# Preparation, characterization and application of synthesized thiourea formaldehyde-calcium alginate in removing of Reactive black 5

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Preparation, characterization and application of synthesized thiourea formaldehyde-calcium alginate in removing of Reactive black 5

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Abstract

Thiourea formaldehyde calcium alginate (TFCA) composite was successfully synthesized and used for removal of Reactive black 5 dye. The synthesized composite was applied and characterized by Fourier transform infrared spectrometer (FT-IR) spectra, scanning electron microscope (SEM)/EDS, Energy Dispersive X-Ray Analysis (EDX) and X-ray diffraction (XRD). SEM and EDX analyses confirm the homogeneity of the sorbent in terms of composition. Batch adsorption experiments were performed to evaluate the adsorption conditions such as pH value, dye concentration, contact time, temperature and sorbent dose, as well as the ionic strength effect. Experimental data have been modeled by using Langmuir, Freundlich, Dubinin Radushkevich (D–R) and Temkin isotherms. Kinetic adsorption data modeled using PFORE, PSORE, Morris Weber and Elovich. Thermodynamic parameters (ΔG, ΔH, and ΔS) were evaluated for the dye adsorbent systems. These data indicated an exothermic spontaneous adsorption process that kinetically followed the pseudo-second-order adsorption process.

Removal of Reactive Black 5 (RB5) dye from aqueous solution the results showed that the maximum adsorption capacity was 0.2 mmol·g⁻¹, observed at pH 1 and temperature 25 °C. Equilibrium adsorption was achieved within 60 min.

Keywords: RB5; composite; isotherm; kinetics; thermodynamics.
1. Introduction

Water pollution is an important environmental problem and receives major worldwide concerns\textsuperscript{1-3}. Dyes discharged together with industrial textile wastewaters are main organic pollutants due to they are highly visible and undesirable even at low concentrations in water\textsuperscript{4-6}. More seriously, most organic dyes are toxic, non-biodegradable, and even teratogenic, carcinogenic, mutagenic, which create the serious threats to human health and marine organisms\textsuperscript{7,8}. Dyes are used in large quantities in various industries including textile, healthcare, paint, printing, leather processing, food processing etc. to color their products. Hence, the dyes must be efficiently removed from the discharged wastewater to solve the ecological, biological and industrial problems. Many treatment methods for dyes removal including chemical, biological and physical. Among many physical methods used for dye removal from aqueous solution including adsorption, electrochemical precipitation, ion exchange, membrane filtration (ultrafiltration, reverse osmosis) irradiation and electro kinetic coagulation\textsuperscript{9,10}. Adsorption techniques have been shown to be a feasible option, both technically and economically. The adsorbents with high capacity and high rate play a critical role in the adsorption removal of dye molecules. Many works have been published investigating the removal of dyes or from industrial effluents. The present study reports the synthesis and characterization of thiourea
formaldehyde calcium alginate (TFCA) and its dye adsorbed efficiency of Reactive black 5 (RB5) dye ions removal by batch technique. TUF resin can be synthesized easily in aqueous solutions by controlling the acidity during the synthesis. The synthesis includes hydroxy methylation and condensation steps. TUF resin has very complex structure depending on the mole ratio of thiourea to formaldehyde that attain high surface area and excellent adsorption capacity\textsuperscript{11}. Alginate is by far the most popular biopolymer for immobilization purposes. Alginate forms sol gel propagules easily, has good acid stability, and remarkable dye ion adsorption properties attributed to the presence of carboxylic groups on the surface of the alginate beads\textsuperscript{12}, modifications of thiourea-formaldehyde sorption properties by incorporation of sorptive materials such as calcium alginate to improved sorption performance of alginate through amine and thio groups of thiourea. To the best of our knowledge there have been no reports on thiourea-formaldehyde crosslinked alginate resin. Experimental parameters affecting the adsorption process such as pH solution, initial adsorbate concentration, contact time, temperature, adsorbent dosage and solution ionic strength were studied. The experimental equilibrium adsorption data was analyzed by isotherm and kinetic models. The thermodynamics of the adsorption indicated spontaneous and endothermic nature of the sorption process.

2. Experimental
2.1. Chemicals and reagents

All chemicals which used were of analytical grade and demineralized water was used for the preparation of all aqueous solutions. Sodium alginate was purchased as alginic acid sodium salt (Fluka Co), Acid dye Reactive black 5 (Table 1) was obtained from (Cromatos SRL), hydrochloric acid (HCl 35%), sodium hydroxide (NaOH 99.9%) and CaCl₂ were supplied by Merck Company (Germany). A stock solution whose concentration was 1x10⁻³ M was used and could be diluted to the required concentration with demineralized water in the experiment. All chemical reagents are analytical grade and were used as received.

2.2. Physical measurements

In order to confirm the functionalization of the sorbent thiourea Formaldehyde Calcium Alginate (TFCA) composite Spectroscopic data of the investigated dye were obtained using the following instruments: Fourier transform infrared (FTIR) spectrophotometer spectra (KBr discs, 4000 – 400 cm⁻¹) by Jasco-4100 spectrophotometer. The SEM results of the MSAB sample before and after the adsorption processes were obtained using (JEOL-JSM-6510 LV) scanning microscope to observe surface modification. The structure of the synthesized adsorbents was examined by X-ray diffraction measurement (XRD) is recorded on X-ray diffract meter in the range of diffraction angle 2θ = 5 – 80°. The elemental distribution of (TFCA) was analyzed using the energy-dispersive X-ray
spectroscopy (EDX) and taken on a Leo1430VP microscope with operating voltage 5 kV. The Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volume which form N2 adsorption/desorption isotherms on MSAB at 77 K measured on a Quantachrome Nova Instruments version 10 were calculated. UV-visible spectrophotometer (Perkin-Elmer AA800 Model AAS) was employed for absorbance measurements of samples. HANNA Instruments pH meter (model 211) and Maxturdy 30 (Wisd) were used for pH adjustment and shaking, respectively.

2.3. Synthesis of thiourea-Formaldehyde Encapsulated Alginate

2.3.1. Synthesis of the thiourea-Formaldehyde polymer

15.2 g (0.2 mol) of thiourea and 40 mL of distilled water were mixed in a 250-mL necked flask equipped with a stirrer and condenser. The flask was heated until thiourea was dissolved. Then 15 mL of formaldehyde (37% aqueous solution, containing 0.2 mol of formaldehyde) was added to the reaction mixture and the solution pH was adjusted to 3 with 2 mL of acetic acid. The reaction was carried out for 6 h with heating (95°C) and stirring. The product was washed with dilute NaOH solution, distilled water, and ethanol.

2.3.2. Encapsulated of Alginate with thiourea-Formaldehyde

Fifty grams of sodium alginate solution (4%, w/v) were mixed with 4 g of thiourea-formaldehyde resin and 48 mL of distilled water. The mixture of alginate
and the resin powder was distributed dropwise into a CaCl$_2$ (20g L$^{-1}$) stirred solution. The gel beads were kept in the CaCl$_2$ solution for 24 h, for complete gelation. Finally, the produced calcium alginate beads encapsulated with thiourea-formaldehyde resin rinsed with distilled water, ethanol and acetone, then dried at room temperature.

**The aim of modification of thiourea-Formaldehyde resin with alginate**

1- Because it was impossible to use the fine particles of thiourea-Formaldehyde resin in column systems (head loss and clogging effect).

2- These composite materials take advantage of the sorption properties of both thiourea-Formaldehyde resin and alginate.

3- Amine and thio groups from thiourea contribute to improved sorption performance of alginate.

**2.4. Batch adsorption studies**

The adsorption experiments of anionic dye RB5 were carried out in batch equilibrium mode. A (0.02 – 0.1 g) sample of (TFCA) composite with 25 mL aqueous solution of a (1.2x10$^{-5}$ – 5x10$^{-5}$ M) (RB5) solution at various pHs (1– 9) reached for 120 min was adjusted by adding a small amount of HCl or NaOH solution (0.01 – 0.1 M) using a pH meter. Samples were collected and filtrated through A Whatman (number 40) filter paper and the filtrates were subjected to quantitative analyses. The equilibrium concentration of each solution was
determined at the wavelength of UV-maximum ($\lambda_{\text{max}}$) at 597 nm using Perkin-Elmer AA800 spectrophotometer Model AAS. Dye adsorption experiments were also accomplished to obtain isotherms at various temperatures (20 – 40 °C) and at a range of (1.2x $10^{-5}$ – 5x $10^{-5}$ M) dye concentrations for 90 min by using a shaker water bath. These experiments were carried out with different ionic strength, dye concentration and adsorbent dosage.

3. Results and discussion

3.1. Characterization of adsorbents

The various constituents of (TFCA) per chemical and analytical techniques are applied and characterized with further analysis as: IR spectroscopy. Scanning electron microscopic photographs revealed the absorptive nature of adsorbent. The presence of (TFCA) was examined by X-ray diffraction measurement (XRD) is recorded on X-ray diffract meter. The elemental distribution of (TFCA) was analyzed using the energy-dispersive X-ray spectroscopy (EDX). N2 adsorption/desorption isotherms on (TFCA) was measured on a Quantachrome Nova Instruments version 10, from which the Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volume were calculated.

3.1.1. Infra-red spectrometry

The FT-IR spectra of (TFCA) Particles Wave number range 4000–400 cm$^{-1}$ (Fig. 1) showed that the broad band's appearing in the range of 3500–3200 cm$^{-1}$ can be
attributed to the hydroxyl group (O-H stretching vibrations) of calcium alginate. The symmetric and asymmetric aliphatic C-H stretching bands were observed at 3046.98 and 2958.27 cm\(^{-1}\), respectively. The bands at 1608.34 and 1546.63 cm\(^{-1}\) were attributed to the asymmetric and symmetric stretching vibrations of carboxylate group of alginates, respectively. The bands at 1434.78 and 1280.5 cm\(^{-1}\) were attributed to the C-O stretching vibration of pyranosyl ring and the C-O stretching with contributions from C-C-H and C-O-H deformations\(^{13}\). The peak at 1145.51 cm\(^{-1}\) for C-O-C stretching was also seen with TF resin. The bands at 960.37 cm\(^{-1}\) for thiourea functional group N-C-S stretching and at 744.38 cm\(^{-1}\) for C-S stretching\(^{14}\). Thus, we inferred that thiourea-formaldehyde capsulated with alginate resin. The spectra of dye loaded (TFCA) sorbent has very similar FT-IR profiles the same bands are appearing on all spectra, the only small differences are observed, a small shift in some of these bands.

3.1.2. scanning electron microscope (SEM)

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent. Scanning electron micrographs of raw (TFCA) and adsorbed (RB5) with the dye are shown in (Fig. 2a, b). (Fig. 2a) shows a granular material of CaCO\(_3\) coating on (TFCA) has considerable numbers of pores.
where, there is a good possibility for dyes to be trapped and adsorbed into these pores. The SEM picture of (TFCA) adsorbed with tested dye (RB5) show very distinguished dark spots (Fig. 2b) which can be taken as a sign for effective adsorption of (RB5) dye molecules in the cavities and pores of this adsorbent.

3.1.3. X-ray Diffraction (XRD) analysis

XRD analysis (Fig. 3) was used for characterizing the crystalline structure of the material, which is induced by the magnetite core. The XRD pattern shows a limited number of peaks characteristics of iron oxides may be identified. The large fraction of polymer may contribute to explain the poor resolution of the XRD pattern. The peaks characteristics of (TFCA) are usually identified at indices: 16.8 (98), 21.94 (158), 43.96 (70), 64.3 (54) and 77.42 (70).

3.1.4. Energy-dispersive X-ray spectroscopy (EDX) analysis

From the EDX analysis of the corresponding surface (Fig. 4), it can be seen that the boundary film was composed of TFCA. EDX analysis of free TFCA: element (Wt %): C 28.71; N 21.40; O 9.92; S 37.40; Ca 2.56, element (At %): C 41.43; N 26.49; O 10.75; S 20.22; Ca 1.11 and element (K-Ratio) C 0.0309; N 0.0206; O 0.0105; S 0.3523; Ca 0.0196.

3.1.5. Barrett-Joyner-Halenda (BJH) pore volume and Brunauer-Emmett-Teller (BET) surface area
N$_2$ adsorption/desorption isotherm determined at 77 K on the prepared sample (TFCA) is illustrated in (Fig. 5). The specific surface area is estimated by application the BET equation in its normal range of applicability with a value of 16.20 Å for the cross-section area of N$_2$ molecule. The total pore volume, taken at P/P$_o$ = 0.9477, and the pore size distribution is estimated by BJH method. The adsorption isotherm of the sample is classified as type (II) with H4 hysteresis loop classified by IUPAC that extending down to [P/Po] = 0.38; this deep hysteresis loop arises from aggregates (assemblage of particles which are loosely coherent) of plate-like form giving rise to slit-shaped pores\textsuperscript{18}. The wide hysteresis loop reveals the remarkable mesoporous structure of the prepared sample. The surface area $A_{\text{BET}} = 55.134$ m$^2$/g, the total pore volume = 0.093 cm$^3$/g and the average pore radius = 33.77 Å which confirms the mesoporosity of the prepared sample. The narrow pore size distribution reveals the homogeneity of the pore size through the sample matrix.

3.1.6. Determination of point of zero charge

The point of zero charge (pH$_{\text{PZC}}$) was determined by solid addition method\textsuperscript{19}. A series of 0.1 M KNO$_3$ solutions (25 ml) were prepared and their pH values (pH$_0$) were adjusted in the range of (1 – 12) by addition of (0.01– 0.1 mol/L) HCl and NaOH. To each solution, 0.1 g of (TFCA) was added and the suspensions were agitated in an orbital shaker at 200 rpm. The final pH values of the supernatant
were determined (pH<sub>f</sub>) after 48 h. The difference between initial (pH<sub>0</sub>) and final (pH<sub>f</sub>) values (∆pH = pH<sub>0</sub> – pH<sub>f</sub>) (Y-axis) was plotted against the initial pH<sub>0</sub> (X-axis). The intersection of resulting curve yielded the pH<sub>PZC</sub> where ∆pH = zero.

3.2. Batch Adsorption Analysis

3.2.1. Effect of pH

The pH definitely affects the adsorption of the dye. In order to determine the adsorption behavior of the dye,<sup>20</sup> tests were carried out at predetermined experimental conditions taking initial dye concentration as $1 \times 10^{-4}$ M, 25 °C and 0.02 g adsorbent dosage. Solutions (0.01, 0.1 M) of NaOH and HCl were employed to adjust the pH of the test solutions. In the case of adsorption of RB5 on (TFCA) a pH range of (1–9) was selected. (TFCA) composite has been proven to be an effective adsorbent for the removal of acid dye (RB5) via adsorption from aqueous solution at pH 1 (Fig. 6). It shows that the adsorption capacity of acid dye RB5 onto (TFCA) composite increases significantly with decreasing pH which is due to neutralization of the positive charge at the surface of the adsorbents by the negatively charged dye molecule. The maximum removal of RB5 for contact time 90 min was carried out at pH 1. at strongly acidic pHs, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and the negatively charged dye molecules (-SO<sub>3</sub>Na)<sup>21</sup>. As the pH of the adsorption system increases, the number of negatively charged sites increases and
the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favor the adsorption of dye anions, due to the electrostatic repulsion. Also, lower adsorption of RB5 at alkaline pH is due to the presence of excess hydroxyl ions competing with the dye anions for the adsorption sites\textsuperscript{22}. Basic conditions favor adsorption of dye; thus pH 1 was considered as optimum pH for the adsorption of the dye.

3.2. Effect of adsorbate concentrations

The removal of RB 5 dye by adsorption on the adsorbent (TFCA) composite was shown to increase with time and attained a maximum value at about 60 min, and thereafter, it remained almost constant (Fig. 7). Adsorption experiment for the dye RB5 were carried out by selecting a concentration range of $1.2 \times 10^{-5}$ to $5 \times 10^{-5}$ M with an adsorbent dosage of 0.02 g of the adsorbent at 25 °C and pH 1. the amount of removed dyes was decreased. It was clear that the removal of the dye was dependent on the initial concentration of the dye because the decrease in the initial dye concentration increased the amount of dye adsorbed. This is very clear because, for a fixed adsorbent dose, the number of active adsorption sites to accommodate adsorbate ions remains unchanged but with increasing adsorbate concentration, the adsorbate ions to be accommodated increase and hence the percentage of adsorption goes down.

3.4. Effect of contact time
The amount of the dye adsorbed at definite intervals of time at 25 °C was monitored for a fixed amount of (TFCA) at a particular concentration. (Fig. 8) indicate that with the increase in time, the adsorption rate of the dye over adsorbent increase with time and attained a maximum value at about 60 min, and thereafter, it remained almost constant 120 min of time was required to bring complete saturation of the active sites of adsorbent.

3.3. Effect of temperature

Temperature dependence of the adsorption process is associated with several thermodynamic parameters. The plot of amount of adsorbate per amount of adsorbent of adsorption as a function of temperature (Fig. 9) shows a small increasing trend with rise in temperature from 25 to about 45 °C. Equilibrium capacity can be changed by temperature of the adsorbent for a particular adsorbate. In our case the experimental data obtained at pH 1, adsorbent dosage of 0.02 g, and initial concentration of $3 \times 10^{-5}$ M show no change in the adsorption capacity at temperatures from 25 to 45 °C. The increase in adsorption with increasing temperature also indicates the endothermic nature of the dye adsorption over adsorbent.

3.4. Effect of adsorbent dosage

The study of the effect of amount of the adsorbents was necessary in order to observe the minimum possible amount, which shows maximum adsorption. The
amount of the adsorbent was varied from (0.02 to 0.1 g). In this experiment, the adsorptive ability of the adsorbent at a definite concentration of 3x 10\(^{-5}\) M dye solution at pH 1 at 25 °C was considered. The graphical presentation is provided in (Fig. 10). Adsorption of dyes as a function of the (TFCA) composite dosage shows that the uptake of dye per gram of adsorbent increases with increasing adsorbent dosage from 0.02 to 0.06 g. This is because a higher dose of adsorbent led to increased surface area and more adsorption sites are available causing higher removal of the dyes\(^{23}\). Further increase in adsorbent dose did not cause any significant increase in % removal of dyes. This was due to the concentration of dyes reached at equilibrium status between solid and solution phase.

3.5. Effect of ionic strength (addition of NaCl)

The effect of chloride ions on RB5 removal was examined, by addition of increasing concentrations of NaCl (Fig. 11). For the studied adsorbents increasing the amount of NaCl slightly decreases the sorption capacity: the sorption capacity decreases by 20%, when NaCl concentration reaches 20 g L\(^{-1}\). This is probably due to the competitor effect of chloride anions against RB5 anions for interaction with adsorption sites. It is noteworthy, that when even NaCl concentration reaches 40 g L\(^{-1}\) the reduction in the adsorption capacity decreases by 1.5%, this indicates that even under these drastic conditions a high adsorption capacity is maintained.

3.5. Adsorption studies
3.5.1. Adsorption isotherms

The main factors that play the key role for the dye–adsorbent interactions are charge and structure of dye, adsorbent surface properties, hydrophobic and hydrophilic nature, hydrogen bonding, electrostatic interaction, steric effect, and Vander Waals forces\textsuperscript{24}. Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which are usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at fixed temperature\textsuperscript{25}. The equilibrium relationships between adsorbent (TFCA) and adsorbate RB5 are best explained by sorption isotherms.

The present investigation deals with the applicability of Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin adsorption isothermal models to the experimental data.

3.5.1.1. Langmuir isotherm

The Langmuir adsorption, which is the monolayer adsorption, depends on the assumption that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption occurs at specific homogeneous sites within the adsorbent. It then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Furthermore, the Langmuir equation assumes of a structurally
homogeneous adsorbent, where all sorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can occur. The saturated or monolayer capacity can be represented as the known linear form of Langmuir equation,

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}K_L} + \frac{C_e}{q_{\text{max}}}
\]

(1)

where \(C_e\) is the equilibrium dye concentration in solution (mol. L\(^{-1}\)), \(q_e\) is the equilibrium dye concentration in the adsorbent (mmol. g\(^{-1}\)), \(q_{\text{max}}\) is the monolayer capacity of the adsorbent (mmol. g\(^{-1}\)) and \(K_L\) is the Langmuir adsorption constant (L. mol\(^{-1}\)). Therefore, a plot of \(C_e/q_e\) vs. \(C_e\) (Fig. 12a) gives a straight line of slope \(1 / q_{\text{max}}\) and the intercept \(1 / (q_{\text{max}}K_L)\). The Langmuir equation is applicable to homogeneous sorption, where the sorption of each sorbate molecule onto the surface is equal to sorption activation energy.

The Langmuir isotherm proposes that the coverage of adsorbate molecules on a solid surface occurs in a monolayer. It is assumed that once the adsorbent site is covered with the dye molecules no further adsorption occurs at that site. It also suggests that all the adsorption sites are of equivalent energy. The equation was developed by Irving Langmuir in 1916\(^{27}\). The equation is stated as:

\[
\frac{C_e}{q_e} = \frac{1}{q_mK_t} + \frac{C_e}{q_m}
\]

(2)
C_e in the above equation denotes the equilibrium concentration in (mol. L\(^{-1}\)) of the adsorbate, q_e, is the amount adsorbed in (mmol. g\(^{-1}\)), q_m is the adsorption capacity (mmol. g\(^{-1}\)), and K_L signifies the Langmuir constant (L. mol\(^{-1}\)). (Fig. 12a) show the plot obtained for 1/q_e against 1/C_e, at 25 °C with the help of which Langmuir constants can be calculated (Table 2).

3.5.1.2. Freundlich isotherm

The Freundlich isotherm is a result of the assumption that the adsorption occurs on a heterogeneous surface and non-uniform distribution of the heat of adsorption over the adsorbent surface takes place, characterized by the heterogeneity factor 1/n, describes reversible adsorption and is not restricted to the formation of the monolayer:

\[
q_e = K_F C_e^{1/n}
\]

(3)

where q_e is the equilibrium dye concentration on adsorbent (mmol. g\(^{-1}\)), C_e is the equilibrium dye concentration in solution (mol. L\(^{-1}\)), K_F is Freundlich constant (L. g\(^{-1}\)) and 1/n is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking Anti logarithms of the equation:

\[
ln q_e = ln K_F + \frac{1}{n} ln C_e
\]

(4)

Therefore, a plot of log q_e vs. log C_e for the adsorption of RB5 onto (TFCA) composite was employed to generate the intercept value of K_F and the slope of 1/n. The graphical presentation for the Freundlich isotherm for the adsorbent along with
its R² values are given in (Fig. 12b). High R² values of the straight lines obtained confirm the validity of Langmuir adsorption isotherm for adsorbent. The Freundlich constants for the adsorbent was calculated are presented in (Table 2).

The Langmuir and Freundlich parameters for the adsorption of RB5 are listed in (Table 2). It is evident from these data that the surface of (TFCA) composite is mostly made up of heterogeneous adsorption patches.

On comparing the regression coefficients obtained for Langmuir and Freundlich it can be very well predicted that the Langmuir isotherm is more favored by the adsorption process. The data presented above clearly show that Langmuir adsorption isotherm graphs (Fig. 12a) are better fit that Freundlich adsorption isotherm graphs (Fig. 12b); this indicates that a monolayer adsorption process, taking place in the present case, is more favorable than multilayer formation of the adsorbate. Based on the above analysis of the adsorption isotherm.

The dimensionless parameter of equilibrium, separation factor ‘r’ suggested by Adam and Chua, Weber and Chakrabarti²⁸ can be calculated as:

\[ r_L = \frac{1}{1 + K_L C_0} \]  

where C₀ is the initial concentration and K_L signifies the Langmuir constant. There are four probabilities for the value of r: (i) for favorable adsorption, 0 < r < 1, (ii) for unfavorable adsorption, r > 1, (iii) for linear adsorption, r = 1, and (iv) for irreversible adsorption, r = 0. The obtained values of separation factor are 0.168,
0.158, 0.148 and 0.14 for (TFCA) at 25 °C temperatures, clearly indicating the favorability of the adsorption process.

The correlation coefficients for Langmuir ($R_L^2$) and for Freundlich ($R_F^2$) values are obtained in (Table 2). One of the Freundlich constants $K_F$ indicates the adsorption capacity of the adsorbent. The other Freundlich constant $n$ is a measure of the deviation from linearity of the adsorption. If a value for $n$ is equal to unity the adsorption is linear. If a value for $n$ is below unity, this implies that adsorption process is chemical, but a value for $n$ is above unity, adsorption is favorable a physical process\textsuperscript{29}. The highest value of $n$ at equilibrium is 2.62 (Table 2), represents favorable adsorption and therefore this would seem to suggest that the adsorption is physical, which is referred the adsorption bond becomes weak\textsuperscript{30} and conducted with Vander Waals forces rather than chemical adsorption.

**3.5.1.3. Dubinin–Radushkevich isotherm**

The linear form of the Dubinin–Radushkevich isotherm\textsuperscript{31,32} is expressed as:

$$\ln q_e = \ln Q_{DR} - K_{DR} \varepsilon^2$$  \hspace{1cm} (6)

where $q_e$ is the amount of the dye adsorbed per unit weight of the adsorbent (mg·g\textsuperscript{-1}), $Q_{DR}$ is the maximum sorption capacity provided by the intercept in (mol·g\textsuperscript{-1}), $K_{DR}$ (mol\textsuperscript{2}·J\textsuperscript{-2}) is obtained from the slope of the straight-line plot of $\ln q_e$ versus $\varepsilon^2$, and $\varepsilon$, the Polanyi potential, can be calculated as:
\[ \varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \]  

(7)

where R is the universal gas constant (in kJ. mol\(^{-1}\) K\(^{-1}\)) and T is the temperature in Kelvin. E, the mean sorption energy, is calculated using the following relation:

\[ E = \frac{1}{\sqrt{-2K_{DR}}} \]  

(8)

(Fig. 13a) present \( \ln q_e \) versus \( \varepsilon^2 \) plots for the RB5–(TFCA), at 25 °C, straight line with regression coefficients almost unity is obtained. The values of E for RB5–(TFCA) was found to be less than 8 kJ mol\(^{-1}\), suggesting that Physisorption\(^{33}\) is responsible for the adsorption process for both systems (Table 2).

3.5.1.3. Temkin isotherm

The Temkin isotherm assumes that the heat of adsorption of all the molecules increases linearly with coverage\(^{34}\). The linear form of this isotherm can be given as:

\[ q_e = \beta_T \ln K_T + \beta_T \ln C_e \]  

(9)

where \( q_e \) is the amount adsorbed at equilibrium in (mmol. g\(^{-1}\)), \( k_1 \) is the Temkin isotherm energy constant in (L mol\(^{-1}\)), and \( k_2 \) is the Temkin isotherm constant.

Plots between \( \ln C_e \) versus \( q_e \) for (TFCA) (Fig. 13b) gave straight lines at 25 °C, thereby verifying the Temkin isotherm in the adsorption of RB5 over adsorbent.

Slopes and intercepts of these straight lines helped in determining the values of Temkin constants and these values are depicted in (Table 2) for the (TFCA).

3.5.2. Adsorption kinetic studies
The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid–solution interface. The rate of removal of RB5 by adsorption was rapid initially and then slowed gradually until it attained an equilibrium beyond which there was significant increase in the rate of removal. The maximum adsorption of RB5 onto (TFCA) composite was observed at 90 min and it is thus fixed as the equilibrium time.

Aiming at evaluating the adsorption kinetics of RB5 onto (TFCA) composite, the pseudo-first-order and pseudo-second-order kinetic models were used to fit the experimental data, according to the below kinetic model equations. The pseudo-first-order rate expression of Lagergren equation\textsuperscript{35,36} is given as:

$$
\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303}t
$$

(10)

The pseudo-second-order kinetic model\textsuperscript{36} is expressed as:

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

(11)

where $q_t$ is the amount of dye adsorbed (mmol. g\textsupers{-1}) at various times $t$, $q_e$ is the maximum adsorption capacity (mmol. g\textsupers{-1}) for pseudo-first-order adsorption, $K_1$ is the pseudo-first-order rate constant for the adsorption process (min\textsupers{-1}), $q_t$ is the maximum adsorption capacity (mmol. g\textsupers{-1}) for the pseudo-second-order adsorption, $K_2$ is the rate constant of pseudo second-order adsorption (g. mol\textsupers{-1} min\textsupers{-1}). The straight-line plots of $\log (q_e - q_t)$ versus $t$ for the pseudo-first-order reaction and $t/q_t$
versus t for the pseudo-second-order reaction (Figs. 14a, b) for adsorption of RB5 onto (TFCA) composite have also been tested to obtain the rate parameters. The \( k_1 \), \( k_2 \), \( q_e \), \( q_b \), and correlation coefficients, \( r_1^2 \) and \( r_2^2 \) for RB5 under different temperatures were calculated from these plots and are given in (Table 3). The correlation coefficients (\( r_1^2 \)) for the pseudo-first-order kinetic model are between 0.9079 and the correlation coefficient (\( r_2^2 \)) for the pseudo-second-order kinetic model is 1.0. It is probable, therefore, that this adsorption system is not a pseudo-first-order reaction; it fits the pseudo-second-order kinetic model.

3.5.3. Thermodynamic parameters

In any adsorption process, both energy and entropy considerations must be considered in order to determine what process will occur spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. The amount of RB5 adsorbed onto (TFCA) composite at equilibrium and at different temperatures (20, 25, 30, 40, 45 °C) has been examined to obtain thermodynamic parameters for the adsorption system. The pseudo-second order rate constant of RB5 adsorption is expressed as a function of temperature by the following Arrhenius type relationship\(^{37}\):

\[
\ln K_2 = \ln A - \frac{E_a}{RT}
\]  

(12)

where \( E_a \) is the Arrhenius activation energy of adsorption, \( A \) is the Arrhenius factor, \( R \) is the gas constant and is equal to 8.314 J mol\(^{-1}\) K\(^{-1}\) and \( T \) is the operating
temperature in Kelvin. A linear plot of ln \( k_2 \) vs 1/T for the adsorption of RB5 onto (TFCA) composite (Fig. 15a) was constructed to generate the activation energy from the slope \((-E_a / R)\). The chemical (chemisorption) or physical (Phys sorption) adsorption mechanism is often an important indicator to describe the type of interactions between RB5 and (TFCA) composite. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. Low activation energies (5 – 40 kJ. mol\(^{-1}\)) are characteristics for Phys sorption, while higher activation energies (40 – 800 kJ. mol\(^{-1}\)) suggest chemisorption\(^{38}\). The result obtained is +5.13 kJ mol\(^{-1}\) (Table 4) for the adsorption of RB5 onto (TFCA) composite, indicating that the adsorption has a low potential barrier and corresponds to a Phys sorption. The other thermodynamic parameters, change in the standard free energy \((\Delta G^0)\), enthalpy \((\Delta H^0)\) and entropy \((\Delta S^0)\) were determined by using following equations:

\[
K_c = \frac{C_e}{C_s}
\]  

(13)

\[
\Delta G^0 = -RT\ln K_c
\]  

(14)

\[
\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]  

(15)

where \( K_c \) is the equilibrium constant, \( C_e \) is the amount of RB5 adsorbed on the (TFCA) composite of the solution at equilibrium (mol. L\(^{-1}\)), \( C_s \) is the equilibrium concentration of the RB5 in the solution (mol. L\(^{-1}\)). The \( K_2 \) of the pseudo-second-order model in Table \( 2 \) was used to obtain \( C_e \) and \( C_s \). T is the solution temperature.
(K) and R is the gas constant. \( \Delta H^o \) and \( \Delta S^o \) were calculated from the slope and the intercept of Van’t Hoff plots of \( \ln K_C \) vs \( 1/T \) (Fig. 15b), the values of adsorption thermodynamic parameters are listed in (Table 4). The negative value of the change of free energy \( (\Delta G^o) \) (-8.23, -9.11, -9.99, -10.88, -12.64) confirms the feasibility of the adsorption process and also indicates spontaneous adsorption of RB5 onto (TFCA) composite in the temperature range studied\(^{39}\). The positive value of the standard enthalpy change \( (\Delta H^o) \) (21.91 kJ mol\(^{-1}\)) indicates that the adsorption is physical in nature involving weak forces of attraction and is also endothermic, thereby demonstrating that the process is stable energetically. At the same time, the low value of \( \Delta H^o \) implies that there was loose bonding between the adsorbate molecules and the adsorbent surface. The positive value of standard entropy change \( (\Delta S^o) \) (0.0794 J mol\(^{-1}\) K\(^{-1}\)) suggests the increased randomness at the solid–solution interface during the adsorption of RB5 onto (TFCA) composite.

The diagram obtained in Langmuir plots further help in the determination of thermodynamic parameters. Gibb’s free energy \( (\Delta G^o) \), change in entropy \( (\Delta S^o) \), and change in enthalpy \( (\Delta H^o) \) were calculated using the following relations\(^{40}\):

\[
\Delta G^o = -RT \ln K_C
\]

\[
\Delta H^o = -R \left( \frac{T_2 T_1}{T_2 - T_1} \right) X \ln \left( \frac{K_{c2}}{K_{c1}} \right)
\]

\[
\Delta G^o = \Delta H^o - T \Delta S^o
\]
In the above equations \( K_c, K_{c1} \) and \( K_2 \) are the Langmuir constants at 20, 30, and 40 \(^\circ\)C, respectively, as obtained from slopes and intercepts of Langmuir isotherms. The positive values of entropy change and enthalpy show the increased randomness and endothermic nature of the process, respectively, whereas the negative values of free energy suggest the feasibility of the process. The above values have been calculated for both adsorption systems presented in (Table 4).

3.6. Desorption studies

Desorption studies help to elucidate the mechanism and recovery of the adsorbate and adsorbent. (TFCA) composite was washed three times with sodium hydroxide solution at pH around 12 then filtered and left to be dried at 50 °C in an oven overnight and stored on desiccator prior to reuse in the adsorption again. As the pH of desorbing solution was increased, the percent of desorption increased. As the pH of the system increases, the number of negatively charged sites increased. A negatively charged site on the adsorbent favors the desorption of dye anions due to the electrostatic repulsion\(^{41}\). At pH 12, a significantly high electrostatic repulsion exists between the negatively charged surface of the adsorbent and anionic dye. The removal of dye by adsorption on the adsorbent (TFCA) was compared before and after recovering process at the same conditions: initial concentration of dye solution 3x10\(^{-5}\) M at about 25 °C, pH 1 and 0.02 g adsorbent dosage for 60 min.
The maximum adsorption of RB5 dye onto (TFCA) composite before the recovering process was 88.10%, while after recovering process was 87.50%.

3.7. Comparison of adsorption of RB5 dye with various sorbents

(Table 5) shows the comparison of maximum sorption capacities of the (TFCA) with a series of values found in the literature (together with the best operating conditions reported by respective authors). The (TFCA) adsorbent has a adsorption capacity of the same order of magnitude as other sorbents; although the utilization of chitin adsorbent\textsuperscript{42}, nano-ZnO/Chitosan composite beads (nano-ZnO/CT-CB)\textsuperscript{43}, The potential of using walnut wood activated carbon as low-cost adsorbents\textsuperscript{44} and The templated crosslinked-chitosan microparticles\textsuperscript{45}, showed better adsorption capacity. It is noteworthy that the (TFCA) sorbent has an important advantage related to their fast kinetics. The high sorption capacity of the (TFCA) adsorbents towards RB5 dye reveals that adsorbent could be promising for practical application in RB5 dye removal from wastewater.

4. Conclusion

The present study clearly demonstrated that (TFCA) can be very effectively employed for the removal of dyestuff RB5 from aqueous solution and wastewaters. These materials are available freely, locally, and have been proven to be much
more efficient than the conventional expensive adsorbents. The preliminary adsorption data were obtained by observing the effect of pH, concentration, contact time, temperature, dose of adsorbent, etc. and their dependence on adsorption was determined. The high adsorption capacity of RB5 onto (TFCA) composite in highly acidic solutions (pH 1) is due to the strong electrostatic interactions between its adsorption site and dye anion. Adsorption isotherm parameters for Langmuir, Freundlich, D–R and Temkin were determined and their constants were calculated. The equilibrium data fit well the Freundlich model of adsorption for RB5 dye. The highest value of n at equilibrium (2.62) suggests that the adsorption is physical. The kinetic data tends to fit very well in the pseudo-second-order kinetic model with high correlation coefficients, the adsorption process is interpreted as film diffusion at all temperatures. The negative values of $\Delta G^o$ indicate the spontaneity of the process, were the negative value of $\Delta H^o$ reveals that the adsorption process was exothermic in nature and a physical adsorption. The positive value of $\Delta S^o$ implies the increment of an orderliness between the adsorbate and the adsorbent molecules. SEM images show well defined and characterized morphological images that are evident for the effective adsorption of RB5 molecules on the cavities and pores of the (TFCA) composite. Desorption studies were conducted and the results showed that (TFCA) composite can be used in adsorption of acid
dyes several times by regeneration process using sodium hydroxide solution at pH around 12.

References


### Tables

**Table 1**: Properties of the adsorbate (RB 5) anionic dye.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Reactive Black 5</td>
</tr>
<tr>
<td>Symbol</td>
<td>RB5</td>
</tr>
<tr>
<td>Type color</td>
<td>anionic</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>( \text{C}<em>{26}\text{H}</em>{21}\text{N}<em>{5}\text{Na}</em>{4}\text{O}<em>{19}\text{S}</em>{6} )</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>991.82</td>
</tr>
<tr>
<td>Wavelength of maximum absorption (nm)</td>
<td>597</td>
</tr>
<tr>
<td>Molar extinction coefficient, ( \varepsilon_{597} ) (M(^{-1}) cm(^{-1}))</td>
<td>34450</td>
</tr>
</tbody>
</table>

Chemical structure of color
Table 2: Adsorption isotherms, linear forms and Parameters of the sorption isotherm models

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>Value of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td>$\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The constants $q_m$ and $K_L$ are calculated by the plot of $C_e/q_e$ versus $C_e$ with slope $1/q_m$ and intercept $1/(q_mK_L)$</td>
<td>$q_m$ (mmole g$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$q_m$ (mmole g$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_L$ (L mg$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$n$</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td>$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>KF and n1 can be calculated from a linear plot of $\ln q_e$ against $\ln C_e$</td>
<td>$K_F$ (L mg$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td><strong>Dubinin–Radushkevich</strong></td>
<td>$\ln q_e = \ln Q_{DR} - K_{DR} \varepsilon^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The slope of the plot of $\ln q_e$ versus $\varepsilon^2$ gives $K_{DR}$ (mol$^2$ (kJ$^2$)$^{-1}$) and the intercept yields the adsorption capacity, $Q_{DR}$ (mg g$^{-1}$)</td>
<td>$Q_{DR}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_{DR}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta_T$</td>
</tr>
<tr>
<td><strong>Temkin</strong></td>
<td>$q_e = \beta_T \ln K_T + \beta_T \ln C_e$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The parameters $B_T$ and $K_T$ are the Temkin constants that can be determined by the plot of $q_e$ versus $\ln C_e$</td>
<td>$K_T$ (L mg$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
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</table>
Table 3: Kinetics models, linear forms and parameters for RB5 adsorption.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>Value of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo-First-order kinetic</strong></td>
<td>log ( (q_e - q_t) = \log q_e - \left( \frac{K_1}{2.303} \right) t )</td>
<td>( k_1 (\text{min}^{-1}) ) 0.0259</td>
</tr>
<tr>
<td></td>
<td>The plot of ln ( (q_e - q_t) ) against ( t ) gives a straight line with the slope (-k_1) and intercept ln( q_e )</td>
<td>( q_e (\text{mmole g}^{-1}) ) 0.3011 ( R^2 ) 0.9079</td>
</tr>
<tr>
<td><strong>Pseudo-second-order kinetic</strong></td>
<td>( \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} )</td>
<td>( k_2 (\text{min}^{-1}) ) 12.9118</td>
</tr>
<tr>
<td></td>
<td>Values of ( k_2 ) and ( q_e ) for different initial concentrations of dye were calculated from the slope and intercept of the linear plot of ( t/q_t ) versus ( t )</td>
<td>( q_e (\text{mmole g}^{-1}) ) 1.97328 ( R^2 ) 1</td>
</tr>
<tr>
<td><strong>Intraparticle diffusion</strong></td>
<td>( q_t = K_i t^{1/2} + X )</td>
<td>( K_i (\text{mg g}^{-1} \text{min}^{-1/2}) ) 0.00109</td>
</tr>
<tr>
<td></td>
<td>The parameters ( K_i ) and ( X ) were determined from the linear plot of ( q_t ) versus ( t^{1/2} )</td>
<td>( X (\text{mg g}^{-1}) ) 1.9634 ( R^2 ) 0.8595</td>
</tr>
<tr>
<td><strong>Elovich</strong></td>
<td>( q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t )</td>
<td>( \beta (\text{g mg}^{-1}) ) 336.7</td>
</tr>
<tr>
<td></td>
<td>The constants ( \alpha ) and ( \beta ) were obtained from the slope and intercept of a line plot of ( q_t ) versus ( \ln t )</td>
<td>( \alpha (\text{mg g}^{-1} \text{min}^{-1}) ) 7.0979 ( R^2 ) 0.9134</td>
</tr>
<tr>
<td><strong>Experimental data</strong></td>
<td></td>
<td>( q_e (\text{exp}) (\text{mmole g}^{-1}) ) 1.9721</td>
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</table>
**Table 4:** Standard enthalpy, entropy and free energy changes for adsorption.

<table>
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<tr>
<th></th>
<th>∆H&lt;sup&gt;o&lt;/sup&gt; (kJ mol&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>∆S&lt;sup&gt;o&lt;/sup&gt; (J mol&lt;sup&gt;-1&lt;/sup&gt; K&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>E&lt;sub&gt;a&lt;/sub&gt; (kJ mol&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>∆G&lt;sup&gt;o&lt;/sup&gt; (kJ mol&lt;sup&gt;-1&lt;/sup&gt;)</th>
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<tbody>
<tr>
<td></td>
<td>21.91</td>
<td>0.0794</td>
<td>5.13</td>
<td>293 K</td>
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<td>298 K</td>
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<td></td>
<td>308 K</td>
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<td>318 K</td>
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<td></td>
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<td>-12.64</td>
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**Table 5:** Comparison of sorption capacity for RB5 dye with various adsorbents

<table>
<thead>
<tr>
<th>Adsorbent material</th>
<th>Initial pH</th>
<th>Contact time (min)</th>
<th>Temperature (°C)</th>
<th>Initial concentration (mg/L)</th>
<th>Sorbent dosage (g L⁻¹)</th>
<th>Sorption capacity (mg g⁻¹)</th>
<th>References</th>
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<tr>
<td>chitin</td>
<td>3.2</td>
<td>300</td>
<td>54</td>
<td>50</td>
<td>-</td>
<td>41.8</td>
<td>42</td>
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<tr>
<td>Nano- ZnO/CT-CB</td>
<td>4.0</td>
<td>360</td>
<td>30</td>
<td>30</td>
<td>0.1</td>
<td>198.44</td>
<td>43</td>
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<tr>
<td>walnut wood activated carbon</td>
<td>5.0</td>
<td>120</td>
<td>30</td>
<td>40</td>
<td>0.6</td>
<td>19.34</td>
<td>44</td>
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<tr>
<td>crosslinked-chitosan</td>
<td>3.0</td>
<td>7200</td>
<td>30</td>
<td>4000</td>
<td>0.4</td>
<td>2941</td>
<td>45</td>
</tr>
<tr>
<td>Thiourea-formaldehyde Alginate</td>
<td>1.0</td>
<td>60</td>
<td>25</td>
<td>0.03</td>
<td>0.02</td>
<td>198.36</td>
<td>This work</td>
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</table>
Captions of Figures:

Fig. 1: FT-IR spectrum of the (TFCA) adsorbent.

Fig. 2: Scanning electron micrographs of; (a) unloaded (TFCA), (b) RB5-loaded (TFCA).

Fig. 3: Powder X-ray diffraction (XRD) pattern of (TFCA) particles.

Fig. 4: Energy-dispersive X-ray spectroscopy (EDX) of (TFCA).

Fig. 5: pore volume and surface area for (TFCA).

Fig. 6: pH effect on adsorption of RB5 using the adsorbent: (T: 25 ± 1°C; C0=1x10-4 M).

Fig. 7: adsorption isotherms onto the adsorbent (pH 1; T: 25 ± 1°C).

Fig. 8: Effect of contact time.

Fig. 9: Effect of temperature.

Fig. 10: Effect of sorbent dose on adsorption (C0: 5x10-4 M; T: 25 ± 1°C; pH 1).

Fig. 11: Effect of ionic strength (addition of NaCl).

Fig. 12: adsorption isotherm models (a) Langmuir (b) Freundlich for removal of RB5 on (TFCA).

Fig. 13: adsorption isotherm models (a) Dubinin–Radushkevich (b) Temkin model.

Fig. 14: Modeling of RB5 kinetic adsorption with (TFCA): (a) PFORE, (b) PSORE (c) intraparticle diffusion (Morris and Weber equation), (d) Elovich.

Fig. 15: Van't Hoff (a) and Arrhenius (b) plots for adsorption onto the adsorbent.
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