Textile & Leather Review

ISSN 2623-6281 | www.tlr-journal.com | 10.31881/TLR

Simultaneous Removal of Cadmium and Disperse Black-9 Dye Using Chemically Modified Rice Husk-Derived Activated Carbon

Md. Mukter Alam, Azmira Sultana, Md. Abdul Jabbar

How to cite: Alam MM, Sultana A, Jabbar MA. Simultaneous Removal of Cadmium and Disperse Black-9 Dye Using Chemically Modified Rice Husk-Derived Activated Carbon. Textile & Leather Review. 2024; 7:806-830. https://doi.org/10.31881/TLR.2024.063

How to link: https://doi.org/10.31881/TLR.2024.063

Published: 20 May 2024

Simultaneous Removal of Cadmium and Disperse Black-9 Dye Using Chemically Modified Rice Husk-Derived Activated Carbon

Md. Mukter ALAM[1], Azmira SULTANA[1], Md. Abdul JABBAR[2*]

[1]Institute of Leather Engineering and Technology, University of Dhaka, Dhaka–1209, Bangladesh

[2]Department of Chemistry, University of Dhaka, Dhaka–1000, Bangladesh

*jabbar@du.ac.bd

Article

https://doi.org/10.31881/TLR.2024.063

Received 21 March 2024; Accepted 13 May 2024; Published 20 May 2024

ABSTRACT

Heavy metals and organic dyes pose significant environmental concerns due to their persistence, toxicity, and tendency to accumulate in the food chain. These pollutants are often discharged from various industrial sources without proper management, resulting in unacceptable damage to the environment. The use of low-cost agricultural by-products can be a sustainable and green solution for the industrial effluent treatment process. In the present research, the effective removal of Cd^{2+} and disperse black–9 (DB–9) dye simultaneously was planned through the adsorption method utilizing specially activated carbon (AC) derived from rice husk. FTIR, SEM, and XRD were used to characterize the produced AC. The adsorption studies showed that approximately 88% of the dye DB–9 and 97% of Cd^{2+} were adsorbed by using optimal dosages of the AC, which were 16 g/L and 12 g/L, respectively. In addition, it was successfully demonstrated that Cd^{2+} adsorbed AC was capable of binding with DB–9 and also DB–9 adsorbed AC is capable of binding with Cd^{2+}. Therefore, a novel strategy for the simultaneous elimination of Cd^{2+} and DB-9 ideas was successfully implemented in the current study. In addition, equilibrium data were examined to assess the adsorbate-adsorbent system's isotherms. The Langmuir isotherm was determined to be the most well-fitting, with a maximum uptake of 11.48 mg/g. Thermodynamic study (ΔG^o) showed that the adsorption process was spontaneous, and the adsorption process followed pseudo-second-order kinetics.

KEYWORDS

cadmium, disperse back–9 dye, rice husk, activated carbon, removal, wastewater

INTRODUCTION

The emission of organic compounds and heavy metals are both significant contributing species that have detrimental effects on humans and the environment [1,2]. Dyes are widely utilized in diverse classes of sectors, including textiles, rubber, plastics, printing, leather, cosmetics, and the manufacturing of coloured goods [3]. Without proper treatment, these chemicals are sustainable, retain their colour and structure under sunlight, and resist microbial breakdown in wastewater treatment systems. As a result, they further perturb the ecosystem of the water [4,5]. Several dyes and their metabolites are harmful to aquatic plants, microbes, fish, and animals [6]. Dye waste exposure

has also been linked to an increased risk of asthma, eczema, and dermatitis, as well as multiple myeloma, leukaemia, and pulmonary oedema. Vomiting, hyperventilation, sleeplessness, profuse diarrhoea, salivation, and eye or skin infections are other side effects [7].

In addition, the issue of pollution from heavy metals stands as a paramount concern within the realm of contemporary environmental challenges. Numerous sectors generate and release waste materials that contain diverse heavy metals into the surrounding environment. These include metal extraction and processing, surface finishing, power generation, chemical manufacturing, fertilizer and pesticide production, steelmaking, electroplating, electrolysis, electro-osmosis, electronics production, the treatment of metal surfaces, the aerospace industry, and the installation of atomic energy [8]. Heavy metals have long been harmful to humans and the environment. Toxicity has the potential to impact various physiological processes, including those related to mental and central nervous system functioning, energy regulation, blood composition, pulmonary function, renal health, hepatic function, and the overall well-being of vital organs [9,10]. In such cases, acute cadmium poisoning can produce pulmonary oedema, vomiting, diarrhoea, hypertension, proteinuria, glucosuria, aminoaciduria, osteomalacia (bone softening), and renal consequences of proteinuria [11–14]. However, heavy metals and dyes can be removed using a variety of treatment methods, including oxidation-reduction, adsorption-desorption, precipitation-dissolution, ion exchange, and membrane processes [15] photocatalytic degradation [16], graphene oxide [17] assisted adsorption, and advanced oxidation processes [18]. Among the various recognized processes, adsorption is recognized as one of the leading technologies for water purification since it is efficient, cost-effective, and environmentally benign. Activated carbon is widely used as an adsorbent. Most of the activated carbon comes from various cellulose-containing materials [19]. Therefore, the utilization of activated carbon continues to be the predominant approach for dye and heavy metal removal through the process of adsorption [20].

Dye and heavy metals are removed from wastewater using activated carbon from various plants. These sources include agricultural waste [21,22]. There have been multiple studies conducted to investigate the potential use of different agricultural waste materials, such as rice husk [20,23,24], rice husk ash [25], coffee grounds [26], orange waste [27], agricultural and household wastes [21,28,29], sugarcane bagasse [30], coconut copra meal [31], wheat bran [32], cornstalk [33], fly ash [34], oil palm shell [35], and neem leaf [36] to remove heavy metals and dyes from wastewater. However, research was conducted to achieve the goal of removing individual components, such as dyes or metals. Very few studies have investigated the simultaneous removal of dye and heavy metal is achieved through the utilization of hierarchically porous carbons generated from banana peels [37], a nanocomposite of magnetic graphene oxide [38], and succinyl-grafted chitosan [39]. According to the earlier studies, no study has investigated the use of activated carbon made from rice husks to remove dye and heavy metals simultaneously from aqueous solutions. The aim of the present research is to aid in the

discovery of less expensive and sustainable adsorbent rice husk-derived activated carbon and its potential applications for the simultaneous removal of dispersed black–9 dye (Figure 1), DB–9 and Cd^{2+}. Rice husk, one of the least expensive agricultural residues, has 20% silica in an amorphous form among the several types of organic waste materials. Additionally, this substance has 60% volatile matter, 15% carbon, and 5% ash components. Rice husk ash contains 90% silica, and is very porous, light, and high surface area [40,41]. Due to its abundance in nature, rice either modified or unmodified drawn a lot of attention as an adsorbent for the removal of pollutants in recent years. DB-9 is often used in the dying operation of leather manufacture, and cadmium is used in the form of pigment for fastening, marking, and surfacing of material. The amount of Cd among the observed parameters is more significant after Cr and shows a potentially dangerous level of pollution [42,43]. Therefore, this research will be helpful to contributing greener technology to retain the sustainable clean environment goal.

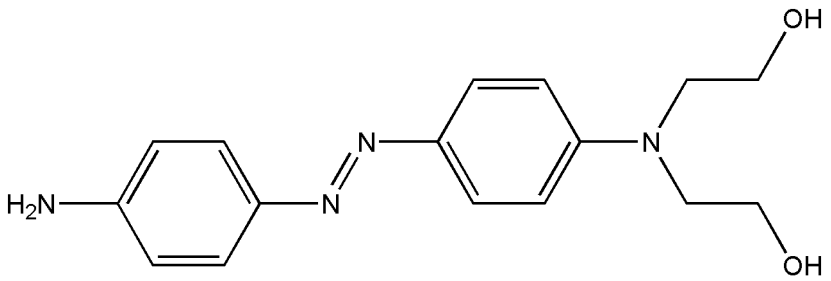

Figure 1. Structure of disperse black–9 dye ($C_{16}H_{20}N_4O_2$), DB–9

EXPERIMENTAL

Materials

Collection of samples

The rice husks used in this experiment were collected from a rice mill in Dhaka, Bangladesh The rice husks utilised in this study were obtained from a rice mill located in Dhaka, Bangladesh and then subjected to a thorough washing process using deionized water, repeated 8–10 times, to eliminate any contaminants present.

Chemicals

The cadmium metal salts ($CdCl_2.H_2O$) and analytical grade acetic acid (99.8%) used in this study were procured from Merck in Germany. Further, deionized water was used to dilute acetic acid to 5% to create activated carbon from rice husk.

Instruments

A variety of specialized instruments were used in the preparation and characterization of the activated carbon derived from rice husk, including a muffle furnace (Model no. SEL-HORN "R-3L", JP SELECTA group), HANNA pH meter, digital weight balance, shaker (Stuart Scientific, SMG model), UV-visible spectrophotometer (Model Spectro, UV-visible dual beam, UVS-2700, Labomed, Inc.), scanning electron microscope-SEM (Model: JSM-6490), Fourier Transformed Infrared Spectroscope-FTIR (84000S Shimadzu, Japan), and an Atomic Absorption Spectrophotometer-AAS (Model AA240, Varian) that measured the concentration of cadmium.

Methods

Preparation of rice husk-derived activated carbon

Activated carbons from rice husks were synthesized by a combination of chemical and physical activation processes following the modified procedure outlined by Pathiraja [44] and Naiya [45]. To prepare the AC, the washed rice husk was taken for oven drying at 110 °C for 3 hours; after drying, it was pulverized to make the ash into a uniform powder. Pulverized ash was then treated with 5% acetic acid for 24 hours. The next day, the mixture was filtered using filter paper. For carbonization, the impregnated ash was placed into a muffle furnace at 800 °C for 1 h. The samples were carbonized, taken out of the furnace to cool, and then crushed. Crushed samples of activated carbon were then washed in deionized water to eliminate any remaining inorganic particles and activating agents. The activated carbon-washed aqueous solution had a pH of about 6.5. After washing, activated carbon samples were dried for 6 hours at 105 °C and used for the adsorption research.

Preparation of adsorbate solution

A stock solution of 1000 ppm was prepared by dissolving 1.0 g of dispersed black–9 dye into deionized water. This stock solution was kept in a volumetric flask, and the additional solutions were prepared from it through careful successive dilution. The stock solutions of cadmium (Cd^{2+}) at a concentration of 200 ppm were prepared by dissolving 0.2 g of $CdCl_2.H_2O$ into deionized water, followed by dilution to a final volume of 1000 mL with water. The calibration curves and equilibrium studies for adsorption were conducted using a series of diluted solutions successively.

Preparation of DB-9 adsorbed activated carbon

The activated carbon, which was initially used to treat with the DB–9 dye solution, was filtered, and collected from filter paper. After filtration, the dye-treated activated carbon was dried in an oven at a temperature of 60 °C until dried, and a powder form of the activated carbon was obtained from the

removal of all moisture. This dye-adsorbed activated carbon (AC-Dye) was further used in different dosages to remove cadmium (Cd^{2+}).

Preparation of metal-adsorbed activated carbon

The activated carbon, which was initially used to remove Cd^{2+} in this research from solutions, was collected from filter paper and dried at a lower temperature of 60 °C in an oven until powder form was obtained and all moisture was removed. This metal-adsorbed activated carbon (AC-Metal) was further used in different dosages to remove DB–9 dye from the solution.

Adsorption studies of DB–9

The DB-9 dye solutions were combined with different dosages of adsorbents, and the resulting mixture was subjected to agitation using a mechanical shaker. The adsorption capabilities for various doses were assessed at specific time intervals while maintaining all other variables constant. The maximum absorption wavelength of the dye was measured using a UV-visible spectrophotometer to determine its residual concentration. For the determination of the DB–9 dye, a calibration curve was plotted with known concentrations of DB–9, using the Beer-Lambert formula ($A=\varepsilon lc$, where A is the absorbance, ε is the molar absorptivity, c is the concentration, and l=the path length of light through the test material cell).

Adsorption studies of cadmium

The adsorption capacity of adsorbents was determined by lab-scale experiments using the liquid-phase batch adsorption technique. Separate flasks containing 50 mL of Cd^{2+} (50 mg/L) were each treated with 1, 2, 4, 8, 12, 16, and 20 g/L of adsorbents and placed in a shaker and subjected to continuous agitation at a speed of 120 rpm for 30 minutes (t) (pH 6.5 was kept constant) at room temperature (T=25 °C). Thus, the metal solution may encounter the adsorbent sites. The samples were taken out of the shaker at different intervals and filtered to remove the suspended adsorbent. Atomic absorption spectroscopy was used to determine the concentration of metals in the solution. The following relationships [46,47] were used to determine the equilibrium adsorption amount uptake of the metal, q_e (mg/g). Where C_0=initial concentration (mg/L), C_e=equilibrium concentration, V=solution volume (l), and W=dry adsorbent mass (g).

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

$$\text{Amount Adsorbed } (q_e) = \frac{(C_o - C_e) \times V}{W} \quad (2)$$

The following diagram (Figure 2) demonstrates the application of activated towards the simultaneous removal of dispersed black–9 and Cd^{2+}.

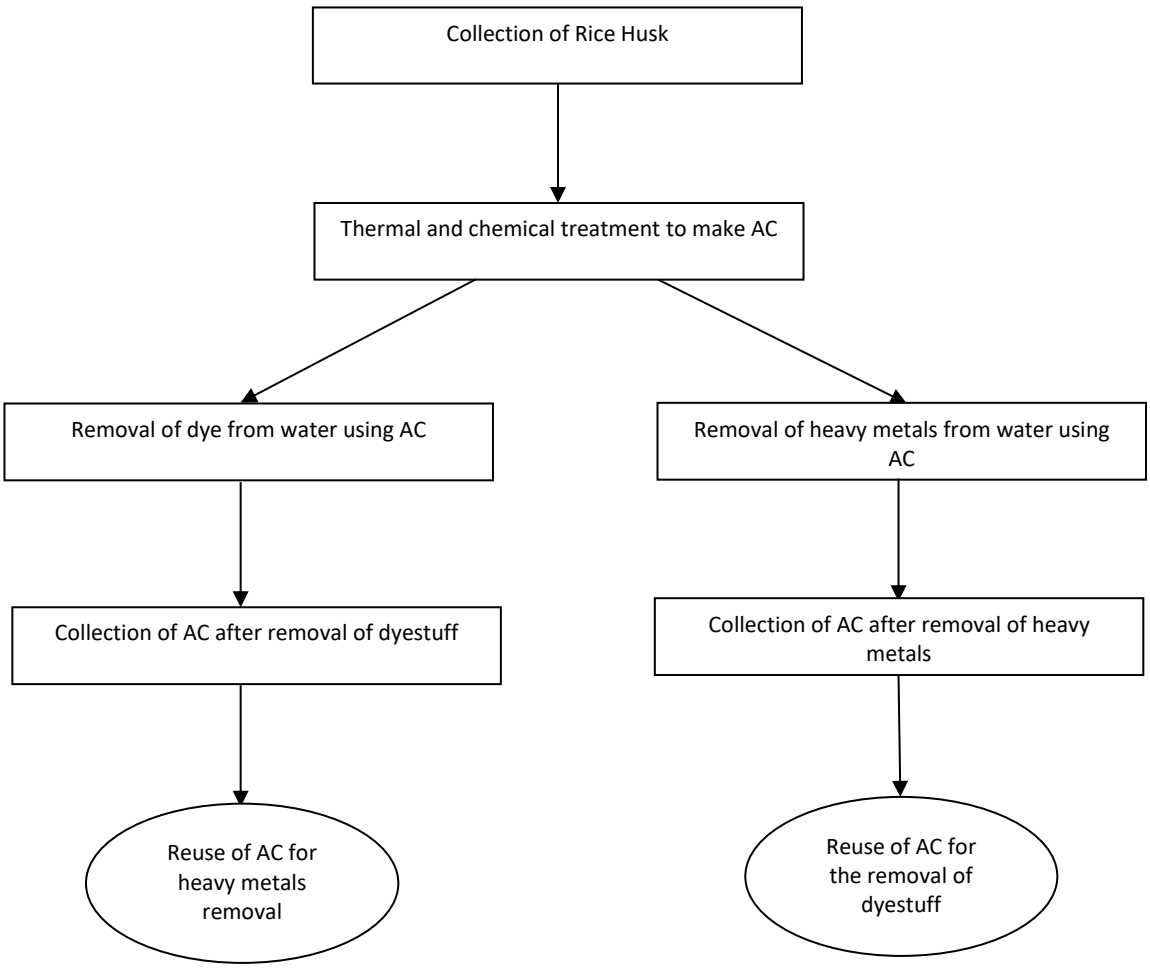

Figure 2. Flow diagram of the simultaneous removal of dye and metal

RESULTS AND DISCUSSION

SEM analysis

The surface morphology of rice husk activated carbon, as well as modified AC (dye-adsorbed), metal-adsorbed AC, and dye-metal-adsorbed AC, was examined using a SEM (Model: JSM-6490). Figure 3 shows the SEM micrograph of AC from rice husk, AC–Dye, AC–Metal, and dye–metal adsorbed AC (2000 X). Figure 3 (a) shows that the AC surface is quite rough and heavily corrugated. AC from rice husk offers a good chance for the dye or heavy metals to be adsorbed because it is a heterogeneous material comprised of particles with uneven forms, having significant layers with pores of different sizes. Dye (disperse black–9) molecules are adsorbed and attached at the outer surface pores of activated carbon, as shown in Figure 3 (b). The incorporation of metal (Cd^{2+}) into AC increases the

uniformity of the surface, as shown in Figure 3 (c). Moreover, Figure 3 (d) shows the metal–dye–AC (metal removal using AC–Dye) complex structure with a homogeneous surface due to metallic species incorporation, a change from Figures 3 (a), 3 (b), and 3 (c). The comparative SEM images show that metal and dyes were adsorbed on the surface of AC simultaneously.

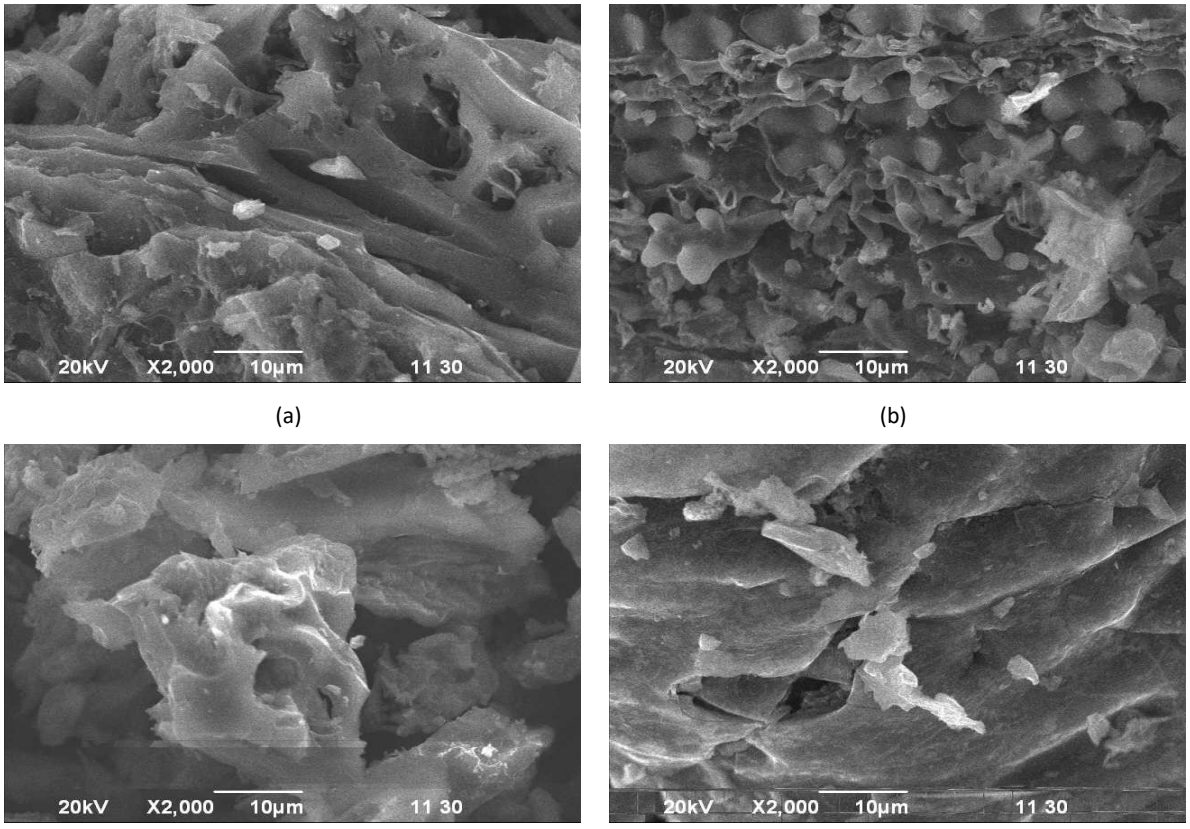

Figure 3. Comparative SEM images of (a) Activated Carbon (AC) from rice husk, (b) AC-Dye, (c) AC–Metal, and (d) Metal–Dye adsorbed AC

FTIR analysis

The FTIR spectra of activated carbon made from rice husk, DB-9, and dye-metal adsorbed activated carbon are displayed in Figure 4. The highest peak occurs near 3300 cm^{-1} due to the vibrational stretching of water and alcoholic groups. The peaks observed at 2925 cm^{-1} correspond to the C-H alkanes functional group, whereas the peak at 1609 cm^{-1} can be attributed to the stretching of the C=O bond, indicating the presence of a carbonyl group. In Figure 4 (a), the peaks at 1442 - 1217 cm^{-1} region indicate the existence of $–CH_2$ bending vibrations, while Figure 4(b)'s ring vibration between 1600 and 1350 cm^{-1} indicates the presence of aromatic rings [48]. As, the dyes utilized in the adsorption research and for surface modification of the activated carbon primarily consist of multifunctional groups, including fused benzene rings.

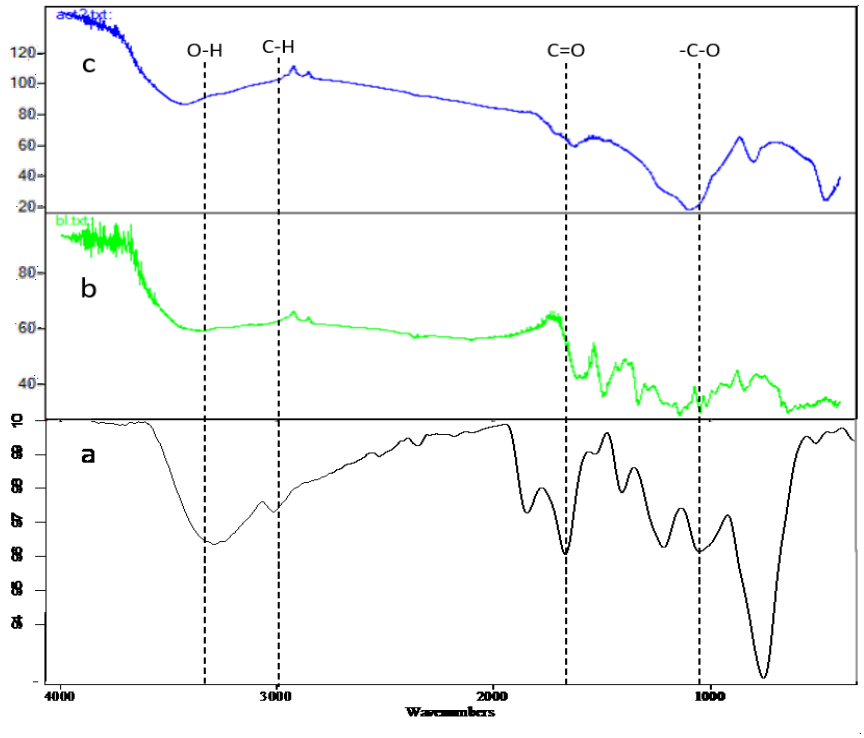

Figure 4. FTIR spectrum of (a) Activated Carbon (AC) from rice husk, (b) disperse black–9 Dye, and (c) Metal–Dye–AC

The produced activated carbon exhibited favourable surface characteristics due to the presence of several active sites for adsorption [49]. Figure 4 illustrates that the AC and dye-metal adsorbed AC exhibit instability in the alcoholic stretching vibrations, which range from 3400 cm^{-1} to 3300 cm^{-1}, as well as in the C=O stretching vibrations, which range from 1700 cm^{-1} to 1609 cm^{-1}. The notable differences in peak provide convincing evidence of the adsorption of dyes and metals, as shown by the changes in transmittance intensities presented in Figure 4 (c) compared to Figures 4 (a) and 4 (b). Following the adsorption process of the respective dye, the alkyl and aryl components become covalently bonded to the activated carbon, resulting in the disappearance of peaks located in the vicinity of the fingerprint region, as illustrated in Figure 4(c).

XRD analysis

The XRD experiment (Model: Ultima IV) was conducted to closely examine the surface alteration of AC. Figure 5 (a) shows the XRD spectrum of AC; Figures 5 (b) and 5 (c) show the XRD spectra of AC after the adsorption of AC–Metal and AC–Dye, respectively; and Figure 5 (d) shows the XRD spectra of Metal–Dye–AC. Sharp peaks with maximal intensity at 2θ=21.5 and 24.9 were identified for the AC, showing that the rice husk-generated AC has an amorphous character [20]. The well-defined, distinct peaks were found for AC–Metal at 2θ=21.7, 26.52, 38.78, 60.07, and for AC–Dye at 2θ=21.31 shown in Figures 5 (b) and 5 (c), respectively. The similarity between Spectra 5 (b) and 5 (d) can be attributed to

the existence of metal ions, as evidenced by the 2θ–value [50] and indicating amorphous nature with a small crystalline region, which may be the result of reactions of DB–9 and Cd^{2+} with AC [51]. Adsorbed on the AC surface, the DB-9 may act as an additional complexion agent, amplifying its affinity for heavy metals. The compound's almost flat shape, with two aromatic rings, enables it to function as an electron donor when interacting with Cd^{2+} [34].

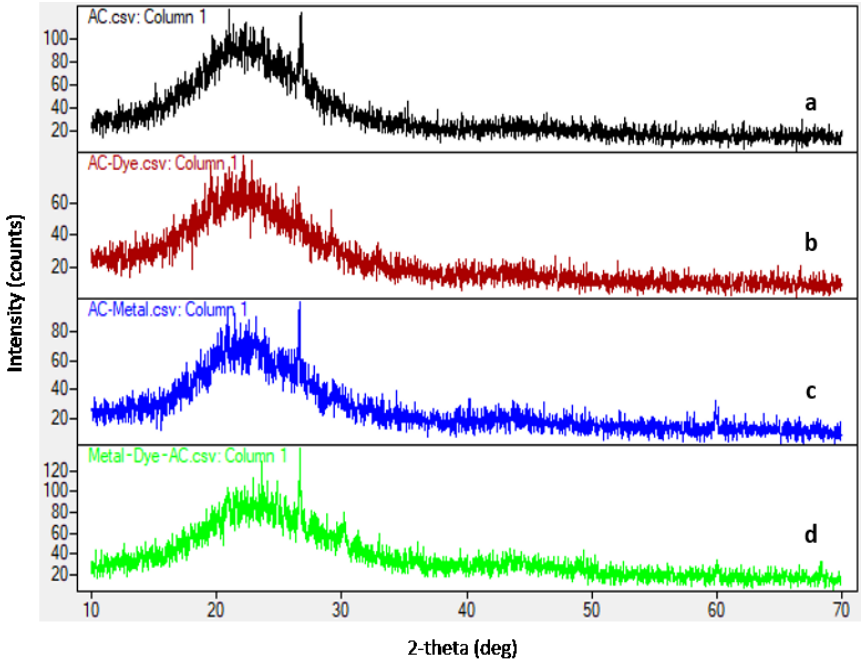

Figure 5. XRD spectra of (a) AC, (b) AC–Metal, (c) AC–Dye, and (d) Metal–Dye–AC

Comparison of DB–9 dye and Cd^{2+} removal using AC

According to Figure 6, increasing dosages remove more disperse black–9 and Cd^{2+}. Increases in adsorption surfaces and sites are responsible for the higher percentage of removal [52]. There was no drastic increase in removal efficiency on increasing the dosage of adsorbent beyond 16 g/L of activated carbon. This may be a consequence of black–9 and Cd^{2+} reaching an equilibrium against the adsorbent, which limits further adsorption [53]. Therefore, from an economic perspective, 16 g/L was the optimum dosage for the removal of disperse black–9 was about 88% and 12 g/L with around 97% removal of Cd^{2+}.

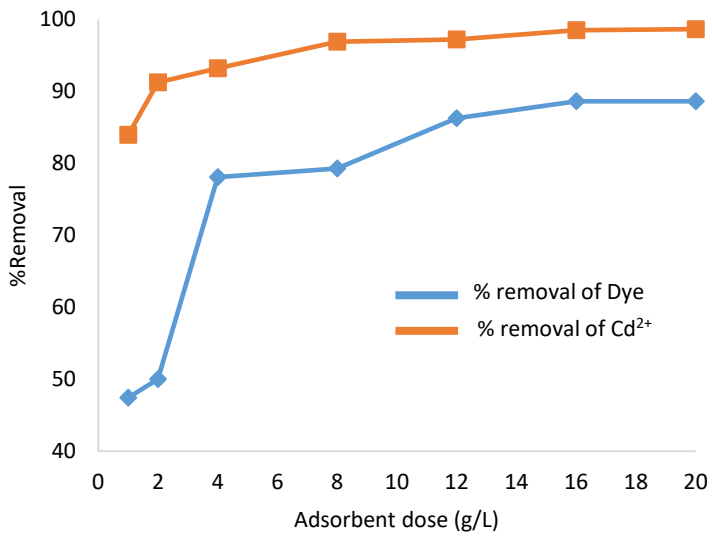

Figure 6. % of disperse black–9 and Cd^{2+} removal using AC, varying adsorbent dosage; C_0=50 mg/L, rpm=120, t=30 min, T=25 °C, and pH=6.5

Comparison of DB–9 dye removal using AC and AC–Metal

A comparable experiment was conducted to demonstrate the efficacy of the removal of DB-9 with bare AC and AC–metal adsorbed species. This experiment was repeated using AC after Cd^{2+} adsorption to assess the potential binding capacity of the metal with the dye and to determine the feasibility of reusing activated carbon after metal adsorption on its surface.

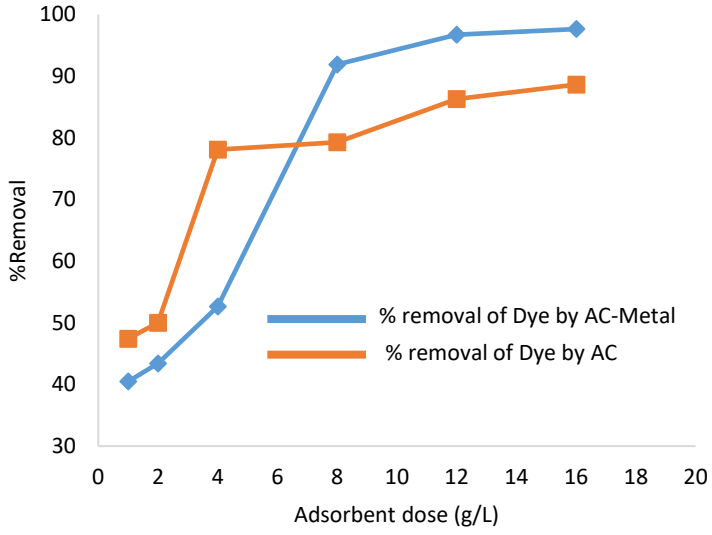

Figure 7. % of disperse black–9 removal with AC–Metal and AC; C_0=50 mg/L, rpm=120, t=30 min, T=25 °C, and pH=6.5

Adsorbent dosage was also changed within this range (1, 2, 4, 8, 12, and 16 g/L). From the data, a higher dose results in a greater percentage of DB–9 being removed like AC alone. Figure 7

demonstrates a notably higher removal efficiency for DB–9 when using AC–Metal compared to AC alone. The presence of positively charged adsorbates following the removal of Cd^{2+} ions may have a significant impact on the adsorption of DB–9 dye [38]. The removal efficiency of 12 g/L was found to be 96.70%, surpassing the removal efficiency of AC, which was seen to be 86.29% for the same mass of 12 g/L.

Comparison of cadmium (Cd^{2+}) removal using AC and AC–Dye

Activated carbon, previously used to remove the DB–9 dye and referred to as AC–Dye for the removal of Cd^{2+}, was utilized in the batch experiment. Effects of doses of AC–Dye on the adsorption of Cd^{2+} ions were conducted at 50 mg/L initial metal concentration, while the AC–Dye doses were varied from 1 g/L to 20 g/L, respectively. Figure 8 depicts the relationship between adsorbent dosages and the rate at which Cd^{2+} is removed. The results show that as the concentration of AC–Dye was increased, Cd^{2+} was removed at a faster rate. When both AC and AC–Dye are dosed similarly, AC is more effective at removing Cd^{2+}. However, AC–Dye outperforms AC when using an adsorbent dosage of 16 g/L. The lower removal efficiency may be due to the lower binding propensity of Cd^{2+} with AC–Dye. Based on these results, the best option to remove Cd^{2+} (about 90%) is 12 g/L at a concentration of 50 mg/L of AC–Dye from an economical perspective. Subsequently, the impact of contact time and starting concentration was examined concerning the adsorption of Cd^{2+} using AC-Dye.

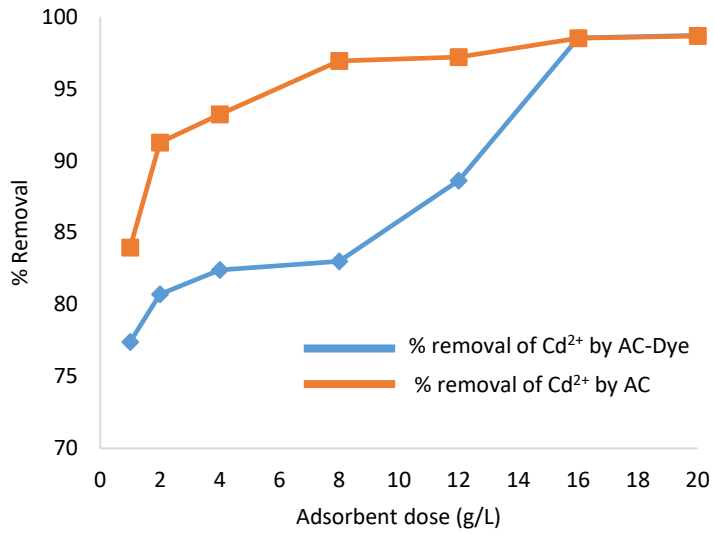

Figure 8. % of removal of Cd^{2+} with AC and AC–Dye; C_0=50 mg/L, rpm=120, t=30 min, T=25 °C, and pH=6.5

Effect of initial concentration

The adsorption of Cd^{2+} was investigated throughout a range of concentrations, specifically from 40 to 100 mg/L with the other five variables held constant (p=6.5, dosage=12 g/L of AC–Dye, rpm=120, T=25

°C, and t=30 min). When Cd^{2+} concentrations were low, the adsorbent quickly absorbed metal ions, but it slowed down after concentrations approached 60 mg/L (Figure 9). The rapid increase in metal uptake at first is believed to result from interactions between Cd^{2+} and the available active sites of the adsorbent [54,55]. The % removal relatively decreased with continuously increasing Cd^{2+} concentration. At a concentration of 90 mg/L, the adsorption exhibited a lower level (82.7%) in comparison to lower concentrations (40 mg/L) of Cd^{2+}. At higher concentrations, a greater number of Cd^{2+} ions remain unabsorbed in the solution due to the saturation of binding sites. This is because there is more metal ion competition for a limited number of active sites on the adsorbent's surface (Figure 10). Increases in metal ions, while maintaining the adsorbent dosage, rapidly saturate the available active sites [53].

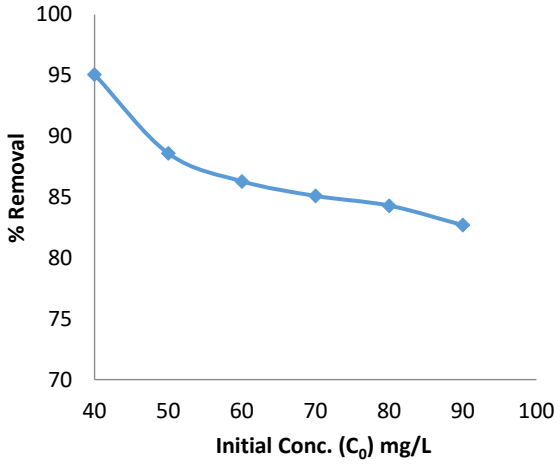

Figure 9. Effect of initial concentration at optimum doses on % removal of Cd^{2+}; dosage=12 g/L of AC–Dye, rpm=120, t=30 min, T=25 °C, and pH=6.5

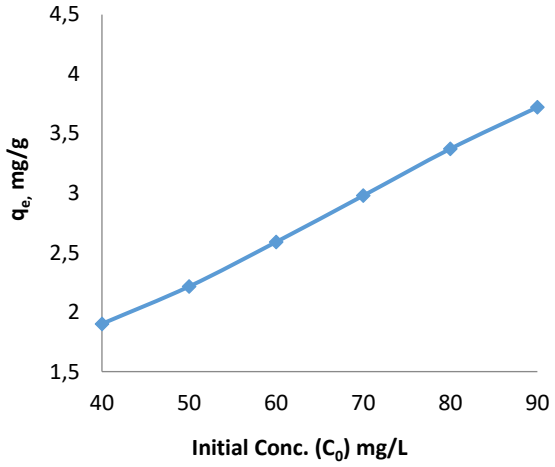

Figure 10. Effect of initial concentration at adsorption capacity for Cd^{2+}

Effect of contact time

The removal of Cd^{2+} was investigated throughout a time range of 5 to 35 minutes while keeping the other five variables constant (pH=6.5, dosage=12 g/L of AC–Dye, rpm=120, T=25 °C, and C_0=50 mg/L). It has been noticed that adsorption increases with contact time. Adsorption increased exponentially in the first 10 minutes until the maximum slope was reached in the next 10 minutes. This may have happened as a result of the large number of binding sites that were available on the adsorbent during the first stage [53]. After a considerable amount of time had passed, steady-state equilibrium was attained (Figure 11). This phenomenon may arise from the repulsive forces exerted on the solid surface by the molecules of the adsorbate. Consequently, the rate at which mass is transferred between solid and liquid phases diminishes as time progresses. In addition, the metal ions must pass through the pores much more deeply and forcefully, which causes the adsorption process to slow down in later stages [24]. However, about 90% of Cd^{2+} has been removed from aqueous solution within 30 minutes.

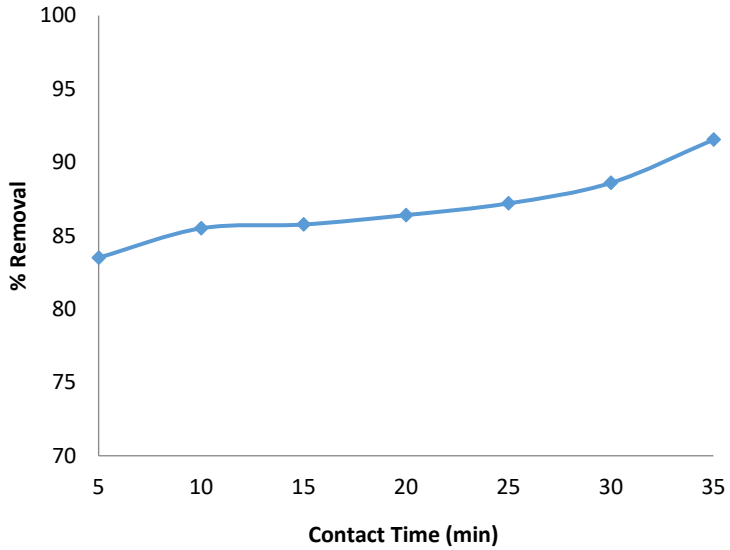

Figure 11. Effect of contact time on % removal of Cd^{2+} with AC–Dye; dosage=12 g/L of AC–Dye, C_0=50 mg/L, rpm=120, T=25 °C, and pH=6.5

Adsorption isotherms

The equilibrium that exists between the concentration of adsorbate in solution and the amount that is absorbed by the adsorbent's surface at a specific temperature is represented by isotherms. In order to best fit the data obtained from this experiment, the Langmuir and Freundlich models were utilized. The adsorption capacity of the adsorbent expressed as a function of its mass at equilibrium (mg/g) is used as a parameter q_e in all the models.

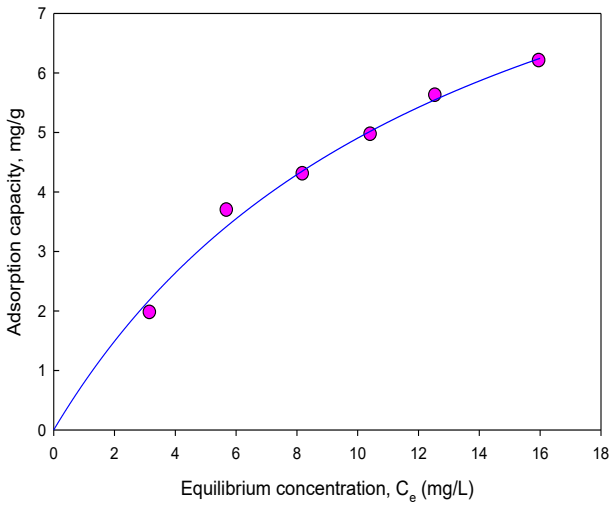

Figure 12. Fitting of adsorption data to Langmuir equation; dosage=12 g/L, t=30 min, T=25 °C, and pH=6.5

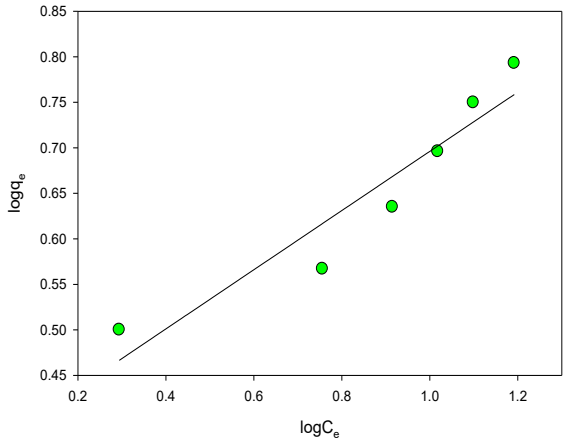

Figure 13: Fitting of adsorption data to Freundlich equation; dosage=12 g/L, t=30 min, T=25 °C, and pH=6.5

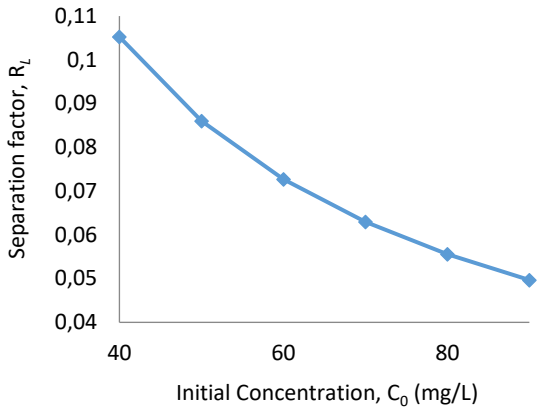

Figure 14. Separation factor of adsorption on AC–Dye for Cd^{2+}

Table 1. Langmuir and Freundlich isotherm Parameters for Cd^{2+}

Langmuir			Freundlich		
$q_{max,}$ (mg/g)	$K_{L,}$ (L/mg)	R	$K_{f,}$ ($mg^{1-(1/n)}L^{1/n}g^{-1}$)	1/n	R
11.480	0.075	0.994	2.349	0.325	0.947

Langmuir model

The Langmuir theory assumes adsorption creates a monolayer without adsorbate-adsorbate interaction. Adsorption occurs at distinct places within the adsorbent material. Each site preserves one chemical molecule of the specified chemical. The equilibrium adsorbent has limited adsorbate capacity. A saturated condition prevents further adsorption. Every site exhibits identical characteristics and possesses equivalent levels of energy. The adsorbent exhibits structural homogeneity [56–58]. The following linear equation represents the Langmuir model.

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (3)$$

Where q_e is the adsorption capacity (mg/g), and C_e is the solution's equilibrium concentration (mg/L). The maximal adsorption capacity (mg/g) is denoted by q_m, and Langmuir constant, K_L (L/mg).

Freundlich model

The most fundamental model for multilayer adsorption is the Freundlich isotherm. It results in an empirical equation that characterizes the system's heterogeneity. Adsorption on heterogeneous

surfaces, where molecules interact with one another, is studied using this model [7]. The following equation describes the Freundlich isotherm:

$$\log q_e = logK_f + {}^{1}/_{n}\, logC_e \quad (4)$$

Where K_f and n represent adsorption capacity ($mg^{1-(1/n)}L^{1/n}g^{-1}$) and intensity, respectively. The magnitude of n indicates adsorption favorability. Where, 1/n=1 shows linearity, 1/n<1 a Freundlich isotherm, and 1/n>1 cooperative adsorption [45,59]. Data were analyzed through the Sigma Plot (Version 10) program, where the Levenberg-Marquardt algorithm was used for the non-linear curve fit and shown as the better-fit solid line in Figure 12, and Figure 13 respectively for Langmuir and Freundlich isotherm. Different parameters that were described in the curve-fitted data are tabulated in Table 1. In contrast to the Freundlich model, the Langmuir model has a substantially higher cadmium regression correlation coefficient (R). Thus, the Langmuir model better described the adsorption data. The linear nature of the plot suggests the formation of a uniform layer of metal ions on the outer surface of the adsorbent [53] with a maximum adsorption capacity for Cd^{2+} is 11.48 mg/g. The equation equation describes the important Langmuir dimensionless constant separation factor, R_L:

$$R_L = \frac{1}{(1+K_L C_0)} \quad (5)$$

Where the initial concentration in mg/L is C_0. Moreover, the nature of the adsorption process can be inferred from the separation factor R_L value as follows [20,45,49]. If,

$R_L=0$, Irreversible adsorption

$R_L=1$, Linear adsorption

$R_L>1$, Unfavourable adsorption

$0<R_L<1$, Favourable adsorption

The R_L value for the Cd^{2+} adsorption on AC–Dye at the initial concentration of 40 mg/L is about 0.105. The data obtained represent favourable adsorption of Cd^{2+} on AC–Dye. As, the $R_L \approx 0$ (Figure 14), suggests that the irreversible Cd^{2+} adsorption by AC–Dye. Additionally, Table 2 summarizes a comparison of the current adsorbent's adsorption capabilities for the removal of Cd^{2+} ions with those of alternative adsorbent materials that have already been described in the literature. The effectiveness of the AC–Dye exhibits comparable performance even after dye removal.

Table 2. Comparative analysis of the adsorption capabilities of different adsorbents used to remove Cd^{2+}

Adsorbent Name	pH	q_m (mg/g)	References
Magnetic graphene oxide nanocomposite	6.0	59.69	[38]
Fly ash	5.3	6.36	[34]
Rice husk ash	6	6.57	[25]
Cornstalk	7	12.73	[33]
Coconut copra meal	5.5	1.84	[32]
Wheat bran	8.6	12.5	[31]
Acid-modified rice husk	6.5	11.48	This study

Batch kinetic studies of adsorbate

The controlling mechanisms of adsorption processes, such as mass transfer and chemical reaction, were investigated in this work using two popular kinetic models: pseudo-first order and pseudo-second order. The following equations reflect pseudo-first and second-order kinetic models [49,60–62].

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e 2} + \frac{t}{q_e} \quad (7)$$

where k_1 (min^{-1}) is the pseudo-first-order adsorption rate constant, k_2 (g mg^{-1} min^{-1}) represents the pseudo-second-order adsorption rate constant, and q_e and q_t are the amounts of Cd^{2+} adsorbed on adsorbent (mg/g) at equilibrium and at the time, t, respectively. The rate constants, k_1 and k_2 of Cd^{2+} under varying concentration ranges were ascertained using straight-line plots of log (q_e−q_t) against t and straight-line plots of t/q_t against t, respectively. The correlation coefficients (R) were calculated for the Cd^{2+} adsorption on rice husk-derived AC after dye adsorption, along with the uptake capacity (q_e) and the pseudo-first-order rate constants, k_1 (min^{-1}) and pseudo-second-order rate constants, k_2 (g mg^{-1} min^{-1}). These values were obtained using equations 6 and 7 and are shown in Table 3. Figures 15 and 16 illustrate the linear plots of log (q_e−q_t) against t and t/q_t against t, respectively, which were employed to verify the relevant kinetic models.

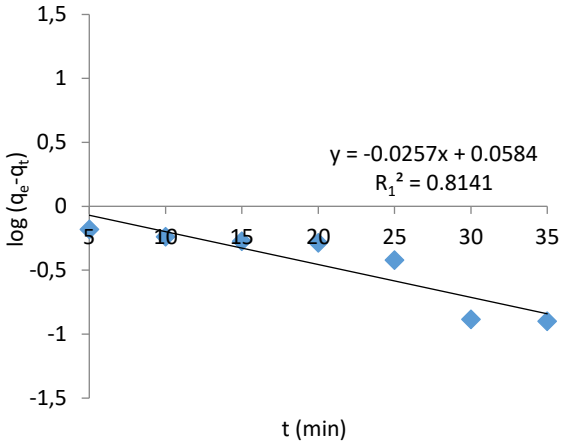

Figure 15. Pseudo first-order kinetic plots for Cd^{2+} adsorption on AC–Dye; dosage = 12 g/L, t= 30 min, T=25 °C, and pH=6.5

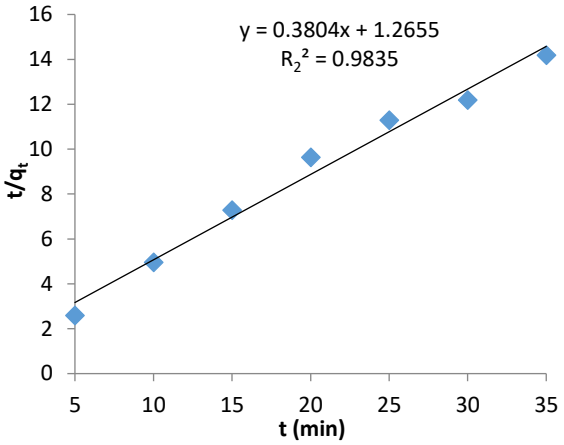

Figure 16. Pseudo second order kinetic plots for Cd^{2+} adsorption on AC–Dye; dosage = 12 g/L, t= 30 min, T=25 °C, and pH=6.5

Table 3. Rate kinetics for adsorption of Cd^{2+} on AC–Dye

C_o (mg/L)	k_2 (g mg^{-1} min^{-1})	q_e (mg/g)	R_2^2	k_1 (min^{-1})	q_e (mg/g)	R_1^2
50	0.214	2.59	0.997	0.055	0.86	0.9044

According to the correlation coefficients presented in Table 3, the regression coefficients for the pseudo-second-order are greater for the adsorbent compared to those of the pseudo-first order. This kinetic model could therefore provide a better description of the Cd^{2+} adsorption kinetics data obtained by AC–Dye. Previous researchers have also observed similar trends of results [38,63]. The adsorption behavior is expected to involve valency forces, where electrons are shared between Cd^{2+} and AC–Dye [49].

Adsorption thermodynamics

To gain a better understanding of the behaviour of Cd adsorption, the adsorption reaction's Gibbs free energy (ΔG^o) was determined by using the following equations.

$$K_L = {}^{q_e}/_{C_e} \quad (8)$$

$$\Delta G^0 = -RTlnK_L \quad (9)$$

where the molar gas constant is R=8.314 J/(K mol), the adsorption temperature is T (K), and K_L (L/mg) is the thermodynamic distribution constant at equilibrium. By employing equation 9, the value of ΔG^o

that was determined to be -1.178 kJ/mol was determined. It is confirmed by the negative result that the adsorption process is spontaneous and thermodynamically favourable.

LIMITATIONS AND FUTURE PROSPECTS

In this simultaneous removal process, the prepared AC and AC-Dye both have shown excellent performance. By using an FTIR, SEM, and XRD analyzer, the prepared AC was investigated. The measurement of activated carbon's unique surface areas could lead to comprehending its adsorption capabilities. The effects of contact time, adsorbate concentration, and adsorbent dosage on the adsorption process were examined in batch investigations. The adsorption process is sensitive to changes in temperature and pH; therefore, those factors could also be studied. This will assist in determining studies related to thermodynamics other than Gibbs free energy (ΔG^o). The results indicate a higher removal efficiency and equilibrium data were analyzed to evaluate the isotherms of the adsorbate-adsorbent system. Additionally, two popular kinetic models, pseudo-first order and pseudo-second order, were utilised to investigate the mechanism that controls adsorption processes in this work. Other adsorption kinetic models, such as the Boyd model, which determines whether film diffusion is the rate-controlling step, the Intra-particle diffusion (IP) model, which looks at the rate-limiting step during adsorption, and the Elovich model, which predicts mass and surface diffusion, activation, and deactivation energy of a system, could also be used. The regeneration of the adsorbent is a crucial factor in determining the adsorption process's economic viability. The adsorption process will be more economically advantageous if the material can be recycled and used again after the first phase [49]. In the future, the reusability and adsorption capacity of the AC and AC-Dye could be analyzed.

CONCLUSION

In this paper, the activated carbon from rice husk was successfully utilized for the simultaneous removal of the dye DB–9 and heavy metal (Cd^{2+}) from an aqueous solution. A higher adsorbent (activated carbon) dosage was shown to result in a higher percentage of DB–9 and Cd^{2+} removal about 88% and 97%, respectively. Furthermore, the research involved investigating the impact of varying adsorbent dosages, contact time, and initial concentration on the removal effectiveness of Cd^{2+} using surface-modified activated carbon (AC–Dye). The results indicate a higher removal efficiency which is about 90%. Both the Langmuir and the Freundlich models were used to depict the adsorption isotherm, however, the Langmuir isotherm provided a better fit with a maximum adsorption of 11.48 mg/g, indicating that the adsorption process was irreversible. The kinetics data indicate that the adsorption of Cd^{2+} conformed well to the pseudo-second-order kinetic model, with a regression coefficient of

0.997. Furthermore, based on thermodynamic analysis, it was revealed that the adsorption process is both spontaneous and favourable. This study concludes that rice husk-derived AC removes dye and metal ions simultaneously from aqueous solutions efficiently. This research will lay the groundwork for designing an efficient and cost-friendly adsorption system.

Author Contributions

Conceptualization – Jabbar MA, Alam MM and Sultana A; methodology – Jabbar MA, Alam MM and Sultana A; formal analysis – Alam MM and Sultana A; investigation – Alam MM and Sultana A; resources – Jabbar MA, Alam MM and Sultana A; writing-original draft preparation – Alam MM and Sultana A; writing-review and editing – Alam MM and Jabbar MA; visualization – Jabbar MA, Alam MM and Sultana A; supervision – Jabbar MA. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

Acknowledgements

The authors would like to acknowledge the financial support of this research work from the Centennial Research Grant (Ref.: Admin–3/47377) of the University of Dhaka. The authors would also like to acknowledge the Institute of Leather Engineering and Technology, Department of Chemistry, and Department of Soil, Water, and Environment of the University of Dhaka for giving us scope to carry out the research.

REFERENCES

[1] Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN. Toxicity, mechanism and health effects of some heavy metals. Interdisciplinary Toxicology. 2014; 7(2):60–72. https://doi.org/10.2478/intox–2014–0009

[2] Nguyen KT, Navidpour AH, Ahmed MB, Mojiri A, Huang Y, Zhou JL. Adsorption and desorption behavior of arsenite and arsenate at river sediment-water interface. Journal of Environmental Management. 2022; 317:115497. https://doi.org/10.1016/j.jenvman.2022.115497

[3] Rai HS, Bhattacharyya MS, Singh J, Bansal TK, Vats P, Banerjee UC. Removal of dyes from the effluent of textile and dye stuff manufacturing industry: A review of emerging techniques with reference to biological treatment. Critical Reviews in Environmental Science and Technology. 2005; 35(3):219–238. https://doi.org/10.1080/10643380590917932

[4] Georgiou D, Aivazidis A, Hatiras J, Gimouhopoulos K. Treatment of cotton textile wastewater using lime and ferrous sulfate. Water Research. 2003; 37(9):2248–2250. https://doi.org/10.1016/S0043–1354(02)00481–5

[5] Ogugbue CJ, Sawidis T. Bioremediation and Detoxification of Synthetic Wastewater Containing Triarylmethane Dyes by *Aeromonas hydrophila* Isolated from Industrial Effluent. Biotechnology Research International. 2011; 2011:967925.https://doi.org/10.4061/2011/967925

[6] Üstün GE, Solmaz SKA, Birgül A. Regeneration of industrial district wastewater using a combination of Fenton process and ion exchange—A case research. Resources, Conservation and Recycling. 2007; 52(2):425–440. https://doi.org/10.1016/j.resconrec.2007.05.006

[7] Foo KY, Hameed BH. Decontamination of textile wastewater via TiO_2/activated carbon composite materials. Advances in Colloid and Interface Science. 2010; 159(2):130–143. https://doi.org/10.1016/j.cis.2010.06.002

[8] Wang JL, Chen C. Biosorbents for heavy metals removal and their future. Biotechnology Advances. 2009; 27(2):195–226. https://doi.org/10.1016/j.biotechadv.2008.11.002

[9] Fu S, Xi S. The effects of heavy metals on human metabolism. Toxicology Mechanisms and Methods. 2020; 30(3):167-176. https://doi.org/10.1080/15376516.2019.1701594

[10] Musilova J, Arvay J, Vollmannova A, Toth T, Tomas J. Environmental Contamination by Heavy Metals in Region with Previous Mining Activity. Bulletin of Environmental Contamination and Toxicology. 2016; 97(4):569–75. https://doi.org/10.1007/s00128-016-1907-3

[11] Ebau W, Rawi CSM, Din Z, Al-Shami SA. Toxicity of cadmium and lead on tropical midge larvae, Chironomus kiiensis Tokunaga and Chironomus javanus Kieffer (Diptera: Chironomidae). Asian Pacific Journal of Tropical Biomedicine. 2012; 2(8):631–634. https://doi.org/10.1016/S2221–1691(12)60110–5

[12] Malik A. Metal bioremediation through growing cells. Environment International. 2004; 30(2):261–278. https://doi.org/10.1016/j.envint.2003.08.001

[13] Mansour SA, Gad MF. Risk assessment of pesticides and heavy metals contaminants in vegetables: A novel bioassay method using Daphnia magna Straus. Food and Toxicology. 2010; 48(1):377–389.https://doi.org/10.1016/j.fct.2009.10.026

[14] Zhang W, Liu X, Cheng H, Zeng EY, Hu Y. Heavy metal pollution in sediments of a typical mariculture zone in South China. Marine Pollution Bulletin. 2012; 64(4):712–720. https://doi.org/10.1016/j.marpolbul.2012.01.042

[15] Areco MM, Hanela S, Duran J, Dos Santos Afonso M. Biosorption of Cu(II), Zn(II), Cd(II) and Pb(II) by dead biomasses of green alga Ulva lactuca and the development of a sustainable matrix for adsorption implementation. Journal of Hazardous Materials. 2012; 213–214(0):123–132. https://doi.org/10.1016/j.jhazmat.2012.01.073

[16] Li S, Lin Q, Liu X, Yang L, Ding J, Dong F, Li Y, Irfan M, Zhang P. Fast photocatalytic degradation of dyes using low-power laser-fabricated Cu_2O–Cu nanocomposites. RSC Advances. 2018; 8(36):20277–20286. https://doi.org/10.1039/C8RA03117G

[17] Deb AK, Sultan, MdZ, Chowdhury, M, Shaikh AA, Sarker MdR, Hossain, MdI. Synthesis and Application of Graphene Oxide (GO) for Removal of Cationic Dyes from Tannery Effluents. Textile & Leather Review. 2020; 3(3):146–157. https://doi.org/10.31881/TLR.2020.12

[18] Bethi B, Sonawane SH, Bhanvase BA, Gumfekar SP. Nanomaterials-based advanced oxidation processes for wastewater treatment: A review. Chemical Engineering and Processing-Process Intensification. 2016; 109:178–189. https://doi.org/10.1016/j.cep.2016.08.016

[19] Nor NM, Lau LC, Lee KT, Mohamed AR. Synthesis of activated carbon from lingo cellulosic biomass and its applications in air pollution control—A review. Journal of Environmental Chemical Engineering. 2013; 1(4):658–666. https://doi.org/10.1016/j.jece.2013.09.017

[20] Mondal MdIH, Chandra Chakraborty S, Rahman MS, Marjuban SMH, Ahmed F, Zhou JL, et al. Adsorbents from rice husk and shrimp shell for effective removal of heavy metals and reactive dyes in water. Environmental Pollution. 2024; 346:123637. https://doi.org/10.1016/j.envpol.2024.123637

[21] Hegazi HA. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. HBRC Journal. 2013; 9(3):276–282. https://doi.org/10.1016/j.hbrcj.2013.08.004

[22] Mojiri A, Zhou JL, Ratnaweera H, Ohashi A, Ozaki N, Aoi Y, et al. Performance optimization of a chitosan/anammox reactor in nitrogen removal from synthetic wastewater. Journal of Environmental Chemical Engineering. 2021; 9(3):105252. https://doi.org/10.1016/j.jece.2021.105252

[23] Foo KY, Hameed BH. Utilization of rice husk ash as novel adsorbent: A judicious recycling of the colloidal agricultural waste. Advances in Colloid and Interface Science. 2009; 152(1–2):39–47. https://doi.org/10.1016/j.cis.2009.09.005

[24] Priya AK, Yogeshwaran V, Rajendran S, Hoang TKA, Soto-Moscoso M, Ghfar AA, et al. Investigation of mechanism of heavy metals (Cr^{6+}, Pb^{2+}& Zn^{2+}) adsorption from aqueous medium using rice husk ash: Kinetic and thermodynamic approach. Chemosphere. 2022; 286:131796.https://doi.org/10.1016/j.chemosphere.2021.131796

[25] Ag ES, Na B, Se G. Adsorption of Heavy Metal Ions from Aqueous Solutions onto Rice Husk Ash Low Cost Adsorbent. Journal of Environmental & Analytical Toxicology. 2018; 08(01). https://doi.org/10.4172/2161-0525.1000543

[26] Azouaou N, Sadaoui Z, Djaafri A, Mokaddem H. Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics. Journal of Hazardous Materials. 2010; 184(1-3):126-134. https://doi.org/10.1016/j.jhazmat.2010.08.014

[27] Pérez-Marín A, Zapata VM, Ortuño J, Aguilar M, Sáez J, Lloréns M. Removal of cadmium from aqueous solutions by adsorption onto orange waste. Journal of Hazardous Materials. 2007; 139(1):122-131. https://doi.org/10.1016/j.jhazmat.2006.06.008

[28] Bhatnagar A, Sillanpää M, Witek-Krowiak A. Agricultural waste peels as versatile biomass for water purification – A review. Chemical Engineering Journal. 2015; 270:244–271. https://doi.org/10.1016/j.cej.2015.01.135

[29] Bhatnagar A, Sillanpaa M. Utilization of Agro-Industrial and Municipal Waste Materials as Potential Adsorbents for Water Treatment: A Review. Chemical Engineering Journal. 2010; 157:277–296. http://dx.doi.org/10.1016/j.cej.2010.01.007

[30] Sultana R, Ahmed S, Tuj-Zohra F. Development of Adsorbent from Sugarcane Bagasse for the Removal of Pollutants from Chrome Tanning Effluents. Textile & Leather Review. 2021; 4(2):65–75. https://doi.org/10.31881/TLR.2020.24

[31] Singh KK, Singh AK, Hasan SH. Low cost bio-sorbent 'wheat bran' for the removal of cadmium from wastewater: Kinetic and equilibrium studies. Bioresource Technology. 2006; 97(8):994–1001. https://doi.org/10.1016/j.biortech.2005.04.043

[32] Ofomaja AE, Ho YS. Effect of pH on cadmium biosorption by coconut copra meal. Journal of Hazardous Materials. 2007; 139(2):356–362. https://doi.org/10.1016/j.jhazmat.2006.06.039

[33] Tang C, Shu Y, Zhang R, Li X, Song J, Li B, et al. Comparison of the removal and adsorption mechanisms of cadmium and lead from aqueous solution by activated carbons prepared from Typha angustifolia and Salix matsudana. RSC Advances. 2017; 7(26):16092–16103. https://doi.org/10.1039/C6RA28035H

[34] Visa M, Bogatu C, Duta A. Simultaneous adsorption of dyes and heavy metals from multicomponent solutions using fly ash. Applied Surface Science. 2010; 256(17):5486–5491. https://doi.org/10.1016/j.apsusc.2009.12.145

[35] Baby R, Hussein MZ, Zainal Z, Abdullah AH. Preparation of Functionalized Palm Kernel Shell Bio-adsorbent for the treatment of heavy metal-contaminated water. Journal of Hazardous Materials Advances. 2023; 10:100253. https://doi.org/10.1016/j.hazadv.2023.100253

[36] Bhattacharyya KG, Sharma A. Azadirachta indica leaf powder as an effective biosorbent for dyes: A case research with aqueous Congo Red solutions. Journal of Environmental Management. 2004; 71(3):217–229. https://doi.org/10.1016/j.jenvman.2004.03.002

[37] Yu D, Wang L, Wu M. Simultaneous removal of dye and heavy metal by banana peels derived hierarchically porous carbons. Journal of the Taiwan Institute of Chemical Engineers. 2018; 93:543–53. https://doi.org/10.1016/j.jtice.2018.08.038

[38] Deng JH, Zhang XR, Zeng GM, Gong JL, Niu QY, Liang J. Simultaneous removal of Cd(II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent. Chemical Engineering Journal. 2013; 226:189–200. https://doi.org/10.1016/j.cej.2013.04.045

[39] Kyzas GZ, Siafaka PI, Pavlidou EG, Chrissafis KJ, Bikiaris DN. Synthesis and adsorption application of succinyl-grafted chitosan for the simultaneous removal of zinc and cationic dye from binary hazardous mixtures. Chemical Engineering Journal. 2015; 259:438–448. https://doi.org/10.1016/j.cej.2014.08.019

[40] Glushankova I, Ketov A, Krasnovskikh M, Rudakova L, Vaisman I. Rice Hulls as a Renewable Complex Material Resource. Resources. 2018; 7(2):31. https://doi.org/10.3390/resources7020031

[41] Rathi BS, Kumar PS. Application of adsorption process for effective removal of emerging contaminants from water and wastewater. Environmental Pollution. 2021; 280:116995. https://doi.org/10.1016/j.envpol.2021.116995

[42] Arti, Mehra R. Analysis of heavy metals and toxicity level in the tannery effluent and the environs. Environmental Monitoring and Assessment. 2023; 195(5):554. https://doi.org/10.1007/s10661-023-11154-4

[43] Bhuiyan MAH, Suruvi NI, Dampare SB, Islam MA, Quraishi SB, Ganyaglo S, et al. Investigation of the possible sources of heavy metal contamination in lagoon and canal water in the tannery industrial area in Dhaka, Bangladesh. Environmental Monitoring and Assessment. 2011; 175(1):633–649. https://doi.org/10.1007/s10661-010-1557-6

[44] Pathiraja GC, De Silva DK, Dhanapala L, Nanayakkara N. Investigating the surface characteristics of chemically modified and unmodified rice husk ash; bottom-up approach for adsorptive removal of water contaminants. Desalination and Water Treatment. 2015; 54(2):547–556. https://doi.org/10.1080/19443994.2014.883133

[45] Naiya TK, Bhattacharya AK, Mandal S, Das SK. The sorption of lead(II) ions on rice husk ash. Journal of Hazardous Materials. 2009; 163(2):1254–1264. https://doi.org/10.1016/j.jhazmat.2008.07.119

[46] Denizli A, Cihangir N, Tüzmen N, Alsancak G. Removal of chlorophenols from aquatic systems using the dried and dead fungus Pleurotus sajor caju. Bioresource Technology. 2005; 96(1):59–62. https://doi.org/10.1016/j.biortech.2003.11.029

[47] Yu W, Yi Y, Wang H, Yang Y, Xing C, Zeng L, et al. Effects of residual pectin composition and content on the properties of cellulose nanofibrils from ramie fibers. Carbohydrate Polymers. 2022; 298:120112. https://doi.org/10.1016/j.carbpol.2022.120112

[48] Manjuladevi M, Anitha R, Manonmani S. Kinetic study on adsorption of Cr(VI), Ni(II), Cd(II) and Pb(II) ions from aqueous solutions using activated carbon prepared from Cucumis melo peel. Applied Water Science. 2018; 8(1):36. https://doi.org/10.1007/s13201-018-0674-1

[49] Vunain E, Njewa JB, Biswick TT, Ipadeola AK. Adsorption of chromium ions from tannery effluents onto activated carbon prepared from rice husk and potato peel by H3PO4 activation. Applied Water Science. 2021; 11(9):150. https://doi.org/10.1007/s13201-021-01477-3

[50] Dizaj Khalili A, Ghaemi A. Utilization of response surface methodology, kinetic and thermodynamic studies on cadmium adsorption from aqueous solution by steel slag. Journal of the Iranian Chemical Society. 2021; 18(11):3031–45. https://doi.org/10.1007/s13738-021-02248-2

[51] Saini S, Katnoria JK, Kaur I. A comparative study for removal of cadmium(II) ions using unmodified and NTA-modified Dendrocalamus strictus charcoal powder. Journal of Environmental Health Science and Engineering. 2019; 17(1):259–272. https://doi.org/10.1007/s40201-019-00345-2

[52] Anwar J, Shafique U, Waheed-uz-Zaman, Salman M, Dar A, Anwar S. Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana. Bioresource technology. 2010; 101(6):1752–1755. https://doi.org/10.1016/j.biortech.2009.10.021

[53] Kardam A, Raj KR, Srivastava S, Srivastava MM. Nanocellulose fibers for biosorption of cadmium, nickel, and lead ions from aqueous solution. Clean Technologies and Environmental Policy. 2014; 16:385–393. https://doi.org/10.1007/s10098-013-0634-2

[54] Garg U, Kaur MP, Jawa GK, Sud D, Garg VK. Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass. Journal of Hazardous Materials. 2008; 154(1–3):1149–1157. https://doi.org/10.1016/j.jhazmat.2007.11.040

[55] Mustafiz S, Basu A, Islam MR, Dewaidar A, Chaalal O. A novel method for heavy metal removal. Energy Sources. 2002; 24(11):1043–1051. https://doi.org/10.1080/00908310290086905

[56] Cazetta AL, Vargas AM, Nogami EM, Kunita MH, Guilherme MR, Martins AC, Silva TL, Moraes JC, Almeida VC. NaOH-activated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption. Chemical Engineering Journal. 2011; 174(1):117–125. https://doi.org/10.1016/j.cej.2011.08.058

[57] Kundu S, Gupta A. Arsenic adsorption onto iron oxide-coated cement (IOCC): Regression analysis of equilibrium data with several isotherm models and their optimization. Chemical Engineering Journal. 2006; 122(1–2):93–106. https://doi.org/10.1016/j.cej.2006.06.002

[58] Limousin G, Gaudet J, Charlet L, Szenknect S, Barthès V, Krimissa M. Sorption isotherms: A review on physical bases, modeling and measurement. Applied Geochemistry. 2007; 22(2):249–275. https://doi.org/10.1016/j.apgeochem.2006.09.010

[59] Fytianos K, Voudrias E, Kokkalis E. Sorption-desorption behaviour of 2,4–dichlorophenol by marine sediments. Chemosphere. 1999; 40(1):3–6. https://doi.org/10.1016/S0045–6535(99)00214–3

[60] Anakhu EA, Ameh VI, Modekwe HU, Ayeleru OO, Ramatsa IM. Remediation of cadmium and chromium using modified *Vitex doniana* waste plant Seed's biochar in quarry site surface water. Environ Funct Mater. 2024.https://doi.org/10.1016/j.efmat.2024.02.002

[61] Kim TK, Kim T, Choe WS, Kim MK, Jung YJ, Zoh KD. Removal of heavy metals in electroplating wastewater by powdered activated carbon (PAC) and sodium diethyldithiocarbamate-modified PAC. Environ Eng Res. 2018; 23(3):301–8.https://doi.org/10.4491/eer.2017.208

[62] Lasheen MR, Ammar NS, Ibrahim HS. Adsorption/desorption of Cd(II), Cu(II) and Pb(II) using chemically modified orange peel: Equilibrium and kinetic studies. Solid State Sci. 2012; 14(2):202–10. https://doi.org/10.1016/j.solidstatesciences.2011.11.029

[63] Ge S, Zhao S, Wang L, Zhao Z, Wang S, Tian C. Exploring adsorption capacity and mechanisms involved in cadmium removal from aqueous solutions by biochar derived from euhalophyte. Sci Rep. 2024; 14(1):450. https://doi.org/10.1038/s41598-023-50525-2