Circular economy approach for rice husk modification: Equilibrium, kinetic, thermodynamic aspects and mechanism of Congo red adsorption

Nina Mladenovic
Ss Cyril and Methodius University in Skopje Faculty of Technology and Metallurgy: Saints Cyril and Methodius University in Skopje Faculty of Technology and Metallurgy

Jovana Petkovska
Ss Cyril and Methodius University in Skopje Faculty of Technology and Metallurgy: Saints Cyril and Methodius University in Skopje Faculty of Technology and Metallurgy

Vesna Dimova
Ss Cyril and Methodius University in Skopje Faculty of Technology and Metallurgy: Saints Cyril and Methodius University in Skopje Faculty of Technology and Metallurgy

Dejan Dimitrovski
Ss Cyril and Methodius University in Skopje Faculty of Technology and Metallurgy: Saints Cyril and Methodius University in Skopje Faculty of Technology and Metallurgy

Igor Jordanov (jordanov@tmf.ukim.edu.mk)
Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University https://orcid.org/0000-0002-9409-8197

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Nina Mladenovic, Jovana Petkovska, Vesna Dimova, Dejan Dimitrovski, Igor Jordanov

Nina Mladenovic

Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University in Skopje, Ruger Boskovic 16, 1000 Skopje, Republic of North Macedonia

Jovana Petkovska

Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University in Skopje, Ruger Boskovic 16, 1000 Skopje, Republic of North Macedonia

Vesna Dimova

Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University in Skopje, Ruger Boskovic 16, 1000 Skopje, Republic of North Macedonia

Dejan Dimitrovski

Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University in Skopje, Ruger Boskovic 16, 1000 Skopje, Republic of North Macedonia
Abstract

Equilibrium, kinetic, thermodynamic aspects and mechanism of Congo red adsorption onto rice husk treated with effluent from cotton pre-treatment are examined by altering the initial dye concentration, contact time, temperature, and adsorbent mass. When a lower mass is applied, the treated rice husk adsorbs the Congo red following the Langmuir model, while at a higher mass, the adsorption follows the Freundlich model. A maximum of 149.1 mg/g Congo red is adsorbed with 10 g/L rice husk at 70°C. This capacity of the chemically modified rice husk is one of the better ones found in the literature. The calculated Dubinin–Radushkevich activation energy indicates the physical nature of Congo red adsorption adsorbed under the pseudo-second-order kinetic model. The thermodynamic analysis confirmed spontaneous and endothermic adsorption with physically created Congo red-rice husk bonds. These results showed the applicability of the circular economy concept in the effort to obtain an efficient adsorbent without wasting additional
chemicals and energy that could be used to create a continuous column-mode process of rice husk modification and purification of colored effluent from the textile industry.

Graphical abstract

Key words: dye removal, modification, rice husk, circular economy, adsorption

Highlights

- Treatment of rice husk with effluent from cotton pretreatment.
- Equilibrium, kinetic, thermodynamic and mechanism of adsorption are tested.
- 149.1 mg/g adsorption capacity of treated rice husk.
- The adsorption is physical, spontaneous and endothermic.
**Introduction**

Direct (substantive) dyes are water-soluble colorants for dyeing cellulosic fabrics when good lightfastness is required, but washing-fastness is not crucial (Broadbend 2001). As sulfonated azo chemicals, they are serious pollutants (Blackburn 2004), because their degradation products are highly carcinogenic (Brown and De Vito 1993). Effluent from dyeing of cellulosic fibers, with 5-30% residual direct dye (Easton 1995) has a negative environmental impact and a toxic influence on aquatic organisms because of its high biochemical oxygen demand that results in the suffocation of aquatic flora and fauna. Several studies for cleaning the colored effluent have been examined. Biological treatment using activated sludge (Abu Elella et al. 2019), chemical treatment with oxidation (Alaton and Teksoy 2007) and ozonation (Ciardelli et al. 2001) and physical methods by implementing membrane technology (Males et al. 2020; Gorgieva et al. 2019), ion-exchange materials (Shao X et al. 2021), polyelectrolytes (Qiao et al. 2021), biomasses (Halysh et al. 2020), nanostructures (Batmaz et al. 2014; Aboamera et al. 2018), cellulose-based hydrogels (Ching et al. 2018; Mohamed et al. 2018) cellulose-based aerogels (Chong et al. 2015) and biopolymers (Perez-Ameneiro et al. 2014) have been explored. Many of these treatments are expensive and have limited effectiveness that requires additional extensive examination. Adsorption of dye molecules is one of the cheapest methods for purifying colored effluent from the textile industry based on employing cheap and highly effective adsorbents. Many adsorbents show effective dye absorbency, but most of them are either expensive or have limited absorptivity. One of the commercially available adsorbents, which possess excellent adsorption ability, is activated carbon (Foo and Hameed 2010). Despite its high efficiency, its expensive fabrication limits its use as a dyed effluent purifier (Abdelwahab et al. 2005).
The latest development in colored effluent cleaning is related to using an agricultural byproduct, or industrial waste, as an adsorbent, that is inexpensive and abundant. Grass waste, leaf, fly ash, sugarcane bagasse, sludge ash, wheat straw, natural fibers, rice husk, etc., have been tested as potential adsorbents (Chakraborty et al. 2011; Gupta et al. 2009; Sanghi and Verma 2013; Sharma et al. 2011; Tarbuk et al. 2020; Toshikj et al. 2019). Some of them are highly efficient, but many require additional modification steps to make them more amenable for dye sorption. Rice husk with its chemical composition containing 32% cellulose, 21% hemicellulose, 21% lignin, 20% silica, 3% crude proteins (Chowdhury et al. 2011), which is similar to the composition of natural cellulose fibers (Ivanovska et al. 2019; Lazic et al. 2018), emphasizes its use as a purifier for colored effluent (Chakraborty et al. 2011; Mladenovic et al. 2020; Shamsollahi and Partovinia 2019). Despite the theoretically good ability for dye adsorption, the content of 21% lignin in its outer protective layer i.e. the hydrophobic lignin-silicone-cellulose shield, makes the rice husk less adsorptive (Ndazi et al. 2007). In order to improve its adsorption capacity, the rice husk was subjected to physical grounding (Vadivelan & Kumar 2005), incineration (Alam et al. 2020), chemical treatments with acids (Abdelwahab et al. 2005), ethylenediamine (Ong et al. 2007) and bases (Chowdhury et al. 2011; Chowdhury et al. 2012). These modifications are effective but require an investment in expensive equipment that operates at high temperatures under pressure.

Alkaline scouring of cotton is a process that uses dilute sodium hydroxide solution and surfactants to remove non-cellulosic hydrophobic components from cotton’s cuticle and to make it hydrophilic (Toshikj et al. 2016; Toshikj et al. 2017; Lazic et al. 2018). The circular economy is a new concept opposite to the linear economy one, which is based on production, use, and throwing away of the products. It is mainly focused on using the products and materials over and...
over, in a continuous loop. In this system, products and wastes are either reused or recycled. The
applicability of the circular economy concept for rice husk modification has been proved in
previous research (Mladenovic et al. 2020). In that study, rice husk was treated with cotton
scouring effluent as an inexpensive way of successful modification by avoiding the need for
additional energy and chemicals. Attenuated total reflectance-infrared spectroscopy (ATR-IR)
and scanning electron microscopy-energy dispersive X-ray (SEM-EDX) was used to observe the
occurred changes after this modification. The results of these analyzes showed that the treatment
with effluent from alkaline scouring effectively removed the lignin-silicone shield from the rice
husk surface. Moreover, this treatment increased the percentage of cellulose in the husk and the
structure became cellulose-dominant and more amenable for purifying the colored effluent.

The present study explored equilibrium, kinetics, thermodynamics, and the adsorption
mechanism of Congo red (CR) onto rice husk modified with cotton scouring effluent (ERH), by
the concept of circular economy. The results show that this approach is effective in obtaining an
efficient adsorbent for dye removal. Moreover, such modified rice husk has an exceptional
absorption capacity higher than other chemically modified rice husks found in the literature.

2. Materials and methods

2.1. Materials

The collected rice husk was sifted through a sieve to eliminate tiny particles with a size less than
1.25 mm and dried at 105 °C for 2 h. Congo red dye - C.I. 20120 (Sigma-Aldrich, Milwaukee,
WI) was used as received. All experimental dye solutions with defined concentrations were
prepared by diluting the stock solution which has 1 g/L concentration. Sodium hydroxide and sodium chloride were supplied by Sigma-Aldrich (Milwaukee, WI). Cotoblanco HTD-N (CHT Switzerland AG), anionic washing surfactant and Kemonecer NI (Kemo Croatia), nonionic wetting surfactant are used as received.

2.2. Rice husk modification

Rice husk was treated with effluent from cotton scouring. The effluent was obtained after cotton yarn scouring, done with a solution containing 25 g/L of sodium hydroxide, 2 mL/L Cotoblanco HTD-N and 1 mL/L Kemonecer NI in a bath with 50:1 liquor ratio at 100°C for 60 min in Ahiba Turbomat TM-6 apparatus. Then, the collected effluent was mixed with the raw rice husk (with a ratio of effluent and husk 20:1) and treated for 30 min in the Linitest apparatus. During this treatment, the effluent temperature decreased from 100°C to 40°C with an average temperature of 70°C. Then, the rice husk was rinsed with effluents from cotton yarn rinsing, performed at 70°C for 15 min (warm rinsing) and 25°C temperature for 15 min (cold rinsing).

2.3. Adsorption studies

The adsorption ability of treated rice husk is examined by employing a batch adsorption process where 2, 4, and 8 g rice husk (i.e. 10, 20, and 40 g/L adsorbent dosage) are added in a 200 mL colored solution (in a glass stoppered Erlenmeyer flask) with an initial dye concentration of 0.1, 0.2, 0.3, 0.4, and 0.5 g/L Congo red, 10 g/L NaCl at pH 7, at 298, 323, and 343 K with constant agitation of 60 min⁻¹ in a GLF-shaking water bath 1083 (EURO lux GmbH & Co. KG Karlstadt-Karlbarg, Germany). Pipetting of the dye solution was done at 10, 20, 30, 40, 60, 90, 120, 360,
720, and 1440 min and the concentration of Congo red (max. wavelength at 507 nm) in the supernatant solution was measured with UV/VIS spectrophotometer (Model Hitachi – 2800, United Kingdom). The calculated values are mean values of three measurements. The dye removal efficiency, expressed as a percentage, was determined using Eq. 1.

\[
\text{Dye removal} \, (\%) = \left[ \frac{C_0 - C_t}{C_0} \right] \times 100 \, (\%)
\]  

(1)

\( C_0 \) (g/L) is the initial concentration of the dye and \( C_t \) (g/L) is the concentration of the dye after sorption at any time. The mass balance equation (Eq. 2) was used to calculate the amount of adsorbed dye onto the rice husk \( Q_e \) (g/g).

\[
Q_e = \frac{(C_0 - C_e)V}{W}
\]  

(2)

\( C_0 \) (g/L) and \( C_e \) (g/L) are the initial concentration and the concentration of dye at equilibrium, respectively, \( V \) (L) is the volume of the solution and \( W \) (g) is the weight of the sorbent used.

3. Results and discussion

The influence of adsorbent dosage, temperature, and initial dye concentration on the adsorption ability of the sorbent has to be inter-correlated to obtain a clear picture of the sorption phenomena for each sorbate-sorbent system. Hence, the adsorption ability of CR employing three masses of ERH, five initial dye concentrations, and three temperatures is examined in this study. The capability of the ERH to remove CR from solution with 0.3 g/L initial dye concentration at 298, 323, and 343 K, tested with 10, 20, and 40 g/L ERH are shown in Fig. 1 (a), (b) and (c), respectively. The increase in the ERH dosage and temperature of the dye solution
increases the percent of removed dye. Increased ERH adsorbent dosage increases the specific area and available adsorption sites, while higher temperatures make the dye molecules more energy-active with a higher potential for adsorption onto the ERH surface. Opposite, a higher initial dye concentration, at a constant adsorbent dosage and temperature of the solution, results in a lower percentage of removed dye (Fig. 2). A constant adsorbent dosage has a defined adsorption ability, so the percentage of removed dye decreases as the initial dye concentration increases. The complete data of the dye removal versus contact time, conducted under all combined parameters, are given as a supplementary file.
Fig. 1 Effect of ERH dosage on dye removal tested with 0.3 g/L CR at 298, 323 and 343 K. (a) 10 g/L, (b) 20 g/L and (c) 40 g/L ERH dosage.
In order to examine, explain and interpret the used adsorbent-adsorbate sorption system, the adsorbent capacity must first be assessed. Langmuir and Freundlich's isotherms are the most used equilibrium relationships between the adsorbate and adsorbent at a given sorption condition. As such, they are essential for the evaluation of the physicochemical interaction between CR and ERH and the dye adsorption equilibrium analysis. According to the Langmuir theory, dye adsorption is achieved through certain functional groups in the adsorbent. During the reaction, these groups are saturated forming a monolayer, which prevents further absorption of the dye. Also, in the Langmuir equation (Eq. 3), the dye concentration in the adsorbent increases with the dye concentration in the bath but to some extent, i.e. until all active centers of the adsorbent are saturated with dye. This isotherm has a linear form, as expressed in Eq. 4.
\[ Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \]  

(3)

\[ \frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e \]  

(4)

Ce (g/L) is the equilibrium concentration of Congo red, Qe (g/g) is the amount of CR adsorbed per unit mass of adsorbent, Qm (g/g) is constant related to adsorption capacity and K_L (L/g) is constant related to rate of adsorption. Qm is calculated from the slope of the straight line when Ce/Qe is plotted against Ce.

The Freundlich equation presented in Eq. 5 explain sorption on a heterogeneous surface with sites of varied affinities.

\[ Q_e = K_F C_e^\frac{1}{n_F} \]  

(5)

The logarithmic form of Freundlich is given by Eq. 6.

\[ \log(Q_e) = \log(K_F) + \frac{1}{n_F} \log(Ce) \]  

(6)

Qe (g/g) is the equilibrium dye concentration, Ce (g/L) is the equilibrium dye concentration in solution, K_F (g/g) (L/g)^1/n is the constant related to adsorption capacity, and n_F is the adsorption isotherm constant. K_F and 1/n_F are calculated from the intercept and slope of the straight line of the plot log(Qe) versus log(Ce), respectively.

The Dubinin-Radushkevich (D-R) isotherm, which rules out the homogenous surface or constant sorption potential, is empirical model for the adsorption of the adsorbate to the volume filling of micropores (Dabrowski 2001). This isotherm is very important for determining the adsorption characteristics of most of the industrial adsorbents with a complex and well-developed porous
structure, including pores of different shapes and sizes, but micropores play the most significant role. The non-linear equations of Dubinin-Radushkevich isotherm can be illustrated as Eq. 7 and 8 (Chen 2015).

\[ Q_e = Q_s \exp(-K_{DR} \varepsilon^2) \quad (7) \]

\[ \varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \quad (8) \]

\( Q_s \) (g/g) is a constant related to adsorption capacity, \( K_{DR} \) (mol\(^2\)/KJ\(^2\)) is a constant related to the mean free energy of adsorption, \( \varepsilon \) is Polanyi potential, \( C_e \) (g/L) is the concentration at equilibrium, \( R \) (J/mol K) is the gas constant, and \( T \) (K) is the absolute temperature.

The linear expression of Dubinin-Radushkevich isotherm model is shown in Eq. 9.

\[ \ln Q_e = \ln Q_m - \beta \varepsilon^2 \quad (9) \]

\( Q_m \) (g/g) is the maximum adsorption capacity and \( \beta \) (mmol\(^2\)/J\(^2\)) is a coefficient related to the mean free energy of adsorption. \( Q_m \) and \( \beta \) are calculated from the intercept and slope of the plot between \( \ln Q_e \) and \( \varepsilon^2 \), respectively.

\( \beta \) is used to calculate \( E \) (KJ/mol), the mean free energy of adsorption per mole of the adsorbate, when the adsorbate is transferred from infinity of the solution to the surface of the solid. The relation between them is shown in Eq. 10 (El Haddad 2016).

\[ E = \frac{1}{\sqrt{2\beta}} \quad (10) \]

\( E \) ranged from 8 to 16 KJ/mol indicates proceeds of the sorption process via chemisorption. Values of \( E < 8 \) KJ/mol indicate a physical sorption process (El Haddad 2016).
The experimental adsorption capacity of ERH, the calculated constants of Langmuir, Freundlich and D-R, and the coefficients of correlation between calculated and experimental data are presented in Table 1. The highest adsorption capacity of 149.1 mg/g is achieved when the lowest adsorbent dosage (10 g/L ERH) and the highest temperature of 343 K are applied. The dye removal is directly proportional, while the adsorption capacity of the ERH, at all temperatures is inversely proportional to the adsorbent dosage. Higher dosage reduces the amount of the adsorbed dye per unit weight of the adsorbents. The experimental adsorption capacity of the ERH, tested with 10 and 20 g/L adsorbent dosage, increases by about 63 % as the temperature of the adsorption testing rises from 298 to 343 K. The adsorption capacities tested with 40 g/L ERH are not that temperature-dependent and increase for about 5 % when the temperature of adsorption increases from 298 to 343 K. The calculated coefficients of correlation presented in Table 1 show that the equilibrium data for 10 g/L ERH fits the Langmuir better than the Freundlich isotherm at all tested temperatures, confirming a monolayer coverage of the Congo Red onto ERH when a lower adsorption dosage is used. The adsorption capacity for 20 g/L ERH at 298 and 323 K, fits the Langmuir isotherm, while the one at 343 K fits the Freundlich isotherm model better. The Freundlich isotherm proved to be a better fit for the equilibrium data for 40 g/L ERH at all tested temperatures. A list of published data on adsorption capacities of chemically modified rice husks (Table 2) and the adsorption capacity of Congo red adsorbed onto different renewable adsorbents (Table 3) indicate that capacity of the treated rice husk obtained in this study is one of the better found in the literature.

The Langmuir isotherm could be also used to determine the dimensionless equilibrium separation parameter $R_L$ calculated by Eq. 11 (Omidi and Kakanejadifard 2018).
\[ R_L = \frac{1}{1+K_LC_0} \]  

(11)

\( R_L \) (L/g) is the Langmuir constant related to adsorption capacity, while \( C_0 \) (g/L) is the initial concentration of the dye solution. When \( R_L < 1 \), the adsorption is favorable, while for values of \( R_L > 1 \), it is unfavorable.

The D-R isotherm is employed to calculate the magnitude of \( E \) which indicates the type of adsorption. As mentioned above, the value of \( E \) higher than 8 KJ/mol is an indicator of chemical ion exchange, while \( E \) below 8 KJ/mol indicates physical sorption (Chakraborty et al. 2011). The \( E \) values presented in Table 1 are lower than 8 KJ/mol in most cases, confirming the physical sorption of the CR onto ERH.

**Table 1** Isotherm parameters for adsorption of Congo red onto ERH

| Isotherm     | Parameters               | Temperature (K) | 298 Adsorbent dosage (g/L) | 323 Adsorbent dosage (g/L) | 343 Adsorbent dosage (g/L) |
|--------------|--------------------------|-----------------|----------------------------|----------------------------|-----------------------------|
|              | Q_{m,exp} (g/g)          | 10 20 40        | 10 20 40                   | 10 20 40                   | 10 20 40                   |
| Langmuir     | Q_{m} (g/g)              | 0.0917 0.0765 0.0579 | 0.1153 0.0992 0.0608       | 0.1491 0.1126 0.0610       |
|              | K_L (l/g)                | 0.440 0.659 0.719 | 1.1039 1.5695 1.0279       | 2.347 1.887 0.968          |
|              | R_L (C_0=0.1 g/L)        | 0.9578 0.9382 0.9329 | 0.9006 0.8643 0.9068       | 0.8099 0.8413 0.9117       |
|              | R^2                      | 0.985 0.988 0.933 | 0.979 0.987 0.550          | 0.985 0.930 0.391          |
| Freundlich   | K_F (g/g)(l/g)^{1/n}     | 0.365 0.365 0.873 | 0.354 0.615 1.081          | 0.470 0.906 2.662          |
|              | n_F                      | 1.544 1.842 1.436 | 2.165 1.768 1.461          | 2.284 1.630 1.438          |
|              | R^2                      | 0.6656 0.738 0.976 | 0.638 0.896 0.989          | 0.778 0.971 0.983          |
| Dubinin-Radushkevich | Q_{m} (g/g) | 0.205 0.181 0.464 | 0.211 0.315 0.785          | 0.268 0.517 0.863          |
|              | \beta (mmol^2/J^2)       | 1.86x1 1.14x1 1.76x1 | 0.88x1 1.12x1 1.61x1       | 0.68x1 1.23x1 1.51x1       |
|              | E (KJ/mol)               | 5.185 6.623 5.330 | 7.538 6.681 5.573          | 8.574 6.376 5.754          |
|              | R^2                      | 0.409 0.479 0.857 | 0.391 0.699 0.975          | 0.521 0.857 0.988          |
### Table 2 Adsorption capacity of chemically treated rice husk for different dyes

| Treatment of rice husk                              | Dye               | Adsorption capacity | References               |
|-----------------------------------------------------|-------------------|---------------------|--------------------------|
| Without any pretreatment                            | Indigo carmine    | 65.90 mg/g          | Lakshmi et al. (2009)    |
| Citric acid                                         | Direct F. Scarlet | ~13 mg/g            | Abdelwahab et al. (2005) |
| H$_3$PO$_4$                                         | 5G blue dye       | 3.84 mg/g           | Costa Junior et al. (2018) |
| Thermally treated at 75 °C                          | Methylene blue    | 24.48 mg/g          | Quansah et al. (2020)    |
|                                                     | Crystal violet    | 25.46 mg/g          | Quansah et al. (2020)    |
| Oxalic acid                                         | Methylene blue    | 53.2 mg/g           | Zou et al. (2011)        |
|                                                     | Malachite green   | 54.0 mg/g           | Zou et al. (2011)        |
| Sodium hydroxide under pressure                     | Crystal violet    | 44.9 mg/g           | Chakraborty et al. (2011) |
|                                                     | Safranine         | 37.9 mg/g           | Chowdhury et al. (2012)  |
|                                                     | Malachite green   | 12.6 mg/g           | Chowdhury et al. (2011)  |
| HCl                                                 | Everdirect Orange-3GL | 29.9 mg/g     | Safa et al. (2011)       |
|                                                     | Direct Blue-67    | 37.9 mg/g           | Safa et al. (2011)       |
| EDTA                                                | Basic blue 3      | 3.3 mg/g            | Ong et al. (2007)        |
|                                                     | Reactive orange 16| 24.9 mg/g           | Ong et al. (2007)        |
| Acetic acid and hydrogen peroxide                   | Rhodamine B       | $5.87 \times 10^{-5}$ mg/g | Jain et al. (2007)       |
| Rise husk ash without pretreatment                  | Brilliant green   | 26.20 mg/g          | Mane et al. (2007)       |
| Effluent from alkaline scouring of cotton           | Congo red         | 149.1 mg/g          | This work                |

### Table 3 Adsorption capacity of Congo red onto different renewable adsorbents

| Adsorbent                                           | Adsorption capacity of Congo red | References               |
|-----------------------------------------------------|----------------------------------|--------------------------|
| Rice hull ash                                       | 171.00 mg/g                      | Chou et al. (2001)       |
| Powder from eucalyptus leaf                         | 29.68 mg/g                       | Kumari et al (2019)      |
| Pellet of rice hull ash, kaolin and starch           | 21.0 mg/g                        | Chou et al. (2001)       |
| Hydrothermally treated Shiitake mushroom             | 217.86 mg/g                      | Yang et al. (2019)       |
| Egg shell membrane                                  | 117.65 mg/g                      | Parvin et al (2019)      |
| Sulfidogenic sludge                                 | 238.90 mg/g                      | Rasool and Lee (2013)    |
| Material                               | Adsorption Capacity | Source                          |
|----------------------------------------|---------------------|---------------------------------|
| Raw pine cone                          | 32.65 mg/g          | Dawood and Sen (2012)           |
| Acid-treated pine cone                 | 40.19 mg/g          | Dawood and Sen (2012)           |
| Clay materials                         | 4.3-19.9 mg/g       | Vimonses et al. (2009)          |
| Rice husk                              | 14.00 mg/g          | Han et al. (2008)               |
| Calcium rich - fly ash                 | 4.47 × 105 mol/g    | Acemioğlu (2004)                |
| Ca-bentonite                           | 107.41 mg/g         | Lian et al. (2009)              |
| Coir pith                              | 6.72 mg/g           | Namasivayam and Kavitha (2002)  |
| Orange peel                            | 22.44 mg/g          | Namasivayam et al. (1996)       |
| Powder from jute stick                 | 35.70 mg/g          | Panda et al. (2008)             |
| Dead *Aspergillus niger* fungus        | 14.72 mg/g          | Fu and Viraraghavan (2002)      |
| Modified rice husk                     | 149.1 mg/g          | This work                       |

**Adsorption kinetics**

The amount of adsorbed CR versus the contact time serves to evaluate the adsorption kinetics. It is essential for the examination of the mechanism by which the adsorption occurs. Pseudo-first-order (Eq. 12), pseudo-second-order (Eq. 13), Elovich (Eq. 14), intraparticle diffusion (Eq. 15) as well as the liquid film diffusion (Eq. 16) models are employed in this study to evaluate the kinetics of adsorption.

\[
\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t 
\]  

(12)

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t 
\]  

(13)

\[
Q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t 
\]  

(14)

\[
Q_t = k_i t^{0.5} 
\]  

(15)

\[
\ln(1 - F) = -k_{fd} t 
\]  

(16)
$k_1$ (min$^{-1}$) and $k_2$ (g/gmin) are rate constants for pseudo-first and pseudo-second-order, respectively. $Q_e$ (g/g) is amount of adsorbate at equilibrium and $Q_t$ (g/g) is amount of adsorbate at time $t$, $\alpha$ (g/gmin) is the initial sorption rate constant, $\beta$ (g/g) is desorption constant, $k_i$ (g/gmin$^{0.5}$) is intraparticle diffusion rate constant, $F$ is fractional attainment of equilibrium, equal to $Q_t/Q_e$ and $K_{fd}$ (min$^{-1}$) is liquid film diffusion rate constant.

The calculated kinetic parameters are presented in Table 4. The coefficients of correlation of the pseudo-second-order vary from 0.9998 to 1, while those of the pseudo-first-order range between 0.1513 and 0.9128. The substantially higher coefficients of correlation of the pseudo-second-order and the small differences between $Q_{m, \text{exp}}$ and $Q_{m, \text{cal}}$ of this kinetic model, reinforce its applicability. The plots $t/Q_t$ versus $t$ of 0.1 to 0.5 g/L initial CR concentration, for 10 g/L adsorbent dosage tested at 298 K show excellent linearity (Fig. 1 in Supplementary file).

Pseudo-second-order rate constant $k_2$ is calculated from the intercept of the slope $t/Q_t$ versus $t$. Since $k_2$ has the highest $R^2$, it is then used for calculation of the initial adsorption rate $h$ according to Eq. (17). The $k_2$ values increase along the adsorbent dosage and temperature of adsorption testing. Increased $k_2$ at a higher temperature (Table 4) indicates the endothermic process of the adsorption of CR onto ERH when the temperature of adsorption increases (Chowdhury et al. 2011). The $h$ value, which is the initial adsorption rate, is useful for creating a continuous adsorption system in which a higher initial adsorption rate is crucial for the proper selection of the adsorbents. Higher $h$ values at elevated temperature and higher ERH dosage favor building a continuous adsorption system filled with more ERH that will work at a higher temperature.

\[
h = k_2 Q e^2 \tag{17}
\]
The Elovich model is another kinetic model used to examine adsorption/desorption kinetic on the solid adsorbent. This equation assumes the heterogeneous nature of the solid surface active sites that exhibit different activation energies for chemisorption (Chowdhury et al. 2011). The correlation coefficients R^2 determined from the Qt vs ln (t) plots are in the range between 0.4579 and 0.9065 (Table 4). In this model, the initial adsorption rate is presented as the constant α, while β is the surface coverage or desorption constant. These constants are temperature-dependent. An increase in temperature is accompanied by an increase in α and β, indicating that both the initial adsorption and the available adsorption area would increase. Moreover, the adsorbent dosage also influences the values of α and β. More rice husk, at the same initial dye concentration, increases both α and β constants.

During the process of dye adsorption onto some adsorbent, the diffusion of the dye from the bulk dye solution to the surface of the rice husk, and the transport from the surface into the solid rice husk may have occurred. Since these mechanisms follow intraparticle diffusion and liquid film diffusion models, these models have been explored to rate CR adsorption onto ERH. The liquid film diffusion parameters calculated from the plots of ln (1−F) versus t have R^2 between 0.1239 and 0.8943 with intercepts ranging from -1.1044 to -4.8625 and k_{fd} ranging from -0.0019 to – 0.0071 min\(^{-1}\) (Table 4). On the other hand, the intraparticle diffusion parameters calculated from the plots Qt versus t^{0.5} have R^2 between 0.1238 and 0.5339, intercepts between 0.0097 and 0.0837 and k_i ranging from 0.0001 to 0.0073 g/gmin^{0.5}. Both models show that the intercepts of linear plots did not pass through the origin. Theoretically, if one of these models intends to be the sole rate-determining step, the plots must have zero intercept. Since the linear plots of both models do not meet this requirement, the applicability of these models in the present adsorption
system is limited. In that case, during the interaction of CR with ERH, surface adsorption and
intraparticle diffusion could both happen.

Table 4 Pseudo-first-order and pseudo-second-order kinetic, Elovich, liquid film diffusion and
intraparticle diffusion kinetic parameters for adsorption of Congo red onto ERH
The activation energy $E_a$ is a crucial parameter for determining the origin of the sorption forces that bind the sorbate and sorbent. Since physical adsorption contains weak forces, $E_a$ is lower than 40 KJ/mol. As chemical adsorption involves much stronger forces than physical adsorption,
Ea is higher than 40 KJ/mol. The activation energy for adsorption of CR onto ERH is determined by the Arrhenius equation (Eq. 17) (Zhu et al 2009).

\[
\ln k = \ln A - \frac{E_a}{RT}
\]  

(17)

k is the rate constant, A is the Arrhenius constant, Ea (kJ/mol) is the activation energy, R (8.314 J/mol K) is the gas constant and T (K) is the temperature. In this study, Ea was obtained from the slope of the linear plot of \(\ln k_2\) (calculated from the pseudo-second-order kinetic model) versus 1/T.

The Eyring equation (Eq. 18) was also used to determine the standard enthalpy of activation (\(\Delta H^\#\)), the entropy of activation (\(\Delta S^\#\)) and free energy of activation (\(\Delta G^\#\)) in the sorption process (Saha and Chowdhury 2011; Chowdhury et al. 2010):

\[
\ln \frac{k}{T} = \ln \frac{k_B}{R} + \frac{\Delta S^\#}{R} - \frac{\Delta H^\#}{RT}
\]  

(18)

where k is the rate constant, T is the temperature (K), \(k_B\) is the Boltzman constant (1.3807 \(\times\) 10\(^{-23}\) J/K), h is the Planck constant (6.6261 \(\times\) 10\(^{-34}\) J s) and R is the gas constant. By plotting \(\ln \frac{k}{T}\) vs 1/T, the values of \(\Delta H^\#\) and \(\Delta S^\#\) were determined from the slope and intercept of the plot, respectively. The free energy of activation (\(\Delta G^\#\)) was calculated by using these values in the following equation:

\[
\Delta G^\# = \Delta H^\# - T\Delta S^\#
\]  

(19)

The results of Eyring’s thermodynamic parameters and energy of activation shown in Table 5 indicate positive \(\Delta G^\#\), positive \(\Delta H^\#\), and negative \(\Delta S^\#\). Positive \(\Delta G^\#\) suggests a requirement of energy to convert reactants into products during the adsorption reaction. The positive \(\Delta H^\#\) indicates an endothermic reaction. The negative \(\Delta S^\#\) suggests an associative mechanism of CR adsorption onto ERH in which dye molecules are intact. The negative \(\Delta S^\#\) values are also an indication of a lack of significant change in the adsorbent’s internal structures during the adsorption (Chowdhury et al. 2011; Chowdhury et al. 2012), meaning the ERH can be reused. The obtained Ea values for the adsorption of CR onto ERH, for all initial concentrations (g/L) and adsorbent mass (g), suggest that the adsorption process is, in fact, physisorption.
### Table 5: Activation parameters for adsorption of Congo red onto ERH

| Model | Initial conc (g/L) | Parameters | Temperature (K) | Adsorbent dosage (g/L) | Adsorbent dosage (g/L) | Adsorbent dosage (g/L) |
|-------|------------------|------------|----------------|------------------------|------------------------|------------------------|
| 0.1   |                  | ΔG# (kJ/mol) | 70.77        | 66.70                  | 59.58                  | 75.70                  |
|       |                  | ΔH# (kJ/mol) | 11.98        | 34.54                  | 22.49                  | 323                    |
|       |                  | ΔS# (J/mol K) | -197.26      | -107.93                | -124.47                | -125.84                |
|       |                  | Ea (kJ/mol)  | 14.64        | 37.18                  | 25.14                  | 343                    |
|       |                  | R²          | 0.9809       | 0.9763                 | 0.9807                 | 1                      |
| 0.2   |                  | ΔG# (kJ/mol) | 73.03        | 70.39                  | 64.53                  | 78.90                  |
|       |                  | ΔH# (kJ/mol) | 3.108        | 26.96                  | 27.03                  | 70.20                  |
|       |                  | ΔS# (J/mol K) | -234.63      | -145.76                | -125.84                | -101.51                |
|       |                  | Ea (kJ/mol)  | 5.76         | 29.61                  | 29.68                  | 473.4                  |
|       |                  | R²          | 0.4734       | 0.9999                 | 0.9221                 | 1                      |
| 0.3   |                  | ΔG# (kJ/mol) | 72.595       | 72.09                  | 67.72                  | 78.90                  |
|       |                  | ΔH# (kJ/mol) | -2.61        | 14.92                  | 37.47                  | 70.26                  |
|       |                  | ΔS# (J/mol K) | -252.35      | -191.84                | -101.51                | -114.51                |
|       |                  | Ea (kJ/mol)  | 0.045        | 17.57                  | 40.12                  | 364                    |
|       |                  | R²          | 0.0009       | 0.7593                 | 0.9323                 | 1                      |
| 0.4   |                  | ΔG# (kJ/mol) | 73.57        | 72.20                  | 69.64                  | 79.08                  |
|       |                  | ΔH# (kJ/mol) | 7.89         | 4.24                   | 34.55                  | 72.58                  |
|       |                  | ΔS# (J/mol K) | -220.40      | -228.03                | -117.74                | -114.51                |
|       |                  | Ea (kJ/mol)  | 10.54        | 6.89                   | 37.20                  | 39.60                  |
|       |                  | R²          | 0.7331       | 0.9803                 | 1                      | 312                    |
| 0.5   |                  | ΔG# (kJ/mol) | 73.86        | 73.25                  | 71.08                  | 79.70                  |
|       |                  | ΔH# (kJ/mol) | 4.17         | 3.54                   | 36.95                  | 73.90                  |
|       |                  | ΔS# (J/mol K) | -233.84      | -233.94                | -114.51                | -114.51                |
|       |                  | Ea (kJ/mol)  | 6.82         | 6.18                   | 39.60                  | 45.39                  |
|       |                  | R²          | 0.3519       | 0.5529                 | 0.9827                 | 1                      |

**Adsorption thermodynamics**

Van Hoff’s classical equation (Eq. 20) is used to calculate the change in Gibbs free energy which is crucial for determining the spontaneity of a process (Saha and Chowdhury 2011):

$$\Delta G^0 = -RT \ln K_C$$  \hspace{1cm} (20)

where R (J/mol K) is the universal gas constant, T (K) is the absolute temperature and $K_C$ is the distribution coefficient for adsorption defined by the Eq. 21:

$$K_C = \frac{C_a}{C_e}$$  \hspace{1cm} (21)

in which $C_a$ (g/L) is the equilibrium dye concentration on the adsorbent and $C_e$ (g/L) is the equilibrium dye concentration in solution. The enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) were calculated using the Eq. 22.
\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \] (22)

By plotting \( \Delta G^0 \) vs T, the values of \( \Delta H^0 \) and \( \Delta S^0 \) were determined from the intercept and slope of the plot, respectively. The calculated values of the thermodynamic parameters for the adsorption of CR onto ERH at all temperatures are listed in Table 6.

Table 6 Thermodynamic parameters for adsorption of Congo red onto ERH.

| Model | Initial con. (g/L) | Parameters | \[\text{Temperature (K)}\] |
|-------|-------------------|------------|--------------------------|
|       |                   |            | 298                      | 323                      | 343                      |
|       |                   |            | Adsorbent dosage (g/L)   | Adsorbent dosage (g/L)   | Adsorbent dosage (g/L)   |
|       |                   |            | 10 20 40                 | 10 20 40                 | 10 20 40                 |
|       |                   | \( K_C \)  | 5.46 34.16 38.78         | 19.41 34.79 44.93        | 39.81 30.06 38.79        |
| 0.1   |                   | \( \Delta G^0 \) (kJ/mol) | -4.21 -8.74 -9.06      | -7.96 -9.53 -10.22       | -10.51 -9.70 -10.43      |
|       |                   | \( \Delta H^0 \) (kJ/mol) | 37.55 2.37 0.0780       | 37.24 16.49 0.955        | 96.2 73.5 15.14          |
|       |                   | \( \Delta S^0 \) (J/mol K) | 140.4 9.18 0.9046       | 5.97 27.98 0.44           | 7.60 23.39 47.78         |
|       |                   | \( R^2 \) | 0.9978 0.9188 0.9046     | 1 0.8121 0.9811          |                          |
| 0.2   |                   | \( K_C \)  | 1.79 9.91 45.51          | 4.17 27.98 50.28         | 7.60 23.39 47.78         |
|       |                   | \( \Delta G^0 \) (kJ/mol) | -1.45 -5.68 -9.46       | -3.84 -8.95 -10.52       | -5.78 -8.99 -11.03       |
|       |                   | \( \Delta H^0 \) (kJ/mol) | 27.24 16.49 0.955       | 96.2 73.5 15.14          | 96.2 73.5 15.14          |
|       |                   | \( \Delta S^0 \) (J/mol K) | 96.2 73.5 15.14         | 1.97 27.98 0.44          | 7.60 23.39 47.78         |
|       |                   | \( R^2 \) | 0.9978 0.9188 0.9046     | 1 0.8121 0.9811          |                          |
| 0.3   |                   | \( K_C \)  | 0.97 4.03 36.45          | 1.53 16.39 50.72         | 3.73 32.33 43.12         |
|       |                   | \( \Delta G^0 \) (kJ/mol) | -0.06 -3.45 -8.91       | -1.14 -7.51 -10.54       | -3.76 -9.91 -10.73       |
|       |                   | \( \Delta H^0 \) (kJ/mol) | 25.20 39.40 3.29        | 100 166 24              | 25.2 39.4 0.32           |
|       |                   | \( \Delta S^0 \) (J/mol K) | 83.4 144.3 41.56        | 2.94 16.39 0.44          | 7.60 23.39 47.78         |
|       |                   | \( R^2 \) | 0.9269 0.9932 0.8726     | 1 0.8121 0.9811          |                          |
| 0.4   |                   | \( K_C \)  | 0.74 1.96 23.84          | 0.91 5.17 42.96          | 1.72 12.24 43.44         |
|       |                   | \( \Delta G^0 \) (kJ/mol) | -0.76 -1.67 -7.86       | 0.258 -4.41 -10.1        | -1.55 -7.14 -10.76       |
|       |                   | \( \Delta H^0 \) (kJ/mol) | 15.89 34.53 11.45       | 50.0 121.2 65.42         | 15.89 34.53 11.45       |
|       |                   | \( \Delta S^0 \) (J/mol K) | 83.4 144.3 41.56        | 0.927 0.8726 0.7328      | 7.60 23.39 47.78         |
|       |                   | \( R^2 \) | 0.9269 0.9932 0.8726     | 1 0.8121 0.9811          |                          |
| 0.5   |                   | \( K_C \)  | 0.58 1.57 12.66          | 0.86 3.85 36.88          | 1.48 9.12 42.10         |
|       |                   | \( \Delta G^0 \) (kJ/mol) | 1.35 -1.13 -6.29        | 0.418 -3.62 -9.69        | -1.11 -6.30 -10.66       |
|       |                   | \( \Delta H^0 \) (kJ/mol) | 17.59 33.08 22.88       | 54.1 114.4 98.83         | 17.59 33.08 22.88       |
|       |                   | \( \Delta S^0 \) (J/mol K) | 54.1 114.4 98.83        | 0.9593 0.9928 0.9411     | 7.60 23.39 47.78         |

The negative \( \Delta G^0 \) values for most of the tested samples indicate a spontaneous adsorption process of CR onto ERH. The positive \( \Delta G^0 \) for ERH tested at 10 g/L adsorption dosage and 0.3, 0.4, and 0.5 g/L initial CR concentration show non-spontaneous adsorption of these samples. The inverse correlation between \( \Delta G^0 \) and the temperature imply more favorable adsorption at high temperatures. The positive \( \Delta H^0 \) indicates an endothermic reaction of adsorption. The positive values of \( \Delta S^0 \) show the modified rice husk’s affinity for CR, an increase in the degree of freedom.
of the adsorbed dye, and increased randomness at the solid/solution interface (Gedam et al.
2019).

Isosteric heat of adsorption

Isosteric heat of adsorption ($\Delta H_X$, KJ/mol), presented as the heat of adsorption at a constant
amount of adsorbed adsorbate, is of great importance for obtaining an optimized adsorption
process. The Clausius–Clapeyron equation is used to estimate this thermodynamic quantity
(Simsek and Beker 2014).

\[
\frac{d(\ln C_e)}{dT} = -\frac{\Delta H_X}{RT^2}
\]  

(23)

In the present study, the calculations for $\Delta H_X$ are made at constant surface coverage of $Q_e =
0.04, 0.06, 0.08$ and $0.1$ g/g. The ln of equilibrium concentration ($C_e$) at a constant amount of
adsorbed dye plotted versus $1/T$ is used to determine $\Delta H_X$ from the slope of the plots. In the case
of physical adsorption, $\Delta H_X$ should be below 80 KJ/mol while for chemisorptions, the $\Delta H_X$
values range between 80 and 400 KJ/mol (Saha and Chowdhury 2011). The calculated values of
isosteric heat of adsorption are presented in Table 7. The values between 2.71 and 72.60 KJ/mol
mean physical adsorption of CR onto ERH.

Table 7 Isosteric heat of adsorption of Congo red onto ERH

| Model                  | Constant Surface Coverage $Q_e$ (g/g) | Parameters | Adsorbent dosage (g/L) |
|------------------------|--------------------------------------|------------|------------------------|
|                        |                                      | $\Delta H_X$ (KJ/mol) | $R^2$ | 10   | 20   | 40   |
| Clausius-Clapeyron     | 0.04                                 | 21.11      | 0.9976 | 0.6938 | 0.331 |
|                        | 0.06                                 | 15.91      | 0.8834 | 0.9944 | 0.3526 |
The results presented above showed physical adsorption of Congo red onto the ERH. Lower values of D-R free energy than 8 KJ/mol, lower energy of activation (Ea) than 40 KJ/mol, and the isosteric heat of adsorption (ΔH_X) below 80 KJ/mol confirm the physical adsorption of CR onto ERH. Congo red is a direct dye that presents Na-salt of diazo dye containing two amino and two sulfonic groups responsible for the creation of hydrogen bonds and determination of the CR solubility, respectively. Theoretically, the adsorption of the direct dye onto cellulose occurs with physical hydrogen bonds (Broadbend, 2001), which confirms the aforementioned statement. Considering the information mentioned above, the proposed schematic of adsorption of CR onto ERH is presented in Fig. 3.
4. Conclusion

Equilibrium, kinetic, thermodynamic aspects and mechanism of Congo red adsorption onto rice husk treated with effluent from the cotton scouring are explored. The initial dye concentration, contact time, the mass of rice husk and temperature are crucial in determining the adsorption efficiency of treated rice husk. Adsorption of Congo red follows the Langmuir model, when the mass of rice husk is lower, and the Freundlich model when the dosage is high. The dye removal increases with an increase in adsorbent dose, but the adsorption capacity of the ERH, performed at all temperatures, decreases when the adsorbent mass increases. The maximum adsorption capacity of 149.1 mg CR per gram ERH was obtained with 10 g/L ERH at 70°C, which is one of
the more remarkable results mentioned in the literature. The activation energy calculated by the Dubinin–Radushkevich isotherm, indicates the physical nature of CR adsorption onto ERH, while the adsorption kinetics follows the pseudo-second-order model. The Energy of activation, standard enthalpy of activation, the entropy of activation and free energy of activation, calculated using the thermodynamic Arrhenius and Eyring equations, have shown the spontaneous endothermic mechanism of adsorption. The isosteric heats of adsorption, estimated by Clausius–Clapeyron equation, with values below 80 KJ/mol, also confirm the physical bonding of the adsorbed CR onto ERH. This modification, performed according to the circular economy concept, acts as a straightforward process for obtaining a cheap adsorbent capable of removing Congo red from an aqueous solution and presents a solid base for creating a continuous column-mode process of rice husk modification and purifying the colored effluent from the textile industry.

Notes

The authors declare no competing financial interest.

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