



Adsorption of hazardous azocoumarin from aqueous solution using activated carbon made from rice straw

Ashraf A. El-Bindary^{1*}, Adel Z. El-Sonbati¹, Ahmad A. Al-Sarawy²,
Khaled S. Mohamed³, Mansour A. Farid¹

¹Department of Chemistry, Faculty of Science, University of Damietta, Damietta 34517, Egypt.

²Department of Mathematical and Physical Engineering, Faculty of Engineering, University of Mansoura, Mansoura, Egypt.

³Engineering Chemistry Department, Higher Institute for Engineering and Technology, Damietta, Egypt.

Received 30 June 2014, Revised 3 Aug 2014, Accepted 3 Aug 2014.

*Corresponding author. E-mail: abindary@yahoo.com (A.A. El-Bindary); Tel.: (+2 01114266996)

Abstract

Batch experiments were conducted to study the adsorption of hazardous azocoumarin onto low cost activated carbon made from rice straw (ACRS) in aqueous solution with respect to concentration of adsorbate, adsorbent dosage, contact time, solution pH and temperature. Surface modification of rice straw using scanning electron microscopy (SEM) was obtained. Surface area and pore volumes of ACRS were determined by nitrogen adsorption/desorption experiments at 77 K. Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were determined. The activation energy of adsorption was also evaluated for the adsorption of azocoumarin onto ACRS. The kinetic data obtained with different initial concentration and temperature were analyzed using a pseudo-first-order and pseudo-second-order equations. The activation energy, change of free energy, enthalpy and entropy of adsorption were also evaluated for the adsorption of azocoumarin onto ACRS. The thermodynamics of the adsorption indicated spontaneous and exothermic nature of the process. The results indicate that ACRS could be employed as low-cost material for the removal of acid dyes from aqueous solution.

Keywords: Adsorption; Activated carbon of rice straw; Azocoumarin; Isotherms; Kinetics.

1. Introduction

Coumarin and its derivatives represent one of the most important classes of compounds possessing numerous biological activities [1]. Coumarin derivatives are widely used as additives in food and cosmetics [2], pharmaceuticals and optical brighteners [3] and fluorescent dyes [4]. Azocoumarin and its derivatives are toxic and carcinogenic in nature. Several methods including adsorption [5,6], coagulation [7], membrane filtration [8] and advanced oxidation [9] have been employed to eliminate dyes from wastewaters. Among them, adsorption has been recognized as a promising technique due to its high efficiency, simplicity of design, ease of operation as well as the wide suitability for diverse types of dyes [10,11]. Because the dye effluent may cause damage to aquatic biota and human by mutagenic and carcinogenic effects, the removal of dye pollutants from wastewater is of great importance [12]. In recent years, the search for low-cost adsorbents that have dye-binding capacities has intensified. This has led many workers to search for cheaper alternatives such as coal, fly ash, silica gel, wool wastes, agricultural wastes, wood wastes and clay minerals [13,14]. Due to its large surface area, high adsorption capacity and surface reactivity.

Activated carbons, the most important commercial adsorbents, adsorption is one of the most often used technologies for the removal of natural or synthetic organic compounds in water. The Egyptian Environmental protection Agency regarded activated carbon adsorption as the best available technology for the removal of organic contaminants limited in the environmental regulations. In Egypt, rice straw is an easily available agricultural waste material, produced in large quantities as a by-product of rice milling and create potential environmental problems. The waste products which are the main contributors to biomass burning are wheat residue and rice straw. The disposal of rice straw by open-field burning frequently causes serious air pollution, hence new economical technologies for rice straw disposal and utilization must be developed. In order to improve the sorption capacity of these biomaterials, the low cost agricultural by-products were converted to activated carbon.

In continuation to our interest in study on dye adsorption onto low cost biomaterials [15-18], we synthesize and characterize of new hazardous azocoumarin and investigate its adsorption onto a low cost activated carbon made from rice straw as adsorbent. Physical and chemical characteristics of the adsorbent (ACRS) were evaluated with N₂ adsorption/desorption experiments at 77 K. The influences of adsorption parameters such as initial adsorbate concentration, adsorbent dosage, contact time, solution pH and temperature on the adsorption performance of azocoumarin were investigated. The kinetic and thermodynamic parameters were also calculated to determine rate constants and adsorption mechanism. The experimental data were fitted into Langmuir and Freundlich equations to determine which isotherm gives the best correlation to experimental data.

2. Materials and methods

2.1. Physical measurements

C, H, N and S were determined on Automatic Analyzer CHNS Vario ELIII, Germany. Spectroscopic data of the azocoumarin dye were obtained using the following instruments: FT-IR spectra (KBr discs, 4000-400 cm⁻¹) by Jasco-4100 spectrophotometer; the ¹H NMR spectrum by Bruker WP 300 MHz using DMSO-d₆ as a solvent containing TMS as the internal standard; Mass spectrum by Shimadzu GC-MS-QP2010 Plus instrument. The SEM results of the RSC sample before and after the adsorption processes were obtained using (JEOL-JSM-6510 LV) scanning microscope to observe surface modification. UV-visible spectrophotometer (Perkin-Elmer AA800 Model AAS) was employed for absorbance measurements of samples. An Orion 900S2 model digital pH meter and a Gallenkamp Orbital Incubator were used for pH adjustment and shaking, respectively. N₂ adsorption/desorption isotherms on ACRS at 77 K 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.

2.2. Synthesis of azocoumarin

4-((3-(4-(4-amino-2-oxo-2H-chromen-3-yl)-5-cyanofuran-2-yl)-4-hydroxyphenyl) diazenyl)benzenesulfonic acid (Fig. 1) was prepared using a method describes in the literature [19]. A well stirred solution of sulphanic acid (0.1 mole) in 2 N hydrochloric acid (125 ml) was cooled in an ice-bath and diazotized with 0.1 N sodium nitrite solution (100 ml). The mixture was stirred at 0-5 °C for 1 h. The above cold diazonium solution compound (2) was added dropwise to a cold solution of compound (1) in sodium hydroxide solution (5 %, 30 ml). The reaction mixture was stirred for 2-3 h until coupling was complete. The solid precipitate was filtered, washed with water, dried and crystallized from absolute ethanol to give compound (3). Yield 65%; yellow solid; mp = 262°C; FTIR spectrum (KBr discs)(ν cm⁻¹): 3436 (OH), 3353, 3312 (NH₂), 2234 (CN); ¹H-NMR spectrum in d₆-DMSO (ppm): 3.80 (br s, 2H, NH₂), 7.00-8.2 (m, 12H, ArH) 9.01 (s, 1H, OH), 9.07 (s, 1H, OH); Mass spectrum, MS m/z 528 (M+). Anal.: Calcd. for C₂₆H₁₆N₄O₇S₂ (528): C, 59.09; H, 3.05; N, 10.60; S, 6.07. Found C, 59.11; H, 3.07; N, 10.63; S, 6.07.

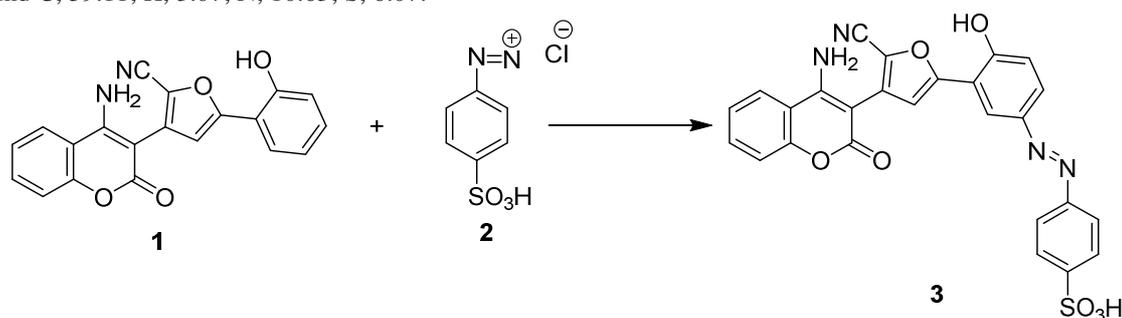


Figure 1: Structure of azocoumarin (3).

2.3. Preparation of activated carbon made from rice straw

Activated carbon made from rice straw (ACRS) as adsorbent was collected from Tammy Amdid, Dakahlia, Egypt Biogas Factory. The concept is based on the burning of waste rice straw in a special incinerator at the temperature of 1000-1200 °C. During the burning process the hydrocarbons are converted to carbon oxides, hydrogen, methane, propane and other gases. The carbon waste was left to cool down. In our laboratory the activated carbon made from rice straw (ACRS) was crushed, ground and sieved through a 200 μm sieve and washed several times with bidistilled water. The adsorbent sample was dried at 120°C for 48 h. preserved in the desiccators over anhydrous CaCl₂ for further use.

2.4. Adsorption experiments

The adsorption experiments of azocoumarin were carried out in batch equilibrium mode. A 0.1-0.9 g sample of ACRS with 100 ml aqueous solution of 30-100 mg.L⁻¹ sodium salt of azocoumarin solution at various pHs (1-9) reached for 120 min. The initial pH of dye solution was adjusted at different values with HCl or NaOH solution (1 M). The optimum pH was determined and used through all adsorption processes. Experiments were conducted for various time intervals to determine when adsorption equilibrium was reached and the maximum removal of the dye was attained. The solution was then

filtered through a Whatmann (number 40) filter paper to remove any organic or inorganic precipitates formed under acidic or basic conditions and the filtrates were subjected to quantitative analyses. The equilibrium concentration of each solution was determined at the wavelengths of UV-maximum (λ_{max}) at 460 nm. Dye adsorption experiments were also accomplished to obtain isotherms at various temperatures (25–60 °C) and at arrange of 30–100 mg L⁻¹ dye concentrations for 120 min by using thermostated shaker with shaking speed of 200 rpm.

Calibration curves were constructed to correlate concentrations to different absorbance values. Construction of this calibration curves was verified and the maximum wavelengths that corresponded to maximum absorbance for the dye was determined.

3. Results and discussion

3.1. Brunauer-Emmett-Teller (BET) surface area.

The Brunauer-Emmett-Teller (BET) [20] surface area and Barrett-Joyner-Halenda (BJH) pore size of ACRS have been investigated using N₂ adsorption/desorption measurements at 77 K (Fig. 2). The BET surface area of ACRS was obtained as 67.4 m²g⁻¹ can supply more surface active sites, leading to an enhancement of adsorption performance. It is suggested that the pore structure of the adsorbent ACRS consists of macropores, mesopores and micropores. The total pore volume (V_p) at $P/P_0 = 0.959$ was obtained as 0.134 cm³g⁻¹, which indicating that ACRS has a mesoporous structure and makes it easy for azocoumarin to penetrate into the mesopores of ACRS.

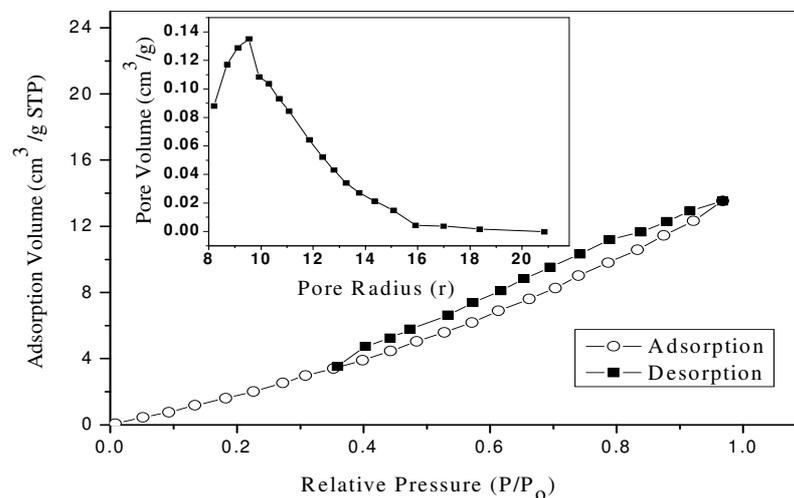


Figure 2: BET adsorption-desorption isotherms and pore volume distribution (insert) of ACRS.

3.2. SEM analysis

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 (ACRS) and adsorbed (ACRS) with the dye are shown in Fig. 3 and 4, respectively. From (Fig. 3), it is clear that, raw (ACRS) has considerable numbers of pores where, there is a good possibility for dyes to be trapped and adsorbed into these pores. The SEM picture (Fig. 4) of (ACRS) adsorbed with tested dye show very distinguished dark spots which can be taken as a sign for effective adsorption of azocoumarin molecules in the cavities and pores of this adsorbent [18].

3.3. Effect of adsorbate concentrations

The removal of azocoumarin by adsorption on the adsorbent (ACRS) was shown to increase with time and attained a maximum value at about 75 min, and thereafter, it remained almost constant (Fig. 5). On changing the initial concentration of dye solution from 30 to 100 mg/L at 25 °C, pH 3 and 0.5 g/L adsorbent dosage 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 increases and hence the percentage of adsorption goes down.

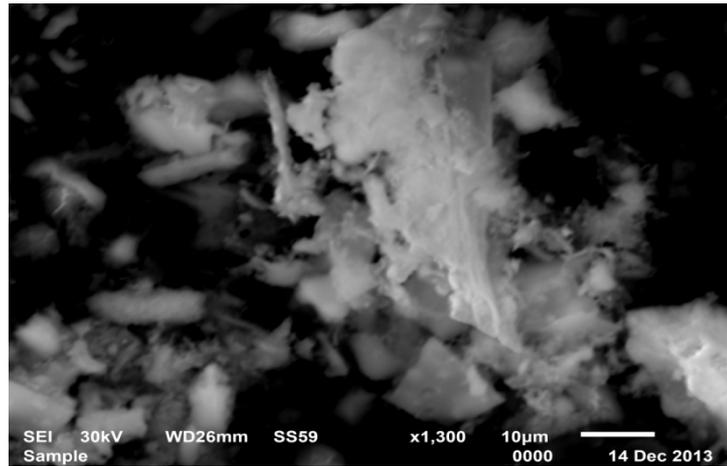


Figure 3:ACRS before adsorption of azocoumarin.

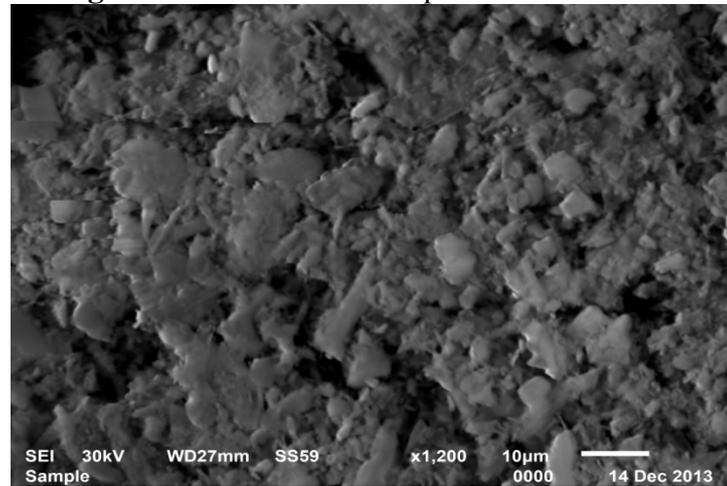


Figure 4:ACRS after adsorption of azocoumarin.

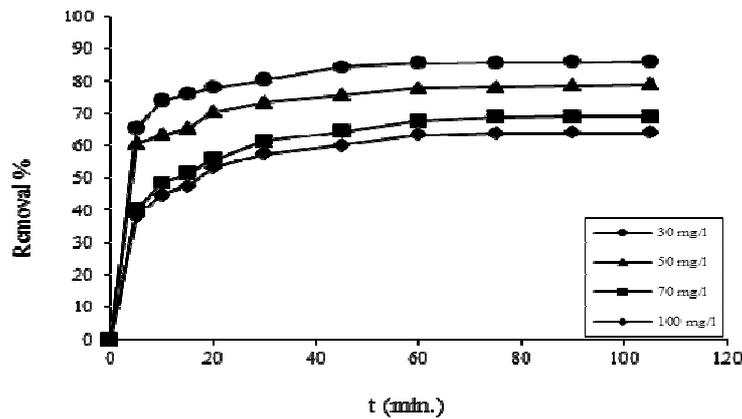


Figure 5: Effect of initial dye concentration on adsorption of azocoumarin onto ACRS, dosage 0.5 g/l, pH = 3 and 25 °C.

3.4. Effect of adsorbent dosage

The uptake of dye with change in adsorbent dosage (0.1–0.9 g) at adsorbate concentrations of 100 mg/L at 25 °C and pH 3 is presented at (Fig.6). Adsorption of dye shows that the uptake of dye per gram of adsorbent increases with increasing adsorbent dosage from 0.1 to 0.9 g. This is because at higher dose of adsorbent, led to increased surface area and more adsorption sites are available causing higher removal of the dye. Further increase in adsorbent dose, did not cause any significant increase in % removal of dye. This was due to the concentration of dyes reached at equilibrium status between solid and solution phase.

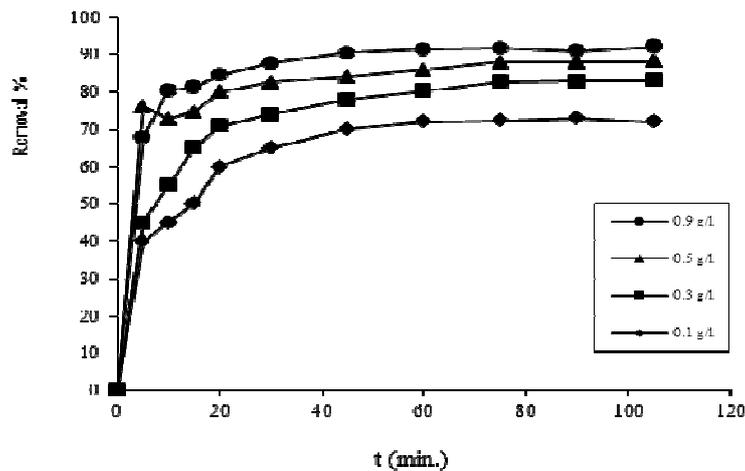


Figure 6: Effect of ACRS dosage on the adsorption of azocumarin at concentration 100 mg/l, pH = 3 and 25 °C.

3.5. 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. 7) shows a small increasing trend with rise in temperature from 25 to about 60 °C. Equilibrium capacity can be changed by temperature of the adsorbent for a particular adsorbate. In our case the experimental data obtained at pH 3, adsorbent dosage 0.5 g/L, and initial concentration of 100 mg/L show that increase in the adsorption capacity at temperature from 25 to 60 °C.

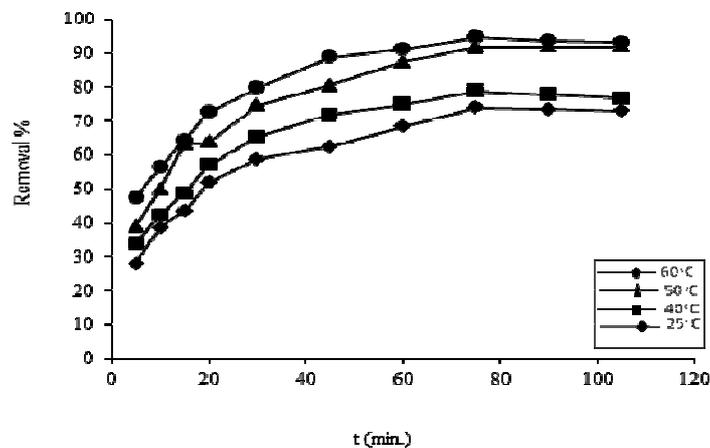


Figure 7: Effect of temperature on adsorption of azocumarin onto ACRS, dosage 0.5 g/l, dye concentration 100 mg/l and pH = 3.

3.6. Effect of pH

The removal of the tested dye by activated carbon of rice straw (ACRS) at different pH values was studied at initial concentrations of 60 mg/L of the dye, 25 °C and 0.5 g/L adsorbent dosage. The pH value of the solution was an important controlling parameter in the adsorption process. ACRS has proved to be an effective adsorbent at pH 3 for the removal of the dye from aqueous solution (Fig. 8). It shows that the adsorption capacity of tested dye onto ACRS increases significantly with decreasing pH. The maximum removals for contact time 75 min was carried out at pH 3. 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 tested dye at alkaline pH is due to the presence of excess hydroxyl ions competing with the dye anions for the adsorption sites [21,22].

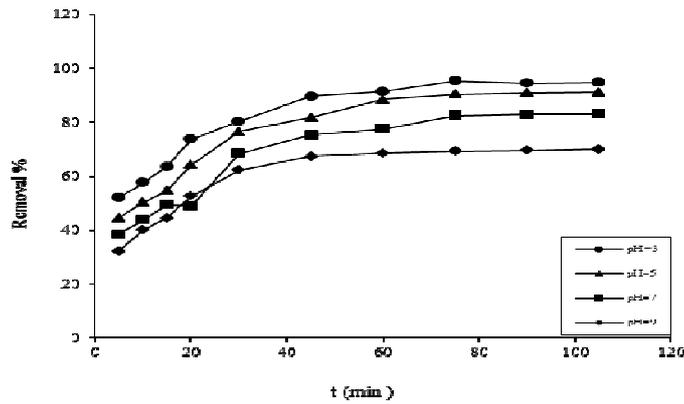


Figure 8: Effect of pH on the adsorption of azocoumarin onto ACRS at dosage 0.5 g/l and temperature 25 °C.

3.7. 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 van der Waal forces etc. [23]. Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at fixed temperature [24–26]. The equilibrium experimental data for the adsorption of the tested dye on the (ACRS) was compared using two isotherm equations namely, Langmuir and Freundlich.

3.7.1. 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 is assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Furthermore, the Langmuir equation is based on the assumption 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 [27-31],

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

where C_e is the equilibrium dye concentration in solution (mol L^{-1}), q_e is the equilibrium dye concentration in the adsorbent (mol g^{-1}), q_{\max} is the monolayer capacity of the adsorbent (mol 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.9), gives a straight line of slope $1/q_{\max}$ and the intercept $1/(q_{\max}K_L)$. The Langmuir equation is applicable to homogeneous sorption, where the sorption of each sorbate molecule onto the surface has equal to sorption activation energy.

3.7.2. Freundlich isotherm

The Freundlich equation [30-32] is an empirical equation employed to describe heterogeneous systems, characterized by the heterogeneity factor $1/n$, describes reversible adsorption and is not restricted to the formation of the monolayer:

$$q_e = K_F \cdot C_e^{1/n} \quad (2)$$

where q_e is the equilibrium dye concentration on adsorbent (mol 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 logarithms of the equation :

$$\log q_e = \log K_F + 1/n \cdot \log C_e \quad (3)$$

Therefore, a plot of $\log q_e$ vs. $\log C_e$ for the adsorption of tested dye onto RSC (Fig. 10) was employed to generate the intercept value of K_F and the slope of $1/n$.

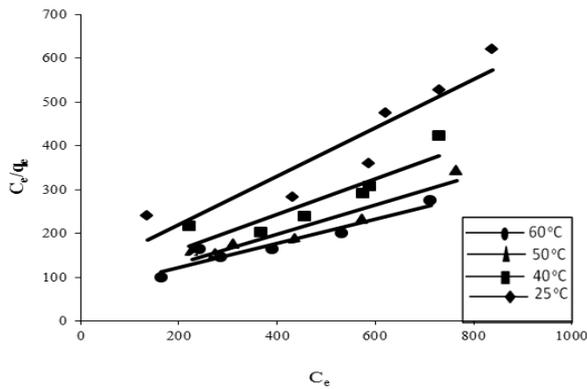


Figure 9: Langmuir plot for adsorption of azocoumarin onto ACRS at different temperatures.

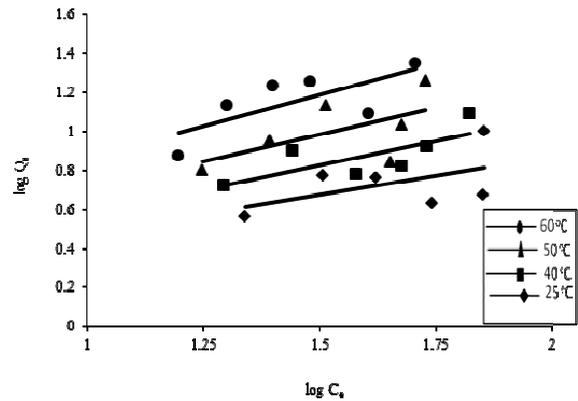


Figure 10: Freundlich plots for adsorption of azocoumarin onto ACRS at different temperatures.

The Langmuir and Freundlich parameters for the adsorption of the dye are listed in Table 1. It is evident from these data that the surface of (ACRS) is mostly made up of heterogeneous adsorption patches. The correlation coefficients for Langmuir (r_L^2) and for Freundlich (r_F^2) values are compared in Table 1.

One of the Freundlich constants K_F indicates the adsorption capacity of the adsorbent. The other Freundlich constants 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 to unity, this implies that adsorption process is chemical, but a value for n is above to unity, adsorption is favorable a physical process [33]. The highest value of n at equilibrium is 1.831 (Table 1), this would seem to suggest that the adsorption is physical [34].

Table 1: Langmuir and Freundlich parameters for the adsorption of azocoumarin onto (ACRS).

Temperature (°C)	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mol g ⁻¹)	K_L (L mol ⁻¹)	r_L^2	K_F (L g ⁻¹)	n	r_F^2
25	53.69	0.0176	0.806	1.639	1.731	0.931
40	64.692	0.0251	0.799	1.707	1.542	0.968
50	136.55	0.0212	0.911	1.904	1.439	0.938
60	146.34	0.0315	0.945	2.123	1.264	0.969

3.8. 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 tested dye 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 was observed at 75 min. and it is thus fixed as the equilibrium time.

Aiming at evaluating the adsorption kinetics of tested dye onto (ACRS), 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 [35,36] is given as:

$$\log (q_e - q_t) = \log q_e - k_1 t \quad (4)$$

The pseudo-second-order kinetic model [36] is expressed as:

$$t/q_t = 1/k_2 q_2^2 + 1/q_2 t \quad (5)$$

where qt is the amount of dye adsorbed (mol g⁻¹) at various times t , q_e is the maximum adsorption capacity (mol g⁻¹) for pseudo-first-order adsorption, k_1 is the pseudo-first-order rate constant for the adsorption process (min⁻¹), q_2 is the maximum adsorption capacity (mol g⁻¹) for the pseudo-second-order adsorption, k_2 is the rate constant of pseudo-second-order adsorption (g mol⁻¹ min⁻¹). The straight-line plots of $\log (q_e - qt)$ versus t for the pseudo-first-order reaction and t/qt versus t for the pseudo-second-order reaction (Figs. 11 and 12) for the adsorption of tested dye onto (ACRS) have also been tested to obtain the rate parameters. The k_1 , k_2 , q_e , q_2 , and correlation coefficients, r_1^2 and r_2^2 for the dye under different temperatures were calculated from these plots and are given in Table 2.

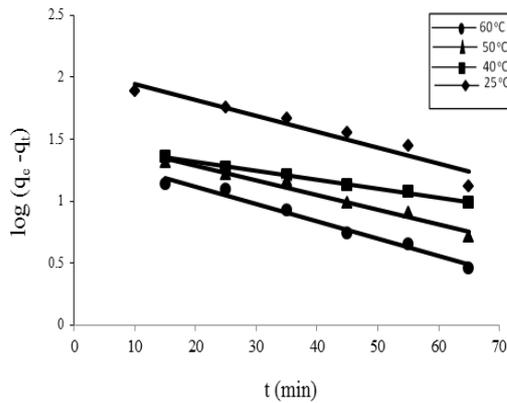


Figure 11: Pseudo-first-order kinetic plot for the adsorption of azocoumarin at different temperatures.

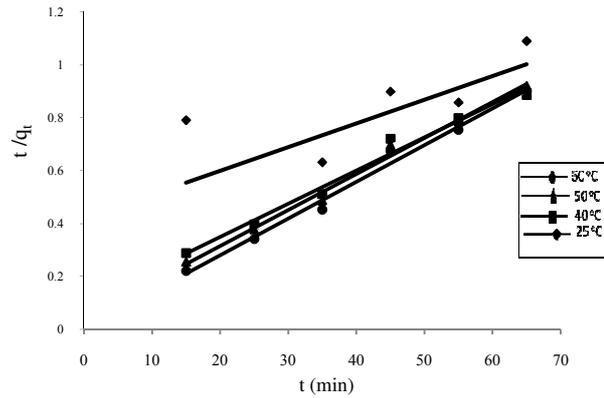


Figure 12: Pseudo-second-order kinetic plot for the adsorption of azocoumarin at different temperatures.

Table 2: Pseudo-first-order, Pseudo-second-order for the adsorption of azocoumarin onto (ACRS).

Temperature (°C)	Pseudo-first-order			Pseudo-second-order		
	q_e (mol g ⁻¹)	k_1 (min ⁻¹)	r_1^2	q_2 (mol g ⁻¹)	k_2 (g mol ⁻¹ min ⁻¹)	r_2^2
25	0.931	4.19	0.979	151.94	0.195	0.998
40	0.944	4.29	0.973	152.37	0.209	0.998
50	0.949	3.38	0.970	151.01	0.498	0.997
60	0.953	3.42	0.968	150.59	0.579	0.997

The correlation coefficients (r_1^2) for the pseudo-first-order kinetic model are between 0.968 and 0.989 and the correlation coefficients (r_2^2), for the pseudo-second-order kinetic model are between 0.998 and 0.999. It is probable, therefore, that this adsorption system is not a pseudo-first-order reaction, it fits the pseudo-second-order kinetic model.

3.9. Thermodynamic parameters

In any adsorption process, both energy and entropy considerations must be taken into account 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 the dye adsorbed onto (ACRS) at equilibrium and at different temperatures 25, 40, 50, 60 °C, have been examined to obtain thermodynamic parameters for the adsorption system. The pseudo-second-order rate constant of tested dye adsorption is expressed as a function of temperature by the following Arrhenius type relationship [37]:

$$\ln k_2 = \ln A - E_a/RT \quad (6)$$

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 operated temperature. A linear plot of $\ln k_2$ vs $1/T$ for the adsorption (Fig. 13) was constructed to generate the activation energy from the slope ($-E_a/R$). The chemical (chemisorption) or physical (physisorption) adsorption mechanism are often an important indicator to describe the type of interactions between tested dye and (ACRS). 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 physisorption, while higher activation energies (40–800 kJ mol⁻¹) suggest chemisorption [38]. The result obtained is +15.56 kJ mol⁻¹ (Table 3) for the adsorption of the dye onto (ACRS), indicating that the adsorption has a low potential barrier and corresponding to a physisorption.

The other thermodynamic parameters, change in the standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined by using following equations:

$$K_C = C_A/C_S \quad (7)$$

$$\Delta G^\circ = -RT \ln K_C \quad (8)$$

$$\ln K_C = \Delta S^\circ/R - \Delta H^\circ/RT \quad (9)$$

where K_C is the equilibrium constant, C_A is the amount of dye adsorbed on the (ACRS) of the solution at equilibrium (mol L⁻¹), C_S is the equilibrium concentration of the dye in the solution (mol L⁻¹). The q_2 of the

pseudo-second-order model in Table 3 was used to obtain C_A and C_S . T is the solution temperature (K) and R is the gas constant. ΔH° and ΔS° were calculated from the slope and the intercept of van't Hoff plot of $\ln K_c$ vs. $1/T$ (Fig. 14). The results are given in Table 3.

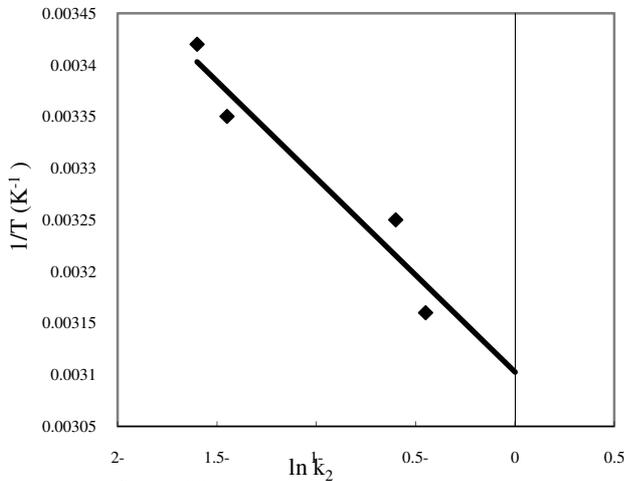


Figure 13: Arrhenius plot of the adsorption of azocoumarin onto ACRS.

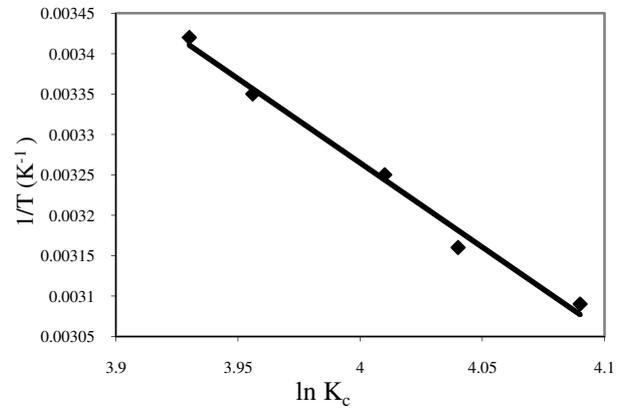


Figure 14: van't Hoff Plot for determination of thermodynamic parameters for the adsorption of azocoumarin onto ACRS.

Table 3: Thermodynamic parameters calculated with the pseudo-second rate constant for azocoumarin onto (ACRS).

Temperature (°C)	K_c	E_a (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J.mol ⁻¹ K ⁻¹)
25	92.643		-33.234		
40	143.056	15.25	-33.654	-12.23	0.092
50	229.374		-33.984		
60	205.754		-34.104		

The values of adsorption thermodynamic parameters are listed in Table 3. The negative value of the change of free energy (ΔG°) confirms the feasibility of the adsorption process and also indicates spontaneous adsorption of tested dye onto (ACRS) in the temperature range studied [39]. The small negative value of the standard enthalpy change (ΔH°) is (-12.23 kJ mol⁻¹) indicate that the adsorption is physical in nature involving weak forces of attraction and is also exothermic, thereby demonstrating that the process is stable energetically. At the same time, the low value of ΔS° implies that there was loose bonding between the adsorbate(0.092J.mol⁻¹K⁻¹) suggest the increased randomness at the solid-solution interface during the adsorption [40].

Conclusion

The present study clearly demonstrated that activated carbon made from rice straw (ACRS) is an effective adsorbent for the removal of azocoumarin from aqueous solution and polluted water. The high adsorption capacity of azocoumarin onto ACRS in highly acidic solutions (pH=3) is due to the strong electrostatic interactions between its adsorption site and dye anion. The Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volume were calculated and found to be 67.4 m²g⁻¹ and 0.134 cm³g⁻¹, respectively. SEM images shows well defined and characterized morphological images that are evident for the effective adsorption of azocoumarin molecules on the cavities and pores of the (ACRS). For the application of Langmuir and Freundlich equations, the experimental results show that the Freundlich model was the best. The highest value of n at equilibrium is 1.831 suggest that the adsorption is physical. The kinetic data tends to fit very well in the pseudo-second-order kinetics model with high correlation coefficients. The ΔG° values were negative, therefore the adsorption was spontaneous in nature. The negative value of ΔH° reveals that the adsorption process was exothermic in nature and a physical adsorption. The positive value of ΔS° suggests the increased of orderliness at the solid-solution interface during the adsorption. Finally, the adsorbent ACRS displayed the main advantages of excellent dispersion in aqueous solution, separation convenience and high adsorption capacity, which implied their application potentials for effective removal of other hazardous pollutants from aqueous solution.

References

1. Flašík R., Stankovičová H., Gáplovský A., Donovalová J., *Molecules* 14 (2009) 4838.
2. Ammar T.A., Abid K.Y., El-Bindary A.A., El-Sonbati A.Z., *Desalination* 352 (2014) 45-51.
3. Kennedy R.O., Thornes R.D., *Coumarins: Biology, Applications and Mode of Action*; John Wiley and Sons, Chichester, UK, (1997).
4. Christie R.M., Morgan K.M., Islam M.S., *Dyes Pigm.* 76 (2008) 741.
5. Fan W., Gao W., Zhang C., Tjiu W.W., Pan J., Liu T., *J. Mater. Chem.* 22 (2012) 25108.
6. Ngah W.S.W., Teong L.C., Hanafiah M., *Carbohydr. Polym.* 83 (2011) 1446.
7. Slokar Y.M., LeMarechal A.M., *Dyes Pigm.* 37 (1998) 335.
8. Madaeni S.S., Jamali Z., Islami N., *Sep. Purif. Technol.* 81 (2011) 116.
9. Serpone N., Horikoshi S., Emeline A.V., *J. Photochem. Photobiol. C* 11 (2010) 114.
10. Dotto G.L., Pinto L.A.A., *Carbohydr. Polym.* 84 (2011) 231.
11. Asgher M., Bhatti H.N., *Ecological Eng.* 38 (2012) 79.
12. Crini G., *Bioresource Technol.* 97 (2006) 1061.
13. Guzel F., Saygili H., Saygili G.A., Koyuncu F., *J. Mol. Liq.* 194 (2014) 130.
14. Jiang X., Sun Y., Liu L., Wang S., Tian X., *Chem. Eng. J.* 235 (2014) 151.
15. El-Deen I.M., Al-Sarawy A.A., El-Halwany M.M., Badawy A.A., *Desal. Water Treat.* 51 (2013) 2564.
16. El-Bindary A.A., Diab M.A., Hussien M.A., El-Sonbati A.Z., Eessa A.M., *Spectrochim. Acta A* 124 (2014) 70.
17. El-Bindary A.A., Hussien M.A., Diab M.A., Eessa A.M., *J. Mol. Liq.* 197 (2014) 236.
18. El-Bindary A.A., El-Sonbati A.Z., Al-Sarawy A.A., Mohamed K.S., Farid M.A., *J. Mol. Liq.*, 199 (2014) 71.
19. Tamam G.H., Bakeer H.M., Abdel-Motelab R.M., Arafa W.A., *J. Chin. Chem. Soc.* 52 (2005) 1191.
20. Brunauer S., Emmett P.H., Teller E., *J. Am. Chem. Soc.* 60 (2002) 309.
21. Alkan M., Demirbas O., Celikcapa S., Dogan M., *J. Hazard. Mater.* 116 (2004) 135.
22. Khan M.R., Ray M., Guha A.K., *Bioresour. Technol.* 102 (2011) 2394.
23. Ahmad R., Kumar R., *J. Environ. Mang.* 91 (2010) 1032.
24. Guendy H.R., *J. Appl. Sci. Res.* 6 (2010) 964.
25. Kiran I., Akar T., Ozcan A.S., Ozcan A., Tunali S., *Biochem. Eng. J.* 31 (2006) 197.
26. Yavuz M., Gode F., Pehlivan E., Ozmert S., Sharma Y.C., *Chem. Eng. J.* 137 (2008) 453.
27. Langmuir I., *J. Am. Chem. Soc.* 38 (1916) 31.
28. Langmuir I., *J. Am. Chem. Soc.* 39 (1917) 1848.
29. Langmuir I., *J. Am. Chem. Soc.* 40 (1918) 1361.
30. Alley A.R., *Water quality control handbook*, McGraw-Hill Education, Europe, London (2000).
31. Woodard F., *Industrial waste treatment handbook*, Butterworth-Heinemann, Boston (2001).
32. Freundlich H.M.F., *Z. Phys. Chem. (Leipzig)* 57A (1906) 385.
33. Tunali S., Ozcan A.S., Ozcan A., Gedikbey T., *J. Hazard. Mater.* B135 (2006) 141.
34. Jiang J.-O., Cooper C., Ouki S., *Chemosphere* 47 (2002) 711.
35. Lagergren S., *Handlingar* 24 (1898) 1.
36. Ho Y.S., McKay G., *Chem. Eng. J.* 70 (1998) 115.
37. Juang R.S., Wu F.C., Tseng R.L., *Environ. Technol.* 18 (1997) 525.
38. Nollet H., Roels M., Lutgen P., Van der Meeren P., Verstraete W., *Chemosphere* 53 (2003) 655.
39. Jaycock M.J., Parfitt G.D., *Chemistry of Interfaces*, Ellis Horwood Ltd, Onichester (1981).
40. Singh D., *Adsorp. Sci. Technol.* 18 (2000) 741.

(2015); <http://www.jmaterenvirosnci.com>