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Use of solid wastes of the soda ash plant as an adsorbent for the removal of anionic dyes: Equilibrium and kinetic studies

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Abstract

Solid wastes (SW) from the distiller waste (DW), which is the by-product of the ammonia-soda process (the Solvay method) for the production of soda ash, has been used as an alternative adsorbent for removing the anionic dyes from aqueous medium. The effects of pH, initial dye concentration and temperature were investigated on kinetics and equilibrium of the adsorption. The results indicated that adsorption was strongly pH dependent. The typical dependence of dye uptake on temperature and the kinetics of adsorption indicated the process to be chemisorption. The results showed that as the pH increased, extent of dye uptake increased and $Ca(OH)_2$ particles precipitated at higher pHs were mainly responsible for the removal of anionic Procion Crimson H-EXL (Reactive Red 231) dye. The necessary time to reach the equilibrium was found to be less than 2 min. Dye uptake process followed the pseudo-second-order rate expression. The Freundlich isotherm best fitted for the adsorption of the dye on SW. Various thermodynamic parameters, such as ΔG°, ΔH° and ΔS° were calculated. The thermodynamics of PC/SW system indicated spontaneous and exothermic nature of the process.

Keywords: Soda ash waste; Wastewater; Dye removal; Adsorption; Isotherm; Kinetics

1. Introduction

The remaining dye molecules, even at very low concentrations in the wastewater of textile industries, are common water pollutants. Their presence in water is highly visible and undesirable and may significantly affect photo-synthetic activity in aquatic life due to reduced light penetration.

Adsorption is an effective process for the removal of dyes from waste effluents [1]. Currently, activated carbons are the most common adsorbents because of their higher adsorption capacities. However, because of its relatively high cost, in relatively recent years, there has been an increasing interest in utilizing low cost adsorbents to remove dyes from wastewater. This has led to a search for industrial wastes, agricultural by-products and natural materials as alternative adsorbents.

Furthermore, anionic dyes are, in general, more problematic than cationic dyes. Mostly, surface charge of these adsorbents is reversed into positive by pre-adsorption of some multivalent cations prior to the adsorption attempt [2].

The utilization of waste materials is increasingly becoming of vital concern because these wastes represent unused resources and, in many cases, present serious disposal problems. During the past decade, a great deal of attention has been given to methods of converting these materials into useful products [3].

Distiller waste (DW) is the main waste material, which is the by-product of the ammonia-soda process (the Solvay method) for the production of soda ash. Nowadays DW, containing $CaCl_2$, unprocessed NaCl, $CaCO_3$, $CaSO_4$, $Ca(OH)_2$ and other substances, creates a huge problem for the ammonia-soda plants [4,5]. The considerable amount of chloride left in the solid wastes restricted to use of them in agriculture and in cement industry.

In this study, the solid waste (SW) from the distiller waste (DW) has been used as an alternative adsorbent for removing the anionic dyes from aqueous medium. The effects of pH, initial dye concentration and temperature were investigated on kinetics and equilibrium of the adsorption. The pseudo-first and pseudo-second-order, and intraparticle diffusion kinetic models were applied. The amount of dye molecules adsorbed at equilibrium was measured. The Langmuir and Freundlich isotherm models were tested for their applicability. The thermodynamic

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Nomenclature

b	Langmuir constant (L/mg)
C_e	equilibrium concentration (mg/L)
C_0	initial dye concentration in solution (mg/L)
ΔG°	Gibbs free energy of adsorption (kJ/mol)
ΔH°	enthalpy change of adsorption (kJ/mol)
k_i	rate parameter of intraparticle diffusion model (mg dye/g adsorbent $min^{-0.5}$)
k_1	rate constant of pseudo-first-order model (min^{-1})
k_2	rate constant of pseudo-second-order model (min g adsorbent/mg dye)
K_F	Freundlich constant ((mg/g)$(L/mg)^{1/n}$)
K_o	sorption equilibrium constant
n	Freundlich constant
q_e	adsorption capacity in equilibrium (mg/g)
q_t	amount of adsorption at time t (mg/g)
Q^0	maximum adsorption capacity (mg/g)
r^2	linear correlation coefficient
R	universal gas constant (=8.314 J/mol K)
ΔS°	entropy change of adsorption (J/mol K)
t	time (min)
T	absolute temperature (K)

parameters were evaluated to define mechanisms of the process.

2. Materials and methods

2.1. Materials

The solid waste (SW) was obtained from the distiller wastewater (DW) provided by Sisecam Mersin Soda Ash Plant, Turkey. The waste sample was analyzed for its chemical composition by using the XRF method and found to contain 112.49 g/L $CaC1_2$, 50.16 g/L NaCl, 3.09 g/L $CaSO_4$, 5.59 g/L $CaCO_3$, 6.43 g/L $Ca(OH)_2$, 1.33 g/L MgO, 1.03 g/L Al_2O_3, 0.43 g/L SiO_2 and 0.13 g/L Fe_2O_3.

Prior to use as an adsorbent, the interference of chloride, which results from NaCl and $CaCl_2$ in the supernatant of the distiller wastewater, was eliminated by elutriation using deionized water. As procedure, the solid was allowed to settle and then the supernatant was decanted (fivefold dilution for each wash). The procedure was repeated five times until it is chloride free. This was checked by the addition of $AgNO_3$ after washing with distilled water to make sure that no precipitate is formed, which is the evidence of chloride existence [4]. The inherent pH of the suspension of the waste without dye was measured as 12.03. A WTW 340i model pH meter was used for measurement of pH of solutions.

The resulted solid sample, which consists mainly of CaO (as $Ca(OH)_2$ in wastewater), $CaCO_3$ and $CaSO_4$ as principle minerals, was dried at 105 °C for 3 h and used as the adsorbent for adsorption studies.

The sample of adsorbent exhibited a uniform particle size distribution. The d_{80} value was determined as about 70 μm by the sub-sieve technique. Bulk and the true density of the sample was measured as 1.42 and 2.47 g/L (by calculation), respectively. The specific surface area of the adsorbent was determined as 10.63 m^2/g by a FlowSorb II-2300 BET apparatus using nitrogen gas as the adsorbate.

An azo reactive Procion Crimson H-EXL (CI Reactive Red 231) having in common the group aminochlorotriazine, a commercially available dye (the purity is above 95% according to the manufacturer) produced by Dystar Textilfarben GmbH & Co., was used as model dye for anionic character without purification. It is solid-dark brown granular powder and soluble in water (140 g/L at 20 °C). The natural pH of the dye solution (500 mg/L) without adsorbent was measured as 7.52. The concentration of the dye in the solution after equilibrium adsorption was determined with Shimadzu brand UV-160 UV visible spectrophotometer by measuring absorbance at λ_{max} of 546 nm for PC.

2.2. Experimental procedure

The adsorption of PC from aqueous solution onto solid waste (SW) was performed using batch equilibrium technique. Adsorption tests were done as a single stage batch test by using Velp DLH model mechanic stirrer. A suspension containing 1 g of adsorbent sample was mixed by stirring the mixture at 200 rpm with a 1 L aqueous solution of dye at a known initial concentration in a flask that immersed in a bath in thermostatted water keeping constant working temperature. An aliquot of the solution was withdrawn at the pre-determined time intervals, and was centrifuged at 5600 rpm for 10 min in order to remove any adsorbent particles. The residual dye concentration in the filtrate was subsequently determined using the spectrophotometer at the wavelength corresponding to the maximum absorbance. The adsorption tests were continued until the equilibrium concentration was reached. The effect of contact time on the amount of dye adsorbed was investigated as a function of initial concentration of dye, pH and temperature. The obtained data from the adsorption tests were then used to calculate the adsorption capacity, q_e (mg/g), of the adsorbent by a mass–balance relationship, which represents the amount of adsorbed dye per the amount of dry adsorbent. All of the experiments were duplicated to check the reproducibility of data and the average value was taken. Replicate experiments showed a maximum deviation of 2.01% in dye uptake measurements.

3. Results and discussion

3.1. Effect of pH on adsorption of PC onto SW

To determine the pH effect on adsorption capacity of SW for PC, dye solutions were prepared at different pH levels within 6–12 after introducing adsorbent at 25 °C and initial dye concentration of 500 mg/L.

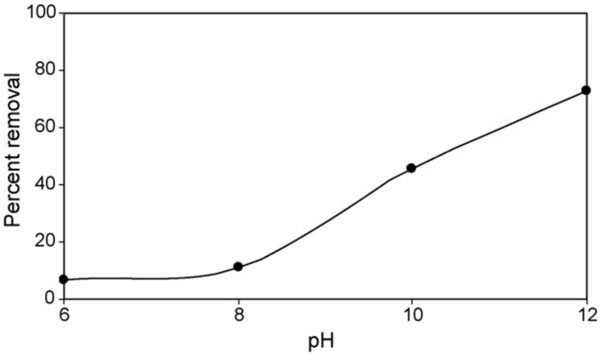

Fig. 1. Effect of pH on the adsorption of PC dye onto SW. Conditions: adsorbent concentration 1 g/L; initial dye concentration 500 mg/L; temperature 25 °C; contact time 10 min; agitation rate 200 rpm.

A plot of the percentage of the removal of PC versus the pH of the solution shown in Fig. 1 indicated that the removal of anionic dye was maximal at a system pH around 12 and decreased as the system pH decreased due to dissolution of the particles in the solution. The percentage of removal increased to 45.29% at pH 10 and to 73.05% at pH 12. The pH effect can be explained with some new adsorption sites developed that is expected due to its solubility constant at pHs greater than 8 [6]. Depending on the pH and Ca^{2+} concentration (112.49 g/L $CaC1_2$ in the DW), calcium may form complexes with OH^- at higher pHs and as a result, calcium hydroxyl species may participate. This implies that the system gradually yielded the insoluble calcium hydroxide complexes through the increasing pH, resulting in the higher capacity of adsorption. The higher adsorption of PC dye molecules at pH value higher than 8 indicated that the precipitated $Ca(OH)_2$ particles were mainly responsible for the removal of PC dye ions, which will be discussed later in adsorption mechanism. Consequently, further experiments were carried out at pH of 12, at which maximum removal obtained for PC.

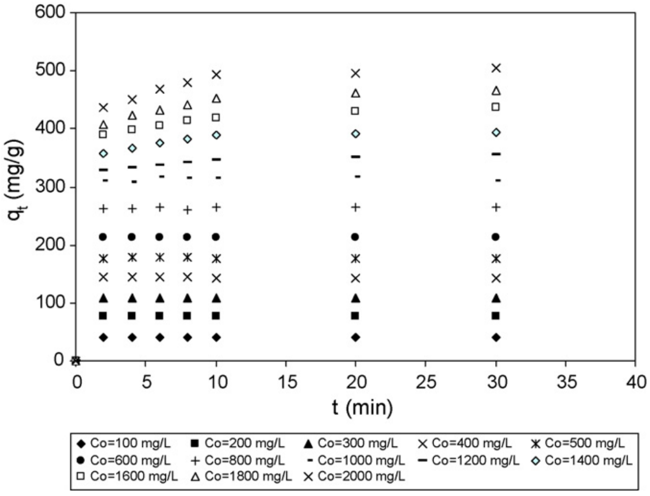

Fig. 2. Effect of contact time and initial concentration on the adsorption of PC onto SW. Conditions: adsorbent concentration 1 g/L; temperature 25 °C; pH 12; agitation rate 200 rpm.

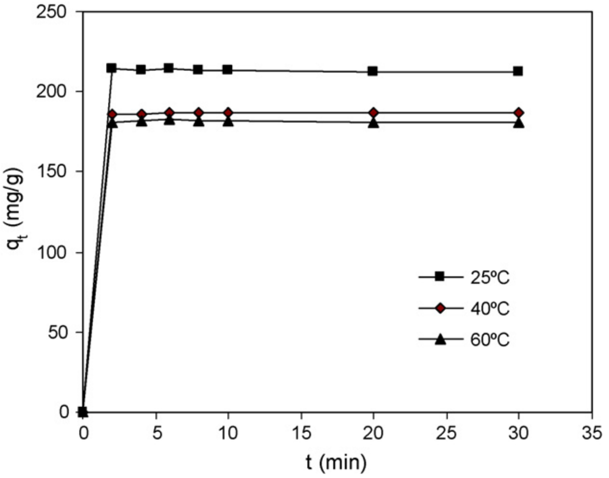

Fig. 3. Effect of temperature on the adsorption of PC onto SW. Conditions: adsorbent concentration 1 g/L; initial dye concentration 600 mg/L; pH 12; agitation rate 200 rpm.

3.2. *Effect of contact time and initial dye concentration on adsorption of PC onto SW*

Fig. 2 shows the effect of initial concentration on the adsorption kinetics of PC onto SW with solid concentration of 1 g/L at 25 °C and pH 12. For all concentrations, there was a rapid uptake of the dye due to surface mass transfer. The kinetics of adsorption represented a shape characterized by a strong increase of the capacity within the first few minutes of contact and gradually tailed off thereafter. This indicated that equilibrium time was independent of concentration. The figure also showed that the necessary time to reach the equilibrium was about 2 min.

The results also showed that an increase in the initial dye concentration produced a reduction in the percentage removal of dyestuff from the water. The removal of PC decreased from 41 to 25% with the increase of initial concentration from 100 to 2000 mg/L at pH 12, showing the process to be highly dependent on the initial concentration.

3.3. *Effect of temperature on adsorption of PC onto SW*

Fig. 3 shows the effect of temperature on adsorption of PC onto SW at pH 12 and initial dye concentration 600 mg/L. Thus, the uptake of the dye decreased from 36 to 30% with increasing the temperature from 25 to 60 °C. The decrease in the extent of equilibrium adsorption of PC with increasing the temperature indicated that a low temperature favored dye removal by adsorption and the adsorption of PC onto SW was controlled by an exothermic process. Equilibrium time for the temperatures studied was found to be 2 min, indicating that the equilibrium time was independent of temperature.

The decrease of adsorption capacity with increasing temperature may be due to a decrease in the chemical potential of the adsorbate. The surface free energy decreased from −1.564 to −1.336 kJ/mol with increasing temperature, as shown in Table 4. It may also be due to an increase in the tendency of dye molecules to escape from the solid phase.

3.4. Kinetics of adsorption

In order to investigate the mechanism of process and potential rate controlling steps such as mass transfer and chemical reaction, the experimental kinetic data for the uptake of PC dye were modeled by the pseudo-first-order by Lagergren [7] and the pseudo-second-order by Ho [8], and the intraparticle diffusion equations by Weber and Morris [9], given in Eqs. (1)–(3), respectively:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (1)$$

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

$$q_t = k_i t^{0.5} + C \quad (3)$$

The effect of the initial dye concentration and temperature was investigated to find the best kinetic model. In all conditions studied, the pseudo-first-order and the intraparticle diffusion equations did not fit well to the whole range of contact. The correlation coefficients (not given in Table 1) for the first-order kinetic and the intraparticle diffusion models were low (<0.4827 and <0.5995, respectively). The calculated q_e values obtained from the first-order kinetic model (data not given) did not give reasonable values, which were too low compared with experimental q_e values. The experimental results did not also follow Eq. (1), indicating that the sorption was not diffusion-controlled and adsorption was not preceded by diffusion through a boundary. This is confirmed by results obtained with the intraparticle model: when the plots do not pass through the origin, this show that the intraparticle diffusion is not the only rate-controlling step, but also other processes (physical adsorption) may control the rate of adsorption.

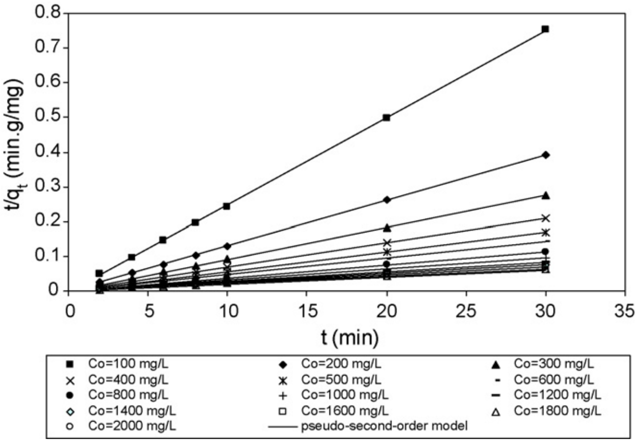

Fig. 4. Pseudo-second-order plots for PC adsorption onto SW at various initial concentrations. Conditions: temperature 25 °C; pH 12; agitation rate 200 rpm.

Table 1
The pseudo-second-order rate constants obtained under different experimental conditions

T (°C)	Co (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-second-order		
			k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	r_2^2
25	100	41.05 ± 0.86	0.4549	39.68	0.9999
	200	77.47 ± 0.47	0.5634	76.92	1.0000
	300	109.44 ± 1.33	0.8463	108.70	1.0000
	400	144.14 ± 1.26	0.4850	142.86	1.0000
	500	178.02 ± 3.15	0.2480	178.57	1.0000
	600	213.95 ± 1.54	0.1104	212.77	1.0000
	800	264.49 ± 2.51	0.0942	263.16	1.0000
	1000	316.38 ± 3.60	0.0690	312.50	0.9998
	1200	355.87 ± 4.38	0.0587	357.14	0.9999
	1400	393.05 ± 3.87	0.0126	394.47	0.9996
	1600	438.10 ± 5.24	0.0090	436.64	0.9998
	1800	466.63 ± 6.71	0.0215	468.00	0.9994
	2000	504.54 ± 7.46	0.0063	509.28	0.9999
40	100	39.44 ± 1.22	2.1505	39.22	1.0000
	300	109.66 ± 0.30	2.4366	109.89	1.0000
	500	179.17 ± 1.75	0.1985	178.57	1.0000
	600	187.31 ± 2.35	0.1512	188.68	1.0000
	800	246.48 ± 1.94	0.0882	243.90	1.0000
	1000	295.23 ± 3.52	0.0613	294.12	1.0000
	1200	318.77 ± 3.04	0.0341	316.40	0.9997
	1400	363.69 ± 4.55	0.0820	363.58	0.9996
	1600	380.45 ± 6.78	0.0266	382.14	0.9999
	1800	402.75 ± 5.44	0.0105	398.77	0.9991
	2000	436.38 ± 6.06	0.0094	440.03	0.9995
60	100	39.36 ± 0.69	2.1670	39.37	0.9999
	300	109.90 ± 1.41	2.7603	109.89	1.0000
	500	160.81 ± 2.27	4.4801	158.73	0.9996
	600	182.66 ± 1.80	0.3511	181.82	0.9999
	800	238.95 ± 3.56	0.0722	238.10	1.0000
	1000	290.12 ± 3.79	0.0341	285.71	0.9996
	1200	297.72 ± 4.21	0.0899	304.35	0.9999
	1400	334.39 ± 5.66	0.0642	337.70	0.9988
	1600	353.54 ± 7.10	0.0403	353.89	0.9999
	1800	378.13 ± 5.41	0.0176	377.10	0.9992
	2000	406.21 ± 6.58	0.0037	407.53	0.9990

The value following "±" is the standard deviation.

Good correlation coefficients (>0.9988) were obtained for the pseudo-second-order kinetic model in all conditions studied, which showed that PC uptake process followed the pseudo-second-order rate expression. So, only linear plots of t/q_t versus t at different initial concentration and at various temperatures are

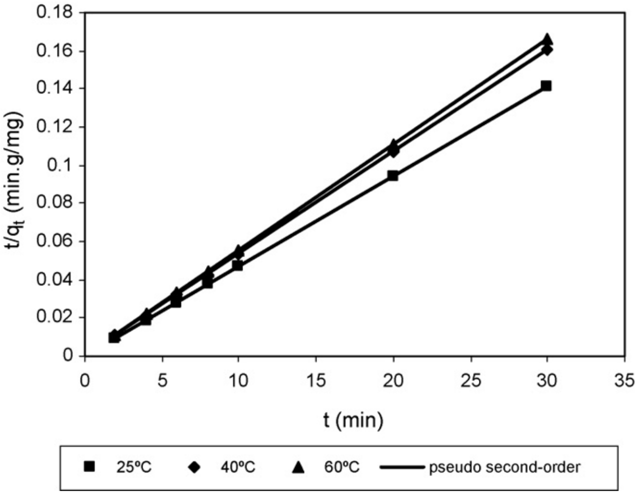

Fig. 5. Pseudo-second-order plots for PC adsorption onto SW at various temperatures. Conditions: Co = 600 mg/L; pH 12; agitation rate 200 rpm.

represented in Figs. 4 and 5, respectively. The pseudo-second-order rate constants, calculated and experimental q_e values for different initial dye concentrations and at various temperatures are given in Table 1. The calculated q_e values agreed very well with the experimental data in the case of pseudo-second-order kinetics. According to the pseudo-second-order model, the adsorption rates became very fast and the equilibrium times were short. Such short equilibrium times coupled with high adsorption capacity indicated a high degree of affinity between PC dye and SW [10,11]. The second-order (and also the first-order) is based on the adsorption capacity: it only predicts the behavior over the "whole" range of studies supporting the validity, and is in agreement with chemisorption being the rate-control.

The pseudo-second-order rate constants increased within the lower initial concentration and then decreased after equilibrium. The decrease in the pseudo-second-order rate constant and a slight increase in correlation coefficients of the pseudo-first-order model with increasing initial concentration might suggest that the process was not only chemically controlled in the rate-controlling step, but also involved some physical adsorption due to the driving force at the higher initial concentrations [12].

3.5. Equilibrium of adsorption

Adsorption isotherms describe how adsorbates interact with adsorbents, and are critical in optimizing the use of adsorbents. Therefore, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption systems [13].

In order to determine the equilibrium concentration and time, the adsorption of PC onto SW was studied as a function of contact time given in Figs. 2 and 3. It represents the quantity of dye removed (q) against the equilibrium concentration of dye molecules in the solution, and it corresponds to the equilibrium distribution of dye molecules between the aqueous and solid phases when the concentration increases. Thirty minutes of contact time, which was chosen on the basis of preliminary results of the kinetics of PC removal by SW for adsorption experiments, were used to obtain equilibrium conditions.

In order to investigate the adsorption isotherm, the experimental data of equilibrium isotherms were interpreted using two equilibrium models: the Freundlich and the Langmuir isotherm equations. This modeling permits us to determine the maximal capacity of removal. The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the regression; i.e. the isotherm giving an r^2 value closest to unity means the best fit.

The Langmuir isotherm [14] predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation assumes that adsorption takes place at specific homogeneous sites within the adsorbent and there is no significant interaction among adsorbed species. The rate of sorption to the surface should be proportional to a driving force which times an area.

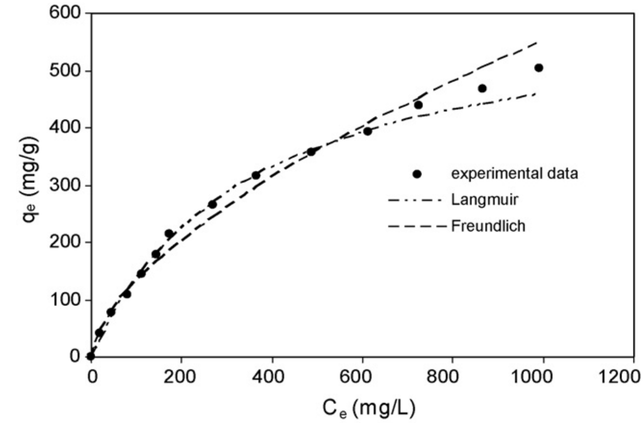

Fig. 6. Equilibrium isotherms for PC adsorption onto SW.

A linear expression of Langmuir equation is

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} C_e \qquad (4)$$

A plot of specific sorption C_e/q_e versus C_e gives a straight line of slope $1/Q^0$ and intercept $1/Q^0 b$, where Q^0 gives the theoretical monolayer saturation capacity. The values of Q^0 and b can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e.

Freundlich isotherm [15] describes the adsorption equation for nonideal adsorption that involves heterogeneous adsorption. This empirical isotherm can be used for nonideal sorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \qquad (5)$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (6)$$

Freundlich constants, K_F and $1/n$, are related to adsorption capacity and intensity of adsorption, respectively. The values of n and K_F can be calculated from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$ derived from Eq. (6). The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption.

Fig. 6 shows plots of q_e against C_e comparing the theoretical Langmuir isotherm and the empirical Freundlich isotherm with experimental data. A comparison of coefficient of determination for the isotherms was given in Table 2. The coefficient of determination for the Freundlich isotherm was greater than that for the Langmuir isotherm. The Langmuir equation describes adsorption on strongly homogeneous surfaces, which is not the case of this adsorbent exhibiting first of all a chemical heterogeneity represented by the different functional groups. It is clear that the Freundlich isotherm has best fitted for the adsorption of PC dye on SW. Freundlich plots (graphs are not given) have high linearity (>0.9825) also indicating the process to have conformed to the empirical Freundlich pattern of adsorption on non-specific, energetically non-uniform, heterogeneous surface in terms of functional groups.

Table 2
A comparison of Freundlich isotherm constants and coefficient at various temperatures

T (°C)	Langmuir isotherm			Freundlich isotherm		
	Q^0 (mg/g)	b (L/mg)	r^2	K_F (mg/g)(L/mg)$^{1/n}$	$1/n$	r^2
25	666.67 ± 7.35	0.00263	0.9528	7.57 ± 0.02	0.6206	0.9882
40	526.32 ± 6.21	0.00318	0.9550	7.43 ± 0.01	0.5784	0.9825
60	476.19 ± 7.54	0.00343	0.9514	7.38 ± 0.02	0.5526	0.9892

The value following "±" is the standard deviation.

The effect of temperature on the adsorption isotherm is shown in Fig. 7. Results indicated that the extent of adsorption of PC decreased with the increase of temperature. This indicated that the adsorption of PC onto SW was controlled by an exothermic process. More significant effect of temperature on the equilibrium isotherm was observed in the higher dye concentration range for adsorption of PC on SW. This may be due to the dissociation of adsorbed dye molecules in the multilayer stage with increasing temperature.

Table 2 also shows the K_F and $1/n$ values at different temperatures. The decrease in the values of K_F at higher temperatures showed that the adsorption rate decreased with a rise in temperature. The values of $0 < 1/n < 1$ showed that adsorption of PC on SW was favorable.

The maximum adsorption of anionic PC dye onto solid waste SW was compared with some anionic dyes and various adsorbents in Table 3. Compared with some data in literature [16–24], the solid waste studied in this work has relatively higher adsorption capacity for anionic PC dye.

3.6. Thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) change of adsorption can be evaluated by using following equations [25,26]:

The Gibbs free energy change, ΔG°, considering the sorption equilibrium constant, K_o, can be calculated by the following equation:

$$\Delta G^\circ = -RT \ln K_o \tag{7}$$

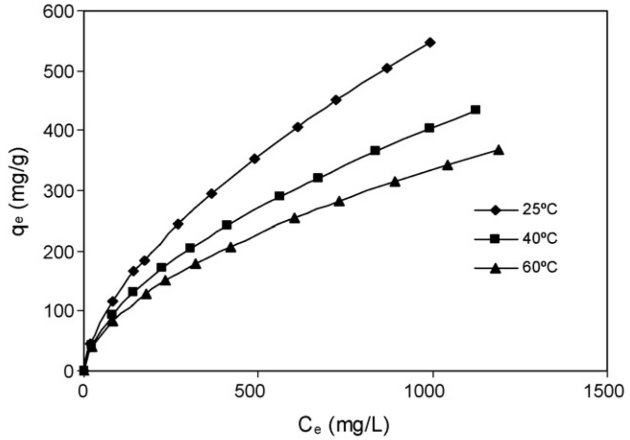

Fig. 7. Freundlich isotherms for the sorption of PC using SW as a function of temperature.

Table 3
Comparison of maximum monolayer adsorption capacity of various adsorbents for some anionic dyes

Adsorbent	Adsorbate (anionic dyes)	Q^0 (mg/g)	References
Waste Fe(III)/Cr(III) hydroxide	Congo Red	44	[16]
Bagasse fly ash	Congo Red	~12	[17]
Activated red mud	Congo Red	7	[18]
Calcined layered double hydroxides	Brilliant Blue R	~615	[19]
Acid-activated bentonite	Acid Red 57	~642	[20]
Activated sludge	Reactive Yellow 2	333	[21]
Chitin	Acid Blue 25	190	[22]
Activated carbon, bentonite, sepiolite	Acid Yellow 194, Acid Blue 349, Acid Red 423	25–100	[23]
Activated carbon	Reactive Yellow 15	116	[24]
Solis waste of soda ash plant	Reactive Red 231	~667	This work

The K_o may also be expressed in terms of the ΔH° (kJ/mol) and ΔS° (J/mol K) as a function of temperature:

$$\ln K_o = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{8}$$

The values of ΔH° and ΔS° can be calculated from the slope and intercept of a van't Hoff linear plot of $\ln K_o$ versus $1/T$.

Thermodynamic parameters during the adsorption process were calculated for 25–60 °C using Eqs. (7) and (8) from the variations of the thermodynamic equilibrium constant K_o. Results

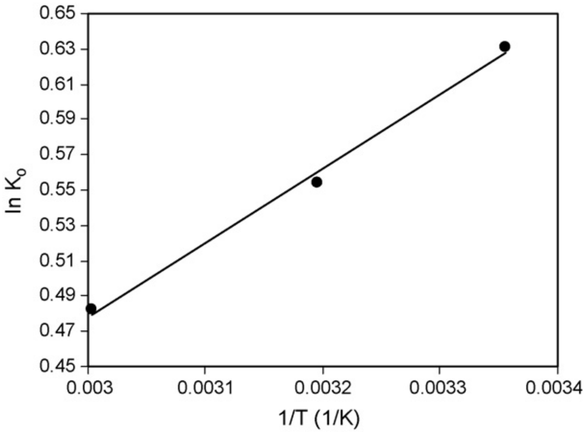

Fig. 8. A plot of $\ln K_o$ against $1/T$ for PC sorption by SW.

Table 4
Thermodynamic parameters for sorption of PC on SW for 25–60 °C

T (°C)	Thermodynamical parameters				
	K_F (mg/g)(L/mg)$^{1/n}$	K_o	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)
25	7.57	1.88	−1.564	−3.495	−6.510
40	7.43	1.74	−1.441		
60	7.38	1.62	−1.336		

are given in Table 4. K_o for the adsorption reactions was determined using the method of Khan and Singh [27] by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e. The decrease in values of K_o with rise in temperature indicated the exothermic nature of the process. A van't Hoff plot of $\ln K_o$ versus $1/T$ (Fig. 8) was found to be linear. Its slope and intercept were used to determine the values of $\Delta H°$ and $\Delta S°$.

The negative values of $\Delta G°$ (Table 4) indicated the feasibility of the process and the spontaneous nature of adsorption. Moreover, the standard-free energy change for the adsorption was more than −20 kJ/mol and less than zero. It should be noted that the magnitude of $\Delta G°$ values is in the range of multilayer adsorption which occurs by both physical adsorption and weak chemical interactions [28,20,29]. This is confirmed with the results of the isotherm of adsorption which followed the Freundlich expression. The value of $\Delta G°$ became less negative with increasing temperature. This showed that an increase in temperature was not favorable for the removal process. The negative value of the enthalpy change, $\Delta H°$ (−3.495 kJ/mol), indicated that the sorption reaction was exothermic and the product was energetically stable. The negative $\Delta S°$ value (−6.510 J/mol K) showed the decreasing randomness at the solid/liquid interface during the sorption of dye ions on SW [30]. The negative value of entropy change suggested the probability of favorable adsorption.

4. Conclusions

This study investigates the adsorption of anionic reactive dye Procion Crimson H-EXL (Reactive Red 231) on solid waste (SW) of soda ash plant, including the effects of temperature and pH on the isotherm, and the effects of the initial dye concentrations and temperature on the kinetics of the adsorption process.

The following results are obtained:

(1) SW can be used successfully as an adsorbent for the removal of anionic PC dye from aqueous solutions.
(2) The pH of the solutions has an important role on the adsorption performance. The maximum uptake of PC dye by SW occurs at an initial pH of 12 at which the adsorbent surface is positively charged, which contributes to enhance the adsorption of the anionic dye via electrostatic interactions.
(3) The pseudo-second-order kinetic model agrees very well with the dynamical behavior for the adsorption of PC dye on solid waste SW under several different initial dye concentrations and temperatures in the whole ranges studied. However, the decrease in the pseudo-second-order rate constant and a slight increase in correlation coefficients of the pseudo-first-order model with increasing initial concentration may suggest that the process is not only chemically controlled in the rate-controlling step, but also involves some physical adsorption due to the driving force at the higher initial concentrations.
(4) Adsorption parameters for Freundlich and Langmuir isotherms were determined and the equilibrium data fit well with the Freundlich model of adsorption for PC dye. The uptake of the dye also decreases with the increasing temperature.
(5) Thermodynamic parameters such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ during the adsorption process are suggested that the adsorption of PC dye ions on SW is of a spontaneous and exothermic nature which is favored at lower temperatures and occurs by both physical adsorption and weak chemical interactions.

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