e(\text{cal.})}$	18.898	21.498
	K_1 (min ⁻¹)	0.01577	0.01881
	R^2	0.8825	0.8551
Second-order pseudo	$q_{e(\text{cal.})}$ (mg/g)	44.997	59.599
	K_2 (g/mg.min))	0.00231	0.00251
	R^2	0.9951	0.9975

model fit the experimental data more closely than the pseudo-first-order model, according to the correlation coefficient (R^2) values. Furthermore, chemisorption was the speed-of-limiting process regulating the adsorption process of reactive dyes onto chestnut shell coated with ZnO nanoparticles, as the estimated q_e was more in line with the pseudo-second-order approach. (Li et al., 2019).

CONCLUSIONS

In this investigation, the capacity of zinc oxide nanoparticle-coated chestnut shells to adsorb and remove Reactive Red-2 and Reactive Blue-19 dyes was explored. The adsorbent was characterized using advanced techniques including BET, XRD, FT-IR, and SEM. The outcomes revealed that the prepared adsorbent performed better overall when the shells were coated with ZnO nanoparticles, as opposed to the coating, which enhanced the adsorption capability and practical utilization. The isotherm study's findings indicated that the adsorbent surface had both homogeneous and heterogeneous adsorption sites that could interact with dye molecules. Both dyes showed the most favorable adsorption capabilities based on the Langmuir model. Furthermore, for each of the two dyes, the pseudo-second-order model fit the kinetic data quite well, indicating that the adsorption process is primarily chemical. The overall findings indicate that CCS is a powerful adsorbent with great promise for dye removal in the treatment of wastewater applications.

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