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Removal of Dye Acid Red 1 from Aqueous Solutions Using Chitosan-*iso*-Vanillin Sorbent Material

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ABSTRACT

Sorption of Acid Red 1 (AR1) from aqueous solutions utilizing low-cost sorbent material; (chitosan-*iso*-vanillin) is studied under batch conditions. The remaining concentrations of the azo dye are measured at λ_{max} = 546 nm by UV spectrophotometric method. Langmuir data reveal that the maximum removal capacity was 555.556 mg/g at pH 3. Freundlich isotherm represents the best fitting model on the removal of AR1 using chemically modified chitosan verifying the sorption takes place on heterogeneous surfaces with multilayer adsorption. Kinetic studies of the sorption process revealed that intraparticle diffusion is not only the rate-determining step but also a chemical reaction takes place as well. The results indicate that high sorption rapidness with almost 90% achieved within 90 min. Thermodynamic investigations suggest that the process favours an exothermic nature. The polymer utilized in the present study is being considered as a feasible sorbent material for the removal of AR1 from waste effluent.

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1. INTRODUCTION

In the current era, environmental management, waste reprocessing, treatment, and removal, contamination control and wastewater have become the mainly significant cases atop the universal schedule (Bilad, 2017; Sulastri & Rahmidar, 2016). Countries that have experienced water pollution caused by toxic metallic, synthetic dyes, organic and metal–organic compounds have seen many catastrophic disasters, at both economic and environmental levels (Anbia *et al.*, 2010).

Synthetic dyes are widely explored in several industries for example textile, paper, carpet, food, cosmetics, plastic and leather tanning (Khanna & Rattan, 2017). These complex materials are discharged into the aqueous effluents causing pollution and environmental crisis (Khuluk *et al*., 2019). Synthetic dyes generally have complex aromatic structures, which possibly come from hydrocarbon based moieties such as benzene, toluene, xylene, naphthalene, etc. The complex nature of these dyes makes them more stable and non biodegradable (Nigam *et al*., 2002; Jabbar *et al*., 2014). Additionally, dyes are toxic, carcinogenic and mutagenic having serious destruction on kidneys, liver, brain, fertility and central nerve system (Shen *et al*., 2009). Therefore, it is very essential to handle the quantity of colored dyes in waste liquids before its entering into the ecological system.

Various treatment methods were improved to dyes removal from industrial effluents. For instance: biological treatment, membrane separation, aerobic coagulation, electrochemical techniques, oxidation and adsorption. The last motioned process is considering one of the universal methods utilized for the removal of toxic organic and inorganic poisons due to its ease, feasibility, and effective sorption ability (Kant, 2012; Wawrzkiewicz & Hubicki, 2010; Mittal *et al*., 2010; Afkhami *et al*., 2007; Anshar *et al*., 2016).

Different types of adsorbent materials are used in removing colored dyes from aqueous solutions effectively. Nevertheless, the high cost and associated handles of renewal and reprocess warrant the investigation for another low-cost sorbents. There are different types of low cost sorbent materials such as: dead bio-mass, seaweed, natural zeolite, and agricultural waste (Ragadhita *et al*., 2019). Natural polymer materials, particularly polysaccharides, have concerned the notice of several scientists during the last years, for exploiting in water remediation, profiting from the huge variety of materials created by living organs (Varma *et al*., 2004; Kurita, 2006). For instance, chitosan, a modified biomaterial attained from chitin, has significant characteristics, including low-cost, biodegradability, non-toxicity, bioactivity and biocompatibility. Chitosan-based derivatives have been widely examined as biosorbents in water treatment studies for removal of heavy metals and dyes even when pollutants exist in low concentrations (Crini & Badot, 2008; Guibal, 2004; Dragan *et al*., 2010; Habiba *et al*., 2017; Haldorai & Shim, 2014; Saha, 2010).

The sorption capacity of chitosan can be enhanced by two chemical modifications: i) crosslinking reaction by attaching multi macromolecule to each other that contains long chain of chitosan molecules, or ii) by grafting a new functional group. Chitosan can react with several substances to produce wide range of chitosan-based materials. One of these reactions is the interaction between the active amino group at C-2 position of chitosan with the aromatic aldehydes or ketones to give a new functional group (imine) by reductive amination yielding chitosan-schiff bases (Zalloum *et al*. 2007).

Recently in our lab, chitosan-vanillin polymeric materials have been investigated for the removal of Pb (II) and Co (II) ions present in aqueous solutions (Alakhras *et al*., 2019; Al-Shahrani *et al*., 2018). Moreover, chitosan-*iso*-vanillin biosorbent is synthesized, characterized and used for the sorption of Cd ions exists in effluents. The study showed that the removal process is chemically controlled with high sorption rates and thermodynamic favourability. In addition, the highest removal capacity with 38.31 mg/g is achieved at pH 5 (Alakhras, 2019).

Acid Red 1 (AR1) is a synthetic mono-azo dye which is widely used for dyeing all kinds of fabrics (Martínez-Huitle & Brillas, 2009) and for baby food colouring. However, in 2007, AR1 was suspended as food colouring in European Union due to its toxicity and carcinogenic effect (European Food Safety Authority, 2007; González-Vargas *et al.*, 2014).

Based on that and a continuity of our work, the scope of this study includes the possible utilization of chitosan-*iso*-vanillin as a low-cost sorbent material for the removal of Acid Red 1 from synthetic solution. Isothermal equilibrium studies, kinetics and thermodynamics of dye removal are investigated.

The presented study will get a positive value on the eastern province of Saudi Arabia, as it is an industrial region which expected to have high level of water pollution of synthetic dyes. It is expected that the outcome of this study will assist in defining and assessing a promising types of sorbent materials toward wastewater treatment which is considered as vital element for most economic and social works.

2. MATERIALS AND METHODS

2.1. Chemicals and Instruments

All chemicals were purchased from commercial resources and were handled as received. Acid Red 1 (**Figure 1a**) with 60% purity was purchased from Aldrich, *iso*-Vanillin (99%) from Spectrum, Chitosan with 85 %deacetylation were received from (RxBiosciences), Sodium hydroxide, Hydrochloric acid, and Ethanol, Acetone, and Methanol were obtained from (AnalaR). Orbital Shaker (Steady Shake, 757), UV-Scanning spectrophotometric (UVD-2950, LABIMED, INC), pH meter (Metrohm, 525A) were used for accomplishing experimental works.

2.2. Preparation and characterization of Chitosan-*iso*-Vanillin sorbent material

Chitosan-*iso*-Vanillin was prepared and described using a process published recently (Alakhras, 2019) which involved refluxing of chitosan (5.7 g) with *iso*-vanillin component (90 mmol) in a solution consisting of methanol (90 mL) and glacial acetic acid (9 mL) for 10 hours. After that, the solid polymer was separated and washed with ethanol and acetone, respectively. Then, the polymer was purified by Soxhlet extraction for 24 hrs. Afterwards, the sorbent was dried at 70°C during the night and then fully characterized using different techniques.

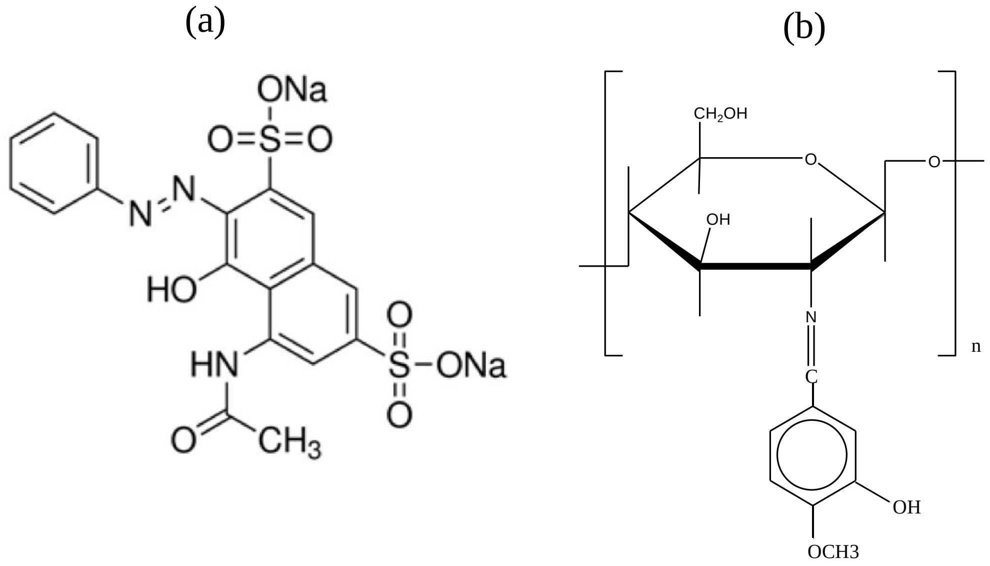

Figure 1. Chemical structure of (a) Acid Red 1 and (b) Chitosan-*iso*-Vanillin biosorbent

2.3. Preparation of stock and working solutions of AR1

Stock solution of AR1 with a concentration of 1000 mg/L was prepared by dissolving the appropriate weight of its salt in deionized water. Working solutions with (50 – 500 mg/L) were obtained from the previous solution in deionized water too.

2.4. Removal of AR1on to the sorbent material

Batch equilibrium method was executed to investigate the removal of AR1 from aqueous solution. Weight of 0.05 g of adsorbent was constantly shaken at 400 rpm with 50 mL of AR1 solution with pH from 3.0 − 10.0 for three hours at 30°C. This temperature was chosen as a moderate one between 20 and 70°C. The initial solution pH was adjusted using 0.1 mol/L of HCl or 0.1 mol/L of NaOH. The isothermal equilibrium studies were done by varying the dye concentration (50 − 500 mg/L). The effect of contact time was explored using similar trials with shaking period started from 0.17 up to 6.0 hrs. The sorbent weight effect was further analyzed using different adsorbent dosage (0.01 − 0.20 g). Same experiments were carried out at different temperature values (20, 30, 50, and 70°C). After conducting each sorption experiment, the mixture was filtered and the remaining concentration of the azo dye was measured at λmax = 546 nm by UV spectrophotometric method. All the measurements were performed in triplicates and the average value was used in the calculations. A calibration curve corresponding to the absorbance vs. known AR1 dye concentrations was used for computing the final dye concentrations.

The equilibrium removal capacity, Qe (mg/g), was calculated by the following relation:

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_e (mg/L) is the remaining concentration at the equilibrium. V (L) is the volume of AR1 solution phase, and W (g) is the mass of biosorbent.

The kinetics studies were performed using the experimental data obtained from the studies on the effect of time, in which the uptake of AR1 at any time, Q_t (mg/g), was determined using C_t (mg/L) as the remaining concentration at pre-specified time 't'.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of sorbent material

The synthesized biosorbent was generally obtained by the reaction between chitosan (**Figure 1a**), which represents the primary amine and *iso*-vanillin derivative presents the active carbonyl group, to afford the polymer material (**Figure 1b**). Structure and comprehensive analyses of the obtained sorbent can be found in our recent work (Alakhras, 2019).

3.2. 3.2. Effect of pH

Displayed in **Figure 2** are results of the effect of pH on the removal of AR1 onto the biosorbent. Results disclosed that the best removal capacity was accomplished at pH 3.0 with 95.53 mg/g.

It is obvious that AR1 dye adsorption onto the adsorbent surface is essentially affected by the surface charge on the adsorbent. Chitosan-iso-vanillin biosorbent has point of zero charge (pHPzc) value at pH 4.8. With decreasing in pH, the charge of the adsorbent becomes more positive and adsorbs more anionic species. In an aqueous solution, AR1 dye dissociates to produce the anion form which in acidic condition the removal is well accomplished due to the electrostatic attraction between the protonated adsorbent surface and the negative sulfonated groups of the dissociated dye molecules (Khanna & Rattan, 2017). On the other hand, at high pH values, the removal is decreased due to the competition with hydroxyl ions that restricted the oncoming of dye anions.

3.3. Effect of initial dye concentration and isothermal investigations

Exposed in **Figure 3** are the results of analysis on the removal of AR1. The impact of initial concentrations on removal effectiveness was investigated between (50-500) mg/L at pH 3 and at 3 hrs of contact time with sorbent mass of 0.05 g. Results demonstrate that, when the initial concentration of dye goes up from 50 to 500 mg/L, the removal capacity increases as well from 48.05 to 420.94 mg/g.

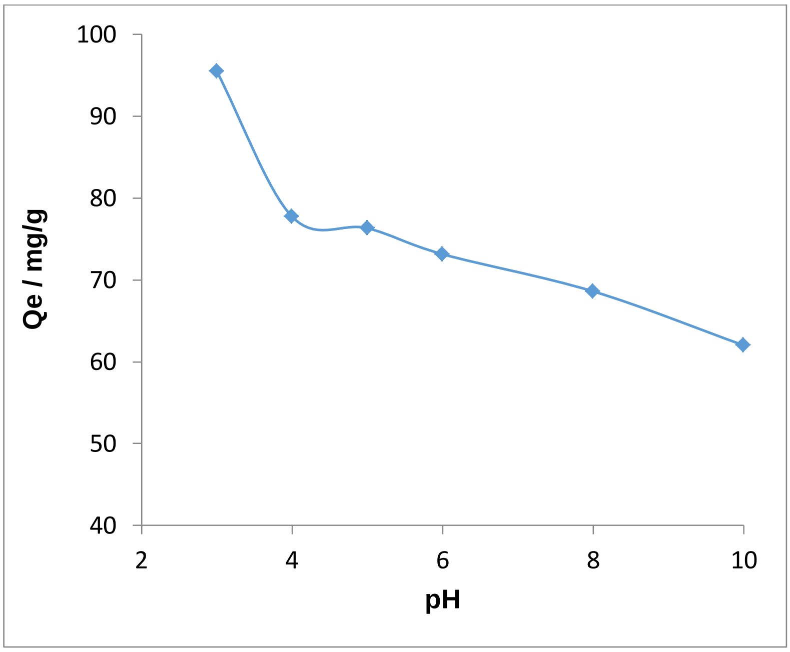

Figure 2. Effect of pH on AR1 removal (C_0 = 100 mg/L, T = 30°C, W = 0.05 g, V= 0.05 L, time = 3 h)

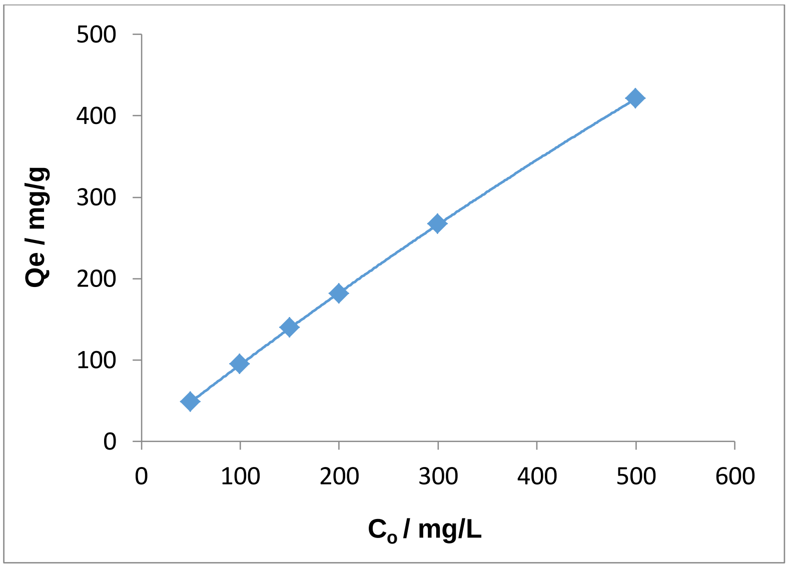

Figure 3. Effect of AR1 amounts on the removal capacity (pH=3, T=30°C, W=0.05 g, V=0.05 L, time=3h)

This behaviour can be assigned to the statement that the initial dye content in the solution is regarded as the driving force for overcoming the mass transfer limitation between the sorbent and the liquid solution (Alakhras *et al*., 2019; Al-Shahrani *et al*., 2018). When the initial dye concentrations increased, mass transport driving force is being improved and consequently the sorption capability is enhanced as well. Therefore, it is concluded that the dye removal efficiency depends on the initial dye concentrations of AR1.

Equilibrium study for a sorption system is a tool to describe the interaction of sorbate and sorbent at equilibrium condition, which is very helpful in the optimization of sorbent usage and designing full-scale plants for treatment of polluted waters and wastewaters. Therefore, three isotherm models, namely Langmuir, Freundlich and Temkin, were performed to convey the equilibrium results.

Langmuir sorption model presumes monolayer sorption of adsorbates onto a sorbent matrix with a fixed number of equal sites (Sajjadi *et al*., 2019). The model and can be depicted as:

$$C_e/Q_e = 1/(Q_0 K_L) + C_e/Q_0 \qquad (2)$$

where C_e is the adsorbate equilibrium concentration of aqueous phase (mg/L), Q_e is the adsorption capacity of the adsorbent at the equilibrium (mg/g), K_L is the Langmuir constant related to the affinity of sorption sites for adsorbate molecules (L/mg), Q_0 is the theoretical maximum sorption capacity of Langmuir model (mg/g). The plot of C_e/Q_e vs. C_e was applied to resolve Q_0 and K_L, and the results were presented in **Table 1**.

Langmuir data reveals that the maximum removal capacity (Q_0) is 555.556 mg/g. The calculated value of Langmuir constant (K_L) shows a proper affinity of sorption sites for AR1 with the chemically modified chitosan. Based on the calculated value of separation factor R_L, its magnitude indicates the shape of the isotherm to be either favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$). For the utilized polymer in this study, the R_L values were less than 1, suggest that the removal process is favourable (Qasemi *et al*., 2018).

The removal capacity for AR1 sorption is compared with other sorbent materials as reported previously (**Table 2**). It is noted that the removal ability of chitosan-*iso*-vanillin toward AR1 is superior. The data demonstrate that sorbent utilized in the current study has a potential competence for the treatment of waste effluents.

Table 1: Langmuir, Freundlich and Temkin isotherm parameters for the removal of AR1

Langmuir isotherm				Freundlich isotherm			Temkin isotherm		
Q_0 (mg/g)	K_L (L mg^{-1})	R_L	R^2	K_F (mg/g)(mg/L)$^{1/n}$	n	R^2	B (J/mol)	A (L/g)	R^2
555.556	0.03448	0.22481	0.9472	34.7776	1.733	0.9961	97.263	0.55044	0.9142

Table 2: Comparison of maximum removal capacities of various sorbents for AR1 obtained by Langmuir adsorption model

Sorbents	**Sorption capacity (mg/g)**	**Ref.**
Cucumis *sativus* (cucumber)	18.76	Khanna & Rattan, 2017
Ferric chloride flocs	250.0	
Aluminium Sulphate flocs	32.60	Munilakshmi *et al.*, 2013
Ferrous Sulphate flocs	6.623	
Surfactant modified titanate nanotubes	285.281	Lain-Chuen *et al.*, 2008
Chitosan-*iso*-Vanillin	555.556	Present study

The Freundlich isotherm is recognized to well illustrate heterogeneous system for nonideal sorption. The model is expressed as (Alakhras, 2019):

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \qquad (3)$$

where, K_F is the Freundlich constant describing the strength of sorption; n ($0 < n < 1$) is an intensity parameter that reveals the surface heterogeneity.

The plotting of log C_e vs. log Q_e yields the values of K_F and n which are presented in **Table 1**.

The value of n was between 1–10 is indicative of heterogeneity and intensity of sorption. Moreover, K_F values revealed that the dye removal capacity onto chitosan-*iso*-vanillin sorbent is favored.

Furthermore, Temkin isotherm suggested that the removal energy declined linearly with enhance in surface coverage due to sorbent-solute attractions (Dada *et al.*, 2012). The model is expressed as:

$$Q_e = B\ln A + B\ln C_e \qquad (4)$$

where A is Temkin constant indicative of the maximum binding energy (L/g), B is Temkin constant related to the heat of sorption process (J/mol). Because of the relatively low value of the correlation coefficient ($R^2 = 0.9142$) attained in case of Temkin isotherm application, it is not further considered.

Data in **Table 1** and based on the high R^2 values disclosed that Freundlich model best describes the sorption process suggesting the removal of AR1 onto chemically modified chitosan is a heterogeneous process.

3.4. Effect of sorbent dosage

To identify the consequence of sorbent mass on dye removal, tests were performed at pH 3.0 with 100 mg/L of AR1 solution by varying the weight from 0.01 to 0.2 g.

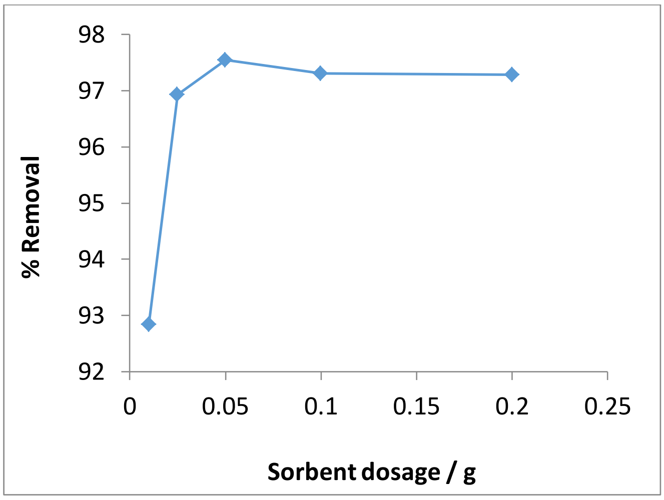

Figure 4. Effect of sorbent dosage on removal of AR1 (C_0=100 mg/L, pH=3, T=30°C, V=0.05 L, time=3h)

As depicted in **Figure 4**, the percentage of dye removal increases with increasing sorbent dosage. The rate of removal process has initially been found to be fast due to the fact that at lower sorbent dosage the dye is more readily attainable. At dose of 0.05 g, 97.54% is almost achieved due to greater availability of sorption sites for AR1 molecules. Nevertheless, as the adsorbent dose further increases, the removal of dye is almost stable. This can be ascribed to the lower exploitation of sorption sites of the sorbent at higher dosage, which may result from possible overlapping or aggregation of sorption sites, leading to an increase in diffusion path and reduction of the available area for sorption process (Bharathi & Ramesh, 2013).

3.5. Effect of contact time and kinetic studies

The influence of time on the extent of sorption is associated with the stability of the complex that may form throughout the sorption process between the adsorbate and the sorbent.

The sorption proportion of acid red 1 based on exposure time was examined by a batch equilibrium process. Herein, 0.05 g of sorbent material was shaken for six hours with dye solution at pH= 3.0. Displayed in **Figure 5** are the results demonstrated the reliance of AR1 removal on contact time. The dye removal was rapid initially. After that, this behavior followed by a slower consequent uptake that slowly reached an equilibrium condition which there was no considerable rise in dye removal. The time needed to accomplish equilibrium was almost 120 min. In addition, the result revealed that the utilized sorbent has fast rates of dye removal with almost 90% achieved within 90 min. This behaviour can be ascribed to the high attraction between the vacant binding sites on the adsorbent surface and the negative sulfonated groups of the dissociated dye molecules.

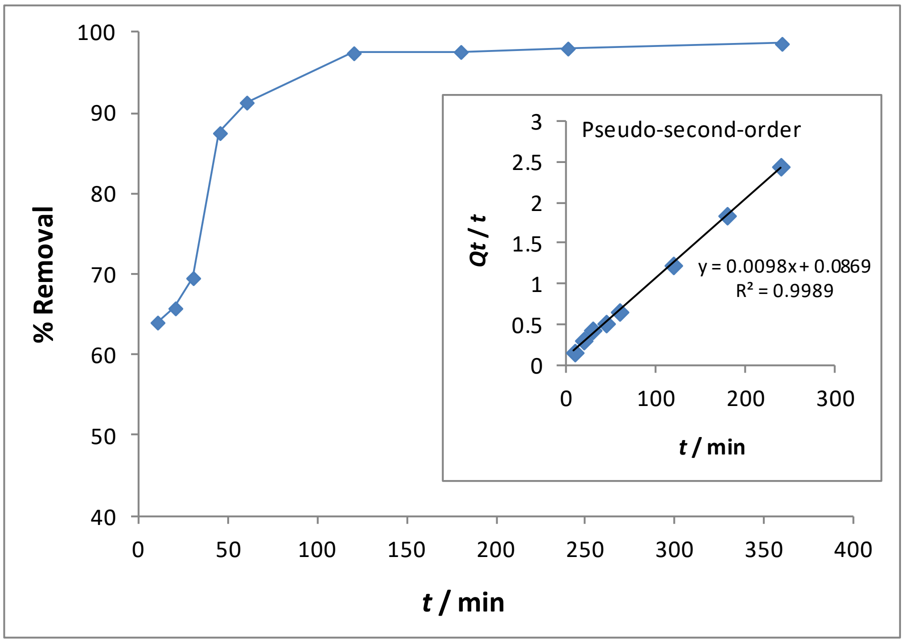

Figure 5. Effect of contact time on AR1 removal (C_0 = 100 mg/L, pH=3, T=30°C, W=0.05 g, V=0.05 L)

The Kinetic data were processed using two adsorption models; pseudo-first-order kinetic (equation 5) and pseudo-second-order kinetic (equation 6). The two models are general expressions describing the kinetic behavior of sorption process on solid surfaces for the liquid–solid system (Lagergren, 1898; Ho & McKay, 1999; Al-Arfaj *et al.*, 2018).

$$ln\,(Q_e - Q_t) = ln\,Q_e - k_1\,t \qquad (5)$$

$$\frac{t}{Q_t} = \frac{1}{k_2\,{Q_e}^2} + \frac{t}{Q_e} \qquad (6)$$

However, the first two models illustrated the whole adsorption process without keeping in mind the diffusion steps where the intraparticle diffusion model is exploited to analyze the sorption mechanism for a solid–liquid removal process (Weber et al., 1963). Weber-Morris model which can usually be represented by three stages is presented by the following equation:

$$Q_t = K_{id}\,t^{½} + C \qquad (7)$$

where K_{id} is the intra-particle diffusion rate constant ($mg.g^{-1}.min^{-½}$), and C is the constant whose values is proportional to the boundary layer (mg/g).

Data in **Table 3** confirm that the theoretical value of Q_e, computed based on pseudo-second-order model, is closer to the experimental one, as compared to those evaluated from the pseudo-first-order model. Furthermore, the higher coefficient of determination (R^2) of the pseudo-second-order kinetic model implies that the experimental results are properly fitted with pseudo-second-order model as the potential form for the sorption behaviour of AR1. Moreover, the closeness of pseudo-second-order model with the experimental data indicates the interaction of dissociated dye molecules with the sorption sites of the polymeric material could be the rate-controlling step for the entire sorption process (Alakhras, 2018; Bulgariu *et al.*, 2019).

Weber-Morris model is also fitted with the experimental data, and **Figure 6** shows that whole plots of Q_t versus $t^{½}$ do not pass through the origin point, and do not have an intercept equal (or close) to zero. However, the Weber-Morris plots for the investigated sorbent display a good linearity, signifying that (i) the intra-particle diffusion is not the rate-controlling step but is involved in the sorption process and (ii) the sorption process is controlled by two or more simultaneous mechanisms. The high value of K_{id} can be ascribed to higher rapidness in the mass transfer and diffusion process of AR1 molecules into the sorbent structure.

Table 3. Kinetic parameters of Pseudo-first-order and Pseudo-second-order for the removal of AR1

$(Q_e)_{Exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	$(Q_e)_{Cal}$ (mg/g)	K_1 (min^{-1})	R_1^2	$(Q_e)_{Cal}$ (mg/g)	K_2 (g/mg.K)	R_2^2	K_{id} ($mg/g.min^{½}$)	C (mg/g)	R^2
98.598	32.87	0.01911	0.9005	102.04	0.00118	0.9989	9.7561	17.963	0.9062

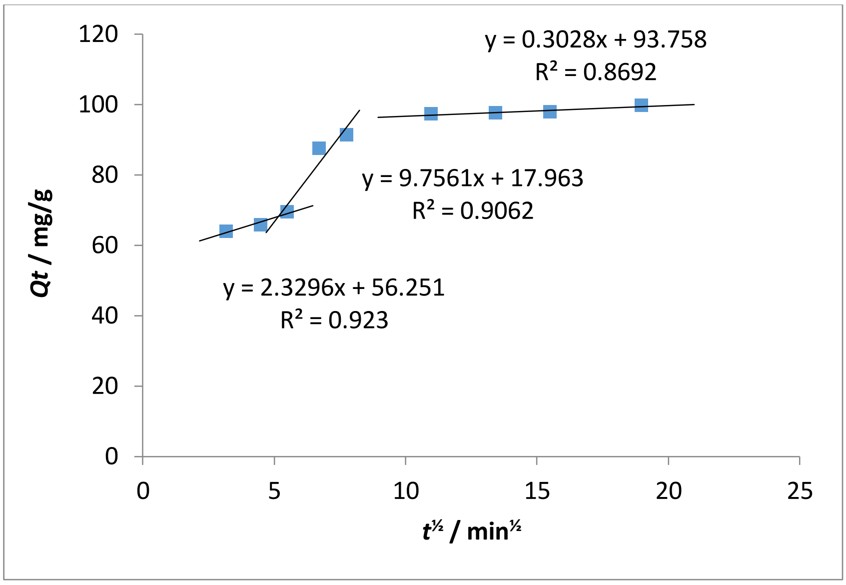

Figure 6. Intraparticle diffusion plots for the removal of AR1 (C_0 = 100 mg/L, pH = 3, T = 30°C, W = 0.05 g, V= 0.05 L)

3.5. Effect of temperature and thermodynamic studies

The influence of temperature on the sorption of AR1 by the investigated polymer was examined between 20 and 70°C, and with an initial dye concentration of 100 mg/L. The data released that the dye removal is decreased as the temperature increased. Upon increasing the temperature from 20 to 70°C the removal uptake was decreased by 7%.

The values of thermodynamic constants which include Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) are calculated using equations 8 and 9 where R (J/mol.K) is the universal gas constant and T (K) is the absolute temperature (Tran *et al.*, 2017; Rahmani-Sani *et al.*, 2017).

$$ln\left(\frac{Qe}{C_e}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (8)$$

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

The negative sign of the Gibbs free energy change confirms that the process is carried with high sorption rate, spontaneous, and feasible at all studied temperatures. Nevertheless, the removal process is more favorable at lower temperatures. The negative value of ΔH designates that the sorption process is exothermic in nature with existence of an energy barrier in the sorption process (Lain-Chuen *et al.*, 2008). The negative value of ΔS suggests decreased randomness at the solid/solution interface and therefore no significant changes arise in the internal structure of the sorbent material during the sorption of AR1 onto the modified chitosan.

Table 4. Thermodynamic parameters for the sorption of AR1 at different temperatures

ΔH (kJ/mol)	*ΔS* (J/mol.K)	*ΔG* (kJ/mol)			
		T= 20°C	*T*= 30°C	*T*= 50°C	*T*= 70°C
-25.871	-54.567	-9.875	-9.329	-8.238	-7.147

Generally, adsorption process can be considered as physical if the absolute magnitude Δ*H* < 40 kJ/mol and as chemical when Δ*H* > 40 kJ/mol (Fu *et al.*, 2016). According to the estimated result, the removal process of AR1 using chitosan-*iso*-vanillin may be regarded as physical sorption method.

4. CONCLUSION

Chitosan-*iso*-vanillin sorbent material has been used for the sorption of AR1 from aquatic media. The removal process is best fitted with Freundlich isotherm model suggesting sorption characteristics for the heterogeneous surface. Results achieved from this study also disclosed that sorption of AR1 onto the utilized polymer is followed by pseudo-second-order kinetics. Weber-Morris model indicates that the removal process is controlled by more than one step and the intraparticle diffusion could be involved in the determination of sorption process. Additionally, results show that, the uptake is favourable, with spontaneous nature and exothermic characteristic. Finally, this study points out that chitosan-based materials are feasible sorbent for the sorption of AR1 from waste effluent samples.

5. ACKNOWLEDGEMENTS

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6. AUTHORS' NOTE

The author(s) declare(s) that there is no conflict of interest regarding the publication of this article. Authors confirmed that the data and the paper are free of plagiarism.

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